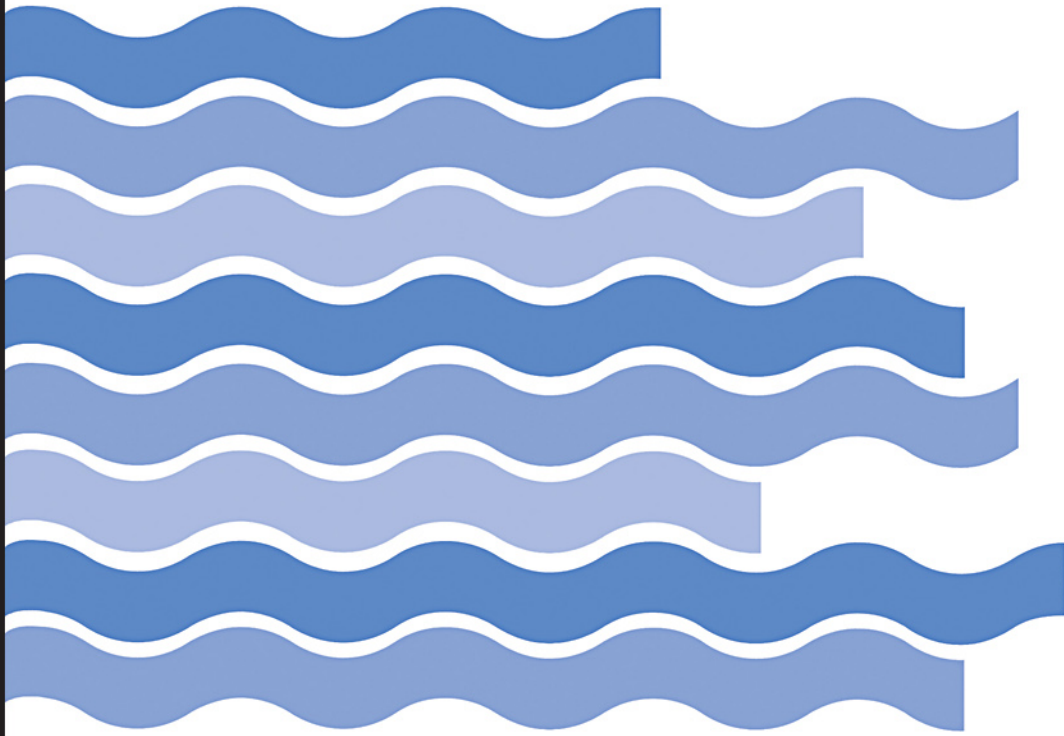

COMPREHENSIVE

*water
analysis*

V O L U M E T W O



treated waters

T R Crompton

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Comprehensive Water Analysis

Volume 2: Treated Waters

Comprehensive Water Analysis

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T.R.CROMPTON

Consultant, Pen Marian, Beaumaris, Gwynedd, UK



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PREFACE

This book covers all aspects of the analysis of treated waters using both classical and the most advanced recently introduced physical techniques. Treated waters are taken to include potable waters, industrial and domestic wastewaters, sewage effluents, trade effluents treated mineral waters, high purity waters, boiler fed waters, swimming pool waters and plant cooling waters.

Determinands covered include all the anions and cations, non-metallic elements including organic nitrogen, halogens, sulphur, phosphorus and the various forms of carbon; miscellaneous determinands such as suspended solids, conductivity, pH, alkalinity, acidity, colour, etc., organic materials, organometallic compounds, oxygen demand parameters, dissolved gases and radioactive elements.

Chromatographic techniques are becoming of increasing importance in water analysis, particularly in the analysis of potable water and effluents and there is a full discussion of these including gas chromatography, high performance liquid chromatography, ion chromatography and others.

Analysis of organics and inorganics is now frequently required at the microgram per litre and submicrogram per litre levels and a full discussion is included of the latest techniques which are capable of meeting these requirements. When particularly low concentrations have to be determined and available instrumentation cannot meet these requirements, then the newly evolving preconcentration techniques are often applicable, whereby the determinand of interest is concentrated into a small volume by suitable treatment of a large volume of the sample prior to carrying out the analysis. A full treatment of the reduction of detection limits by preconcentration techniques is included.

The book is intended to be a source book to anyone with an interest in the analysis of natural waters, the implementation of directives concerned with water quality, environmentalists and students.

The book will be of particular interest to water scientists and engineers, regulatory pollution control authorities, government departments, environmental organizations, industrialists and all who are concerned with monitoring and control of the impact—environments, social and political—of water pollutants.

T.R.Crompton

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Chapter 1

POTABLE WATERS

1.1 Anions

1.1.1 *Bicarbonate*

Ion-exclusion chromatography

Tanaka and Fritz¹ have described a procedure for the determination of bicarbonate and carbon dioxide in water by ion-exclusion chromatography using water as the eluent and an electrical conductivity detector. The sensitivity of detection is improved approximately 10 fold by the use of two ion exchange enhancement columns inserted in series between the separating column and the detector. The first enhancement column converts carbonic acid to potassium bicarbonate and the second enhancement column converts the potassium bicarbonate to potassium hydroxide.

The plastic separating column was 7.5×100 mm and was packed with a cation-exchange resin in the H⁺ form TSK SCX 5 μm (polystyrene divinyl benzene copolymer-based material with a high cation exchange capacity).

The first enhancement column was constructed of plastic (4.6×50 mm) and packed with a cation-exchange resin in the K⁺ form (TSK SCX T μm; TSK IC-Cation for cation chromatographic use, 10 μm silicon based material with low cation-exchange capacity).

The second enhancement column was constructed of plastic (4.6×50 mm) and packed with an anion-exchange resin in the OH⁺ form TSK SAX (5 μm). The precolumn was constructed of plastic (7.5×100 mm) and packed with an anion exchange resin in the OH⁺ form (TSK SAX, 5 μm).

All samples were filtered with a 0.45 μm polytetrafluoroethylene (PTFE) membrane filter before injection into the column.

Tanaka and Fritz¹ applied this procedure to the determination of bicarbonate or carbon dioxide in some potable water samples. Fig. 1 shows the ion-exclusion chromatograms obtained before and after a softening treatment. The results indicated that the method is useful in the field of water quality control of water treatment facilities.

Environmental waters such as river, lake and well waters were analysed for carbon dioxide and bicarbonate by the three column ion-exclusion method without any difficulty. It may be possible to use the first peak to

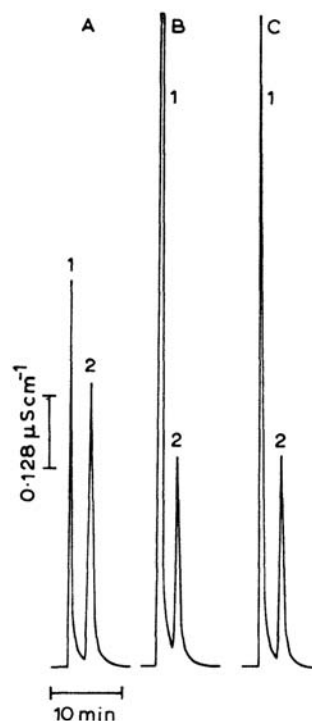


Fig. 1. Ion exclusion chromatograms of in some tap waters: (A) raw tap water of City of Ames, IA, after 10 fold dilution ($0.653 \text{ mM} \times 10$); (B) potable water after softening treatment (0.466 mM); (C) potable water (La Salle, IL) after 20 fold dilution ($0.470 \text{ mM} \times 10$). Peak 1 is strong acid anions and peak 2 is .

estimate the total salts of strong acids (such as chloride and sulphate) in water samples. The detection limit for bicarbonate was about $2 \mu\text{M}$ and the relative standard deviation about 1 per cent.

Strong acids and salts of strong acids, which are converted to acids by the separation column, pass rapidly through ion-exchange columns and do not interfere with the carbon dioxide/bicarbonate peak which elutes later. The effect of weak acids or salts of weak acids was determined by adding various carboxylic acids to samples containing a known amount of sodium bicarbonate. Fig. 1 shows chromatograms obtained by the one-column, two-column and three-column ion-exclusion methods. No interference was observed from equal molar amounts of formic, acetic or butyric acids. Propionic acid has almost the same retention time as carbonic acids and therefore constitutes an interference. Oxalic, tartaric, citric, lactic, malic and malonic acids elute before carbonic acid and therefore do not interfere.

1.1.2 Chloride

Gas chromatography

Bachmann and Matusca² have described a gas chromatographic method for the determination of $\mu\text{g l}^{-1}$ quantities of chloride, bromide and iodide in potable water. This method involves reaction of the halide with

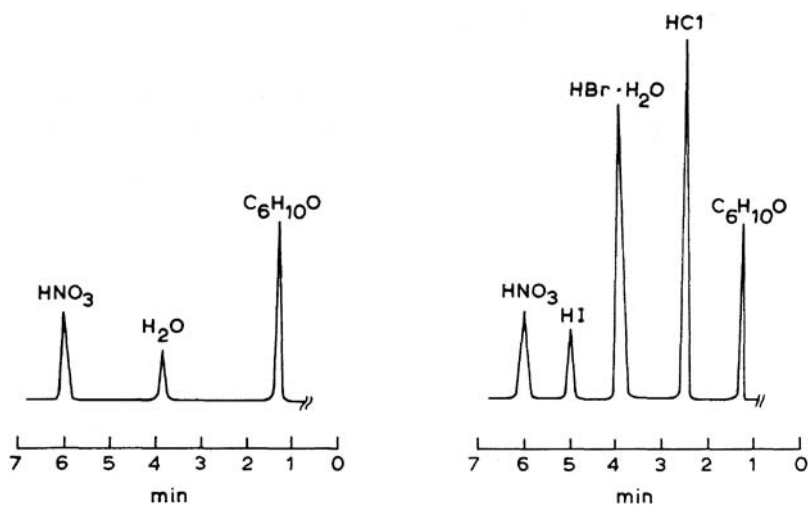


Fig. 2. Gas chromatogram of halogen mixture.

an acetone solution of 7-oxabicyclo-(4,1,0)heptane in the presence of nitric acid to form halogenated derivatives of cyclohexanol and cyclohexanol nitrate.

The column effluent passes through a pyrolysis chamber at 800°C and then through a conductivity detector. The solution is injected on to a gas chromatographic column (OV-10-Chromosorb W-HPI, 80–100 mesh, 150 cm, 0.2 cm dia.) operated at 50°C. Hydrogen is used as carrier gas. Chloride contents determined by this method were $5.0 \pm 1.8 \mu\text{g l}^{-1}$ chloride in potable water, $20.0 \pm 1.5 \mu\text{g l}^{-1}$ in drinking water. A typical gas chromatogram is shown in fig. 2 showing peaks for the three halogens.

1.1.3 Bromide

Spectrophotometric method

Moxon and Dixon³ have described an automated method for the determination of $\mu\text{g l}^{-1}$ amounts of bromide in potable water which is based on the catalytic effect of the bromide ion on the oxidation of iodine to iodate by permanganate and colorimetric measurement of residual iodine in carbon tetrachloride. A Technicon AutoAnalyser 1 is used. The system is kept at $0 \pm 0.2^\circ\text{C}$ using an insulated ice bath. An automatic chloride method of similar sensitivity, accuracy and reproducibility is used to estimate chloride interference. The detection limit of the method is $4 \mu\text{g l}^{-1}$ and the precision is of the order of 6 per cent.

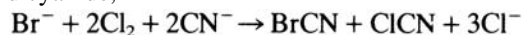
For most potable waters the effects of interferences except for that of chloride will be negligible. Some contaminated drinking waters can contain elements such as iron and manganese in amounts which could give substantial interference and these could be diluted to a level where the interference was removed.

Based on the bromine contents, bromide and bromate give the same response in this technique indicating that bromide and bromate have a similar catalytic activity. Excellent precision data were obtained for this procedure, coefficients of variation ranging from 2.2 per cent at the $100 \mu\text{g l}^{-1}$ bromide level to 7.0 per cent

at the $5 \mu\text{g l}^{-1}$ bromide level. Spiking experiments gave recoveries between 98 and 103 per cent, i.e. excellent accuracy.

Gas chromatography

Nota et al⁴ have devised a simple and sensitive method for the determination of amounts of bromide down to 0.05 mg l^{-1} in water. The procedure is in two stages. Cyanogen bromide is formed by the reaction between bromide, chlorine and cyanide,



Cyanogen bromide is then separated by gas chromatography and selectively detected with an electron capture detector.

It should be noted that the internal standard (nitromethane) must always be introduced after the addition of cyanide in order to prevent rapid darkening of the solutions, which causes non-reproducible results. No interferences are caused by oxidizing or reducing substances or by mercury or cadmium at concentrations below 200 mg l^{-1} . Mercury and cadmium are, among the metals, the strongest complex-forming agents with bromide.

Even small amounts of aromatic compounds are likely to produce some interferences owing to their tendency to bind bromine, which is formed by reaction with chlorine water.

Bromide and iodide

GAS CHROMATOGRAPHY: Grandet et al⁵ have described a method for the determination of traces of bromide and iodide in potable water which permits determination of $50 \mu\text{g bromide l}^{-1}$ and $5 \mu\text{g iodide l}^{-1}$, without preconcentration of the sample or $0.5 \mu\text{g bromide}$ and $0.2 \mu\text{g iodide l}^{-1}$ after preconcentration. The method is based on the transformation of the halides into 2-bromo- or 2-iodo-ethanol. These derivatives are extracted with ethyl acetate and determined with an electron capture detector. The difference in the retention periods enables both halides to be determined simultaneously in one sample. The method is substantially free of interferences and is suitable for use on many types of water.

Ion chromatography

In studies of the formation of bromoforms produced during the disinfection of water supplies it is necessary to have a method capable of determining bromide ion at the $\mu\text{g l}^{-1}$ level. Morrow and Minear⁶ have developed an ion chromatographic procedure using a concentrator column to improve sensitivity. This analysis, which was carried out on a Dionex model 125 ion loop, coupled with an auto-sampler, allowed detection at the $\mu\text{g l}^{-1}$ level. A chromatograph equipped with concentrator column in place of an injection concentrator column is a short separator column used to strip ions from a measured volume of matrix leading to a lowering of detection limits by several orders of magnitude. The concentrated sample was flushed into the system using $0.003 \text{ M sodium bicarbonate}/0.0024 \text{ M sodium carbonate}$ eluant.

When using conventional ion chromatographic separation techniques, it is possible that other matrix anions also common to natural waters may coelute with bromide. For example, bromide and nitrate elute simultaneously using a standard anion separator column (Dionex No. 30065), standard anion suppressor (Dionex No. 30366) and standard eluant ($0.003 \text{ M sodium bicarbonate}/0.0024 \text{ M sodium carbonate}$).

A representative chromatogram is shown in [fig. 3\(a\)](#).

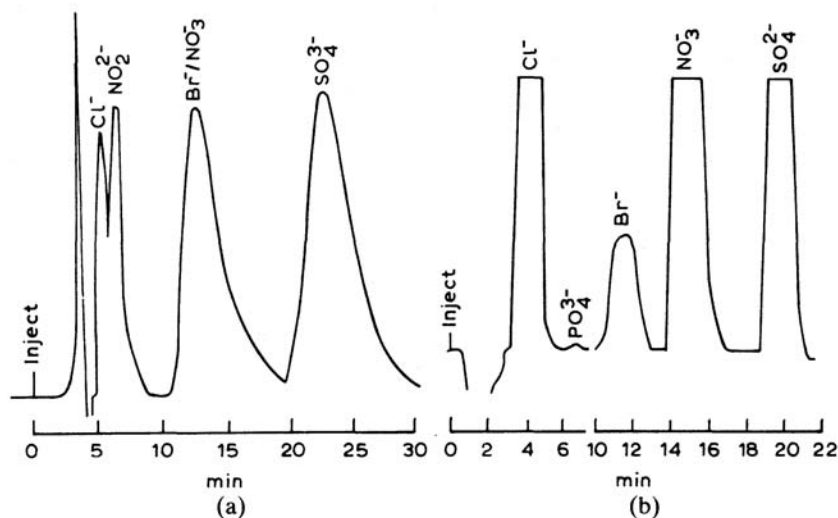


Fig. 3. Ion chromatography on anions in potable water. (a) Simultaneous elution of bromide and nitrate using standard eluant; (b) Separation of bromide and nitrate using trace anion separator and standard eluant.

Separation of bromide from all other matrix anions was shown to be possible using a trace anion separator (Dionex No. 30827), a standard anion suppressor and slightly weakened standard eluent. A chromatogram is presented in [fig. 3\(b\)](#).

Chloride, nitrate and sulphate were the only ions found to be present in any significant quantities in the representative raw waters analysed. To determine whether response for bromide remained the same regardless of the concentration of these anions, recovery tests were performed on bromide standard solutions of $80 \mu\text{g l}^{-1}$ spiked with varying concentrations of chloride, nitrate and sulphate, using the concentrator found to have the highest μ -equivalent capacity. In the presence of 100 mg l^{-1} chloride, there was 100 per cent recovery of $80 \mu\text{g l}^{-1}$ bromide. Chloride was not expected to interfere with the elution of bromide at any concentration since bromide is held preferentially over chloride by the concentrator column. In the presence of 100 mg l^{-1} nitrate only 16.2 per cent of the bromide was recovered, indicating the concentrator's preference for the nitrate ion. There was no response for $80 \mu\text{g l}^{-1}$ bromide in the presence of 1000 mg l^{-1} sulphate, indicating 0 per cent recovery.

Nitrate in excess of 17 mg l^{-1} interfered with the elution of bromide and sulphate in excess of 25 mg l^{-1} interfered with the elution of bromide.

1.1.4 Fluoride

Spectrophotometric methods

One method is based on the bleaching effect of fluoride on the colour of the zirconium erichrome organic R complex⁷. This method is applicable over the range 2–25 μg fluoride. Sulphate does not interfere in the determination. Lanthanum-alizarin complexan has been used to determine fluoride⁸. The main interfering ions are removed from the sample with a strongly acidic cation exchanger. The reagent (a buffered (pH 4.3)

mixture of 3-amino-methylalizarin-*NN*-diacetic acid and lanthanum nitrate with added acetone) is added, and the red chelate is allowed to develop in the dark for about 20 min and the extinction determined against a reagent blank at 620 nm. If very high sulphate and chloride concentrations are present in the sample, the results must be corrected by reference to a calibration graph. Water samples containing aluminium (greater than 0.1 mg l⁻¹) must be adjusted to pH 9 with potassium hydroxide solution before analysis, to ensure quantitative ion exchange.

Wierzbicki and Pawlita observed that free chlorine⁹ and ozone¹⁰ interfere in the determination of fluoride by the zirconium-Alizarin Red-S-spectrophotometric method. Chlorine partially decolorizes the lake formed; this is prevented by the addition of sodium thiosulphate in an equivalent amount to the concentration of free chlorine present. Ozone interferes at concentrations as low as 0.1 mg l⁻¹ and its effect can also be overcome by the addition of a slight excess of sodium thiosulphate.

Mehra and Lambert¹¹ used a solid ion-association reagent comprising Buffalo Black and Brilliant Green dyes supported on activated alumina. When this solid is added to the sample, Brilliant Green reacts with fluoride releasing an equivalent amount of Buffalo Black for spectrophotometric determination at 618 nm. The test solution is passed through a column of the reagent and any Brilliant Green released is selectively decomposed by adding solid sodium bisulphite to the percolate before measurement of the extinction. The calibration graph is rectilinear for up to 10 mg l⁻¹ fluoride and the detection limit is 1 µg. Interfering ions, especially sulphate and bicarbonate must first be removed by adsorption on Amberlite IRA 400 (NO₃-form) and preferential elution of fluoride with 0.1 M sodium nitrate; this treatment also serves to concentrate fluoride.

Cherian and Gupta¹² have described a method for determining fluoride which involves decomposition of the coloured thorium-chromotrope 2R complex to form the more stable fluoride-thorium complex which is measured spectrophotometrically at 570 µm.

Capitan-Vallvey et al¹³ reacted fluoride with zirconium and xylenol orange to produce a changed complex which was preconcentrated in an ion-exchange resin (Duvex 1-X8). Absorbance was measured directly at 580 and 750 µm. The detection limit was 1 µg l⁻¹ fluoride in a 500 ml sample.

Fluoride selective electrodes

Nicolson and Dutt¹⁴ have carried out a detailed study of an optimum buffer system for use with a fluoride selective electrode. They examined eleven buffer systems to determine maximum complexing ability, with optimal reproducibility and sensitivity, in the determination of fluoride in water by the direct potentiometric electrode method. A buffer system containing triammonium citrate was found to have the best masking ability as well as satisfying the other criteria. Only aluminium and magnesium and borate posed interference problems. It is recommended that a minimum decomplexing time of 20 min (and preferably 24 hours) be allowed and fresh buffer solutions be prepared after a maximum storage period of two weeks.

The composition of this buffer is as follows:

TISAB III M. tri-ammonium citrate
 58 g sodium chloride
 57 ml glacial acetic acid
 4 g CDTA (LRG)
 243 g tri-ammonium citrate

The method employed in the determination of fluoride was that of direct potentiometry using a calibration curve constructed from standard solutions. Subsequent aliquots of the same standard or sample solution were analysed until two emf readings within 0.5 mV were obtained.

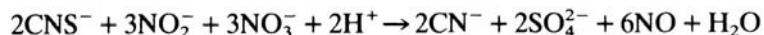
Ballcizo¹⁵ carried out direct potentiometric determinations of fluoride in potable water. This was carried out with the aid of tiron (pyrocatechol 3,5-disodium disulphonate) as a decomplexing agent. This substance releases fluoride from a wide range of complex fluoride ions (e.g. aluminium, iron, titanyl, magnesium, silica and boric acid) and thus permits the determination of total fluoride content, even in the presence of appreciable amounts of aluminium. As the fluoride electrode is also highly sensitive to hydroxyl ions the pH value must be kept at or slightly below neutral, but not so low as to allow the formation of hydrochloric acid. The buffering action of tiron is also sufficient to enable the use of any additional buffers such as those for ionic strength adjustment, to be dispensed with.

1.1.5

Iodide

Spectrophotometric method

Manual¹⁶ and automated¹⁷ spectrophotometric methods have been described for the determination of iodide in potable water. Moxon¹⁷ describes an automated procedure capable of determining iodide ion in potable water in amounts down to 0.4 $\mu\text{g l}^{-1}$ and total inorganic iodine (including iodate) in amounts down to 0.2 $\mu\text{g l}^{-1}$. The methods are based on the catalytic effect of iodide on the destruction of the thiocyanate ion by the nitrite ion;



The methods are applicable to normal drinking waters with possible interfering ions having negligible effects. The system is easy to use and can handle 20 samples per hour.

When series of drinking waters were run by this method, the peaks were found to be irregular and erratic. It was found that there was a relationship between the hardness of the waters and the peak irregularity, and this was removed when the alkaline earth metals were precipitated out with potassium carbonate. Subsequently, samples and standards were made up in 0.3 per cent potassium carbonate solution. This addition of alkali prolonged the stability of the standard solutions from 6 hours to 8 days, but led to a decrease in the sensitivity of the method. Chloride at a level of 400 mg l^{-1} gave a 20 per cent increase in the response to a 4 $\mu\text{g l}^{-1}$ of iodide standard solution. To overcome this interference, a large excess of chloride in the form of sodium chloride solution was introduced into the sample stream and it was found that as well as removing the interference effect of chloride, the sensitivity of the method was greatly increased.

A considerable proportion of the total inorganic iodide present in water can consist of iodate. System A, described in [fig. 4](#) recovered iodate quantitatively and gave a measure of the total inorganic iodine in solution. In order to determine free iodide only, the oxidation-reduction potential of the reaction mixture was adjusted so that iodate was not reduced to iodine or iodide. This was achieved by (a) reducing the concentration of nitric acid in the ammonium iron III sulphate reagent, (b) reducing the concentration of the sodium chloride reagent and (c) reducing the concentration of the potassium thiocyanate reagent. These changes caused a corresponding decrease in sensitivity. The manifold system shown in [fig. 4](#) has two different sets of reagents. Set A was used for the determination of total inorganic iodine in water over the range 0.2–5.0 $\mu\text{g l}^{-1}$ of iodide and set B was used for the determination of free iodide in water over the range 0.4–5.0 $\mu\text{g l}^{-1}$ of iodide.

The effects of ions commonly occurring in drinking waters that could cause possible interference were tested and the results, representing a mean of three determinations, are shown in Table 1. The results show that interferences do not present any major problems in the analysis of drinking waters for either total inorganic iodide or free iodide.

1.1.6 *Chlorate and chlorite*

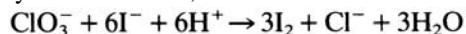
Titration methods

Chlorate ion concentration at the sub mg l⁻¹ level has been measured with high precision and accuracy by a modified iodometric method¹⁸. The chlorate

TABLE 1
Effect of added ions on the determination of (A) total inorganic iodine concentration and (B) free iodide concentration in a 4 µg l⁻¹ standard iodide solution

Element added	Concentration mg l ⁻¹	Maximum concentration in drinking waters (mg l ⁻¹)	(A) Total I found (µg l ⁻¹)	(B) Free I found (µg l ⁻¹)
Zn ²⁻	1	0.69	4.0	3.9
Cu ²⁻	1	0.36	4.0	3.8
Li ²⁺	1	0.01	4.1	3.8
Pb ²⁺	0.1	0.046	4.0	3.9
Fe ³⁺	2	1.5	4.0	3.8
Mn ³⁺	1	0.06	3.9	3.9
Ni ²⁺	0.2	0.013	4.0	4.2
Hg ²⁺	0.005	0.001	3.9	4.2
Co ²⁺	0.2	0.011	4.0	4.2
Mg ²⁺	30	23	4.1	4.0
Cl ⁻	400	245	4.0	4.0
Br ⁻	1	—	4.0	4.1
F ⁻	1	—	4.1	4.3
IO ₃ ⁻	0.004	—	8.0	4.0
SO ₄ ²⁻	200	—	4.1	4.5
Humic acid	20	—	3.9	0.0
Iodoform	1	—	5.6	5.6
Methyl iodide	0.1	—	4.2	4.2

is reduced by iodide ion in 6 M hydrochloric acid;



Oxidation of iodide ion by air is prevented by removing the air with pure hexane and scrubbed nitrogen. Saturated disodium phosphate was used to neutralize the acid. The iodometric end point was detected either with thyodene as the indicator or the colour of iodine in the hexane layer. The precision of the method is

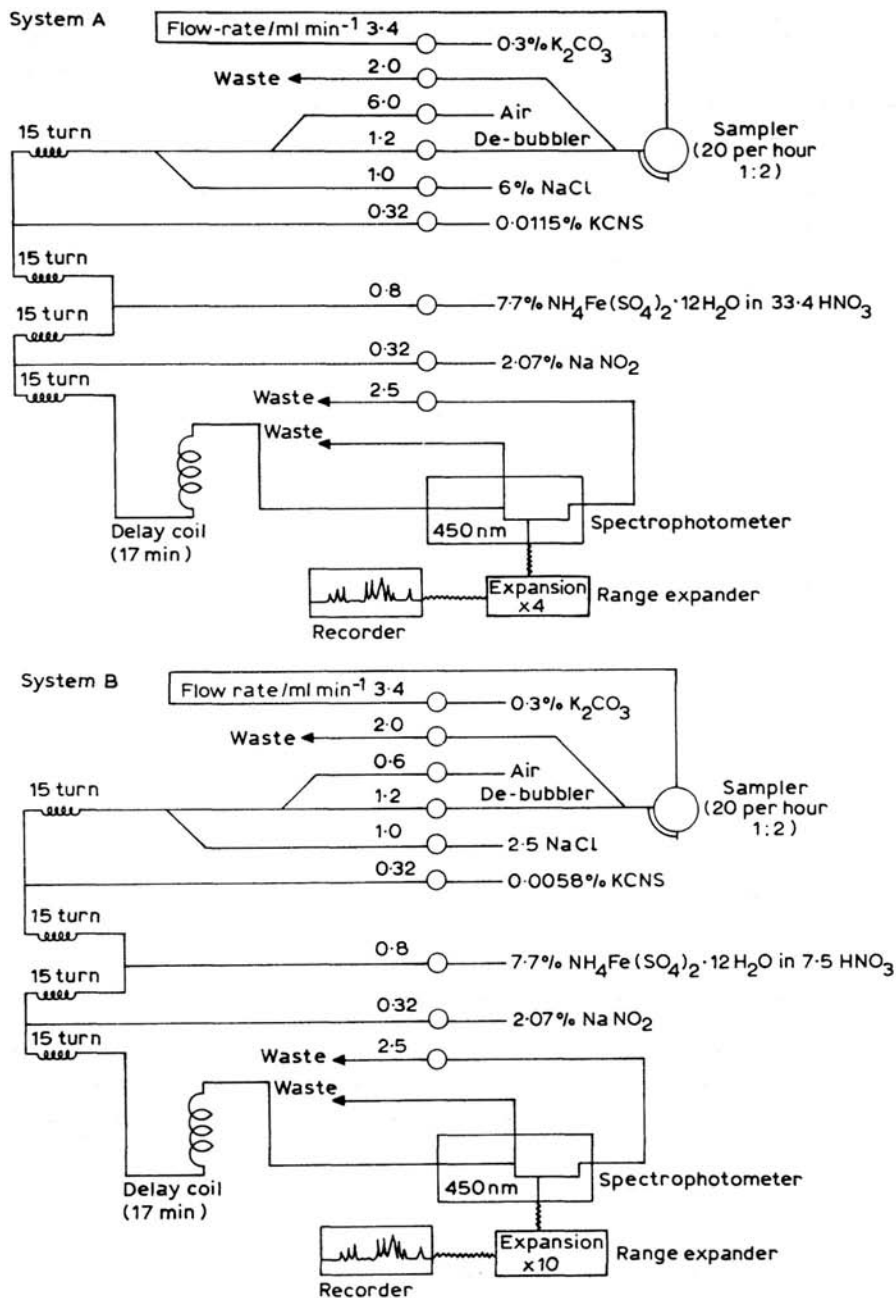


Fig. 4. Flow diagrams for the determination of total inorganic iodine in waters (system A) and free iodide in waters (system B).

better than 1 per cent. For concentrations of chlorate below 3.5 mg l⁻¹ potentiometric titration is recommended.

Miller et al¹⁹ have described two approaches to the determination of trace levels of chlorate ion based on the reaction of chlorate ion with iodide to produce iodine. High hydrochloric acid concentrations accelerated the reaction. Flow injection analysis, which excluded air from the flow stream, was used. The first method could detect chlorate ions at levels of 10 μM and the second method, using a stopped flow condition, could detect levels of 1 μM . Gordon²⁰ has described a procedure for the determination of down to 0.1 mg l⁻¹ of chlorite and hypochlorite by a modified iodometric technique.

1.1.7

Nitrate

Spectrophotometric methods

Spectrophotometric methods employing brucine²¹ and Devarda's alloy reduction to ammonia followed by Nesslerization²² and the use of dihydroxycoumarin²³ have all been employed for the determination of nitrate in water. Apart possibly, from the dihydroxycoumarin²³ method, which employs an ethyl acetate extraction step, none of these methods is sufficiently sensitive for the determination of nitrate in potable water. More recent spectroscopic methods for measurement of nitrate are based on measurements in the ultraviolet region.

Ultraviolet spectroscopy

This technique has been investigated by several workers²⁴⁻²⁶.

Rennie et al²⁵ describe a method for determining down to 6 $\mu\text{g l}^{-1}$ nitrate nitrogen in raw and potable waters which uses an activated carbon filter, at an elevated pH, to eliminate interference from organic matter. Interference from several cations that are precipitated out of solution is also removed by this system. The results obtained using the technique show that the method is precise.

Rennie et al²⁵ utilized absorbances at 210 and 275 nm to indicate the presence of nitrate and organic matter respectively. The absorbance at 275 nm was used as an indicator of the presence or absence of organic matter that could absorb also at 210 nm.

Although some workers have corrected measurements of nitrate made at 210 nm for organic absorbance based on measurements at or near 275 nm, this method of correction becomes decreasingly reliable when low nitrate contents are being measured. Hence, in the method described by Rennie et al²⁵, organic matter is completely removed from the sample prior to ultraviolet spectroscopy. This method is based on the observation that at pH values above 12 one particular grade of carbon black ADC 33 (Sutcliffe Speakman Co.) will adsorb 98–100 per cent of organic compounds from the water sample and, unlike many other grades of carbon black, will retain no nitrate. An analytical grade carbon filter paper (Schleicher and Schiill No. 58) was also satisfactory in this respect and permitted organics removal from the alkaline sample to be conducted in a filtration assembly. Nitrite interference is overcome by the presence of sulphamic acid in the mixed reagent.

The effects of certain concentrations of the adventitious contaminants are 210 nm equivalent to 0.02 mg l⁻¹ N is defined as the interference limit for the summarized in Table 2 and the concentration that gave an absorbance at method (denoted by a superscript 'a') in Table 2. The lack of an interference effect, compared with that found by direct UV spectrophotometry, of the sodium salt of dodecylbenzene-sulphonic acid is due to the effectiveness of removal of organic matter by the filter. Whereas iron II and iron III interfere significantly in direct UV methods, such interference is eliminated in this

TABLE 2
Interference effects

Interfering substance Species	Concentration (mg l ⁻¹)	Interference effect (mg l ⁻¹ N)	
		With carbon filtration	Without carbon filtration
Chloride (Cl ⁻)	2500 ^a	0.02	0.02
	5000	0.06	0.06
Bromide (Br ⁻)	1.0 ^a	0.02	0.02
	2.0	0.04	0.04
Iodide (I ⁻)	0.65 ^a	0.02	0.02
	1.30	0.05	0.05
Iron (Fe ²⁺)	13.5	<0.02	<0.02
	27	<0.02	0.08
	1000 ^b	<0.02	1.4
Iron (Fe ³⁺)	0.2	<0.02	>0.02
	0.4	<0.02	0.08
	1000 ^b	<0.02	1.75
Dichromate (Cr ₂ O ₇ ³⁻)	0.15a	0.02	0.02
	0.30	0.08	0.08
Manganese (Mn ²⁺)	100	<0.02	>0.02
	1000 ^b	<0.02	0.4
Dodecylbenzenesulphonic acid, sodium salt	3.5	<0.02	>0.02
	7.0	<0.02	0.06
	1000 ^b	<0.02	1.8

^a Indicates 'interference limit'.

^b Indicates highest concentration investigated.

method as a result of the formation of insoluble hydroxides at the elevated pH, the precipitates being removed by the GF/C paper on the filter. It is apparent that the interference effects of anions are not reduced by carbon treatment.

Continuous flow analysis

Thompson and Blankley²⁶ have described an automatic ultraviolet continuous flow determination of nitrate in raw and potable water. The method has a linear calibration range of 0–30 µg l⁻¹ nitrate N and a detection limit of 0.01 µg l⁻¹.

The incorporation of a dialysis membrane minimized the effect of humic acid type substances that did not freely diffuse through the membrane, and also avoided the necessity to filter water samples prior to measurement.

The method requires no sample pre-treatment or dilution. It utilizes a conventional dialysis membrane to minimize interference effects from suspended, colloidal and organic matter. Excellent precision is obtained by this procedure.

The dialysis membrane minimized the ultraviolet absorption interference from organic matter present in water as the efficiency of transfer of this matter through the membrane was significantly lower than that of nitrate ions. The nitrate concentrations of three highly coloured raw Pennine waters were determined by the conventional continuous-flow reduction method²⁷ and the manual nitrate method²⁸ (using unfiltered samples) and the above dialysis method. The results show that the dialysis method eliminates the ultraviolet absorption contribution from organic matter observed with the manual method and that there is good agreement between the dialysis method and the continuous-flow reduction method. The manual method (no dialysis) is prone to very significant positive interference from the naturally occurring organic matter.

The interference effect of other substances is given in Table 3 and it can be seen that the method is relatively free of interference effects for its intended uses. There was a small positive bias from chromium VI, acetone and humic acid, a somewhat larger bias from fulvic acid and the benzoate ion. However,

TABLE 3

Effect of other substances on nitrate. If other substances did not interfere, the results would be expected (95 per cent confidence) to be in the following ranges: $10.00 \pm 0.33 \mu\text{g ml}^{-1}$ and $0.00 \pm 0.05 \mu\text{g ml}^{-1}$. Negligible interference was observed from the presence of Ca ($200 \mu\text{g ml}^{-1}$), Mg ($200 \mu\text{g ml}^{-1}$), K ($200 \mu\text{g ml}^{-1}$) and NH_4 ($100 \mu\text{g ml}^{-1}$ N); all present as chlorides

Substance	Concentration $\mu\text{g ml}^{-1}$)	Added as	Measured nitrate concentration ^a ($\mu\text{g ml}^{-1}$ of N)	
Cl	1000	NaCl	10.19	0.02
SO ₄	1000	Na ₂ SO ₄	10.09	0.00
PO ₄ (as P)	5	KH ₂ PO ₄	9.74	0.01
F	5	NAF	9.70	0.00
Humic acid	250	—	10.15	0.33
Fulvic acid	250	—	11.58	1.36
Fe(II)	10	FeSO ₄	10.27	0.06
Fe(III)	10	FeCl ₃	9.89	0.00
NO ₂ (as N)	50	NaNO ₂	10.01	0.00
Cr(VI)	10	K ₂ Cr ₂ O ₇	9.85	0.13
Persil ^b	10	—	9.85	0.00
Al	2	Al ₂ (SO ₄) ₃	9.76	0.00
Mn	2	MnSO ₄	9.92	0.02
I	5	KI	10.03	0.00
Br	5	KBr	10.17	0.00
Glucose	100	—	9.98	0.00
Acetate	100	CH ₃ COONa	10.25	0.00
Benzoate	100	C ₆ H ₅ COONa	10.25	4.62
Acetone	100	—	14.80	0.45
			10.75	

^a Results in the first column have an added nitrate concentration of $10 \mu\text{g ml}^{-1}$ of N.

^b Proprietary detergent.

the interference tests were carried out at concentrations of these determinands considerably in excess of levels likely to be encountered in potable natural waters.

Miscellaneous

Nitrate has been determined by a nitrate selective electrode²⁹ consisting of a porous polymer wick sealed with liquid ion-exchanger (tris(4,7-diphenyl-1,10-phenanthroline) nickel II in 2-nitro-*p*-cymene). Chloride and bicarbonate interferences are overcome by the addition of silver sulphate and 0.5 M phosphate buffer, pH 2 respectively.

Marecek et al³⁰ investigated the feasibility of using a hanging drop electrode for the determination of nitrate, perchlorate, and iodide in potable water. A 3-electrode system was used with a polarographic analyser. The potential range of the method was increased by using crystal violet dicarbollycobaltate electrolyte in the nitrobenzene phase and magnesium sulphate in the aqueous phase, with a lead/lead sulphate reference electrode.

A nitrogen-15 isotopic tracking method has been used³¹ to identify the origin of nitrates of some aquifers in the Paris basin.

High performance liquid chromatography

Schroeder³² determined nitrate in potable water using high performance liquid chromatography with a reversed phase octadecyl C18 column using aqueous phosphoric acid and dihydrogen phosphate as a mobile phase and UV detection. Detection limits were $7 \mu\text{g l}^{-1}$.

1.1.8

Nitrite and nitrate

Spectrophotometric method

NITRITE: 3,3'-dimethylbenzidine has been used as a chromogenic reagent for the determination of down to $5 \mu\text{g l}^{-1}$ nitrite N in potable water. Spectrophotometric measurements are carried out at $437 \mu\text{m}$ ³³. Iron and copper interfere in this procedure. Two modifications have been described³⁴ of the Griess-Ilosvay method for determination of nitrites in drinking water. The first is based on modification of the reaction between the diazonium salt of aniline-4-sulphonic acid with *N*-phenyl-1-naphthylamine-8-sulphonic acid. The second is based on the reaction of the diazonium salt of aniline-4-sulphonic acid with *N*-ethyl-1-naphthylamine. The first produces a red violet coloration measured photometrically at 554 nm and the second a red coloration measured at 537 nm. Absorbance increased linearly over the range $1-3 \mu\text{g l}^{-1}$ of sample. Both methods were equally suitable for the determination of nitrites.

NITRITE AND NITRATE: Zhou and Xie³⁵ give details of a rapid spectrophotometric method for the determination of traces of nitrite and nitrate in water. In this method, nitrate is quickly reduced to nitrite at pH 3.0 in 5 min with freshly prepared cadmium sponge, which is produced in-situ by the action of zinc powder in a dilute solution of cadmium chloride in the presence of ammonium chloride. At pH 2.0, nitrous acid diazotizes with *p*-aminoacetophenone, which is then coupled with *N*-(1-naphthyl)-ethylene-diamine. The azodye formed is extracted into *n*-butanol at pH 2.0 in the presence of 1-naphthyl sulphonic acid and aluminium nitrate. The absorbance is measured at 550 nm. The molar absorptivity of the extract is about $4.8 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$. The ions normally present in water do not interfere when sodium metaphosphate is added as a masking agent.

Differential pulse polarography

Barsotti et al³⁶ determined nitrate in amounts down to $0.4 \mu\text{g l}^{-1}$ N and nitrate by this technique. Nitrate is reduced on a cadmium column to diphenylnitrosamine and then determined polarographically. Cadmium interference is removed by adjustment of pH and complexing with EDTA. Nitrite is determined directly as the diphenylnitrosamine.

In order to separate the cadmium II peak from that of diphenyl nitrosamine, advantage was taken of the fact that organic polarograms are usually pH dependent, while those of reversible inorganic ions are not. Changing the pH from 1.0 to 4.0 shifts the diphenyl nitrosamine peak, without loss of peak height, hence sensitivity, but causes no change in the cadmium II peak. A pH of 1.0 is used for the formation of diphenyl nitrosamine since the rate is fast at that pH with no decomposition. At a pH of 4.0 a peak separation of 140 mV occurs which is sufficient to determine nitrite ion in the presence of cadmium II to a level of approximately $200 \mu\text{g l}^{-1}$. At this pH the EDTA complex of cadmium II has a stability constant of approximately 10^{16} . Thus, the addition of EDTA at a pH of 4.0 results in the complete disappearance of the cadmium II peak and total removal of any interference. Therefore, by an adjustment of pH and the addition of EDTA to the nitrite ion procedure, nitrate could be determined.

Gas chromatography

A method has been described^{37,38} for determining aqueous nitrates by conversion to nitrobenzene followed by electron capture gas chromatography. The procedure can also be used to determine aqueous nitrites and gaseous oxides of nitrogen if they are first converted to nitrates. The procedure was evaluated by analysing drinking water for nitrate over a period of one month. The method is sensitive and capable of measuring typical environmental levels of nitrogen compounds. The detection limit for nitrobenzene is about 10^{-12} g.

Ion-exchange chromatography

Gerritse³⁹ separated nitrate and nitrite on a cellulose anion-exchanger column and detected them in a spectrophotometric flow through cell at 210 nm. The detection limit was $1\text{--}5 \mu\text{g l}^{-1}$ as nitrogen with a sample volume of $100\text{--}200 \mu\text{l}$ and the linear range extends up to 20mg l^{-1} as nitrogen.

A stainless steel column (SS 316) of length 30 cm and i.d. 0.3 cm was filled with a mixture of Kieselguhr and Ecteola ET 41 cellulose anion exchanger (Whatman: W & R Balston, Maidstone, Great Britain). The eluent used was 0.03 M potassium sulphate solution and 0.01 M Tris buffer at pH 7 in water.

A ratio of Kieselguhr to Ecteola of 1:2 (by weight) was used. The column was operated at a pressure of 40 bar. The eluant was monitored with a Cecil CE-212 spectrophotometric flow through detector at a wavelength of 210 nm. The temperature of the column was ambient. Samples were injected with the aid of a sample injection valve (Valvo C20) using a sample loop of $60 \mu\text{l}$.

Examples of chromatograms of potable water and of sludge solution resulting from aeration of anaerobically digested sewage sludge are shown in [fig. 5](#). The sludge was centrifuged at $40\,000 \text{g}$ for 1 hour, then the supernatant was diluted 1:100 with distilled water and injected into the column. Potable water was injected undiluted. Without dilution, samples with concentrations of up to 20mg l^{-1} each (as nitrogen) of nitrite and nitrate could be injected.

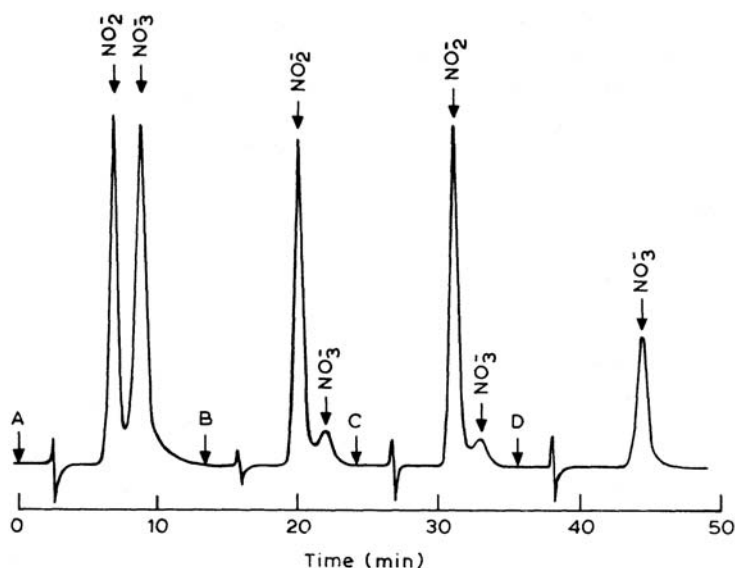


Fig. 5. Chromatograms resulting from the injection of samples containing nitrate and nitrite into a mixed bed column containing Kieselguhr and Ecteola ET 41 cellulose anion exchanger. Eluant: 0.03 M K_2SO_4 , 0.01 M Tris buffer (pH 7); A. Standard mixture containing 1.4 mg l^{-1} as nitrogen of both nitrite and nitrate (attenuated 0.1); B, sewage sludge sample, diluted 1:100 containing 2.7 mg l^{-1} as nitrogen of nitrite and 0.35 mg l^{-1} as nitrogen of nitrate (attenuation 0.2); C, sewage sludge sample, diluted 1:100 containing 1.4 mg l^{-1} as nitrogen of nitrite and 0.1 mg l^{-1} as nitrogen of nitrate (attenuation 0.1); D, potable water containing 0.45 mg l^{-1} as nitrogen of nitrate (attenuation 0.1).

1.1.9

Phosphate and arsenate

Matsubara et al⁴⁰ determined trace amounts of phosphate and arsenate in potable water by spectrophotometric detection at 627 nm of their heteropoly acid-malachite green aggregates following preconcentration by nitrocellulose membrane filtration.

1.1.10

Silicate

Polarographic method

Iyer et al⁴¹ converted trace amounts of silica in potable water to silicomolybdate by addition of ammonium molybdate, followed by methylethylketone to ensure that only the beta form of silicomolybdate was present. Buffering with citrate masked any phosphate or excess molybdate. The initial potential of the hanging mercury drop electrode was kept at -0.2 V for 2 min and silicomolybdate accumulated by adsorption in the interface. Its bulk concentration was determined by measuring the peak height at -0.36 V . The reduction of the silicomolybdate gives a well defined peak at -0.36 V , followed by reduction of the molybdate ion at -0.52 kV . With increasing the concentration of silica only the first peak at -0.36 V increased linearly unlike that of the second peak.

1.1.11 *Sulphate*

Nephelometry⁴², flow injection⁴³ analysis and atomic absorption^{44,45} spectroscopy have been applied to the determination of sulphate in potable waters.

Nephelometric method

Regnet and Quentin⁴² describe a nephelometric method for determining up to 50 mg l⁻¹ sulphate in which a suspension of barium sulphate is produced by addition of a specially prepared barium chloride reagent, and the turbidity measured at 490 nm after a reaction time of 45 min. The calibration curve can be considered as made up of two linear portions of different slope, which intersect at about 30 mg l⁻¹ sulphate ion. The procedures for calibration and determination, taking about 2 hours are outlined. Other ionic constituents do not interfere at concentrations normally encountered, nitrate can cause discrepancies if present in excess of 100 mg l⁻¹.

Van Staden⁴³ reported the application of an active pre-activated carbon filter, for the turbidimetric determination of sulphate in potable waters. The filter is incorporated into an automatic flow injection system, between the sampler and the sampling valve system, to remove suspended and coloured materials which interfere with the spectrophotometric determination of turbidity. The method has been applied to the analysis of sulphate at concentrations up to 200 mg l⁻¹ at a sampling rate of up to 60 samples per hour, with a coefficient of variation less than 1 per cent. The accuracy is similar to that of a standard automated segmented method and standard flow injection methods.

Atomic absorption spectrometry

Montiel⁴⁴ reacted sulphate in a buffered medium with excess standard barium chloride. Unreacted barium was then determined by atomic absorption spectrometry at 553.55 μm and the concentration of sulphate in the sample calculated. Errors due to the presence of alkali and alkaline-earth metals are corrected for by the incorporation of calcium in the standard solution and by the presence of sodium in the buffer solution.

Siemer et al⁴⁵ determined sulphate in potable waters by non-resonance line furnace atomic absorption spectroscopy. Direct sulphur determination is not routinely performed by flame or non-flame atomic absorption because of difficulties associated with the use of the far-UV resonance lines of that element. Therefore, efforts were directed at precipitation of the sulphate with a metal ion followed by determination of the metal retained on a porous graphite filter after washing off excess precipitant. Siemer et al⁴⁵ discovered that non-resonance atomic absorption at 405.7 nm of the lead in a lead sulphate precipitate served the purpose.

At a furnace temperature of 1550°C lead sulphate gives reasonable absorbance values for the amounts of sulphate in potable water. From 50 to 75 per cent of ethyl alcohol was incorporated during the lead sulphate precipitation and washing steps to decrease solubility errors. An excess of lead ions was added to the sample in this medium and excess lead ions determined.

Flow injection analysis

Koch⁴⁶ modified the standard ASTM 15/84 (Techstar) flow injecting method for the determination of sulphate in potable water by adding methyl thymol blue to barium ions in an alkaline alcoholic solution to

produce a blue complex with absorption maximum at 620 μm . Sulphate precipitated out of the barium sulphate complex resulting in a loss of coloration which was measured photometrically.

1.1.12 *Selenate*

Fluorimetric method

Selenate has been determined in potable water fluorimetrically using naphthalene-2,3-diamine⁴⁷. The complex is extracted into cyclohexane and evaluated at 521 nm (excitation 389 nm). The calibration graph is rectilinear in the range 0.02–1.0 μg of selenium. The coefficient of variation for samples containing 0.5 and 1.0 ng of selenium was 6.3 per cent and a 1000 fold excess of nitrate, barium, cadmium, calcium, chromium III, cobalt, copper II, iron III, magnesium, manganese II, nickel II or zinc did not interfere.

1.1.13 *Sulphite and cyanide*

Goodwin et al⁴⁸ determined traces of sulphite in clear or turbid potable waters by a procedure based on gas dialysis/ion chromatography. The detection limit was 2 $\mu\text{g l}^{-1}$. Ascorbic acid was required as an antioxidant to obtain good recoveries for potable and well waters.

Jovanovic and Jovanovic⁴⁹ determined low levels of sulphide and cyanide using a deposited on wire silver-silver sulphide electrode.

1.2 **Cations**

1.2.1 *Aluminium*

Spectrophotometric methods

A British Standard method⁵⁰ is based upon the formation of a blue coloured complex by reaction with pyrocatechol violet in a suitably buffered solution and spectrophotometric measurement at 585 nm. Interference due to iron is avoided by the addition of 1,10-phenanthroline/hydroxyammonium chloride reagent which converts this metal to a stable ferrous iron chelate. Acidification of samples is normally sufficient to convert different forms of aluminium to those capable of reacting with the chromophore, although some samples may require more rigorous treatment. For fluoridated potable waters a specially prepared calibration curve is required. The method is applicable over the range 0–0.3 mg l^{-1} with a limit of detection of 0.013 mg l^{-1} aluminium.

Narayanan and Pantony⁵¹ have described a procedure for the determination of traces of aluminium in water by spectrophotometry after extraction with 8-quinolinol. Other metal ions which interfere with this method are removed by preliminary extraction using 2-iso-propyl-8-quinolinol.

The standard deviation of this method in each of the concentrations ranges 10–36, 36–50, and 50–103 $\mu\text{g l}^{-1}$ of aluminium was 4 $\mu\text{g l}^{-1}$. The method has a better precision than the catechol violet method at

comparable levels. It can detect aluminium as low as $10 \mu\text{g l}^{-1}$ although the relative error with respect to aluminium at this level would be ± 40 per cent. Such an error can be expected in view of the low concentration determined.

Spectrofluorimetric method

Rojas et al⁵² used *N*-(-3-hydroxy-2-pyridyl) salicylaldehyde as a reagent for the determination of 3.5–400 $\mu\text{g l}^{-1}$ aluminium in potable water.

Atomic absorption spectroscopy

Prayle et al⁵³ described a graphite furnace atomic absorption method for determining down to $50 \mu\text{g l}^{-1}$ aluminium in water and compared results with those obtained by the ferron spectrophotometric method⁵⁴ and the lumogallion spectrofluorimetric methods^{55–58}.

It was found that standard additions generally gave more reliable results than calibrations against a standard curve. The ferron method gave unreliable results below about $50 \mu\text{g l}^{-1}$ aluminium. The lumogallion and a.a.s. methods yielded similar results and when a large difference between the two methods occurred, it may have been because atomic absorption spectrometry measures total aluminium while the lumogallion method does not measure unreactive aluminium.

Many interferences on the lumogallion method occur only at high concentrations not often found in potable water. Sulphate, phosphate, and silicate do not interfere at molar concentrations of up to 100 times that of the aluminium.

No interference with the lumogallion method was found from up to 2.7 mg zirconium VI added to a solution of $80 \mu\text{g}$ aluminium. Titanium IV at greater than 0.48 mg l^{-1} , gave apparent concentrations 5 per cent higher than aluminium standards. Humic acid contributes about 0.5 per cent aluminium by dry weight to a sample through contamination but does not interfere through fluorescence on its own or with lumogallion.

Fluoride concentrations of 0.1, 1.0, and 3.8 mg l^{-1} added to $50 \mu\text{g l}^{-1}$ aluminium standards resulted in apparent aluminium concentrations of 48, 28 and $9 \mu\text{g l}^{-1}$ respectively. Iron concentrations above $170 \mu\text{g l}^{-1}$ interfered above $50 \mu\text{g l}^{-1}$ aluminium. This interference can be overcome by diluting a sample so that the aluminium concentration is less than $50 \mu\text{g l}^{-1}$. Manganese and zinc at concentrations up to 220 and $70 \mu\text{g l}^{-1}$ respectively increased the apparent aluminium concentrations by a maximum of only $1 \mu\text{g l}^{-1}$ in the range $10\text{--}50 \mu\text{g l}^{-1}$ aluminium.

Iron interference with the ferron method is corrected by the addition of 1,10-phenanthroline after reduction of iron III. Manganese and fluoride and other ions create small interferences.

Detection limits between 0.05 and $0.1 \mu\text{g}$ aluminium l^{-1} have been reported for the lumogallion method^{50–53}. The signal was linear up to about $120 \mu\text{g}$ aluminium l^{-1} . The lower limit of usefulness of the ferron method was about $50 \mu\text{g}$ aluminium l^{-1} and the linear range was $50\text{--}1500 \mu\text{g l}^{-1}$.

Carrondo et al⁵⁹ have described a direct electrothermal atomic absorption method for the determination of aluminium in potable water, waste water and sewage. For flame analysis they used an atomic absorption spectrometer with a deuterium background correction and a nitrous oxide acetylene reducing flame. To suppress the ionization, samples and standards were made up to 2 mg l^{-1} in potassium chloride. For electrothermal analysis they used a heated graphite atomizer with argon as the inert gas. The conditions were: sample injected, $20 \mu\text{l}$, drying 100°C for 30 s, two stage ashing from 100°C to 400°C in 45 s followed by electrothermal ashing at 1200°C for 30 s, atomization at 2770°C for 8 s. The 257.5 nm line was used.

Using this method it was found that a potable water containing $20 \mu\text{g l}^{-1}$ aluminium after spiking with $1050 \mu\text{g l}^{-1}$ aluminium gave a result of $1030 \mu\text{g l}^{-1}$ aluminium, i.e. a recovery of 96 per cent. Relative standard deviations were always less than 7 per cent.

The atomic absorption spectrometry of aluminium is also discussed in [section 1.2.31](#) (multi-cation analysis).

Miscellaneous

The Standing Committee of Analysts (UK)⁶⁰ have reviewed methods for the determination of acid soluble aluminium in raw and potable waters.

Preconcentration

Aluminium has been preconcentrated as its Chrome Azurol S-3 ephiramine complex on a membrane filter prior to its spectrophotometric determination. Down to $2 \mu\text{g l}^{-1}$ aluminium could be determined by this procedure⁶¹.

Sarzanini et al⁶² compared two ion-exchange methods for the preconcentration of aluminium from potable water. In the first method, the aluminium pyrocatechol blue complex was formed then eluted through a anion-exchange column. In the other the pyrocatechol was loaded onto the resin then the sample passed through the column. The fast method gave the better recovery of aluminium.

1.2.2

Antimony

The determination of antimony is discussed in [section 1.2.31](#) (multi-cation analysis).

1.2.3

Arsenic

Miscellaneous

Spectrophotometry⁶³⁻⁶⁵, polarography⁶³ and atomic absorption spectroscopy have all been employed to determine arsenic in potable waters. Nyamah and Torgbor⁶³ described a spectrophotometric method based on the reaction of pentavalent arsenic with potassium iodide in the presence of sulphuric acid to release an equivalent amount of iodine which gave a pink colour to a carbon tetrachloride extract; the colour was then measured at 515 nm. No interference was caused by trivalent arsenic, trivalent iron, hexavalent chromium, or tetravalent lead. The limit of detection was $5 \mu\text{g l}^{-1}$.

Coprecipitation with ferric hydroxide followed by spectrometry of the silver diethyldithiocarbamate complex⁶⁵ has been used to determine $1 \mu\text{g l}^{-1}$ arsenic in potable water. Linear sweep cathode ray polarography⁶⁶ has been used to determine down to $5 \mu\text{g l}^{-1}$ arsenic in well water.

Schmidt and Royer⁶⁷ determined down to $0.1 \mu\text{g l}^{-1}$ arsenic, also selenium, antimony and bismuth, in potable water using a sodium tetrahydroboride based hydride generation atomic absorption method.

Other methods used to determine arsenic in multi-cation mixtures include atomic absorption spectrometry, hydride generation atomic absorption spectrometry and hydride generation inductively coupled plasma atomic emission spectrometry ([section 1.2.31](#)).

1.2.4 Barium

Atomic absorption spectrometry

Kubota⁶⁸ determined barium in potable waters by carbon furnace atomic emission spectrometry.

The atomic absorption spectrometry of barium is also discussed in [section 1.2.31](#) (multi-cation analysis).

1.2.5 Beryllium

Atomic absorption spectroscopy

Korkisch et al⁶⁹ determined beryllium after separation by solvent extraction and cation exchange. The beryllium was first isolated from natural waters by chloroform extraction of its acetylacetonate from a solution at pH 7 and containing EDTA. The chloroform extract was then mixed in the ratio of 3:6:1 with tetrahydrofuran and methanol containing nitric acid and passed through a column of Dowex 50×8 (H⁺ form). After removal of acetylacetone, chloroform and tetrahydrofuran by washing the resin bed with methanol-nitric acid, beryllium was eluted with 6 M hydrochloric acid and determined by atomic absorption spectroscopy.

In this method only iron and copper are coeluted with beryllium and these do not interfere in the atomic absorption determination. The detection limit is 0.01 $\mu\text{g l}^{-1}$. Up to 2.3 $\mu\text{g l}^{-1}$ beryllium was found in potable water samples.

The atomic absorption spectrometry of beryllium is also discussed in [section 1.2.31](#) (multi-cation analysis).

Gas chromatography

Kuo et al⁷⁰ determined down to 2×10^{-11} g (0.02 $\mu\text{g l}^{-1}$) of beryllium in potable water by gas chromatography with electron capture detection. After mixing with an ethanolic solution of *N*-trifluoroacetylacetone the Be(TFA)₂ complex formed is extracted with cyclohexane. To the excess of free *N*-trifluoroacetylacetone is added sodium bicarbonate solution with shaking for at least 15 s. The pH must be above 7.5, preferably in the range 8.5–9.0. Deionized water showed no detectable levels of beryllium, while Taiwan tap water had a level of 0.18 $\mu\text{g l}^{-1}$.

The peak height of Be(TFA)₂, at a retention time of 1.9 min, was taken for the quantitative determination of beryllium as shown in [fig. 6\(a\)](#). In the chromatogram ([fig. 6\(b\)](#)) the solvent peak of cyclohexane (retention time ca. 1 min) was a tailing that resulted from incomplete removal of free HTFA, in which a random determination would be obtained. The calibration curve of Be(TFA)₂ was obtained from the measurement of standard aqueous solutions or standard solutions of Be(TFA)₂ in cyclohexane.

Data for unknown samples were calculated by the known addition method. It was performed by adding an appropriate amount of Be(TFA) standard solution (Be, 0.26 mg l⁻¹) to 1 ml of the final organic extractants.

Low recovery, due to the interference of the fluoride ion seriously interferes with the determination of beryllium.

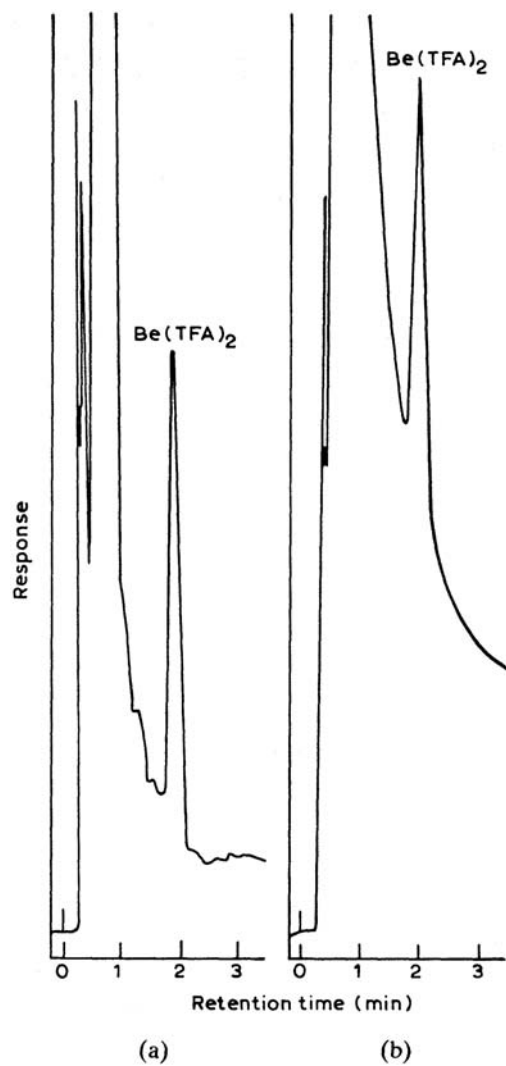


Fig. 6. Chromatograms of $\text{Be}(\text{TFA})_2$ in cyclohexane medium; (a) peak of $\text{Be}(\text{TFA})_2$ with complete washing at 1.9 min retention time; (b) tailing peak for incomplete removal of free HTFA.

1.2.6 *Bismuth*

The determination of bismuth is discussed in [section 1.2.31](#) (multi-cation analysis).

Preconcentration

See [section 1.2.32](#).

200–450 $\mu\text{g l}^{-1}$ bismuth have been determined⁷¹ by sorbing the coloured bismuth iodide complex on to a polyether polyurethane foam and measuring its net absorbance at 495 and 600 nm against a blank foam in benzene. Copper and silver ions interfere in this procedure.

1.2.7

Cadmium

The determination of cadmium is discussed in [section 1.2.31](#) (multi-cation analysis).

Preconcentration

Cadmium has been preconcentrated by extraction of its ammonium pyrrolidine dithiocarbonate into methyl isobutyl ketone followed by determination by atomic absorption spectrometry.⁷²

Jha et al⁷³ investigated the efficiency of removal of cadmium from potable water using chitosan. Studies with potable water showed that cadmium removal capacity was not affected by the presence of calcium, bicarbonate or chloride ion.

The preconcentration of cadmium is also discussed in [section 1.2.31](#) (multi-cation analysis).

1.2.8

Calcium and magnesium

Titration methods

Christiansen et al⁷⁴ carried out a successive titration of calcium and magnesium in potable water using an indicator electrode sensitive to the calcium ion and EDTA as the titrant in a solution containing 3,4-dihydroxybenzoic acid or acetylacetone. In this solution, the ratio between EDTA's conditional stability constants for calcium and magnesium is increased, so that two pronounced inflection points are obtained on the titration curve. The inflection points are determined in a stepwise computer-controlled titration.

Spectrophotometric method

Ishizuki et al⁷⁵ give details for the preparation of a new reagent, 2-(2-(8-hydroxyquinolyl)azo-1-naphthol) for the spectrophotometric determination of calcium in potable water at 610 nm. The reagent formed a soluble complex with calcium in 50 per cent (v/v) dioxane/water at pH greater than 8.5. It also formed complexes with other divalent cations, but such interference could be avoided except for manganese, by adjusting pH or adding masking agents.

Flow injection analysis

Canete et al⁷⁶ simultaneously determined calcium and magnesium in potable water by flow injection analysis with spectrophotometric detection.

The determination of magnesium by flow injection analysis is also discussed in [section 1.2.31](#) (multi-cation analysis).

Atomic absorption spectrometry

Basson and Van Staden⁷⁷ have described a simple, rapid, automated procedure for the simultaneous determination of sodium, calcium and potassium in water. The sample is inserted automatically into an apparatus containing a carrier stream, a lithium nitrate/caesium chloride reagent solution, a sodium/potassium flame photometer and a calcium/magnesium atomic absorption apparatus. The flow injection sampler has a capacity of 128 samples per hour and a peristaltic pump is used to circulate solutions.

The application of atomic absorption spectrometry and energy dispersive X-ray fluorescence spectrometry to the determination of calcium in potable waters is discussed in [section 1.2.31](#) (multi-cation analysis).

Ion selective electrodes

Wada et al⁷⁸ have described the preparation of calcium ion selective electrodes for use as detectors in flow through cells of flow injection analysis systems.

1.2.9

Chromium

Atomic absorption spectrometry

Workers at the Department of the Environment UK⁷⁹ have described two methods for the determination of chromium in potable and raw waters and sewage. The first method is based on fivefold concentration of the sample by evaporation followed by atomic absorption spectrophotometry. The second method is based on the formation of a coloured complex with diphenylcarpotable waters, up to a maximum chromium concentration of $100 \mu\text{g l}^{-1}$ while baziide and determination of the absorption at 540 nm; it is suitable for raw and the first method can be employed up to $400 \mu\text{g l}^{-1}$.

Thompson and Wagstaff⁸⁰ have described an atomic absorption spectrophotometric method for chromium designed to meet the World Health Organization and EEC requirements for a method capable of determining down to $50 \mu\text{g l}^{-1}$ chromium in potable water and waters intended for the abstraction of potable water.

This method utilizes a concentration by evaporation technique, in which ammonium perchlorate is incorporated into the sample solution in order to minimize inter-element effects from the sample matrix. The determination is carried out in an air-acetylene flame.

Automatic background correction at the 357.9 nm chromium line is not recommended as balancing the hydrogen and chromium lamp intensities at this wavelength is not easy and a severely degraded chromium detection limit is normally observed. Sequential background correction using the lead 357.3 nm non-resonance line was used and found to be satisfactory. The presence of sulphate significantly enhances the background absorption from calcium and magnesium. However, the background absorption signals for most natural water and sewage effluent samples are relatively small.

Aliquots of a potable water sample, were spiked with equal amounts (40 and $400 \mu\text{g l}^{-1}$) of chromium III and chromium VI and taken through the procedure, and no significant difference in response for the two oxidation states was detected.

The atomic absorption spectrometry of chromium is also discussed in [section 1.2.31](#) together with the applications of energy dispersive X-ray fluorescence spectrometry and proton induced X-ray emission spectrometry.

Preconcentration

See [section 1.2.32](#).

1.2.10

Cobalt

The determination of cobalt by energy dispersive X-ray fluorescence spectrometry is discussed in [section 1.2.31](#) (multi-cation analysis).

Preconcentration

See [section 1.2.31](#).

1.2.11

Copper

Spectrophotometric methods

Jardim and Rohwedder⁸¹ determined copper in potable waters by adding sodium tetraborate buffer solution (0.01 M, 5 ml) and hydroxylamine solution (0.1 M, 0.3 ml) to 10 ml of water. A suitable period of time was allowed for copper II ion catalysed oxidation of hydroxylamine to nitrite. Final nitrite concentrations were then measured spectrophotometrically. Absorbances at 540 nm were converted to concentrations using a calibration curve. For total copper determinations, the water samples were digested prior to analysis by adding concentrated nitric acid. Using differential pulse anodic stripping voltammetry the total copper found in a sample of potable water was 0.494 plus or minus 0.06 μmol , whereas using the catalytic reaction, the value obtained was 0.43 plus or minus 0.01 μmol .

Themelis and Vasilikiotis⁸² determined traces of divalent copper using the catalytic effect of copper on the oxidation of chromotropic acid by hydrogen peroxide and spectrophotometric measurement of the rate of change of absorbance at 430 nm. Copper concentrations in the range 12–200 $\mu\text{g l}^{-1}$ could be measured.

Zeeman atomic absorption spectrometry

Atsuya et al⁸³ carried out studies on the effect of various factors on the determination of copper by atomic absorption spectrometry in a graphite cup type furnace and optimal conditions to minimize the effects of these variables were established. These workers showed that copper can be determined in tap water after co-precipitation with lead sulphide.

In particular, Atsuya et al⁸³ discuss the effects of hydrochloric acid and large amounts of iron under various heating conditions on the atomic absorption spectrometric determination of copper with a graphite cup-type furnace.

These effects of up to 1000 mg l⁻¹ iron on the absorbance of copper varied with change of drying temperature and carrier gas flow rate, when the ashing

TABLE 4

Effect of other metals (10 ppm) on results for 0.20 ppm copper in 1 M HCl

Element	Al	Cd	Co	Cr	Fe	Mn	Ni	Pb	Zn
Recovery (%)	102 ^a	101	102	98	99 ^b	98	103	99	101

^a Relative standard deviation of 1.94 ($n=5$).

^b Relative standard deviation of 0.88 ($n=5$).

temperature was fixed at 700 or 800°C. However, these effects were eliminated when the ashing temperature was fixed at 800°C or 900°C with a 20 ml min⁻¹ carrier gas flow.

The results in Table 4 show that under the conditions used in this procedure a wide range of metals do not interfere in the determination of copper.

Down to 10 µg l⁻¹ copper can be determined by this procedure.

Ion-selective electrodes

Standard addition potentiometry using a copper selective electrode has been used⁸⁴ to determine copper at the µg l⁻¹ level in potable water.

Hulanicki et al⁸⁵ determined copper in potable water by means of a chalcocite copper ion selective electrode. This electrode is based on a cuprous sulphide membrane. Determinations can be carried out down to 6 µg l⁻¹ when the standard addition procedure is used. These workers used a TFB (tris fluoride) buffer consisting of 0.02 M tris (2-amino-2-hydroxymethyl-propanediol-1,3), 0.1 M potassium nitrate and 0.02 M potassium fluoride. After mixing this buffer with the sample the initial pH being 9.3–9.7 was adjusted to 7 with nitric acid.

Appreciable errors in copper determinations below 25 µg l⁻¹ were observed by this procedure unless the solution was boiled prior to measurement. At pH 7 any iron in the sample should be masked by hydroxide ions but this process is probably slow and may be made more effective when the solution is heated to boiling before measurements. Without boiling the results show a large scatter and they have as a rule a positive error of several hundred per cent. In the heated samples, the precision is only slightly better, but no systematic error occurs.

All results were obtained in this procedure by the standard additions technique.

The determination of copper is also discussed in section 1.2.31 (multi-cation analysis).

Preconcentration

See section 1.2.32.

1.2.12 *Gallium*

Fluorescence spectrometry

Derivative synchronous fluorescence spectrometry using salicylaldehyde thiocarbohydrazone as the reagent has been used to determine down to $2 \mu\text{l}^{-1}$ gallium (and $20 \mu\text{g l}^{-1}$ zinc) in potable water⁸⁶.

Pozo et al⁸⁷ simultaneously determined gallium and zinc in potable water by derivative synchronous fluorescence spectrometry using salicylaldehyde thiosemicarbazone. Peak to peak measurements were made at 400–450 nm (zinc).

1.2.13 *Iron*

Spectrophotometric method

Rychkova and Rychkov⁸⁸ have described a semi-automated kinetic method for the determination of iron in potable water. This is based on the observation that at pH 4.2–5.2 and in the presence of 2,2'-bipyridyl, ferric iron catalyses the oxidation of o-toluidine with potassium iodate and produces a violet colour with a maximum absorption at 540 nm. The rate of reaction is rectilinearly proportional to the concentration of ferric iron between 0.5 and $50 \mu\text{g l}^{-1}$. The reaction rate is determined from extinction measurements at various time intervals. In this method the concentration of manganese II and manganese VII must be less than $30 \mu\text{g l}^{-1}$ and that of chromium below $100 \mu\text{g l}^{-1}$. Three fold excesses of sodium, calcium, magnesium, copper, zinc, aluminium, nickel, cobalt, chloride or sulphate do not interfere.

Zotou and Papadopoulos⁸⁹ determined down to $1 \mu\text{g l}^{-1}$ iron by a technique based on the catalytic effect of iron on the oxidation of 3,5-diaminobenzoic acid and dihydrochloride by hydrogen peroxide and spectrophotometric measurement of the rate of change of absorbance with time at 540 nm.

The determination of iron by energy dispersive X-ray fluorescence spectrography is discussed in [section 1.2.31](#) (multi-cation analysis).

Preconcentration

Wang and Mahmoud⁹⁰ described a preconcentration procedure based on the interfacial accumulation of iron III-Solochrome violet RS chelate on the hanging mercury drop electrode. A preconcentration potential of -0.4 V was applied, then the voltammogram recorded at -1.10 V . The limit of detection achieved was $0.04 \mu\text{g l}^{-1}$.

See also [section 1.2.32](#).

1.2.14

*Lead**Electrothermal atomic absorption spectrometry*

Numerous publications have appeared on the determination of lead in potable water by electrothermal techniques⁹¹⁻⁹⁷. An early method using the Delves cup procedure claims a detection limit of $5 \mu\text{g l}^{-1}$.⁹⁸ Atom trapping techniques have also been used⁹⁹.

Regan and Warren⁹⁶ analysed potable water samples from England and Wales using carbon furnace atomic absorption spectrophotometry. Spiking experiments carried out in order to determine the severity of the matrix interference revealed a suppression of the lead signals ranged from 22 to 84 per cent. No relationship was found to exist between the hardness of a water sample and its suppression effect.

Further spiking experiments carried out in the presence of 1 per cent m/V of ascorbic acid showed that the suppression effect was reduced to a level of less than 5 per cent.

The natural lead contents of these potable waters were determined both by carbon furnace atomic absorption spectrophotometry in the presence of ascorbic acid and by a method that involves solvent extraction—flame atomic absorption. Statistical analysis, using a *t*-test, indicated that there was no significant difference (at the 95 per cent confidence level) in the results obtained by using the two techniques.

Mitcham⁹⁵ also showed that the determination of lead in potable waters using electrothermal atomizers suffer from serious suppression effects. He developed a semi-micro technique that chelates and separates lead as the tetramethylenedithiocarbamate extract (4-methylpentan-2-one) prior to analysis. The extract is then injected directly into the electrically heated graphite furnace atomizer without the need to separate the two phases.

The method has a linear working range up to approximately $75 \mu\text{g l}^{-1}$ of lead. Three types of waters were selected, which were known to cause severe interference effects. The waters were acidified to pH 2.5 (± 0.3) with nitric acid and 0.1 mg of lead was added to 11 of each. These aqueous samples were first analysed by direct injection into the furnace, and subsequently using the above procedure, by extraction with ammonium tetramethylenedithiocarbamate. To establish that the improved recovery was not simply a function of added ammonium tetramethylenedithiocarbamate, the aqueous solutions were also analysed for lead after the addition of the complexing agent. The results for the lead determinations are given in [Table 5](#).

The results in [Table 5](#) illustrate clearly how the response of 0.10 mg l^{-1} of lead is reduced in water containing high levels of dissolved salts. Sample 2 is a particularly good example of suppression effects as absorption is reduced by almost 50 per cent in comparison with the distilled water standard. The addition of the complexing agent has further reduced the absorbance signals, in two instances by almost 40 per cent of their original values. The results for the organic extracts, however, agree well with those for the extracted standard. The lowest result represents a 94 per cent recovery.

It was possible to compare bias and standard deviation results for two independent standards analysed by the proposed method and the solvent extraction flame method. [Table 6](#) gives the results of this exercise.

It is apparent from these results that the method is comparable to the recognized solvent extraction flame technique and is also capable of obtaining the standards for bias and standard deviation required by the water industry.

TABLE 5

Absorbance of 0.10 mg l⁻¹ of lead in different waters

Sample No.	Type of water		Aqueous sample			Aqueous +sampling agent		Organic extract	
	Absorbance	R.S.D., ^a %	Absorbance	R.S.D., ^a %	Absorbance	R.S.D., ^a %			
—	Acidified distilled water		0.330	7.7		0.253	0.2	0.290	1.5
1	Acidified potable water		0.282	5.1		0.265	4.6	0.302	1.8
2	Acidified well water		0.183	15.7		0.107	4.4	0.273	1.8
3	Acidified well water		0.215	11.9		0.140	5.1	0.310	5.3
	Composition	Electrical conductivity/ ($\mu\text{S cm}^{-1}$)	Content (mg l ⁻¹)						
	Sample	Ca ²⁺	Mg ²⁺	Na ⁺	Cl ⁻	SO ₄ ²⁻	SiO ₂	PO ₄ ³⁻	
1	Potable water	786	40	13	112	93	171	6.1	0.20
2	Well	1618	102	57	225	299	188	16.0	<0.01
3	Well	1600	19	15	356	336	74	10.9	0.16

^a R.S.D.=relative standard deviation.

The results are the means of 10 determinations and are corrected for the blank.

Bertenshaw et al⁹⁷ adopted another approach to overcome sample matrix interference problems. They used a lanthanum pre-treatment technique. This pre-treatment can be either impregnation of the furnace tube with lanthanum or the addition of lanthanum (as lanthanum chloride) to each sample. The procedure has a limit of detection of less than 1.0 $\mu\text{g l}^{-1}$ a total standard deviation of less than 1.5 $\mu\text{g l}^{-1}$, or 5 per cent of the concentration and a bias of less than 5 $\mu\text{g l}^{-1}$ or 10 per cent of the concentration over a working range of 0–100 $\mu\text{g l}^{-1}$ for both manual and automated injection of samples.

All samples tested were collected and stored in polythene containers and were acidified by the addition of 10 ml nitric acid l⁻¹. Blanks and standard

TABLE 6
Results of an inter-laboratory control exercise

Technique	True value (mg l ⁻¹)	Mean concentration obtained (mg l ⁻¹)	Standard deviation (mg l ⁻¹)	Relative standard deviation, %	Bias at 95% confidence, %
Micro-extraction, electrothermal atomization	0.0959	0.0951	0.0022	2.3	1.9
Solvent extraction, flame atomization	0.0959	0.0967	0.0026	2.7	2.9
Micro-extraction, electrothermal atomization	0.0501	0.0509	0.0015	2.9	3.0

Technique	True value (mg l ⁻¹)	Mean concentration obtained (mg l ⁻¹)	Standard deviation (mg l ⁻¹)	Relative standard deviation, %	Bias at 95% confidence, %
Solvent extraction, flame atomization	0.0501	0.0500	0.0021	4.2	3.2

solutions were prepared in polythene calibrated flasks and contained 1 ml of nitric acid per 100 ml.

Where addition of lanthanum to samples was used, the samples were adjusted to contain 0.1 per cent m/V of lanthanum (as lanthanum chloride) for manual injection and 0.01 per cent m/V of lanthanum (as lanthanum chloride) for automated injection. New furnace tubes were preconditioned by treatment with five replicate injections of solutions containing 0.5 per cent m/V of lanthanum (as lanthanum chloride).

Where tubes were impregnated with lanthanum, this was achieved by immersing the tube in the minimum volume of a concentrated solution of lanthanum nitrate and leaving in a vacuum desiccator until all the solution had been absorbed. Furnace tubes prepared in this way were conditioned by operating the furnace programme a few times, without sample injection.

Standard deviations (within batch) obtained from single randomized replicate injections of 0–40 $\mu\text{g l}^{-1}$ lead to potable water, with lanthanum added demonstrate that for standard solutions there is no significant difference between the standard deviations obtained by manual or automated injection

TABLE 7

(a) Precision tests on standards (results obtained from ten randomized replicate analyses of each standard)

Injection method	Statistical test	Lead standard solutions ($\mu\text{g l}^{-1}$)				
		1	5	10	20	40
Manual injection	Standard deviation ($\mu\text{g l}^{-1}$)	0.14	0.13	0.28	0.90	0.84
	Relative standard deviation, %	14	2.6	2.7	4.5	2.1
Automated	Standard deviation ($\mu\text{g l}^{-1}$)	0.13	0.23	0.46	0.58	1.47
	Relative standard deviation, %	13	4.6	4.6	2.9	3.7

(b) Precision tests on spiked potable water

Concentration of spike ($\mu\text{g l}^{-1}$)	Standard deviation/ $\mu\text{g l}^{-1}$		
	Within-batch (S_w)	Between-batch (S_b)	Total ^a (S_t)
0.0	0.24	0.00	0.24
2.0	0.24	0.00	0.24
5.0	0.43	0.00	0.43
10.0	0.59	0.00	0.59
20.0	0.87	1.39	1.63 ^b
50.0	2.63	1.44	3.00 (6.0%) ^b
100.0	4.01	0.00	4.01 (4.0%)

^a Requirement is a total standard deviation not greater than 1.5 $\mu\text{g l}^{-1}$ or 5 per cent of the concentration (whichever is the greater).

(a) Precision tests on standards (results obtained from ten randomized replicate analyses of each standard)

Injection method	Statistical test	Lead standard solutions ($\mu\text{g l}^{-1}$)		
1	5	10	20	40

^bNot significantly different from the target at the 95 per cent confidence level.

(Table 7(a)). Precision tests on spiked potable water are summarized in Table 7(b).

The limit of detection of the electrothermal atomization technique was thus calculated as 0.65 and 0.60 $\mu\text{g l}^{-1}$ for the manual and automated injections, respectively, both of which were well within the limit of 5 $\mu\text{g l}^{-1}$ recommended by the WRC.

The bias (accuracy) of the electrothermal atomization technique using lanthanum treatment was assessed by comparing the results obtained for the above range of potable waters with those obtained by the standard additions technique. The standard additions technique, although not entirely free from interference effects, is generally accepted as giving the best estimate of the true concentration of a determinand. The results obtained for this comparison are given in Table 8 from which the bias of individual results has been calculated.

Bertenshaw et al⁹⁷ did not encounter any interference by chloride in their method. They demonstrated that lead may be successfully determined in potable water by electrothermal atomization, using the lanthanum treatment technique to overcome suppressive interference effects of matrix constituents. Either pre-treatment of the furnace tube by impregnation with lanthanum or the addition of lanthanum (as lanthanum chloride) to each sample is equally effective, but for the electrothermal atomizer used for their investigation the latter provides a much longer furnace tube lifetime and is therefore preferred.

Tests on drinking water samples from a variety of sources within the Severn-Trent Water Authority show that electrothermal atomization together with the lanthanum treatment technique meets the recommended criteria of performance for the determination of lead in potable waters in respect of concentration range, standard deviation, bias and limit of detection.

Sthapit et al⁹³ also investigated the suppression of interferences in the determination of lead in potable and natural waters by graphite furnace atomic absorption spectrometry. Examination of the individual effects of various matrix components, including sodium, chloride, potassium chloride, magnesium chloride, calcium chloride, sodium sulphate, potassium dihydrogenorthophosphate and magnesium nitrate, showed that magnesium chloride and sodium sulphate caused the most severe interference. The use of the L'vov platform and the use of a mixture of lanthanum (as the chloride) and nitric acid, to suppress interference were tested, and the effectiveness of the treatment was assessed by comparing results with those obtained by using either flame atomic absorption spectrometry or flame atomic fluorescence spectrometry.

Webster and Wood⁹¹ also investigated lanthanum impregnation of the graphite tube. The precision and bias obtained were acceptable and good recoveries were obtained from a wide range of raw and treated waters. Results were compared with those obtained using concentration either by evaporation, or extraction of the ammonium tetramethyldithiocarbamate complex into isobutyl methyl ketone, both followed by flame atomic absorption spectrophotometry. A statistical comparison of data from all three procedures showed

TABLE 8

Comparison of results for lead in potable waters by the standard additions technique and lanthanum treatment technique

Sample	True concentration of lead by standard additions technique ($\mu\text{g l}^{-1}$)	Concentration of lead by direct analysis in presence of lanthanum ($\mu\text{g l}^{-1}$)	Mean bias ($\mu\text{g l}^{-1}$)	Maximum possible bias ^a ($\mu\text{g l}^{-1}$)
A	7.3	6.6±0.3	-0.7	-1.0
B	2.9	2.6±0.1	-0.3	-0.4
C	1.0	0.9±0.1	-0.1	-0.2
D	2.7	2.8±0.2	+0.1	+0.3
E	3.2	3.6±0.3	+0.4	+0.7
F	2.7	2.6±0.1	-0.1	-0.2
G	76	79±1.8	+3.0	+4.8
H	99	100±1.6	+1.0	+2.6
I	45	47±0.7	+2.0	+2.7
J	69	65±2.4	-4.0	-6.4 (9.3%)
K	12	11.5±0.8	-0.5	-1.3
L	3.6	4.0±0.4	+0.4	+0.8
M	12.4	13.0±0.8	+0.6	+1.4
N	<0.6	<0.6	—	—

Sample composition			Concentration (mg l^{-1})						
Sample	Type of water sample	Electrical conductivity ($\mu\text{S cm}^{-1}$)	Ca ²⁺	Mg ²⁺	Total hardness (CaCO ₃)	Na ⁺	K ⁺	SO ₄ ³⁻	Cl ⁻
A	Treated water	180	31	3.5	92	6.4	3.1	47	21
B	Borehole	626	75	9.5	227	32	3.1	71	61
C	Borehole	430	52	31	258	9.1	2.5	25	24
D	Borehole	960	106	40	430	17	2.8	163	26
E	Borehole	364	200	26	607	54	3.8	432	26
F	Tap water	62	55	15	199	6.0	2.7	31	19
G	Tap water	62	6	1	19	4.2	0.4	3	12
H	Tap water	62	6	1	19	4.2	0.5	3	12
I	Tap water	66	6	1	19	4.2	0.4	4	12
J	Tap water	430	7	1	22	3.9	0.5	5	13
K	Tap water	66	44	7	140	24	3.6	39	47
L	Tap water	615	6	2	23	30	7.6	104	13
M	Tap water	300	78	28	310	33	5.6	124	59
N	Tap water		37	31	221	5.1	4.4	60	80

^a Requirement is a bias of not more than $5 \mu\text{g l}^{-1}$ or 10 per cent of the concentration (whichever is the greater). 90 per cent confidence limits.

good agreement. The atomization procedure was more accurate than flame atomic absorption spectrometry procedure in the 5–15 $\mu\text{g l}^{-1}$ lead range.

Hunt and Winnard⁹² appraised various techniques for overcoming matrix interference effects. Bulk samples of water, collected at source from hard and soft water areas, and a range of river samples were spiked with cadmium and lead. To assess matrix interference effects in the determination of these two metals, analyses were performed using graphite furnace atomic absorption spectrometry, each sample being analysed by eight different procedures. Techniques involving the use of lanthanum as a matrix modifier (without a furnace platform) or the stabilized temperature platform furnace showed marked reductions in interference effects. A combination of platform and matrix modifier provided the most accurate results.

As mentioned previously, Sthapit et al⁹³ investigated the application of flame atomic fluorescence spectrometry to the determination of lead in potable water. Further developments of this procedure have produced a method capable of detecting down to 2.5 $\mu\text{g l}^{-1}$ lead⁹⁴. Samples were acidified with nitric acid before direct aspiration into the nitrogen shielded air-hydrogen or air-acetylene flame of the spectrometer. The method was interference free. For greater sensitivity, a procedure is described which was compatible with this method, and involved preconcentration of water samples using isobutyl methyl ketone-ammonium tetramethylene-dithiocarbamate extraction and chelation. A detection limit of 0.4 $\mu\text{g l}^{-1}$ was thereby achieved.

Sthapit et al⁹⁴ analysed samples of water obtained from various domestic water supplies for their lead content by the flame atomic fluorescence system using both air-hydrogen and air-acetylene flames and also by a carbon furnace atomic absorption method after prior extraction and chelation with isobutyl methyl ketone-ammonium tetramethylenedithiocarbamate. The results show good agreement.

Vandegans et al¹⁰⁰ have studied some interferences by salts, rather than anions or cations in the determination of lead by flameless atomic absorption spectrometry, magnesium chloride, for example, caused considerable interference.

The atomic absorption spectrometry of lead is also discussed in [section 1.2.31](#) (multi-cation analysis).

Hydride generation techniques

Vijan and Sadana¹⁰¹ observe that copper and nickel present in potable waters interfere with the determination of lead by the hydride generation atomic absorption spectrometric technique. They eliminated this interference by coprecipitating lead with manganese and nitric acid and the evolved plumbane analysed by an automated hydride-atomic absorption method.

In [Table 9](#) are reported results on potable water samples obtained by this technique, also by direct injection atomic absorption spectroscopy, graphite furnace atomic absorption spectroscopy, and differential pulse anodic scanning voltammetry. The graphite furnace method employed did not allow for matrix

TABLE 9
Determination of lead in drinking water by four methods ($\mu\text{g/l}$)

Sample	Atomic absorption spectrometry	Hydride atomic absorption spectrometry	Graphite furnace atomic absorption spectrometry		Differential pulse anodic scanning voltammetry	
			As received	Co-precipitated	As received	Digested with nitric acid
1	64	49	38	54	45	55
2	41	35	44	30	27	33

Sample	Atomic absorption spectrometry	Hydride atomic absorption spectrometry	Graphite furnace atomic absorption spectrometry		Differential pulse anodic scanning voltammetry	
			As received	Co-precipitated	As received	Digested with nitric acid
3	69	80	48	54	50	54
4	67	78	60	88	48	60
5	76	75	48	110	57	75
6	184	166	124	168	153	210
7	539	567	201	565	498	482
8	14	14	39	12	9	14
9	118	117	58	111	88	101
10	10	10	33	12	7	9
11	462	416	171	392	380	450
12	82	90	38	73	75	89
13	130	155	76	141	126	155
14	344	348	132	304	277	370
15	34	37	25	35	26	31
16	113	102	53	105	88	116
17	40	35	33	30	21	33
18	8	8	5	8	6	8
19	42	31	24	32	28	39
20	32	31	14	20	17	21
21	142	116	56	120	101	130
22	140	155	54	120	106	150

interference and this is seen in the poor agreement of lead contents obtained between this and the other methods.

The results obtained by conventional flame atomic absorption spectrophotometry are included in [Table 9](#). The method requires at least a tenfold preconcentration in order for reliable signals to be obtained for the low lead levels. The accuracy of measurement at these concentrations is limited and necessitates the use of high damping and scale expansion in addition to background correction.

The results obtained by differential pulse anodic scanning voltammetry when nitric acid digestion is employed, are in good agreement with those obtained by graphite furnace atomic absorption spectrometry with manganese dioxide coprecipitation and hydride graphite furnace atomic absorption spectrometry with manganese dioxide coprecipitation.

Smith¹⁰² has also applied hydride generation atomic absorption spectrometry to the determination of lead in potable water. This method incorporates the use of potassium cyanide solution for the reduction of copper interference. The sample, together with 7.5 per cent tartaric acid solution, is mixed with 3 per

TABLE 10

Results obtained by hydride-generation technique on reference samples of known lead concentration

Sample	Pb concn found ($\mu\text{g/l}$)	Certified Pb values ($\mu\text{g/l}$)	Certified Cu values ($\mu\text{g/l}$)
EPA quality control samples:			
476-1	28	30	9
476-2 (10×dilution)	37	38.3	37.4
476-3 (10×dilution)	11	11.3	3.7
IWR interlaboratory comparison study 80/B:			
Sample 1 (10×dilution)	41	41.5	39

cent potassium cyanide and 3 per cent potassium dichromate and reacted with sodium borohydride. The optimum pH is 1.5–2.2 for the reaction. The released hydride is measured for absorbance at 217.0 nm. Recoveries of 93 per cent and 110 per cent were recorded from five replicate samples containing $10 \mu\text{g l}^{-1}$ and $30 \mu\text{g l}^{-1}$ lead. Approximately 30 determinations per hour can be carried out.

Studies on the interference effects of aluminium, barium, cadmium, cobalt, zinc (up to 5 mg l^{-1}) in the presence of $50 \mu\text{g l}^{-1}$ lead and calcium, magnesium, copper, chromium, iron (di- and trivalent), manganese, nickel, strontium, and potassium and sodium (up to $100 \mu\text{g l}^{-1}$) in the presence of $50 \mu\text{g l}^{-1}$ lead showed that only copper exhibited significant interference effects. Interference effects from nickel and iron were not observed. Addition of potassium cyanide considerably reduced the copper interference. Optimum control of copper interference was achieved by the addition of 1 ml of 3 per cent potassium cyanide solution to the test solution.

Results obtained by this method on Environmental Protection Agency and National Institute for Water Research reference samples of known lead concentrations are given in [Table 10](#). Actual copper concentrations are also given.

The detection limit of this procedure is about $5 \mu\text{g l}^{-1}$ and the relative standard deviation 2.9 per cent at the $34 \mu\text{g l}^{-1}$ lead level in potable water.

Polarography

Lead has been determined in potable water by polarography as its 3-hydroxypyridine-2-thiol chelate¹⁰³.

The voltammetric determination of lead is also discussed in [section 1.2.31](#) (multi-cation analysis).

Miscellaneous

Bermejo Barrera et al¹⁰⁴ described a spectrophotometric method using dithizone to determine the lead content of drinking water in La Coruna, Spain. The results showed that in 61 per cent of the samples lead contamination was below the 0.05 mg l^{-1} levels specified by the U.S. Public Health Service.

Miller et al¹⁰⁵ studied the influence of time of acidification after sample collection on the preservation of potable water samples for lead determination. Potable water samples containing known concentrations of lead between 26 and $105 \mu\text{g l}^{-1}$ were acidified at different time intervals after collection, up to 14 days. The water samples were then stored at room temperature for varying times prior to lead determination by flameless atomic absorption spectrometry with deuterium background correction. All acidified spiked samples gave a higher lead value than unacidified samples having comparable lead concentrations. In general, all acidified samples had average lead recoveries within 10 per cent of their initial control values. It

was concluded that acidification of water samples could be delayed by up to 14 days without adversely affecting lead concentration data.

The application of energy dispersive X-ray fluorescence spectroscopy and isotope dilution mass spectrometry is discussed in [section 1.2.31](#) (multi-cation analysis).

Preconcentration

Ammonium pyrrolidine dithiocarbamate precipitation followed by extraction with methyl isobutyl ketone has been used to preconcentrate lead from potable water prior to its determination by atomic absorption spectrometry.¹⁰⁶

Coprecipitation with tris-(pyrrolidine dithiocarbamate cobalt III) has been used to preconcentrate lead from potable water prior to its determination by atomic absorption spectrometry¹⁰⁷.

Coprecipitation as the phosphate has also been used¹⁰⁸ to preconcentrate lead in potable water at levels down to $50 \mu\text{g l}^{-1}$ prior to polarographic analysis.

Polystyrene supported polymaleic anhydride resin has been used to preconcentrate lead in potable water prior to determination by flame atomic absorption spectrometry¹⁰⁹. Chelex 100 in the calcium form proved unsuitable for lead preconcentration. This method met the European Community directive limiting the content of lead in potable water to $50 \mu\text{g l}^{-1}$.¹¹⁰

A plumbo solvent potable water having a low alkalinity (18 mg l^{-1} as CaCO_3) and low pH (6.58) had most of the lead in the smaller size fractions but a significant proportion is particulate (i.e. $>0.4 \mu\text{m}$). The Ca-Chelex 100 extraction was not 100 per cent efficient for lead removal from any of the subsamples. Incomplete recoveries may be due to the presence of colloidal species or to non-Chelex labile organic complexes of lead or both. Slow dissociation of complexes relative to the solution/resin contact time may also have an effect. The polystyrene supported poly(maleic anhydride) resin behaved in a significantly different manner. The column extraction (50 ml of sample) gave 100 per cent lead removal from the 0.4 and $0.08 \mu\text{m}$ filtered waters but particulate lead was not recovered from the unfiltered and $12 \mu\text{m}$ filtered samples. A batch extraction on the unfiltered sample after passage through the column chelated all the remaining lead from solution thereby indicating its potential for total lead determinations.

Some potable water samples of relatively high alkalinity were examined because such waters can attack lead. Total lead in unfiltered samples was determined by a.a.s. directly and following a 48 h batch extraction of 50 ml of water. Lead removal by the poly (maleic anhydride) resin was complete for both high and low alkalinity samples.

Activated alumina

Lead has been deposited on a microcolumn of activated alumina and eluted with nitric acid prior to its determination by flame atomic absorption spectrometry¹¹¹. A detection limit of $0.36 \mu\text{g l}^{-1}$ was achieved.

Ammonia precipitation

Martinez-Gomez et al¹¹² give details of a preconcentration procedure whereby lead is continuously precipitated with ammonia from water prior to its determination by atomic absorption spectrometry. Lead can be determined over the range $1\text{--}2 \mu\text{g l}^{-1}$ with a sampling frequency of up to 15 samples per hour.

The preconcentration of lead is also discussed in [section 1.2.31](#) (multi-cation analysis).

1.2.15 *Lithium*

Ion selective electrodes

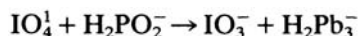
Hildebrandt and Pool¹¹³ have used a liquid ion-exchange membrane electrode for the determination of lithium in potable water. This electrode uses n-decanol as both liquid membrane and ion-exchanger. Its selectivity for lithium relative to sodium and potassium is similar to that of the LAS 15–25 glass electrode for lithium. Stringent pH control is required to detect low activities. Nevertheless, these workers feel that the electrode would be of limited use for lithium determinations in other than pure lithium solutions.

1.2.16 *Manganese*

Spectrophotometric methods

In a Standard Department of the Environment UK procedure¹¹⁴ the manganese is reacted with formaldoxime to form a coloured complex and the absorbion measured at 450 nm. The limit of detection is 0.005 mg l⁻¹ and the response is linear up to at least 1.0 mg l⁻¹. Interference due to cobalt and both ferrous and ferric ions may occur and preliminary treatment of samples containing suspended or organically bound manganese may be necessary to convert it to a form capable of reacting with formaldoxime.

Nikolelis and Hadjioannou^{115,116} have described a kinetic micro-determination of manganese in potable and natural water. The method is based on the catalytic effect of manganese on the periodate-acetylacetone reaction. The time required for the formation of a small predetermined amount of coloured product is measured automatically and related to the trace metal or inhibitor concentration



Down to 1 µg l⁻¹ manganese can be determined by this procedure. No serious interferences are to be expected in the determination of manganese by this procedure. Potassium, sodium, calcium and magnesium did not interfere when flow concentrations were several thousand that of the manganese.

Atomic absorption spectrometry

The application of atomic absorption spectrometry to the determination of manganese in potable water is discussed in [section 1.2.31](#) (multi-cation analysis).

Preconcentration

See [section 1.2.32](#).

1.2.17 Mercury

Atomic absorption spectrometry

Determinations of mercury by atomic absorption spectrometry are usually based on the cold vapour technique. Mercury is normally generated from solution by reduction procedures with tin II chloride in acidic solutions, but many other reductants including stannate in alkaline medium, ascorbic acid, hydrazine sulphate or sodium borohydride, can also be used. Preliminary retention of mercury vapours by amalgamation with gold, silver, or copper wires, gold wool, etc. or by sorption on active carbon, has been widely applied for preconcentration of traces of mercury from various matrices, mercury is then easily released by heating.

The determination of mercury in a graphite furnace has only limited sensitivity, although this can be slightly improved by addition of oxidizing agents or sulphide. Electrothermal atomization from copper, silver, or gold wires after amalgamation from solutions, seems more promising.

Kunert et al¹¹⁷ used cold vapour graphite furnace atomic absorption spectrometry and cold vapour atomic absorption spectrometry to determine mercury in potable water. They found that the sensitivity of the graphite furnace method could be improved by covering the graphite surface with gold or silver foil.

The determination of mercury in graphite furnaces is of rather low sensitivity because the reduction of mercury II to elemental mercury by carbon occurs almost at room temperature, and mercury volatilizes in the pre-atomization periods. Accordingly, Kunert et al¹¹⁷ compared the responses from graphite, gold and silver surface in the Perkin flames HGA-74 optimized conditions. For this purpose 10 μl aliquots of mercury II nitrate solution in 0.01 M nitric acid (60 $\mu\text{g ml}^{-1}$ for graphite and 2 $\mu\text{g ml}^{-1}$ for metallic surfaces) were injected into the furnace, dried at 60°C during 15 s, ashed at 100°C, 150°C or 150°C during 10s in a nitrogen flow of 350 ml min^{-1} and finally atomized at 700, 950 or 900°C during 10s (under stopped flow conditions) from the graphite, gold or silver surfaces, respectively. The furnace was finally heated at 2700°C, 1050°C or 950°C respectively, during 5 s to prevent memory effects. The use of metallic surfaces permitted higher temperatures for sample decomposition without loss of mercury, because a prior amalgamation process occurred from the sample solution and the mercury amalgam was then quantitatively decomposed. This allowed a 27 fold increase in sensitivity for the metallic surfaces compared with the graphite surface. Strong acids, except hydrochloric acid, suppressed the absorbance signal even at moderate concentrations, especially sulphuric and perchloric acids. There was no signal for 10 ng Hg in 1 M perchloric acid but 10^{-4} M concentrations of acid were without effect.

An increase in sensitivity was found in the presence of sulphide or oxidizing agents on the graphite surfaces because of decreased losses of mercury during the pre-atomization periods. The addition of 10 μl of 1 M sodium sulphide, 0.3 M potassium permanganate, 1 M potassium dichromate or 10 per cent hydrogen peroxide to an aliquot containing 0.20 $\mu\text{g Hg}$ increased the sensitivity for mercury II 6.5, 6 or 7 times, respectively.

The influence of various salts at concentrations of 0.1 M is summarized in Table 11 for the different surfaces, a deuterium background corrector was used. A large suppressing effect was observed for thiocyanate and perchlorate, but in general the largest effects were observed on metallic surfaces.

Very low atomic yield from graphite was found during the atomization step ($[\text{Hg}]_{\text{at}}/C_{\text{Hg}}=0.021$) but the value was 0.40 for silver or gold surfaces, as indicated by the ratio of the slopes for the theoretical and experimental plots of absorbance vs. mercury concentration. Thus, the atomization recorded for an uncovered graphite surface gave only about 1/50th of the theoretically possible sensitivity; when the

graphite surface was covered with gold or silver foil, almost half the possible efficiency of the method was achieved. The calculated theoretical sensitivities are valid only for the particular internal volume of the HGA-74, furnace, the sample solution volume, and the heating mode used.

Oda and Ingle¹¹⁸ have described a speciation scheme whereby ultratrace levels of inorganic and organomercury are selectively reduced by stannous chloride and sodium borohydride respectively. The volatilized elemental mercury is determined by cold vapour atomic absorption. The detection limits for inorganic and organomercury species are in the 0.003–0.005 μl^{-1} range and both types of mercury can be determined in a 1 ml sample in about 3 min. Analysis is performed by cold vapour atomic absorption spectrometry^{119–121}.

The discrete sampling reduction vessel^{119–122} is a modified coarse frit sealing tube in which the carrier gas (85 ml min^{-1} flow rate) passes up through the frit, through the reaction mixture solution with vigorous bubbling and out of a side

TABLE 11

The influence of some salt solutions (0.1 M) on the atomization of mercury from various surfaces in the HGA-74 graphite furnace^a

Salt	$A \times 100/A_0^b$		
	Au foil	Ag foil	Graphite
$\text{Na}_2\text{S}_2\text{O}_3$	94	93	94
KI	87	99	96
KBr	89	97	90
KSCN	27	25	99
NaCl	82	65	92
NaClO_4	34	74	96
ZnSO_4	86	79	86
CuSO_4	70	98	79
CdSO_4	35	72	82
NiSO_4	38	62	81
CoSO_4	41	81	80
$\text{Fe}_2(\text{SO}_4)_3$	43	72	90

^a 0.010 μg Hg if atomized from the graphite and 0.010 μg Hg from Au or Ag foil.

^b A_0 is the absorbance for Hg^{2+} solution in the absence of salt.

arm tube at the top of the reduction vessel into the 60 cm path length absorption cell which is electrically heated to 130°C.

The speciation scheme for inorganic and organomercury is based on the different reducing strengths of stannous chloride and sodium borohydride. First tin chloride is used to reduce only the inorganic mercury in the sample. The resultant elemental mercury is swept into nitrogen and carried into an observation cell where the absorbance at 253.7 nm is measured. Next, sodium borohydride is injected into the reduction cell and the organomercury is reduced, volatilized, and carried to the observation cell. Ideally the measured peak absorbance due to stannous chloride reduction is due only to inorganic mercury and the measured peak absorbance due to sodium borohydride reduction is due only to organomercury.

Typical recorder tracings for the determination of 1 and 0.03 $\mu\text{g l}^{-1}$ mixtures of inorganic mercury and methyl mercury chloride and a blank are shown in fig. 7. In fig. 7(b) and (c), a small narrow peak (<0.005

AU) appears at the time of injection of both reducing agents. This results from minutely varying gas flows as syringe needles are inserted and removed and solution is sprayed onto the frit and the injection peak is readily distinguished from the mercury peaks because of its immediate response.

The calibration sensitivities and detection limits achieved for inorganic and organomercury species were as follows: inorganic mercury $0.003 \mu\text{g l}^{-1}$, CH_3HgCl and $\text{CH}_3\text{CH}_2\text{HgCl}$ $0.003 \mu\text{g l}^{-1}$ and $\text{C}_6\text{H}_5\text{HgCl}$ $0.005 \mu\text{g l}^{-1}$. The calibration curves were linear from the detection limit to at least $3 \mu\text{g l}^{-1}$.

Wittman¹²³ has described a cold vapour method for the determination of inorganic mercury in which samples are heated in an electric furnace and the mercury released is trapped by amalgamation on a gold wire. The mercury is then vaporized and carried through the absorption cell by a flow of air, so that the mercury atomic absorption signal at 253.7 nm increases sharply to a maximum and quickly returns to zero.

The apparatus is shown in [fig. 8](#). Place the sample (10–1000 mg) in a quartz boat. Heat solid or liquid samples in an electric furnace, decomposition products being transported by a carrier gas over $100 \mu\text{m}$ diameter pure gold wire maintained at 170°C used to trap the mercury by amalgamation and then being vented to atmosphere. The mercury trapped is then vaporized by heating the gold with an electric furnace to $600\text{--}700^\circ\text{C}$ and the mercury vapour carried through.

Preconcentration of mercury on gold or silver wire or foil is an interesting idea which has been pursued by other workers. Thus Temmerman et al¹²⁴ evaluated and optimized reduction aeration/amalgamation as a method for the analysis of down to $6.6 \mu\text{g l}^{-1}$ mercury in potable water by cold vapour atomic absorption spectrometry. Parameters investigated were: aeration time, aeration gas flow rate, type of gas distributor, amount of reductant and mercury concentration. The aerated mercury was preconcentrated on a gold-coated quartz sand absorber and subsequently thermally desorbed. This enabled interference by water vapour to be avoided and calibration to be simplified. The detection limit was 0.6 ng l^{-1} and reproducibility was better than 10 per cent.

For the analysis of the samples, the inside of the aeration flasks ([fig. 9](#)) is first equilibrated with the potable water sample passing through the vessel for about 15 min. Next, the flask is emptied and filled with 11 of the potable water sample. After acidification with 10 ml 36 N sulphuric acid or 5 ml 12 N hydrochloric acid 1 ml of a 30 per cent stannous chloride solution is added and the aeration is started under the conditions as described below. The mercury is collected on a gold coated absorber and measured by thermal desorption and cold vapour atomic absorption spectrometer. Blanks are obtained by aerating the analysed samples again 2 or 3 times, after addition of all the reagents.

EXPERIMENTAL CONDITIONS:

Aeration time: 1 hour.

Aeration flow rate: For an aeration time of 60 min and with a glass fitted gas distributor (porosity D2) a flow rate between 250 and 700 ml min⁻¹ is advisable.

The collected water can be removed by passing dry nitrogen through the absorbing tube for 1 or 2 min before connecting it to the second absorber.

The mean recovery obtained by this method on potable water spiked with 1–8 mg mercury was 98.8 per cent. Reproducibility is better than 10 per cent for solutions containing more than 1 ng mercury.

In [fig. 10](#) are shown mercury contents obtained over a two month period on a city potable water supply. The mercury content of the samples varied from less than 1 ng l^{-1} to 10 ng l^{-1} with a geometric mean of 3.1 ng l^{-1} . The results show that the analysed drinking water meets the requirements of the WHO and EEC ($1 \mu\text{g l}^{-1}$ total mercury¹²⁵).

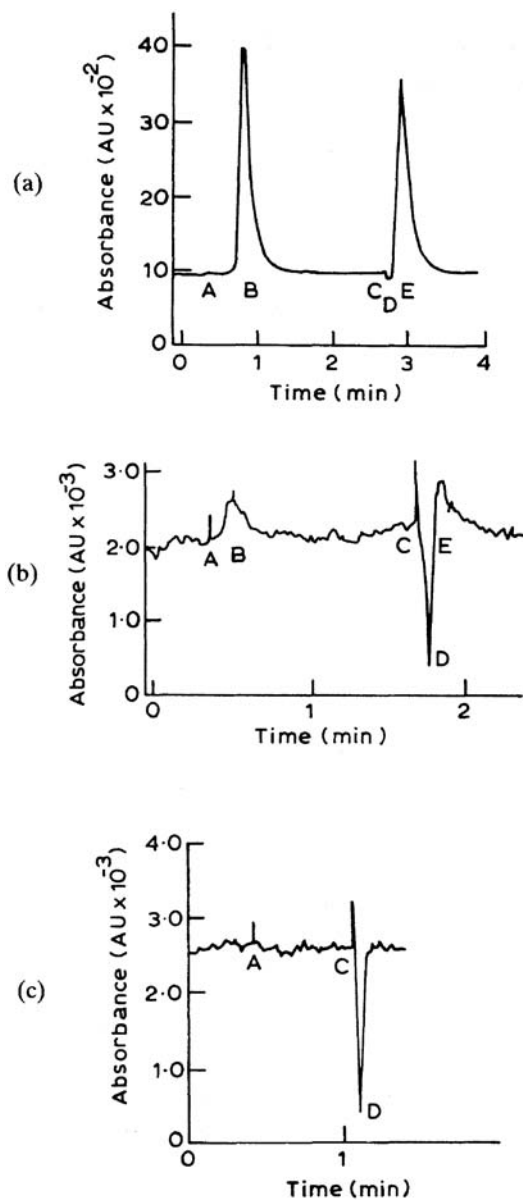


Fig. 7. Typical recorder outputs for speciation analyses: (a) mixtures of $1 \mu\text{g l}^{-1}$ (with respect to Hg) of Hg^{2+} and CH_3Hg^+ ; (A) sample injection spike, (B) inorganic Hg^{2+} peak, (C) NaBH_4 injection spike, (D) negative peak from H_2 (E) organomercury peak; (b) mixture of $0.030 \mu\text{g l}^{-1}$ (with respect to Hg) of Hg^{2+} and CH_3Hg^+ : (A) sample injection spike, (B) inorganic Hg^{2+} peak, (C) NaBH_4 injection spike, (D) negative peak from H_2 , (E) organomercury peak; (c) water blank; (A) blank injection spike, (C) NaBH_4 injection spike, (D) negative peak from H_2 .

Flow potentiometric and constant current stripping analysis

Huiliang et al¹²⁶ have investigated the feasibility of using gold or platinum coated carbon electrodes as flow sensors for determining traces of mercury in potable water. The gold fibre electrode was considered best for

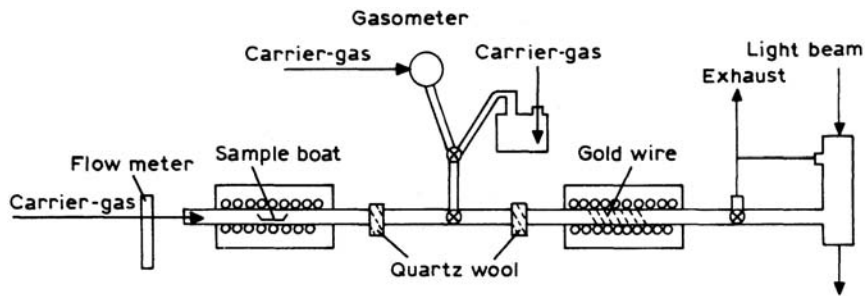


Fig. 8. Schematic diagram of the apparatus for mercury determination.

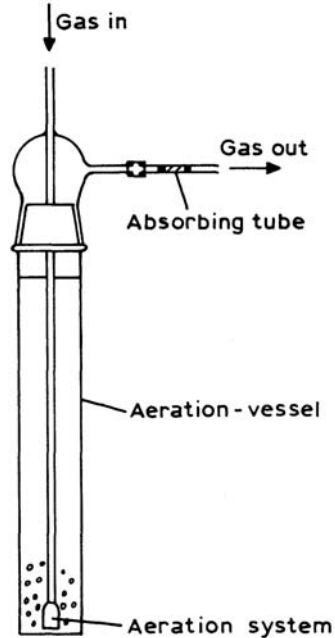


Fig. 9. Aeration vessel (1:50 cm, i.d.: 55 mm). routine use.

Energy dispersive X-ray fluorescence spectrometry

This technique has been applied to the determination of mercury in potable water, see [section 1.2.31](#) (multi-cation analysis).

Preconcentration

Bertenshaw and Wagstaffe¹²⁷ have described a preconcentration technique for use in the cold vapour atomic fluorescence determination of mercury in potable water. This method employs a trap containing potassium permanganate. Mercury can be determined in the concentration range 4–700 ng l⁻¹.

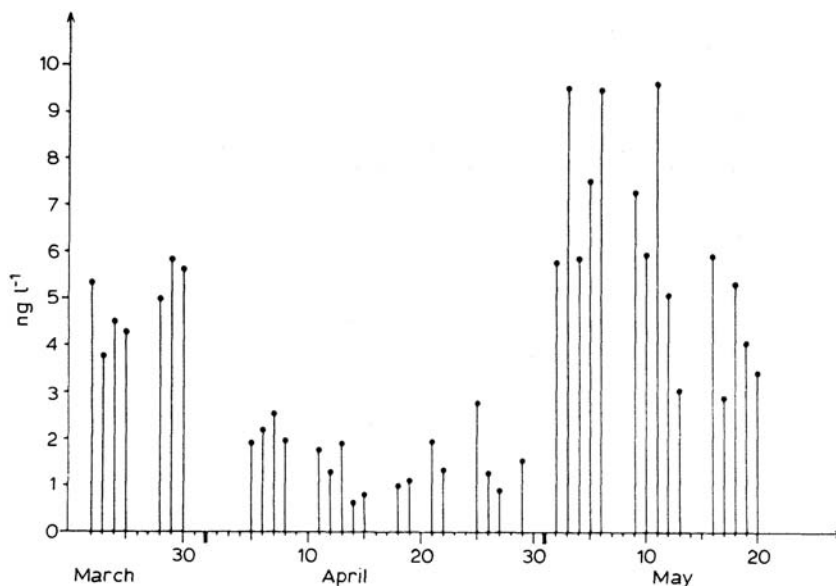


Fig. 10. Mercury concentration of city potable water.

1.2.18 *Molybdenum*

Spectrophotometric kinetic methods have been described for the determination of molybdenum in potable water^{128,129}. These methods are based on the molybdenum catalysed oxidation of quinol with iodate¹²⁸ and acetylacetone with periodate¹²⁹. Both methods are capable of determining down to $1 \mu\text{g l}^{-1}$ molybdenum.

In the acetylacetone periodate method¹²⁹ the sample is pipetted into the reaction cell containing the reagents, acetylacetone is injected to start the reaction and the time taken to reach a particular optical density is recorded. Ultramicro amounts of molybdenum in the range 6–60 ng were determined with an average error and relative standard deviation of ca. 2 per cent and measurement times of 40–180 s.

The following ions do not affect the rate of the manganese-molybdenum catalysed reaction, even when their concentrations were several thousand times that of the manganese: potassium, sodium, calcium, magnesium, zinc, nickel, copper, and lead.

The molybdenum catalysed periodate-acetylacetone reactions are critically pH-dependent; the pH should be kept constant to better than ± 0.1 pH until in the range pH 6.1–6.2.

If the reaction rate in all samples was constant for a fixed molybdenum concentration, the calibration curves would have the same slope and the product of the molybdenum concentration in $\mu\text{g l}^{-1}$ (including the blank) multiplied by the measurement times in seconds, would be the same for all samples. This is not the case because interfering substances affect the reaction rate. Any substance that oxidizes acetylacetone or reduces periodate, under the conditions of the procedure, constitutes a potential interference. In addition, large amounts of salts decrease the reaction rate. To compensate for the effect of interfering substances, the composition of the standard molybdenum solutions should be similar to that of the samples but as interfering substances may be present in different amounts in different samples, it is not feasible to prepare such standard solutions. Calibration curves obtained with pure solutions of molybdenum in distilled water

can therefore lead to erroneous results. By applying the standard addition method, the concentration of all substances (except molybdenum) is the same in all the solutions used in each analysis.

Atomic absorption spectrometry

This technique has been applied to the determination of molybdenum in potable water, see [section 1.2.31](#) (multi-cation analysis).

Preconcentration

Hidalgo et al¹³⁰ preconcentrated molybdenum VI by co-flotation on iron III hydroxide prior to analysis by differential pulse polarography co-flotation was achieved by octadecylamine.

1.2.19

Nickel

See [section 1.2.31](#) (multi-cation analysis).

Preconcentration

Nickel in potable water has been preconcentrated by conversion to its chelate with ammonium, pyrrolidine dithiocarbonate followed by solvent extraction and determination by atomic absorption spectrometry¹³¹. The preconcentration of nickel is also discussed in [section 1.2.31](#) (multi-cation analysis).

1.2.20

Osmium

Spectrophotometric method

Nikolelis and Hadjiioannou¹³² have described a kinetic micro-determination of osmium in potable water based on the catalytic effect of osmium on the periodate-phosphinate reaction.

1.2.21

Potassium

Miscellaneous

The Department of the Environment (UK)¹³³ have described two methods for the determination of potassium in potable waters. The first based on flame photometry and the second on atomic absorption spectrometry.

Flow injection analysis has also been applied to the determination of potassium in potable waters, see [section 1.2.31](#) (multi-cation analysis).

1.2.22
Thallium

The determination of thallium by isotope dilution mass spectrometry is discussed in [section 1.2.31](#) (multi-cation analysis).

1.2.23
Selenium

Miscellaneous

Hammer¹³⁴ has reviewed Government standards for the determination of selenium in potable water.

Selenium in potable water is likely to appear as a mixture of selenite and selenate depending on the solubility of the selenium salts, the aquifer and the redox potential and pH of the ground water¹³⁵. Little is known about the valence state of selenium in waters because the standard analysis has been for total selenium by either atomic absorption spectrophotometry or the diaminobenzidine method¹³⁶. Selenite has been differentiated from other forms by using a fluorimetric technique.

Atomic absorption spectrometry, hydride generation atomic absorption spectrometry, hydride generation inductivity coupled plasma atomic emission spectrometry and energy dispersive X-ray fluorescence spectroscopy have all been applied to the determination of selenium in potable water, see [section 1.2.31](#) (multi-cation analysis).

1.2.24
Silver

Spectrophotometric methods

Methods based on spectrophotometry with *p*-dimethylaminobenzylidenerhodanine and dithizone¹³⁷ and on the ring oven technique¹³⁸ have been described for the determination of silver in potable water but these are only capable of determining silver in the mg l⁻¹ range. Bancells et al¹³⁹ have described an inductively coupled plasma emission spectroscopic technique for the determination of down to 2 µg l⁻¹ silver in potable water. These workers compared determinations of silver obtained by this technique with those obtained by extraction with ammonium pyrrolidine dithiocarbamate, diethylammonium diethyldithiocarbamate and methylisobutylketone, followed by for silver by flame atomic absorption spectrometry. was 0.3 µg l⁻¹. Matrix determination by flame atomic absorption spectrometry. The detection limit interference studies were performed. Sodium and iron caused interference. The inductively coupled plasma method was faster and easier than the extraction method.

Potentiometric titration

Frevent¹⁴⁰ carried out a potentiometric determination of silver ions in potable water containing silver as a disinfectant. The measurement cell consisted of a silver sulphide coated wire connected to a silver/silver chloride reference electrode. Measurements in the range 1–100 µg l⁻¹ silver had a linear response.

Preconcentration

See [section 1.2.32](#).

*1.2.25**Sodium**Miscellaneous*

The Department of the Environment (UK)¹⁴¹ has described two methods for the determination of sodium in raw and potable waters. The first is based on flame photometry and the second on atomic absorption spectrophotometry. A third method based on atomic emission spectrophotometry, was considered but found to be too sensitive for the purpose and to offer no advantages in practice over the atomic absorption method.

Determination of sodium by flow injection analysis is discussed in [section 1.2.31](#) (multi-cation analysis).

*1.2.26**Strontium*

See [section 1.2.31](#) (multi-cation analysis).

*1.2.27**Tungsten**Preconcentration*

See [section 1.2.32](#).

*1.2.28**Uranium**Neutron activation analysis*

Nazaki et al¹⁴² used neutron activation analysis to determine down to 9 ng l^{-1} uranium in potable water. The water sample was irradiated for 30 min in a thermal neutron flux of 2×10^{12} neutrons per cm^2 to effect the $^{238}\text{U}(n, \gamma)^{239}\text{U}$ reaction. After rapid radiochemical separation in the presence of uranium carrier by a series of solvent extractions, the ^{239}U is determined by measuring the 74 keV γ -radiation in a well type crystal connected to a single channel analyser. The carrier recovery is from 60 to 70 per cent.

Galinier and Zikovsky¹⁴³ also applied neutron activation analysis to the measurement of uranium (and thorium) in potable water. Uranium was found in samples of potable water at levels ranging from 0.4 to $7 \mu\text{g l}^{-1}$. An empirical method was developed for estimating the detection limit for uranium as a function of the mineral salt content of a water.

1.2.29 *Vanadium*

See [section 1.2.31](#) (multi-cation analysis).

Preconcentration

Vanadium has been preconcentrated by chelation with nerolic acid (s-amine-2-anilino-benzene sulphane acid) followed by extraction with toluene and spectrophotometric determination¹⁴⁴.

1.2.30 *Zinc*

Atomic absorption spectrometry

The determination of zinc in potable waters by this technique has been discussed by several workers. Workers at the Department of the Environment (UK)¹⁴⁵ claimed a working range of 2–100 $\mu\text{g l}^{-1}$ and observed slight interferences from 10 mg l^{-1} potassium and 1 mg l^{-1} ferric iron.

Dong¹⁴⁶ used an air-acetylene flame and discusses the effect of sample pH on absorbance. Pande¹⁴⁷ carried out a comparative evaluation of the estimation of zinc by the spectrophotometric Zincon method and by atomic absorption spectrophotometry.

The interference from most ions was negligible using other methods, and iron and manganese did not interfere up to 5 $\mu\text{g l}^{-1}$ in the Zincon method and up to 200 mg l^{-1} using atomic absorption spectrometry. The sensitivity of the Zincon method was 30 $\mu\text{g l}^{-1}$ zinc and the limit of detection The figures for the atomic absorption spectrometric method were 20 and 4 $\mu\text{g l}^{-1}$. Synchronous fluorescence spectrometry has been used to¹⁴⁸ determine down to 20 $\mu\text{g l}^{-1}$ of zinc in potable water. The method is based on the formation of fluorescent complexes with salicylaldehyde thiocarbohydrazone.

See also [section 1.2.31](#) (multi-cation analysis).

Preconcentration

See [section 1.2.31](#) (multi-cation analysis).

1.2.31 *Multi-cation analysis of potable water*

The Department of the Environment¹⁴⁹ (UK) have reviewed the applicability of a number of techniques to the determination of metals in potable water. The methods are grouped under the headings of electrochemical methods, spectrophotometric methods and chromatography. Following a general introduction to the scope of these methods and problems of examination of an unknown material, each of the above categories is considered in turn. For each method the basic principles are outlined, together with the advantages and disadvantages in terms of equipment cost or ease of construction, background and interference effects, sensitivity and suitability for various types of sample. Brief reference is made to multiple channel automatic analysers and thermogravimetry, including differential thermal analysis.

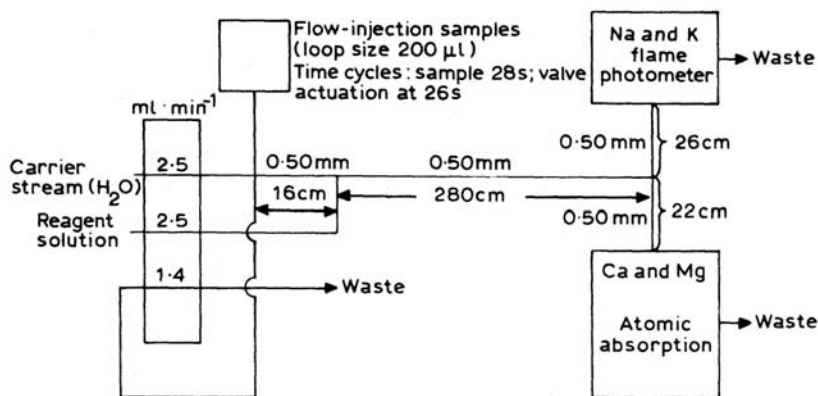


Fig. 11. Flow system for the simultaneous determination of sodium, potassium, calcium and magnesium. Sampling rate 128 samples per hour. Tube length and i.d. are given in cm and mm respectively.

Ranson¹⁵⁰ has reviewed the applicability to potable water analysis of spark source mass spectrometry, X-ray fluorescence spectrometry and neutron activation analysis. She comments that aspects of performance such as limit of detection, precision and bias can vary markedly from element to element and from one technique to another. Accordingly, the exact requirements of any proposed analysis need to be defined before a choice of the optimal technique can be made. Of the techniques examined inductively coupled plasma direct reading optical emission spectrometry has many attractive features for multielement analysis, although it does not at present allow inadequately small detection limits for a number of elements of interest in potable water analysis.

Automated flow injection analysis of sodium, potassium, magnesium and calcium

Basson and Van Staden¹⁵¹ have described a simple, rapid, automated procedure for the simultaneous determination of these elements in potable water, based on the principles of the flow injection technique in combination with flame photometry and atomic absorption spectrometry. The method is suitable for the simultaneous analysis of sodium, potassium, calcium and magnesium at a rate of up to 128 samples per hour with a coefficient of variation of better than 2.1 per cent for sodium, 1.7 per cent for potassium, 2.7 per cent for calcium and 1.8 per cent for magnesium.

A schematic flow diagram of the system used for the simultaneous determination of sodium, potassium, calcium and chloride is shown in [fig. 11](#). The manifold consists of Tygon tubing with tube lengths and inside diameters as indicated in the figure.

The sample is inserted automatically into the system by means of a Breda Scientific flow-injection sampler. A 28 s sampling cycle is used between successive samples giving a capacity of 128 samples per hour. The valve system is actuated on a time basis which is correlated with the sampler unit. The sampling valve actuates whilst a peak minimum is recorded.

The settings on the atomic absorption apparatus are:

Lamp current=3 mA

Wavelength Ca=422.7 nm, Mg=285.2 nm

Spectral band pass=1.0 nm

Carry over is less than 1 per cent. The coefficient of variation for sodium is less than 2.1 per cent, for potassium less than 1.7 per cent, for calcium less than 2.7 per cent and for magnesium less than 1.8 per cent.

The flow injection analysis compares favourably with the standard automated flame photometry method for sodium and potassium and also with the standard automated atomic absorption spectrophotometric method.

Atomic absorption spectrometry

This technique has been used for the following multielement analysis of potable water: Vanadium and molybdenum¹⁵²; cadmium, lead, copper, zinc, chromium and barium¹⁵³; and sodium, potassium, barium, arsenic and selenium. Anion exchange separation was used prior to the determination of vanadium and molybdenum¹⁵².

Hallam and Thompson¹⁵⁴ determined lead and cadmium in potable waters by atomic trapping.

The large sample dilution normally associated with conventional flame atomic absorption spectrophotometry was minimized by the use of a water cooled silica tube system as an atom trapping device. Sample water was nebulized for a pre-set time of 2 min. Condensed determinands were released into the optical path of the instrument by rapid heating. Detection limits of 2.0 and 0.25 $\mu\text{g l}^{-1}$ for lead and cadmium respectively are reported. Basic performance characteristics for arsenic, selenium, copper and silver are also reported.

Graphite furnace atomic emission spectrometry

Graphite furnace atomic emission spectrometry differs from graphite furnace atomic absorption spectrometry in that the furnace is employed as the spectral excitation source as well as the atomization cell, and light intensity due to radiational deactivation of excited atoms in the furnace is measured, rather than the attenuation of a light beam due to absorption processes.

Copper, manganese, barium, aluminium, molybdenum, nickel and beryllium

Epstein et al¹⁵⁵ used this technique to determine the above elements in nanogram quantities in potable water and compared precision and accuracy with those obtained by atomic absorption techniques.

The apparatus used by these workers for graphite furnace atomic emission spectrometry consisted of an HGA-2100 graphite furnace, quartz optics, a 0.5 m monochromator, and associated electronics. Wavelength modulation is employed as a background correction system. The monochromator was modified for wavelength modulation by placing a vibrating quartz refractor plate mounted on a torque motor between the entrance slit and the collimating mirror. The modulation apparatus is driven by the sinusoidal signal from a function generator and audio amplifier, and the signal from the photodetector is processed by a phase sensitive synchronous amplifier referenced to the second harmonic of the modulation frequency. Quantitation is performed by peak height measurements of signal tracings from a chart recorder.

Analysis by graphite furnace atomic absorption spectrometry was performed using a Perkin-Elmer Model 603 atomic absorption spectrometer and the HGA-2100. Electronic peak height detection and deuterium-arc background correction were used.

The limit of detection using graphite furnace atomic emission spectrometry is significantly lower than those obtained by graphite furnace atomic absorption spectrophotometry for several elements whose

resonance lines lie in the visible region of the spectrum (sodium, barium, potassium). Limits of detection for many other elements are similar, as shown in Table 12.

The major interfering element was found to be calcium which caused a severe depression of absorption and emission signals for some elements and an enhancement of signals for others. In order to compensate for this interference, calcium was added to all standard solutions at a concentration similar to that present in the sample.

Precision data obtained on a standard potable water sample by both the absorption and emission methods are listed in Table 13. The variability of the emission results exceeds that of the absorption results for the analysis of aluminium, beryllium, manganese, nickel and copper. No differences were found for barium and molybdenum.

The reproducibility of the emission signal will depend on the reproducibility of the heating rate of the tube and the tube temperature, as well as the factors which affect the atomic concentration. Long-term signal drift may also be more significant in emission since changes in the tube resistance may affect its temperature.

TABLE 12
Comparison of furnace atomic emission and absorption detection limits (ng l^{-1})^a

Element	GFAAS ^b	GFAES ^c
Aluminium	0.1	0.04
Barium	2	0.08
Beryllium	0.06	2
Chromium	0.2	0.4
Cobalt	0.8	3
Copper	0.1	0.4
Lead	04	60
Magnesium	0.06 ^d	2
Manganese	0.02	0.7
Molybdenum	1	1
Nickel	2	4
Sodium	0.2 ^d	0.002 ^e
Titanium	40	10
Potassium	0.1 ^d	0.002 ^e

^a Relative detection limits based on a 50- μl sample volume. Detection limits from this laboratory calculated as the analyte signal equivalent to two times the estimated maximum standard deviation of the background or blank signal during the atomization step.

^b Graphite Furnace Atomic Absorption Spectrometry (26).

^c Graphite Furnace Atomic Emission Spectrometry, HGA-2100 (3), except where noted.

^d Sensitivity (ng/ml for 0.0044 absorbance unit).

^e Carbon Furnace Atomic Emission Spectrometry, HGA-2000.

TABLE 13

Results from the analysis of SRM 1643

Concentration ($\mu\text{g l}^{-1}$)							
Element	GFAAS			GFAES			Certificate value ^d
	n^a	\bar{X}^b	s^c	n	\bar{X}		
Aluminium	16	824	1.4	21	77.1	5.7	77±1
Beryllium	10	18.3	0.4	17	21.3	5.5	19±1
Copper	8	14.0	0.3	18	16.2	1.8	16±1
Manganese	10	27.5	0.7	12	28.0	2.5	29±1
Molybdenum	8	104	3	5	110	5	105±3
Nickel	7	49.8	0.3	17	51.3	4.2	49±1
Barium	10	18.7	0.7	10	19.7	1.0	(18) ^e

^a Number of analyses included in the average.

^b Average value of analyses.

^c One standard deviation.

^d Based also on several other techniques besides those discussed here (Neutron Activation, Isotope Dilution Mass Spectrometry, and Polarography).

^e Information value. Barium is not certified because of the large difference between its initial concentration (39 ng/ml) corresponding to the amount added to water and the stabilized concentration (18 ng/ml).

Epstein et al¹⁵⁵ make the following comments regarding the determination of individual elements by both techniques:

Barium, furnace emission method was sensitive
 Manganese and beryllium, furnace absorption method was sensitive
 Molybdenum, shows strong memory effects by both methods
 Aluminium, furnace emission technique preferred

Hydride generation atomic absorption spectrometry

ARSENIC AND SELENIUM: Gunn¹⁵⁶ has reviewed the application of this technique to the determination of arsenic and selenium in potable waters. He concluded that the technique is rapid and convenient and is able to reach the required limits of detection for potable water analysis. Interference by other hydride forming elements present in water is unlikely. Regarding the chemistry of the process, he further concludes that the most suitable reductant is sodium borohydride. For the determination of selenium it is necessary to include a pre-reduction step involving heating the sample with hydrochloric acid to convert any selenium VI present to selenium IV. In the case of arsenic pre-reduction of arsenic V to arsenic III with an alkali metal iodide is advisable. Organic arsenic compounds are not completely included in the determination and they must first be decomposed to inorganic arsenic by acid persulphate digestion.

Schmidt and Royer¹⁵⁷ determined sub microgram quantities of arsenic, selenium, antimony and bismuth in potable water by atomic absorption spectrophotometry using sodium borohydride reduction. Detection limits were 0.1 $\mu\text{g l}^{-1}$ for arsenic and antimony, and 1 $\mu\text{g l}^{-1}$ for selenium and bismuth.

Inductively coupled plasma atomic emission spectrometry

Various workers have applied this technique to the determination of metals in potable waters^{150,158,159}. This technique has been compared for 32 elements with alternative systems including spark-source mass spectrometry, X-ray fluorescence spectrometry and neutron activation analysis.

Taylor and Floyd¹⁵⁹ compared the use of ultrasonic and pneumatic nebulizers in inductively coupled plasma/atomic emission spectrometry for analysing samples and the findings are reported with the aid of tables and diagrams. It was found that ultrasonic nebulization is capable of much lower detection limits than the pneumatic system (Table 14) and it has less problems when nebulizer plugging occurs.

In Table 15 are shown some analyses of a potable water sample obtained by both modifications of the technique.

In analysis of such samples where concentrations allow comparison of data acquired with pneumatic and ultrasonic nebulizer systems, the two systems show good agreement. The major differences in the two nebulizer systems to be noted from these data are the lowest quantitative determinable values that can be stated for each system. Rinse times between samples for both nebulizer

TABLE 14
Maximum contaminant levels for inorganic chemicals in drinking water and ICP detection limit data

Contaminant	Maximum level (mg l ⁻¹)	ICP Nebulizer			
		Pneumatic		Ultrasonic	
DL ^a (mg l ⁻¹)	LQD ^b (mg l ⁻¹)	DL ^a (mg l ⁻¹)	LQD ^b (mg l ⁻¹)		
Arsenic	0.05	0.06	0.210 ^c	0.006	0.020
Barium	1	0.003	0.009	0.0009	0.0003
Cadmium	0.010	0.005	0.015 ^c	0.0003	0.001
Chromium	0.05	0.005	0.015	0.0003	0.001
Lead	0.5	0.030	0.100 ^c	0.002	0.005
Mercury	0.002	0.015	0.050 ^c	0.004	0.015 ^c
Selenium	0.01	0.060	0.300 ^c	0.003	0.010
Silver	0.05	0.005	0.025	0.008	0.0025

^a Detection limit (DL) is three times the standard deviation of background emission.

^b Lowest quantitative determinable concentration (LQD) is 10 times the standard deviation of background emission.

^c Underscored values indicate LQD exceeds maximum contaminant level concentration.

TABLE 15
Analysis of drinking water

Element	Conc (mg l ⁻¹) ^a		Element	Conc (mg l ⁻¹) ^a	
	ICP pneumatic	ICP ultrasonic		ICP pneumatic	ICP ultrasonic
Ag	<0.003	<0.025	Mo	<0.007	<0.040
Al	0.034	0.038	Na	1.61	<5
As	<0.020	<0.21	Ni	<0.003	<0.10
B	<0.013	<0.030	Pb	<0.007	<0.10
Ba	0.002	0.001	Sb	<0.013	<0.17
Be	<0.0001	<0.0004	Se	<0.010	<0.30

Element	Conc (mg l ⁻¹) ^a		Element	Conc (mg l ⁻¹) ^a	
	ICP ultrasonic	ICP pneumatic		ICP ultrasonic	ICP pneumatic
Bi	<0.030	<0.17	Sn	<0.013	<0.17
Ca	19.0	19.1	Sr	0.074	0.071
Cd	<0.001	<0.015	Te	<0.030	<0.17
Co	<0.001	<0.020	Th	<0.004	<0.04
Cr	<0.001	<0.015	Ti	<0.0007	<0.007
Cu	<0.003	<0.010	Tl	<0.060	<0.25
Fe	0.045	0.041	V	<0.001	<0.007
Hg	<0.015	<0.05	Y	<0.0003	<0.003
Mg	0.701	0.715	Zn	<0.002	<0.02
Mn	0.001	<0.002			

^a <values are calculated lowest quantitative determinable concentration (10 times the standard deviation of background emission).

systems were found to be the same for the sample types analysed in these studies.

Hydride generation—inductively coupled plasma atomic emission spectrometry

ARSENIC AND SELENIUM: Pruszkowska et al¹⁶⁰ evaluated the performance of this technique comprising a commercially available continuous flow hydride generator interfaced with a segmented inductively coupled plasma system in the determination of arsenic and selenium in potable water. Samples and standards were adjusted to 6 M concentration with respect to hydrochloric acid. The reduction reagent consisted of 1 per cent w/v sodium borohydride in 0.1 M sodium hydroxide. A schematic diagram of the gas and liquid flow streams is shown in [fig. 12](#). The liquid streams—a sample, a blank, and a reducing reagent are pumped continuously. The uptake rate of the blank and the sample solution is about 7 ml min⁻¹. The reducing reagent solution is pumped at 2 ml min⁻¹. Two liquid streams, the sample or the blank solution and the reducing reagent solution, are mixed at a T piece where the reaction occurs, while the third stream is going to the drain. Switching between the blank solution and the sample solution is controlled by a pneumatic valve. The mixture of liquid and gaseous products is continuously pumped from the T-piece into the glass interface vessel. The gaseous products are swept from the interface into the plasma system by a continuous stream of argon. An individual rotameter control valve was added to the Plasma-Therm unit to provide a steady stream of argon. The gas stream is introduced directly into the plasma through the torch injection tube (2 mm). Since the analyte at this point is a gas, no nebulizer/spray chamber device is needed. With acid solution and reagent solution being continuously pumped, a steady stream of hydrides, hydrogen, and argon is continuously introduced into the plasma, and a stable discharge is obtained.

Detection limits achieved in this procedure were as follows:

- 0.3 µg l⁻¹ for the arsenic 193.69 and 189.04 nm lines
- 0.5 µg l⁻¹ for the 228.81 nm arsenic line
- 0.3 µg l⁻¹ for the 196.02 nm selenium line
- 1.5 µg l⁻¹ for selenium at 206.28 nm

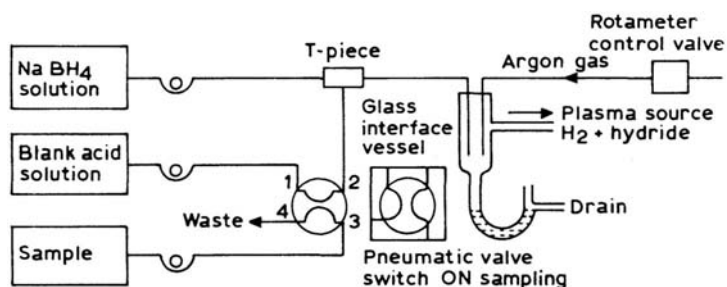


Fig. 12. Schematic diagram of the ICP-hydride system

Pruszkowska et al¹⁶⁰ found that potassium iodide pre-reduces arsenic V to arsenic III and enhances the intensity of emission from the analyte. In potable water samples (diluted 1:1 with 37 per cent hydrochloric acid) they found that no less than 1 per cent potassium iodide was required in order to get 100 per cent recovery of arsenic. A concentration of 2 per cent potassium iodide is recommended for pre-reduction of arsenic V to arsenic III.

Good agreement was obtained in this procedure for arsenic and selenium determinations on a standard water and a potable water sample.

Differential pulse anodic stripping voltammetry

Anodic stripping voltammetry with collection is a technique that was invented for the rotated ring-disk electrode, but which may be performed at two tubular electrodes in series on a flowing stream. Trace metal cations are deposited on the upstream electrode from the flowing sample solution, stripping from that electrode with an anodic potential scan, and are collected by deposition on the downstream electrode, which is held at a constant cathodic deposition potential. The constant potential applied to the collection (analytical) electrode eliminates the charging current normally encountered with conventional anodic stripping voltammetry.

This subject has been reviewed by Pandya¹⁶¹.

CADMIUM, LEAD AND COPPER: Schieffer and Blaedel¹⁶² have described a portable battery operated anodic stripping voltammeter which they used for the determination of subnanomolar quantities of cadmium, lead and copper in potable water.

The elements are collected at two mercury coated glassy carbon tubular electrodes in series. By operating the collection electrode at a constant cathodic potential, charging current backgrounds are reduced greatly, permitting better perception of peak currents than with conventional anodic scanning voltammetry.

Anodic scanning voltammetry with collection at a twin tubular electrode using a dual potentiostat is a sensitive and precise technique which might be a useful alternative to differential pulse stripping voltammetry at mercury film electrodes. At thin film electrodes, the pulse technique does not yield a significant improvement in sensitivity over linear scans for many anodic scanning voltammetric determinations and is generally restricted to low scan rates. It does, on the other hand, give a significant reduction in both the magnitude and noise of the background current, allowing more precise, sensitive analysis and the use of relatively fast scan rates.

Upon application of anodic scanning voltammetry with collection to the analysis of potable water for copper, it was found that the result was much higher than the cupric ion activity or the cation exchangeable copper ion activity. It was also found that the copper content was less than the total determined by carbon

furnace atomic absorption spectroscopy. A similar conclusion applied to cadmium and lead. These discrepancies have not been resolved.

LEAD, CADMIUM, COPPER AND ZINC: Frimmel and Immerz¹⁶³ determined these elements in amounts down to $0.1 \mu\text{g l}^{-1}$ by differential pulse anodic scanning voltammetry. Matrix interference in the case of copper determinations in ground water tended to give flattened peaks, and hence low values, but this could be counteracted by a preliminary extraction step. Heavy metal contents in potable water were influenced by the stagnation period, and samples drawn after standing could give results ten times as great as those after flushing the system until the sample temperature had dropped to the level of the mains supply.

Pandya¹⁶⁴ developed a method for the automatic simultaneous determination of lead, cadmium, copper and zinc in potable water by anodic stripping voltammetry using the hanging mercury drop electrode. The software of this system is split into two independent programs, the 'parameter input' program and the 'analysis control' program. This enables readjustment of the optimal parameters over a large range before every voltammetric analysis. The time consuming repetition of the whole analysis is avoided by various test subroutines that control the state of the three electrodes and of the important parts of the device after every measurement. After the analysis the whole voltammetric curve is plotted, every peak in an optimal current sensitivity range and the heading containing important information about the analysis is printed out.

A buffered medium like acetate at pH 5-8 yielded readily measurable current peaks for zinc, cadmium, lead and copper, and the differences between the half peak potentials were large enough for simultaneous recording of their peaks. The accuracy is satisfactory with coefficient of variation less than 20.08 per cent and the standard deviation is less than 0.007 mg l^{-1} .

Arts et al¹⁶⁵ evaluated the performance of the Princeton Applied Research Model PAR 384 automated polarograph for the determination of heavy metals in potable water. Numerous improvements were suggested both in the operation of the polarograph to ensure more reproducible mercury drop formation and in the design of the software to give more acceptable presentation of results and to eliminate errors from the calculations. The method provided a cheaper method of equal sensitivity to atomic absorption spectrometry for routine multi-element determination of heavy metals in drinking water.

Schulze et al¹⁶⁶ described a flow cell detection system for the determination of lead in potable water based on potentiometric stripping analysis and atomic absorption spectrometry.

Spark source mass spectrometry

Vanderborcht and Van Grieken¹⁶⁷ combined spark source mass spectrometry with an enrichment procedure in which the transition metals in solutions are chelated by oxine and subsequently adsorbed into activated carbon. The metal ions are collected after chelation but naturally occurring metal/organic and colloidal components are also concentrated. Very high enrichment factors and recoveries are obtained, with an error of around 30 per cent. The collection substrate is also suitable for direct determination by X-ray fluorescence or neutron activation analysis. For analysis by spark source mass spectrometry, the substrate must be ashed to remove organic material and this improves the strength of electrodes prepared after mixing with graphite. This method has been used for simultaneous determination of 10-25 elements in potable water, surface and ground water samples.

Energy dispersive X-ray fluorescence spectrometry

The field of X-ray spectrometry is rapidly progressing. There has been a breakthrough resulting from the development of semi-conductor detectors with high resolving power which allows the easy quantitative

multi-element analysis with moderate to high precision. The method is particularly interesting for the analysis of environmental samples. The high sensitivity measurement of the fluorescence radiation allowed by the use of the energy-dispersive detector resulted in the possibility of exploiting almost perfectly monochromatized X-ray beams for the excitation. This has a prominent impact on the development of mathematical correction and calibration procedures because the excitation and fluorescence conditions become easy and straightforward. At the same time the mathematical treatment of the data is enhanced by the availability of small computing facilities. This technique has been applied¹⁶⁸ to the determination of 20 elements in 5–20 min in potable and rain water. Computer techniques are used for the subsequent data reduction of the X-ray spectra. The technique is applicable to suspended material in water which is filtered on a 0.45 μm pore size filter paper and to dissolved trace elements which are evaporated on cellulose filter paper or are collected on a thin ion-exchange loaded paper.

With this instrument a 170 eV energy resolution at 5.9 KeV is capable of resolving K α -X-rays with a 50:1 to 1:50 intensity ratio for all adjacent elements, but is not sufficient to resolve a number of K α -K β or K-L interferences. The count rate characteristics are excellent. There are no significant displacements of peak maxima nor is there a significant decrease in energy resolution or deterioration of peak shape. For the molybdenum K-secondary radiation the intensity ratio of coherently scattered Mo K radiation to recorded intensity is close to 1000:1 at the energy region of 5–7 KeV.

To prevent the difficulties involved in calibration of the instrument for each different sample type individually, a calibration was performed with a set of homogeneously thin pure compound standards.

These are commercially available and are obtained by vacuum evaporation of the pure elements or compounds onto the mylar backings. Taking into account the cross-sections of fluorescent X-ray production, absorption jump ratios, Auger yields, absorption in the air, and the beryllium window of the detector and finally in the detector itself, a calibration could be obtained with an estimated accuracy of better than ± 5 per cent for the elements chlorine to strontium and lead which was determined through its L-radiation.

To overcome any instability in the X-ray generator an internal reference was generated in each spectrum by using a thin wire which was positioned reproducibly in the radiation path just below the sample. The selection of a suitable element and an adequate thickness provides an easily measurable calibration peak in the spectrum. For molybdenum excitation a pure zirconium metal wire with a diameter of 50 μm was used. It gives rise to K α , K β fluorescence radiation which does not interfere with the detection of the other elements except by the small increase in continuous radiation background.

When toxic metals in potable water are collected on Chelex 100 filters and examined by this technique, detection limits of 1 $\mu\text{g l}^{-1}$ were achieved by Van Espen et al¹⁶⁸.

CALCIUM, IRON, COBALT, NICKEL, COPPER, ZINC, LEAD, MERCURY, CHROMIUM AND SELENIUM: Ho and Lin¹⁶⁹ have also applied energy dispersive X-ray fluorescence spectrometry to the simultaneous determination of several elements in potable, surface and ground waters.

In their system, water samples are passed repeatedly through a filter paper coated with a suitable ion-exchange resin. This filter is then exposed to X-ray pulses and the secondary spectra caused by the metals trapped in it are analysed by dedicated computer. Qualitative evidence of the presence of unsuspected metals may also be had. Detection limits as low as 0.54 $\mu\text{g l}^{-1}$ are possible for iron.

A sample preparation and collection module processes the water samples through resin loaded filter paper in which the metal ions contained in the samples are concentrated by the ion-exchange resins. Once this is completed, the filter paper is then ready for X-ray analysis.

Energy dispersive X-ray analysis is a multielement technique inasmuch as all the elements present on the filter paper are measured simultaneously. The sample is excited by an X-ray tube and the secondary X-rays subsequently generated are detected. The pulse X-ray tube which is coupled to the X-ray detector, is turned

off when the detector processes the incoming X-rays from the sample, permitting a more efficient collection of the incoming X-rays. The net effect of using a pulse X-ray tube is the storage of more counts, or incoming X-rays, per unit of time, which therefore shortens analysis time. A pre-amplifier takes the charge, or pulse, presented by the detector and converts it to a voltage signal proportional to the energy deposited on the detector. A main amplifier then takes the preamplifier signals and amplifies them for presentation to the multi channel analyser which qualitatively and quantitatively extracts information from the input signal and generates the spectra which are stored in a memory for further processing.

Ho and Lin¹⁶⁹ applied this system to the determination of 10 elements; calcium, iron, cobalt, nickel, copper, zinc and lead, were easily exchanged in a strong and resin loaded SA-2 filter paper. Mercury, selenium and chromium could not be retained on SA-2 paper (Amberlite IR-120 ion exchange resin, Whatman Inc) and were collected on a strong base resin loaded SB-2 filter paper (Amberlite LRS-400 ion-exchange resin).

Calibration plots for the 10 metals are shown in *figs 13(a)–(c)*. The next X-ray intensities were expressed in counts per second and the concentrations were expressed in micrograms. For each metal ion, a straight line was obtained for samples in the metal ion contents ranging from 50 to 200 μg in a 500 ml solution.

Table 16 shows the detection limit for the 10 metal ions based on a 100 s analysis time and a 500 ml water sample. The detection limit for these 10 metal ions varies from 0.54 $\mu\text{g l}^{-1}$ for iron to 9.14 $\mu\text{g l}^{-1}$ for selenium.

Pella et al¹⁷⁰ prepared samples for energy dispersive X-ray spectrometric analysis by evaporation of the water and fusion of the residue with sodium borate. This technique overcomes particle size and inhomogeneity effects on the analysis.

Proton induced X-ray emission spectrometry

In this technique, the sample in a vacuum chamber is bombarded with 2.55 meV protons and the X-ray spectra produced are detected by a silicon lithium detector used in conjunction with a pulse height analyser. Several workers have examined the applicability of this technique to potable water analysis^{171–173}.

Saleh¹⁷³ dried small drops (0.75 μl) of potable water samples on 25 cm^{-2} sections of Hostophan foil leaving thin spots as targets for proton induced X-ray emission analysis. With this method, detection limits range from 2 to 5 $\mu\text{g l}^{-1}$. Samples were acidified to pH 1–1.5 with ultrapure nitric acid.

TABLE 16
Detection limits for various metal ions in SA-2 and SB-2 resin-loaded papers

Resin-loaded paper	Metal ion	Spectral line measured (keV)	Detection limit ^a ($\mu\text{g cm}^{-2}$)	Detection limit ^b ($\mu\text{g l}^{-1}$)
SA-2	Ca	3.690	0.21	1.00
SA-2	Fe	6.398	0.11	0.54
SA-2	Co	6.924	0.15	0.70
SA-2	Ni	7.471	0.15	0.74
SA-2	Cu	8.040	0.19	0.90
SA-2	Zn	8.630	0.21	1.00
SA-2	Pb	10.550	0.79	3.80
SB-2	Cr	5.411	0.24	1.04
SB-2	Hg	9.987	0.91	4.36
SB-2	Se	11.207	1.90	9.14

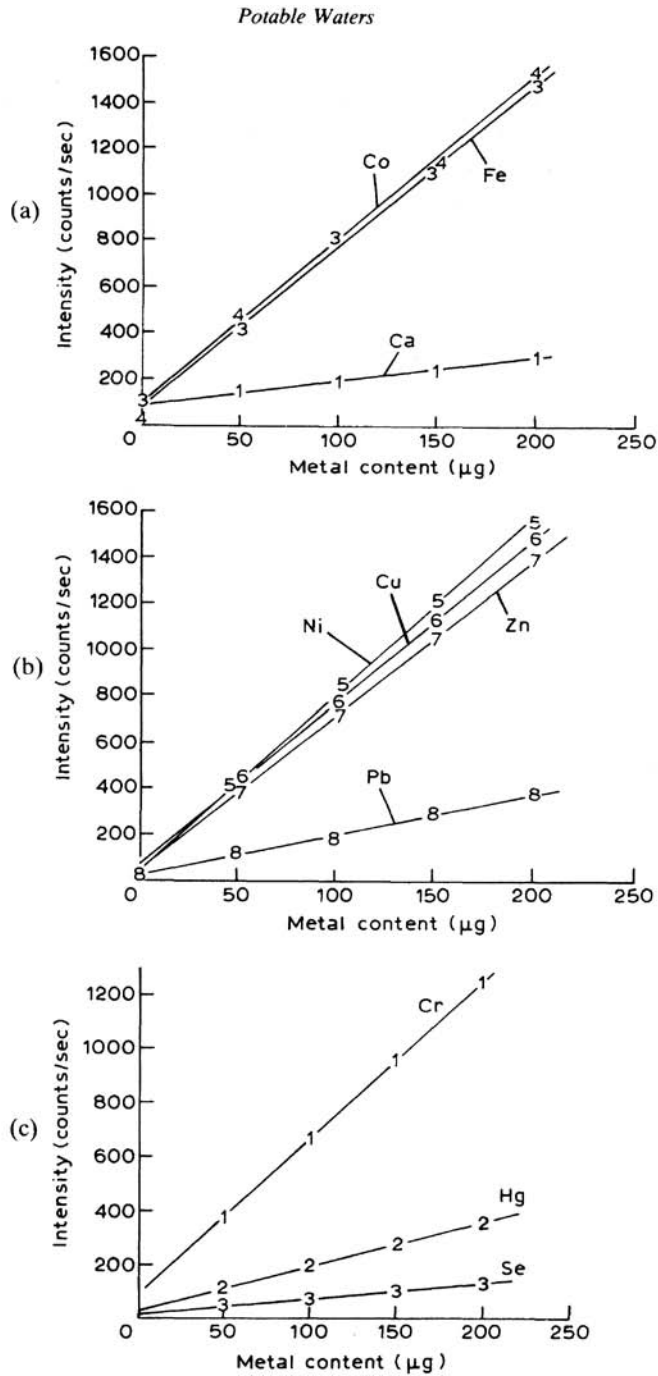


Fig. 13. Energy dispersive X-ray analysis of potable water. (a) Calibration curves for Co, Fe and Ca analysis on SA-2 filter paper; (b) calibration curves for Ni, Cu, Zn and Pb analysis on SA-2 filter paper; (c) calibration curves for Cr, Hg and Se analysis on SB-2 filter paper.

Resin-loaded paper	Metal ion	Spectral line measured (keV)	Detection limit ^a ($\mu\text{g cm}^{-2}$)	Detection limit ^b ($\mu\text{g l}^{-1}$)
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^a Based on 2.4-cm² area.

^b Based on 500-ml sample.

Preconcentration was not required to achieve the required detection limits. Detection limits achieved range from 2 $\mu\text{g l}^{-1}$ for nickel and copper to 5 $\mu\text{g l}^{-1}$ for vanadium and chromium. This can be compared with data obtained by Simms and Rickey¹⁷² using the same technique who obtained detection limits ranging between 0.1 and 100 $\mu\text{g l}^{-1}$ for the 76 elements they examined in potable water supplies.

Neutron activation analysis

Brune¹⁷⁴ carried out neutron activation analysis of frozen potable water samples.

Isotope dilution mass spectrometry

Trettenbach and Heumann¹⁷⁵ used cathodic electrodeposition for the initial separation of lead, cadmium and thallium from potable water samples prior to their determination in the $\mu\text{g l}^{-1}$ and ng l^{-1} ranges by isotope dilution mass spectrometry. A solution containing lead-206 and cadmium-116 was added to the sample. Positive thermal ions of the respective elements were measured successively by raising the temperature of the single filament ion source.

1.2.32

Preconcentration of multi-cations

Chelation-solvent extraction procedures

Subramanian and Meranger¹⁷⁶ made a critical study of the solution conditions and other factors affecting the reliability of the ammonium pyrrolidine dithiocarbamate-methyl isobutyl ketone extraction system for the determination of silver, cadmium, cobalt, chromium, copper, iron, manganese, nickel and lead in potable water. Graphite furnace atomic absorption spectrometry was used for the finish.

The following parameters were investigated in detail: pH of the aqueous phase prior to extraction, amount of ammonium pyrrolidine diethyl dithiocarbamate added to the solution following pH adjustment the length of time needed for complete extraction and the time stability of the chelate in the organic phase. Except for silver and chromium which were quantitatively extracted only in a very narrow pH range (1.0–2.0 and 1.8–3.0 respectively) and cadmium and lead which were stable in the extracted methylisobutyl ketone phase only for 2–3 hours, the solution conditions for quantitative extraction were not critical for the other metals. Simultaneous extraction of all the metals except cadmium and lead was also investigated. Good recoveries (100±10 per cent) were obtained for a number of spiked raw treated and distributed potable water samples covering a wide range of hardness. They concluded that the procedure is reliable and precise under proper solution conditions.

In [fig. 14](#) is shown the effect of sample pH on the extraction efficiency of several metals. [Fig. 15](#) shows the effect of complexing agent: metal ratio on extraction efficiency. Metal recoveries are satisfactory as shown in [Table 17](#).

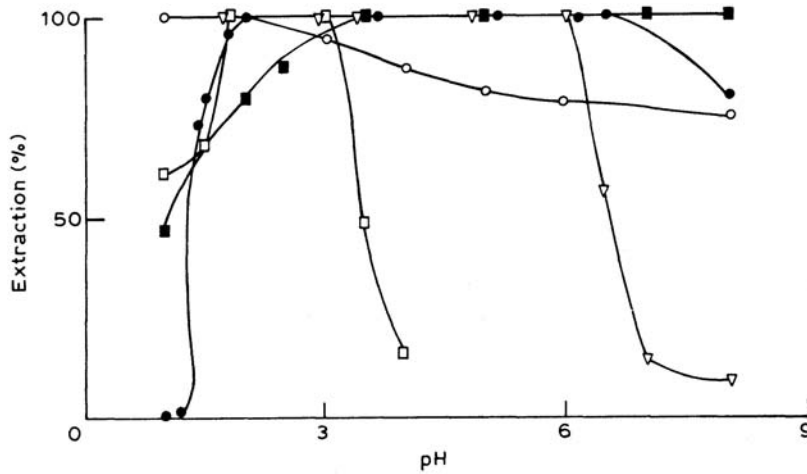


Fig. 14. Effect of pH on the extraction of some trace metals using the APDC-MIBK procedure (aqueous/organic=5); Ag, $4 \mu\text{g l}^{-1}$; Cr, $20 \mu\text{g l}^{-1}$; Fe, $20 \mu\text{g l}^{-1}$; Mn, $6 \mu\text{g l}^{-1}$; Pb, $8 \mu\text{g l}^{-1}$.

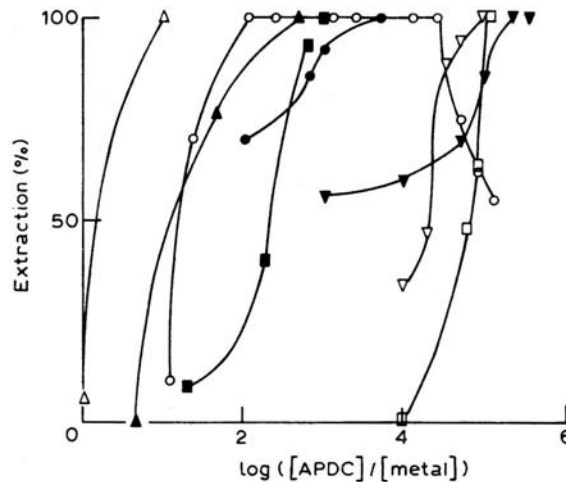


Fig. 15. Effect of APDC on the extraction of some trace metals using the APDCMIBK procedure: Ag, $4 \mu\text{g l}^{-1}$; Cd, $0.2 \mu\text{g l}^{-1}$; Co, $20 \mu\text{g l}^{-1}$; Cr, $20 \mu\text{g l}^{-1}$; Cu, $20 \mu\text{g l}^{-1}$; Fe, 20ng l^{-1} ; Ni, $50 \mu\text{g l}^{-1}$; Pb, $8 \mu\text{g l}^{-1}$.

Cadmium-exchange resin techniques

Kempster and Van Vliet¹⁷⁷ have described a semi-automated resin concentration method for the preconcentration of trace metals (chromium, manganese, iron, cobalt, nickel, copper, zinc, cadmium and lead) in potable water, prior to atomic absorption analysis. A peristaltic pump was used to control the flow of

TABLE 17

Percent recovery of metals in spiked samples of raw, treated and distributed potable water using APDC-MIBK-GFAA

Concentration of spike (ng ml ⁻¹)	% Recovery								
Ag	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	
0.2	—	96±7 ^a	—	—	—	—	—	—	—
0.4	100±3	101±4	—	—	—	—	94±6	—	—
0.6	104±2	98±3	—	—	—	—	—	—	—
0.8	—	95±4	—	—	—	—	103±5	—	—
2.0	103±3	—	—	92±6	97±4	—	93±4	—	104±5
4.0	100±4	—	94±5	96±3	105±2	98±3	97±3	—	—
6.0	98±3	—	—	—	101±3	—	—	—	95±5
8.0	—	—	96±3	97±2	105±2	—	—	—	98±6
10.0	—	—	—	97±4	104±3	96±1	98±2	—	101±5
20.0	—	—	97±2	91±6	95±2	93±2	—	101±1	—
40.0	—	—	97±4	—	—	102±4	—	104±1	—
50.0	—	—	—	—	—	98±1	—	—	—
80.0	—	—	—	—	—	—	—	102±4	—
100.0	—	—	95±5	—	—	—	—	100±5	—
200.0	—	—	—	—	—	—	—	104±2	—

^a Values given represent the average of the triplicate analyses each of 20 raw, treated and distributed potable water samples ranging in hardness from 1 to 554 mgCaCO₃ l⁻¹. The values are more or less the same for single as well as simultaneous extractions. The measure of precision is the standard deviation.

water samples through columns of a cation-exchange resin (Amberlite IR-120/H form), the samples being stabilized with ascorbic acid (0.5 g l⁻¹) at a pH of 2.5 during the sorption stage.

The water samples analysed were treated as follows: the samples, collected in precleaned polyethylene bottles and preserved with concentrated nitric acid (5 ml l⁻¹) were filtered through a 0.45 µm pore size membrane filter to remove particulate matter. Ascorbic acid (0.5 g l⁻¹) was then added, and the pH adjusted to between 2.0 and 2.5 with concentrated ammonia solution using the pH indicator paper.

The samples were then pumped through the cleaned resin columns (at 0.42 ml min⁻¹) to sorb the metals onto the resin. The time necessary to pump 500 ml sample volumes through the resin columns was just under 20 hours. With subsequent elution of the sorbed metals to a volume of 50 ml, a concentration factor of 10× was obtained. The volume of each sample passed through the resin columns was measured to determine the exact concentration ratio.

To elute the metals from the resin columns, 25 ml 5 M hydrochloric acid followed by 12ml of deionized water was pumped through each column, the eluate being collected in 50 ml volumetric flasks. Concentrated ammonia solution (3.5 ml) was then added to the elute in each 50 ml volumetric flask to reduce the excessive acidity, which was found to produce noisy signals in the subsequent atomic absorption analysis. The pH of the eluate after the addition of ammonia solution was found to be less than 2. The eluate was made up to 50 ml with deionized water and transferred to 50 ml polyethylene bottles until analysis by flame atomic absorption spectroscopy.

The resin columns were then regenerated for the next batch of samples with 25 ml 3 M hydrochloric acid (redistilled AR). Of the nine elements mentioned above, eight gave a recovery through the whole procedure of between 88 and 99 per cent whilst iron had a recovery of 75 per cent. Detection limits were as follows: Cr $3 \mu\text{g l}^{-1}$, Mn $0.5 \mu\text{g l}^{-1}$, Co $1 \mu\text{g l}^{-1}$, Cu $0.5 \mu\text{g l}^{-1}$, Zn $2 \mu\text{g l}^{-1}$, Cd $0.1 \mu\text{g l}^{-1}$, Pb $6 \mu\text{g l}^{-1}$.

This method is useful for the pre-concentration of a large number of samples, does away with the tedium characteristic of manual enrichment techniques and gives good recovery for the nine metals tested.

Difficulty was experienced in obtaining consistent results for iron but it was found that with the addition of ascorbic acid to the samples, prior to sorption onto the resin, more consistent results were obtained. Ascorbic acid serves as a complexing agent to counteract hydrolysis of iron.

Brajter et al¹⁷⁸ pre-concentrated metal ions (bismuth III, copper II, indium III, copper II and nickel II), by adsorption on Amberlite XAD-2 resin loaded with pyrocatechol violet prior to desorption and determination by atomic absorption spectrometry.

Chelex 100 resin techniques

Subramanian et al¹⁷⁹ have discussed on-site sampling with pre-concentration for the determination of some Chelex-100 levels of labile metals (cadmium, copper, lead and zinc) in potable water. The on-site pump integrated water sampler coupled with a Chelex-100 pre-concentration unit is described in detail. Metals in the concentrate were determined by graphite furnace atomic absorption spectrophotometry.

Chelex 100 will remove only that fraction of the trace metal level that is 'Chelex labile'. For example, only 44–63 per cent of lead and copper in potable water is labile, presumably due to the presence of humic acid and possibly other chelators in the water.

Zolotov et al¹⁸⁰ used Chelex 100 resin to pre-concentrate 0.5–1000 μg copper from 50–500 ml samples of water.

1.3

Elemental analysis

1.3.1

Total organic nitrogen

Titration method

Moore and McNulty¹⁸¹ used microcoulometric titration to determine 0.2–10 mg l^{-1} total organic nitrogen in potable water. The sample is pyrolysed over a granular nickel catalyst at 800°C in a stream of humidified hydrogen, converting nitrogen to ammonia which is absorbed in sodium sulphate solution. Ammonia is then titrated by the electrogeneration of hydrogen ions in the presence of a pH electrode until the original pH of the solution is restored.

Albat et al¹⁸² describe a method for the determination of total Kjeldahl nitrogen content which is designed to meet the requirements of the EEC directive setting the limit in water supplies at 1 mg l^{-1} . The conventional method has been improved by introducing a potentiometric end-point indication instead of the colorimetric technique. The coefficients of variation of the method did not exceed 17 per cent, in the range 0.2–0.8 mg l^{-1} N. Losses during all stages of the analysis were negligible. During a six month study at Mery-Sur-Oise, France, no samples exceeded the EEC limit.

1.3.2

*Organic chlorine**Titration method*

Van Steenderen¹⁸³ has described the construction of a total organohalogen analysis system, which is applicable to potable water. It is based on a coulometric titration system. In this method an aliquot of sample extract is injected into a pyrolysis tube and mixed with reagent gas, from which the gas is eluted through a heated capillary inlet tube into a titration cell which is specific for the measurement of chloride, bromide and/or iodine derived from the combusted halogenated organic compounds present in the sample. Halides entering the titration cell form insoluble precipitates with silver ions in a 13.2 mol l⁻¹ acetic acid solution. The most sensitive cell conditions occur when the silver ion concentration is equal to the chloride ion concentration. For water the chloride ion concentration is 10⁻⁵ mol l⁻¹ while for acetic acid this is at less than 10⁻⁷ mol l⁻¹.

1.3.3

Bromine and iodine

Leddicote and Navarette¹⁸⁴ determined down to 1 ng of bromine in water by neutron activation analysis.

Sadisivan and Anand¹⁸⁵ have developed a neutron activation analysis procedure for the determination of bromine and iodine in potable water.

1.3.4

*Total organic carbon**Peroxydisulphate oxidation*

Van Steenderen et al¹⁸⁶ give details of the direct automated determination of trace levels of organic carbon in potable water. It involves a wet chemical oxidation technique using silver peroxydisulphate, and measurement of the liberated carbon dioxide by infrared photometry.

The technique is that of continuous flow analysis and utilizes an automatic sampler, a multiple channel proportioning pump, and an appropriate analytical system (manifold). Samples are acidified, oxygen segmented and passed through a heated inorganic carbon stripper. The stripped liquid is resampled, mixed with silver peroxydisulphate solution and digested at 70°C. The liberated carbon dioxide is measured by means of infrared photometry. Complete inorganic carbon removal was not possible. From a 30 mg l⁻¹ inorganic carbon solution 0.1 per cent residual remained after stripping. Using a sample volume of 6.3 cm³ min⁻¹, full scale recorder deflection could be obtained for a 1 mg l⁻¹ organic carbon standard solution with a relative standard deviation of 0.9 per cent. The lower detection limit of practical significance is 50 µg l⁻¹ organic carbon. The analysis rate is 20 samples per hour. Certain synthetic organic materials resisted complete oxidation including the amino acids glycine, l-alanine, leucine, iso-leucine and valine.

Ultraviolet oxidation

Ultraviolet oxidation has been used¹⁸⁷ to determine total organic carbon in potable water. The analyser is based on ultraviolet oxidation at low temperature, with an infrared detector for the carbon dioxide evolved.

The components are a highly efficient reactor with a submerged ultraviolet tube, a stable, highly sensitive, non-dispersive infrared detector, a microprocessor and a digital display unit for results. The potassium persulphate reagent is fed continuously via a dosing pump and the sample is acidified and oxygenated before injection to the ultraviolet reactor. The calibration and determinations are rapid and simple and the instrument is capable of continuous measurement. Replicate measurements of a sample containing 0.3 mg l^{-1} had a reproducibility of plus or minus 0.011 mg l^{-1} .

Kehoe¹⁸⁸ discusses the limitations of the total organic carbon method for analysis of water including the limits of detection and the efficiency of conversion of carbonaceous material to carbon dioxide. The correlation of total organic carbon with biochemical oxygen removal and chemical oxygen demand is also considered briefly.

1.3.5

Biodegradable dissolved organic carbon

Servais et al¹⁸⁹ give details of two procedures for the determination of biodegradable dissolved organic carbon in potable water. In both procedures the sterile filtered sample is reinoculated with a natural bacterial population from the same region as the sample and incubated in the dark for 10 days at 20°C . In one procedure dissolved organic carbon is measured until a plateau is reached, the difference between the initial and final dissolved organic carbon being taken as the biodegradable organic carbon. In the other procedure bacterial biomass and mortality rate are followed and integrated flux of mortality during the incubation period calculated and divided by the growth yield to give an estimate of biodegradable dissolved organic carbon.

1.3.6

Total inorganic carbon

Spectrophotometric method

Gravelet-Blondin et al¹⁹⁰ have described a simple automated method for the determination of total inorganic carbon using an adapted Technicon AutoAnalyser. The sample is segmented with carbon dioxide free air, acidified and heated to 37°C , then passed under the dialysis membrane to ensure that a constant fraction of the carbon dioxide diffused through the membrane into the buffered thymol indicator stream. The method has been successfully used in the range $50\text{--}500 \text{ mg l}^{-1}$ bicarbonate for total inorganic carbon measurements. Recoveries for 102 mg l^{-1} averaged 98.4 per cent and for 310 mg l^{-1} , 101.3 per cent. The coefficient of variation was less than 1 per cent.

Miscellaneous

Wilson¹⁹¹ has considered the potential effects of humic buffering capacity on total inorganic carbon determinations. The buffer capacity of humic substances is described mathematically and the effects of pH values, carbonate species concentration and humic concentration on total inorganic carbon are quantified. Humic substances are shown to be poor buffers, even when present in high concentrations.

1.4 Miscellaneous determinands

1.4.1 Alkalinity

Spectrophotometric method

Van Staden and Van Vleit¹⁹² have described simple, automated procedure for determining total alkalinity in surface water, groundwater and potable water. Up to 120 samples per hour can be analysed with a coefficient of variation of better than 1.40 per cent.

Flow injection analysis

Canate et al¹⁹³ have described a flow injection analysis system for the simultaneous determination of the alkalinity, pH and total ionic concentration of potable water. The pH measurements are performed by means of a glass calomel microelectrode inserted in the water stream. The alkalinity and total ionic concentration are determined by flow injection analysis titrations, acid base reactions and spectrophotometric detection. In addition, the determination of the total ionic concentration requires the incorporation of an ion-exchange minicolumn. The results obtained are in agreement with those obtained by conventional methods for the determination of these parameters and are obtained with a higher degree of automation, which results in a smaller reagent consumption, greater convenience and higher reproducibility and sampling frequency. A microcomputer is installed for on-line data collection and the treatment and display of results.

TABLE 18
Features of the simultaneous determination of pH, alkalinity and total ionic concentration

Parameter	Detection method	Range of determination ^a	Equation of calibration graph ^b	Regression coefficient	R.s.d., % (concentration)
pH	Potentiometric (continuous control)	3–11			
Alkalinity	Spectrophotometric	$t: 5.0\text{--}600 \mu\text{g ml}^{-1} \text{CaCO}_3$	$t=31.28 \log C + 151.5$	0.9952	$\pm 1.5(11.9 \mu\text{g ml}^{-1})$
		$S: 10.0\text{--}600 \mu\text{g ml}^{-1} \text{CaCO}_3$	$S=3.48 \log C + 17.3$	0.9965	$\pm 1.7(11.9 \mu\text{g ml}^{-1})$
Concentration	Spectrophotometric	$0.7\text{--}2.8 \text{ mequiv.l}^{-1} \text{Cl}^{-}$	$S=3.09 \log C + 9.4$	0.9998	$\pm 3.4(1.27 \text{ mequiv.l}^{-1})$
		0.9994	$\pm 2.1(7.04 \text{ mequiv.l}^{-1})$	0.9790	
		$2.8\text{--}27 \text{ mequiv.l}^{-1} \text{Cl}^{-}$	$S=2.53 \log C + 7.4$		$\pm 3.5(7.04 \text{ mequiv.l}^{-1})$

^a t =peak width/s; S =peak area covered by the base line and the measured height.

^b C =analyte concentration.

TABLE 19
Determination of pH, alkalinity and total ionic concentration in synthetic samples

Sample composition, p.p.m.	pH	Alkalinity ($\mu\text{g ml}^{-1} \text{CaCO}_3$)	Error, %	Total ionic concentration (mequiv.l ⁻¹)	Error, %
Cl ⁻ , 5; SO ₄ ²⁻ , 5; NO ₃ ⁻ , 5; HCO ₃ ⁻ , 10	6.74	15.84	-3.4	0.666	1.9
Cl ⁻ , 25; SO ₄ ²⁻ , 30; NO ₃ ⁻ , 10; HCO ₃ ⁻ , 30	7.34	46.59	-5.3	2.519	1.9
Cl ⁻ , 60; SO ₄ ²⁻ , 60; NO ₃ ⁻ , 20; HCO ₃ ⁻ , 60	7.65	99.95	1.5	5.363	2.6
Cl ⁻ , 125; SO ₄ ²⁻ , 150; NO ₃ ⁻ , 40; HCO ₃ ⁻ , 150	8.24	252.9	2.7	12.010	-1.5
Cl ⁻ , 250; SO ₄ ²⁻ , 250; NO ₃ ⁻ , 50; HCO ₃ ⁻ , 175	8.30	301.4	4.9	18.637	-0.7
Cl ⁻ , 350; SO ₄ ²⁻ , 350; NO ₃ ⁻ , 50; HCO ₃ ⁻ , 250	8.38	420.3	2.4	25.564	1.63

Table 18 summarizes the features of the simultaneous determination of alkalinity, pH and total ionic concentration.

Canate et al¹⁹³ tested the validity of their procedure by analysing a series of synthetic samples, the composition and results of which are shown in Table 19. In general, the errors in the determination of alkalinity are higher than those of the total ionic concentration.

The method was also applied to the determination of these parameters in potable water. The results (Table 20) have been compared with those of conventional manual methods (e.g. for alkalinity titration with hydrochloric acid and methyl orange as indicator and for total ionic concentration, passage of the water sample through a cationic ion-exchange column in acidic form and titration of the eluate with sodium hydroxide and phenolphthalein as in

TABLE 20
Determination of pH, alkalinity and total ionic concentration in natural and potable water by the curate and conventional

Sample	pH	Alkalinity ($\mu\text{g ml}^{-1} \text{CaCO}_3$)		Total ionic concentration (mequiv.l ⁻¹)	
		FIA	Conventional ^a	FIA	Conventional ^a
<i>Bottled waters—</i>					
Font-bella	7.99	194.79	195.47	4.856	4.760
Cabras	8.58	481.11	453.21	12.373	12.444
<i>Unbottled waters—</i>					
C rdoba (urban)	7.95	134.64	137.62	4.689	4.781
La Rambla (urban)	7.96	400.68	393.81	17.933	17.808
La Rambla (well)	7.51	366.79	366.29	13.145	13.340

^a See text.

dicator). The results obtained were in good agreement with these conventional methods.

1.4.2 *Hardness*

Titration procedures

Various titrimetric procedures have been described for the determination of the hardness of potable water^{194–196}. The UK Department of the Environment method¹⁹⁵ consisted of two titrimetric procedures for the direct determination of total hardness and calcium hardness respectively, the magnesium hardness being obtained by difference. Both methods are based on complexometric titration against standard EDTA solution (0.01 M) and are applicable up to 1000 mg l⁻¹ (expressed as calcium carbonate) in each case.

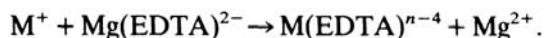
Virojanavat and Huber¹⁹⁶ have described a potentiometric end point detection in the chelometric titration of water hardness, calcium, or magnesium with EDTA. The potentiometric electrode system consists of a wax-bound lead dioxide versus a wax bound lead sulphide electrode. Both are solid state and easily maintained. Both electrodes respond to EDTA but with opposite signs, thus a large 'break' in potential between the electrodes occurs at the end point. For routine applications the titration end point can be conveniently indicated by a simple sensing comparator circuit. A light emitting diode is used to mark the end point at a preset potential. Plotting the titration curves to locate the end point is not necessary. The average error was less than 1 per cent for the samples containing calcium carbonate at 20–60 mg l⁻¹ at titrant flow rates of 1.05 and 2.05 ml min⁻¹. The error increases at the higher flow rates.

Excellent agreement is obtained between the potentiometric titration procedure and a manual standard Eriochrome Black-T method.

Bellomo et al¹⁹⁷ have described a labour saving semi-automatic method of measuring electrically the change in absorbance during an EDTA titration of calcium and magnesium in potable water when Eriochrome Black-T is used as an indicator. In this method red radiation (max=630 nm) emitted by a light emitting diode passes through the solution under examination, which is coloured red by the indicator, and impinges on a phototransistor placed on the other side of the titration vessel. At the end point the solution becomes blue and thus absorbs the red radiation; under these conditions the phototransistor is de-energized. This transition is treated electronically to send a signal to stop the flow of titrant from an automatic burette, adjusted to add equal increments of 0.01 ml.

Polarographic method

Cheney et al¹⁹⁸ have described a method for the determination of water hardness based on the polarographic reduction of magnesium ion. Magnesium is displaced from its EDTA complex by cations contributing to the water hardness



M=zinc, calcium, lead, copper, iron, calcium or magnesium.

The liberated ion is reduced at the dropping mercury electrode via a catalytic process. The enhanced current which results, yields approximately 100 fold amplification over that obtained from a conventional diffusion controlled process. Precision and accuracy comparable to that obtained using standard EDTA titrations are achieved by this more rapid technique. This hardness measurement technique is based on the stoichiometric displacement of magnesium from its relatively weak EDTA complex by most divalent metal ions. Though the relationship between observed catalytic current and concentration of magnesium ion is linear over a relatively narrow range of concentration, the technique offers a rapid and sensitive method for determination of water hardness.

Samples of potable water, well water and an artificially prepared hard water containing 25.0 mg l⁻¹ calcium and 20.2 mg l⁻¹ magnesium were analysed by the polarographic method and by the standard EDTA titration method. For the polarographic method, the starting solutions were adjusted to the linear concentration range with magnesium and the sample sizes chosen to keep the final concentrations less than 80 μM (total current, 80 μA). The polarogram was recorded for the starting solution and again after sample addition. The change in the maximum current for these two runs, divided by the slope of the calibration curve, gave the increase in Mg²⁺ attributable to the sample; a volumetric correction was applied. Results are accurate to within 1 per cent of the titration values and precision is of the order of ±1 per cent.

Since diffusion controlled waves are much smaller for a given reactant concentration than the catalytic wave used for this method, this technique may be used to discriminate against metal ions, which, although reducible at these potentials, do not contribute to the catalytic wave, e.g. alkali metals and ammonium.

Flow injection analysis

Canete et al¹⁹⁹ have described a method for the simultaneous determination of calcium and magnesium (hardness) in water by flow injection analysis. The method is applied to the determination of these parameters in natural, potable urban and bottled waters. The determinations are performed by a flow injection analysis titration with spectrophotometric detection. The chemical systems used are conventional, i.e. murexide-EDTA for calcium and Eriochrome Black-T EDTA for the sum of calcium and magnesium, the concentration of the latter being obtained by difference. The usefulness of this method has been demonstrated through the resolution of synthetic calcium and magnesium mixtures. Table 21(a) shows the results obtained which are in good agreement with the amount of these analytes added to the samples. Table 21(b) lists the results of the application of this method to the determination of these parameters in real samples.

TABLE 21

(a) Determination of calcium and magnesium in synthetic samples

Added (mg l ⁻¹)		Found(mgl l ⁻¹)		Error, %	
Ca ^{II}	Mg ^{II}	Ca ^{II}	Mg ^{II}	Ca ^{II}	Mg ^{II}
15.0	9.0	14.7	8.5	-2.0	-5.5
20.0	5.0	20.6	5.3	3.0	6.0
25.0	30.0	24.1	28.7	-3.6	-4.3
60.0	15.0	60.9	14.6	1.5	-2.6
75.0	31.2	74.8	31.4	-0.2	0.6
125.0	50.0	126.3	51.2	1.0	2.4

(b) Determination of calcium and magnesium in real samples

Type of water	Source	[Ca ^{II}] (mg l ⁻¹)	[Mg ^{II}] (mg l ⁻¹)	Hardness (mg l ⁻¹ CaCO ₃)
Natural	Well ₁ (La Rambla)	96.1	17.9	313.6
	Well ₂ (La Rambla)	63.2	16.1	224.1
Urban	C rdoba	15.6	10.5	82.2
	La Rambla	69.0	13.3	227.0
Bottled	Font-bella	22.9	4.8	76.9
	Lanjar n	30.3	10.4	118.5

(a) Determination of calcium and magnesium in synthetic samples

Added (mg l ⁻¹)	Found(mgl l ⁻¹)	Error, %	
Cabras	37.0	16.6	160.7

1.4.3

Odour and taste

Alexander et al²⁰⁰ have reported the results of a study to generate data on odour and taste for use in emergencies caused by chemical spills into potable waters during transport or storage. The odour thresholds for 63 industrial chemicals and the taste threshold for 43 of them have been evaluated using 1-butanol as a standard odour comparison and reported literature values. Threshold values were determined with water at 60°C but it is considered that the values obtained should be applicable at ambient temperature. The lowest odour threshold value observed was 0.0008 mg l⁻¹ for number 2 fuel oil, while naphtha had the lowest taste threshold of 0.02 mg l⁻¹.

Odour threshold values are measured as the least detectable odour perceived by panelists and reported as milligrams of compound per litre of odour free water at 60°C. The least detectable taste of compounds in water at 40°C observed by panelists is the taste threshold value. Taste threshold value is reported in milligrams of compound per litre of odour free water.

Evaluation of a compound for odour and taste thresholds requires definitive environmental and procedural controls.

All tests were performed in an odour free room (a closed room with closed circulation through an activated carbon filter). A constant temperature of 21°C and a relative humidity of approximately 50 per cent were maintained. All equipment used in the tests was cleaned thoroughly. Glassware was cleaned with hydrochloric acid, rinsed with distilled water and then rinsed several times with odour free water. Equipment used in testing was stored in the odour free room and used only for these tests.

Odour free water was obtained by passing tap water through a charcoal column. The column contained 4.61 of activated carbon (6×16 mesh grain size). The flow rate through the column was approximately 200 ml/min.

Persons involved in running an odour and taste test must wash their hands and face with an odourless detergent and warm water followed by a thorough rinsing with warm water.

Odours associated with soaps, perfumes or lotions must be removed or they will interfere with the tests. Odour free water should be checked to ensure that it has no off odour or taste. An odour and taste free water will smell and taste different from tap water to a new tester, but this water must be accepted as a standard. Once tests are started, they should be free of unnecessary interruptions by unauthorized personnel.

Test samples were dissolved in odour free water at a known concentration to form a stock solution. Normally, the primary stock solutions (1 g l⁻¹) were prepared outside the odour free room. The TOC, COD or TOD was determined to verify the concentration of the primary stock solution. Necessary dilutions were made from this stock solution with odour free water. Calculations of the threshold value were based on the actual dilution used in the odour or taste testing.

Odour threshold

Odour threshold values were obtained by using a modification of the ASTM method D 1292²⁰¹. Stock solutions of the compounds were made by dissolving the chemicals in odour free water. The solution was

diluted whenever a compound was very odorous, and a smaller amount ($<1\text{g l}^{-1}$) of a chemical was used to prepare the stock solution when the chemical had a low solubility.

Odour thresholds of compounds were determined by comparison with odour free water. Three 500 ml, glass stoppered, dark brown Erlenmeyer flasks were used as the testing flasks. Each flask was filled with 250 ml of solution that was kept at a constant temperature of 60°C by using an electric, variable control hot plate. In the triangle procedure, each of the three flasks was presented individually to a panelist. Two flasks contained odour free water, and one flask contained the test compound. The tester would shake the flask, remove the glass stopper and smell the vapours. The initial concentration was usually high enough for the panelist to detect and to characterize the odour. Then, the concentration was increased or decreased for each panelist. The threshold odour is defined as the lowest concentration detected. The concentration at which odour was detected and any comments by the panelist concerning the characteristic of the odour were recorded.

Taste threshold

Taste thresholds were determined by panelists who made a judgement as to the least detectable concentration of a compound that they could taste. The taste threshold determination was carried out with the same rigorous environmental and procedural controls used during the odour threshold evaluation. The technique used for taste testing was similar to that used for odour testing.

Taste tests were conducted at 40°C which is near body temperature, so that no sensation of hot or cold would be encountered by the panelists. Again, the panelist was presented with three flasks for taste evaluation. One flask contained the diluted chemical, and two flasks contained taste free water. The panelist is instructed to swirl each flask in turn, take a sample (10–15 ml) into the mouth, hold it for a few seconds and then discharge it. As with the odour tests, the panelist's response and comments for the taste tests are recorded; the calculation of taste threshold is based on the dilution of the sample.

A modification in procedure was necessary when testing a very odorous compound. The panelist was instructed to swirl the flask, inhale, and hold his breath while going through the taste procedure.

1.4.4

Turbidity

The term turbidity is a parameter which is often used to characterize the water quality. The difficulty is, however, that this parameter only represents a relative value which is strongly influenced by the size, shape and refractive index of the solid particles in the water as well as by the applied measuring instruments and calibration method. Pieper²⁰² gives recommendations for a uniform performance of the turbidity measurement. It is considered of primary importance that all turbidity meters are calibrated with a standard suspension. In view of the experience gained by the Water Research Centre UK, the 'Deutscher Verein von Gas- und Wasserfachmännern' and Pieper's own results, the formazin suspension prepared in accordance with Standard Methods, 13th edition, appeared to be the most satisfactory.

Turbidity measurements are often carried out in order to obtain indications about the weight concentration of solid particles. The turbidity is therefore an important parameter for characterizing the water quality. This is the reason why it is continuously controlled during many processes of water treatment. It should be realized, however, that the weight concentration of solid particles in water cannot be determined directly and exactly by means of turbidity measurements. Only in special cases it is possible to measure the concentration of these particles by recording the correlation between the optical property given

by the turbidity and the concentration of the solid particles. When the nature of the particles changes the correlation should be checked periodically because the light scattering is not only dependent on the concentration of solid particles but also on the size, shape and refractive index of these particles.

It is necessary to take into account the fact that dissolved substances like colouring matter, will absorb light as well as particulate matter. With regard to the colour of the water it may be noticed that this colour is partly caused by the suspended matter causing the turbidity. This means that the true colour of water can be determined only after removal of the suspended matter by means of centrifugation or membrane filtration. When the influence of the suspended matter is also measured one speaks of an apparent colour.

Turbidity can either be determined by means of optical instruments or by means of direct visual observation. The latter method, which of course is far less objective, is called 'visual method'. As for the measuring principle, optical turbidity measuring instruments can be divided into two groups: the nephelometers and the transmissometers. Nephelometers measure the intensity of dispersed light; the direction of the incident light is scattered by the particles present in the fluid (Tyndall effect). This measurement is carried out by means of a photoelectric cell placed at an angle with respect to the incident light beam. This angle varies according to the type of nephelometer.

Transmissometers—the principle of transmissometers is based on the measurement of the relationship between the intensity of light transmitted in a straight line and the incident light. These instruments actually measure the light absorption. Light absorption by dissolved substances like colouring matter is measured as well by these instruments, which of course influences the obtained results.

Nephelometers have a greater accuracy than transmissometers for low turbidity measurements. At higher turbidities the nephelometers no longer give reliable results unless they are provided with a measuring cell fitted with windows. This is caused by the repeated scattering of the light beam and possibly because the windows became dirty. At higher turbidities, it is necessary to switch over to another nephelometer (for example the 'surface scatter' type), or a transmissometer. For a transmissometer the mutual relationship between turbidity and deflection of the meter is not linear. Hence, when using transmissometers one often works with a logarithmic graduation. The sensitivity of a transmissometer can be increased by extending the distance to be covered by the light passing through the sample.

The visual method ascertains the turbidity by determining the so-called visibility depth. A disk (the Secchi disk) is placed in the sample at such a depth so that it is just perceptible. This depth, the visibility depth, is therefore an indication for the degree of turbidity. Directives for this way of determining turbidity have been formulated by the Fachausschuss 'Flockung und Filtration' of BVGW²⁰³.

The optical turbidity measuring instruments presently available are developed from the Jackson-candlelight turbidity meters. The measuring unit JTU (=Jackson Turbidity Unit) was derived from this standard instrument. As this instrument was used to measure the absorption of candlelight it was in general unsuitable for measurements of the usually low turbidities of treated water. For modern turbidimeters the restrictions of the Jackson-candlelight-turbidimeters were met by:

- using incandescent light as a light source, having a broader light spectrum
- the application of comparative measurements (see [fig. 16](#))

In an optical turbidity meter ([fig. 16\(a\)](#)), two light beams are derived from one light source (1), one of which is transmitted through the sample (4) whereas the other is scattered (3). By modulating the intensity of the transmitted light beam (10) the degree of turbidity can be determined from the modulation in a situation where the light intensity of both outgoing beams is equal. This is the case when the beams, flowing into the photocell, generate a current of equal strength.

Quite a large number of different types of turbidity instruments are now available. Many of these instruments operate according to different measuring principles. The accuracy, among other things, depends on whether or not a comparison light beam is used.

The usual types of nephelometers are:

- The incidence type, measuring the scattered light at an angle of 90° , with respect to the incident light beam; see [fig. 16\(b\)](#).
- The falling stream type, measuring the scattered light of the through going beam from a free falling fluid stream, see [fig. 16\(c\)](#).
- The surface scatter type, where the incident light beam enters an open surface at an angle and the scattered light is measured perpendicular to this surface, see [fig. 16\(d\)](#).

To calibrate a turbidimeter one needs standard samples with different degrees of turbidity. In the past suspension of diatomaceous earth was often used for this purpose.

A drawback of this method is that there are several kinds of diatomaceous earth on the market. The Water Research Centre (UK) has therefore used Fullers Earth Fulbent 570. This product offers a reasonable reproducibility and a quite stable suspension of synthetic sodium montmorillonite. Nowadays, both the WRC and DVGW prefer to use formazin standard suspension as described in the 13th edition of Standard Methods (American Public Health Authority). Formazine calibration samples can be prepared artificially by mixing hydrazine sulphate and hexamethylenetetramine in a given proportion and a given amount of water to produce a standard of 400 Formazin Turbidity Units (F.T.U.). In this way a well reproducible calibration sample is obtained and standard calibration samples of a given turbidity can be prepared.

Differences between the results of turbidity measurements may arise from the following causes.

The measurements in question measure the light as a function of the optical properties of the suspended matter. These optical properties are determined by the size, shape, colour, refractive index and nature of suspended and colloid particles. If only one of these factors varies, the turbidity will change as well. The influence of the particle size on the light scattering is explained by means of the graph given in [fig. 17](#).

This graph shows three different areas:

- The region where the particle size is greater than $1 \mu\text{m}$. In this area the light scattering appears to be changed inversely proportional to the particle size, in other words the smaller the particle the greater the light scattering.
- The region where the particles are smaller than $1 \mu\text{m}$. In this case light scattering decreases strongly when the particle diameter decreases.
- Between the above mentioned regions there is a transitional area.

Figs [18\(a\)](#) and [\(b\)](#) show the light scattering in the regions for particles smaller than $0.05 \mu\text{m}$ and greater than $1 \mu\text{m}$. For these figures the light enters from the left. From these figures it appears that the light scattering of particles smaller than $0.05 \mu\text{m}$ has an almost equal strength in every direction, this in contrast with larger particles, where it comes to an obvious light scattering in forward direction.

With respect to the refractive index it should be noted that the refractive indices of both the particles and the liquid will influence light scattering. This seems to be the reason for silica having a higher turbidity in water than in a sugar solution.

During the turbidity measurements with optical instruments stray light arises. This stray light is produced by the optical equipment, the measuring cell windows and the internal surface of the measuring cell. Both

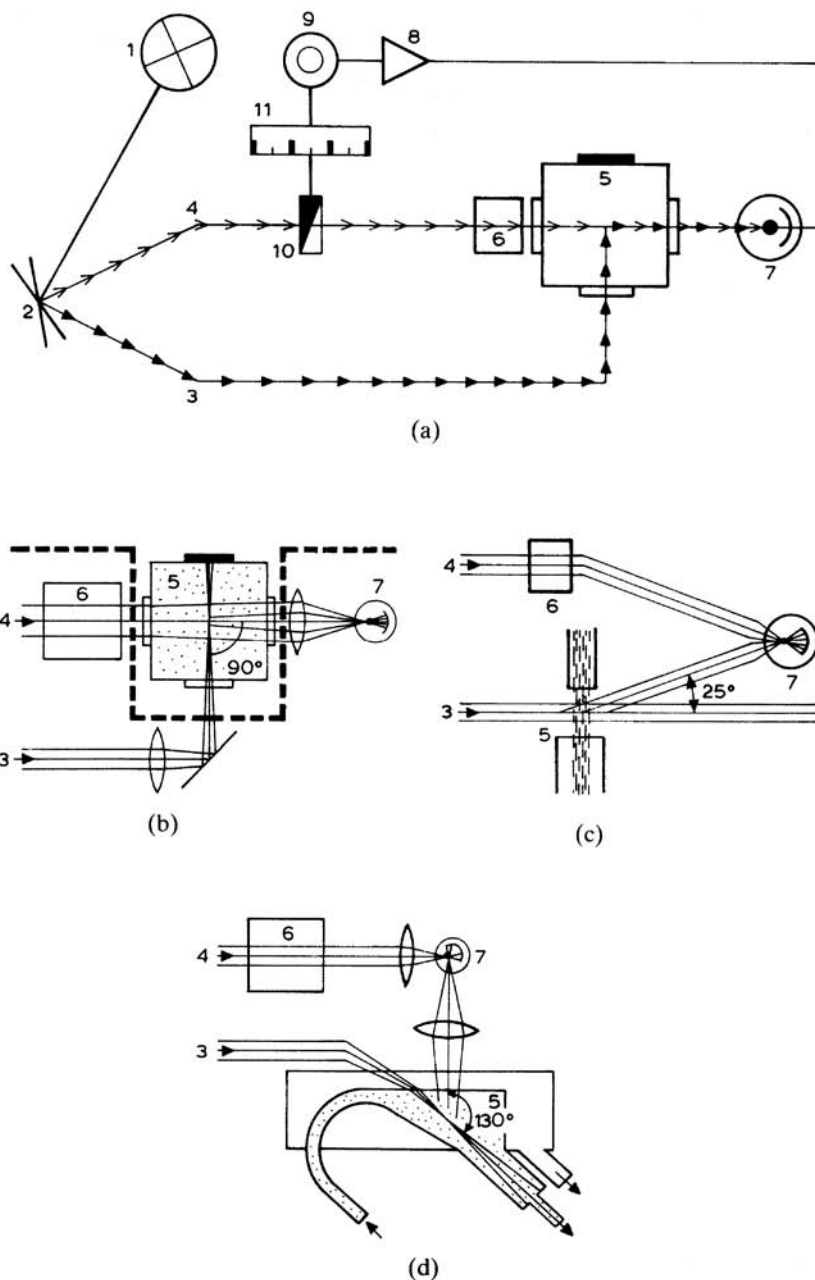


Fig. 16. (a) Measuring principle of the Sigrist nephelometer: 1, light source; 2, mirror; 3, measuring beam; 4, comparison beam; 5, measuring cell; 6, comparison standard; 7, photocell; 8, amplifier; 9, servomotor; 10, shutter; 11, reading/registration. (b) scattered light nephelometer; (c) falling stream nephelometer; (d) surface scatter nephelometer.

the light scattering of the measuring beam and the stray light are received by the photocell, which means that the influence of the stray light is measured as well. As the strength of the stray light changes from

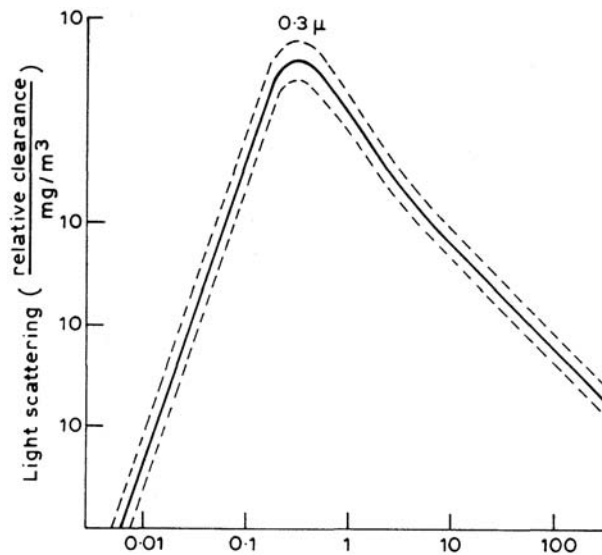


Fig. 17. Light scattering as a function of the particle size.

moment to moment, this implies a source of inaccuracy, the influence of which on the results increases according as lower turbidities are measured. It is clear that the influence of this stray light should be restricted to the minimum especially for instruments measuring low turbidities. In practice this appears difficult to realize and it can be assumed that the extent of applicability of this technique to low turbidities is, among other things, determined by the extent in which the influence of the stray light is eliminated.

When measuring the light scattering with the nephelometer, the measuring angle with respect to the incident light is of great importance. Measurements at different angles carried out with exactly the same suspension might give different measuring results. This particularly applies to particles greater than $1 \mu\text{m}$. All these factors make it impossible to speak in absolute terms of the turbidity of a certain type of water. The term turbidity has only a relative meaning which is strongly dependent on the type of pollution of the water, the measuring instrument applied as well as the calibration method applied. The WRC recommends therefore that when reporting turbidity, the standard suspension and the type of measuring instrument should be mentioned.

Other sources of measurement error include fouling of measuring cell windows, imperfections in cell windows, the effect of flow velocity through the cell and the formation of air bubbles.

To reduce these various sources of error to a minimum, Pieper²⁰² recommends that the following criteria are adopted.

Turbidimeters should be calibrated with a formazin standard suspension. For the turbidimeter, calibrated as given above, the correlation factors should be determined with respect to an accurate laboratory meter, which has also been calibrated with formazin. It is admitted further investigations in this field are still required.

Preparation of formazin standard suspensions according to standard methods 13th edition, 1971.

Preparation of a stock standard suspension of 400 FTU

This suspension is prepared by mixing the following solutions 1 and 2.

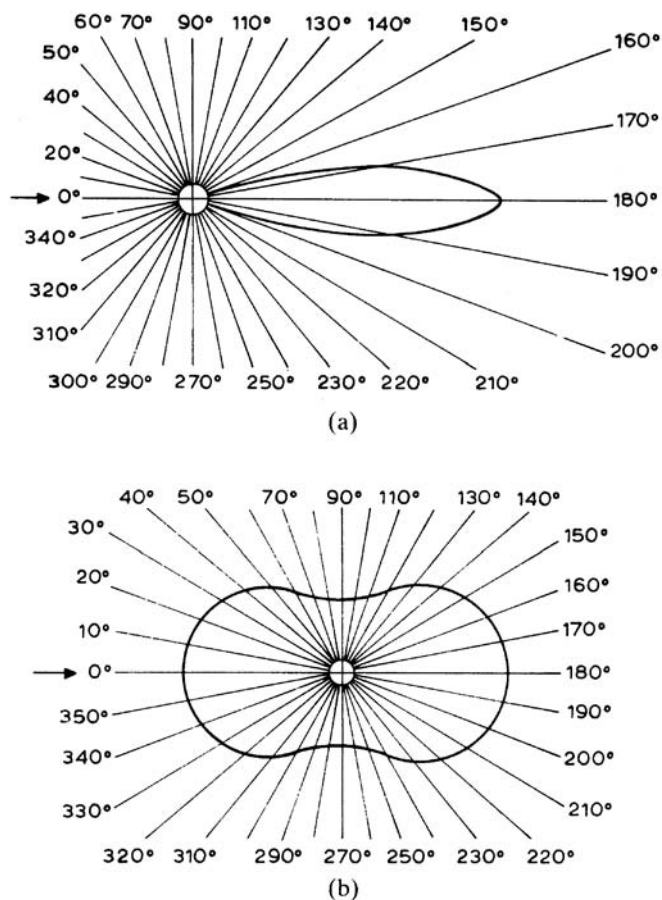


Fig. 18. (a) Light scattering for particles smaller than $0.05 \mu\text{m}$; (b) light scattering for particles larger than $1 \mu\text{m}$.

Solution 1—dissolve 1.000 g hydrazine sulphate $(\text{NH}_2)_2\text{H}_2\text{SO}_4$ in distilled water and dilute the solution to 100 ml in a volumetric flask.

Solution 2—dissolve 10.00 g hexamethylenetetramine, $(\text{CH}_2)_6\text{N}_4$, in distilled water and dilute the solution to 100 ml in a volumetric flask.

Mix 5.0 ml of solution 1 with 5.0 ml of solution 2 in a 100 ml volumetric flask. Store it for 24 hours at $25 \pm 3^\circ\text{C}$, and then dilute the mixture to 100 ml and mix again. The turbidity of the suspension obtained is equal to 400 formazin units. These solutions and suspensions should be prepared monthly.

Preparation of a standard solution of 40 and 4 FTU

When diluting quantities of 1.00 ml and 10.00 ml of the 400 FTU standard suspension, up to 100 ml with turbidity free water, standard suspensions are obtained of 4 and 40 FTU respectively. These standard suspensions should be prepared weekly.

Turbidity free water is prepared by passing distilled water through a membrane filter having a pore size smaller than 100 μm if such filtered water shows a lower turbidity than distilled water. Discard the first 200 ml. If the filtered water does not show a lower turbidity than distilled water, distilled water may be used.

Singh²⁰⁴ criticizes the use of silica and formazin units for the measurement of turbidity and suggests that a rational unit should be based on measurement of the fraction of light lost in transmission through the sample after correction for colour. Advantages claimed for this system are that the measurement of turbidity is not dependent on arbitrary standards; correction for colour can be applied accurately to determine true turbidity; the source of light need not be standard as the transmission coefficient of light is independent of the intensity of illumination to a large extent; the instrument can be quickly calibrated in the laboratory when the source of light is altered, the partial loss of sensitivity of the photocell of the instrument does not affect the results if photocell voltage is measured each time; galvanometer readings can be directly interpreted without reference to graphs, and measurements are not only reproducible but also accurate.

Cathelain and Robbe²⁰⁵ have presented a review of the theory of turbidity and a discussion of turbidity measurements and the equipment used. The relationship between the turbidity of water and the suspended material content cannot be established by the present commercially available equipment, because of the influence of the particle size distribution. The concentration of suspended material can be monitored, in waters of reasonably stable quality, by turbidimeters in fixed positions. Instruments based on diffused light are affected by coloured waters but can serve as an alarm system for sudden inputs of pollution; those based on transmitted light, such as spectrophotometers are not applicable to coloured solutions, since they depend on a monochromatic beam. The Drott nephelometer, which uses a beam focused across the liquid contained in a cuvette, on to a photoelectric cell, was capable of compensating for such factors as the colour of solutions.

1.4.5

Chrysotile asbestos

Electron microscopy

Hallenbeck et al²⁰⁶ carried out detailed examinations of potable water samples to determine the precision of analysis for chrysotile asbestos by transmission electron microscopy. Since the frequency distribution of counts fit a Poisson distribution, several statistical inferences were made including (1) an estimate of precision and (2) a model for determining the probability of observing chrysotile as a function of its concentration in water and magnitude of area scanned by transmission electron microscopy. The concentration of asbestos in water is generally reported in terms of fibre or fibrils per litre. Hallenbeck et al²⁰⁶ suggest that it is very important to define the precision of electron microscopy methodology since only a very small percentage of a collected sample is actually examined. For example, only about 0.01 per cent of a water sample is actually examined by electron microscopy.

The procedure used to estimate asbestos fibres in potable water is summarized below:

1. A sample was mixed by multiple inversions.
2. 200 ml of water were filtrated through a Millipore membrane filter of 0.45 μm pore size and 47 mm diameter with 24 hours of collection.
3. The filter was placed in a petri dish and allowed to dry in a vacuum desiccator.
4. A randomly selected 3.05 mm punch from each filter was placed on a 200 mesh copper TEM grid of equal diameter. The grid substrate was carbon coated 0.25 per cent formvar.

5. Acetone was filtered through a 0.1 μm Nucleopore membrane filter and used to charge the boiler of a condensation washer for 2 hours with an acetone reflux rate of approximately 1 drop s^{-1} .
6. Ten grid squares were randomly selected and examined by transmission electron microscopy at 26280 \times and 100 kV. Chrysotile asbestos was confirmed by both morphology and selected area electron diffraction pattern.
7. Steps 4–6 were repeated for 9 more punches from the same membrane filter. Thus 10 punches were randomly selected from each membrane filter.

For each of the two potable water samples 10 grid squares from each of the 10 grids were scanned for their content of chrysotile units. Hence the basic unit of observation is a single grid square. Table 22(a) presents the frequency distributions of counts. Selected descriptive statistics and estimation values are presented in Table 22(b). The variance test was performed to test the Poisson goodness-of-fit for the distribution of chrysotile units per grid square. The results given in item 4 of Table 22(b) show a good fit for both water samples. Thus, it may be stated that the number of chrysotile units per grid square follows a Poisson distribution.

The number of chrysotile units is usually presented in terms of number per

TABLE 22

Count of chrysotile units/grid square		Number of grid squares	
Sample A	Sample B		
0		95	93
1		4	7
2		1	0
		Total 100	100
(b) Selected descriptive statistics and estimation values			
		Sample A	Sample B
(1)	Number of grid squares scanned, N	100	100
(2)	Standard deviation, s (units/grid square)	0.28	0.26
(3)	Variance, s^2	0.08	0.07
(4)	Variance test $\chi^2=(N-1)s^2/\bar{x}$	127.4	93.1
	p -value	0.06	0.70
(5)	Point estimates and confidence interval		
	(a) Mean, \bar{x} (units/grid square)	0.06	0.07
	(b) $8.41 \times 10^5 \bar{x}$ (units l^{-1})	5.05×10^4	5.89×10^4
	95% confidence interval		
	Lower limit (units l^{-1})	1.85×10^4	2.36×10^4
	Upper limit (units l^{-1})	1.10×10^5	1.21×10^5

litre of water. The conversion from average units per grid square to units per litre is as follows:

$$\text{Area of one grid square} = 8.236 \times 10^{-5} \text{ cm}^2$$

$$\text{Effective filter area} = 13.847 \text{ cm}^2$$

Volume of water filtered=200 ml

Since it is recognized that the number of chrysotile units per grid square follows a Poisson distribution, confidence intervals can readily be obtained. The 95 per cent confidence intervals are given in item 5 of Table 22(b). It is interesting to note that the 95 per cent confidence limits for counting 100 grid squares with are 0 and $3 \cdot 10 \times 10^4$ units per litre.

The identification and measurement of asbestos fibres in potable water has also been discussed by Axelrod²⁰⁷.

1.4.6

Hydrogen peroxide

Bader et al²⁰⁸ have described a photometric method for the determination of down to $0 \cdot 2 \mu\text{g l}^{-1}$ hydrogen peroxide in potable water by the peroxide catalysed oxidation of *N, N*-diethyl *p*-phenylene diamine.

1.5

Organic substances

1.5.1

Aliphatic hydrocarbons

Gas chromatography

Swinnerton and Linnenbom²⁰⁹ were the first to examine the applicability of gas stripping methods to the determination of hydrocarbons in water. They determined C_1 – C_6 hydrocarbons by stripping them from water with a stream of helium.

After gas stripping the hydrocarbons can be either passed direct to a gas chromatograph or, to increase sensitivity, trapped in a cold trap then released into the gas chromatograph. Alternatively, the stripped hydrocarbons can be trapped in, for example, active carbon, then released into the gas chromatograph. This method offers the possibility of determining trace amounts of organic compounds in water even below the $\mu\text{g l}^{-1}$ level, particularly for the more volatile compounds²¹⁰. Many factors, such as interference by artefacts because of impurities in the stripping gas, the large amount of water passing the trap, adsorption of less volatile compounds in drying filters, the selection of sorbents and the adsorption and desorption efficiency, are serious drawbacks of the method, particularly for quantitative analyses. However, Grob and co-workers^{211–214} reported an impressive improvement of the method by using a closed loop system, provided with a small volume effective charcoal filter but several precautions are necessary when working at such low concentrations. The complicated procedure and the sophisticated equipment required result in many more or less unknown factors and a semiquantitative analysis. In view of the absolute amounts of pollutants involved, their overall results were excellent.

Desbaumes and Imhoff²¹⁵ swept volatile hydrocarbons and their halogenated derivatives from water contained in a heated metallic column by a current of purified air and their concentrations were determined with a flame ionization detector. The condensed vapours are analysed qualitatively by gas chromatography. Details and diagrams of the equipment are given and the operating procedure is described. Samples must be

stored only in glass or stainless steel containers. Substantial losses may still occur if the storage time is more than 10 hours.

Novak et al²¹⁶ have analysed for simple hydrocarbons in potable water. The hydrocarbons were extracted by bubbling an inert gas through the water, and the compounds were separated and identified by combined gas chromatography-mass spectrometry.

Preconcentration

The preconcentration of hydrocarbons (aliphatic, aromatic) is discussed in [section 1.5.31](#).

1.5.2

Polyaromatic hydrocarbons

The Environmental Protection Agency has been bound, under a Consent Decree, to set maximum concentration limits in effluent waters for a group of unambiguous priority pollutants²¹⁷. Included on this list are several polycyclic aromatic hydrocarbons. The World Health Organization has recommended that the total concentration of six specific PAH compounds, fluoranthene, benzo(d)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, benzo(ghi)perylene and indeno(1,2,3-ed)pyrene, not exceed 200 ng l⁻¹ in domestic water^{218,219}. The Federal Republic of Germany has legislated a maximum limit of PAHs of 250 ng carbon l⁻¹ of potable water. The basic assembly of the apparatus employed was similar to that previously described by Kirkbright and De Lima²²⁰.

Spectrofluorimetric methods

Ogan et al²²¹ have described a fluorimetric procedure capable of determining as little as 0.2 ng l⁻¹ of 7 H benz(de)anthracene-7-one (benzanthrone), fluoranthene, perylene, benzo(a)pyrene and benzo(ghi)perylene in potable water samples. The polycyclic aromatic hydrocarbons are determined by adsorption on to an extraction column, followed by desorption and separation in a single step using reversed phase liquid chromatography.

Most of the work described by Ogan et al²²¹ was concerned with the analysis of synthetic solutions although some results are reported for actual potable water samples.

Further work on the fluorimetric determination of benzo(a)pyrene in water was conducted by Monarca et al²²². These workers utilized low temperature spectrofluorimetry using the Shpol'skii effect²²³⁻²²⁵. This technique is capable of high selectivity and sensitivity in the determination of PAH components at 77 K and can permit this determination in mixtures without lengthy initial chromatographic separation procedures. The aim in this work was to develop a method sufficiently sensitive to determine benzo(a)pyrene at the 0.3 ng l⁻¹ level.

To analyse water samples Monarca et al²²² extracted the samples (5 l) with cyclohexane and the extract was diluted with 1 ml of octane-cyclohexane (9:1) solvent solution; excited at 375 (and 325) nm and the luminescence emission intensities obtained at 403 nm were compared with those obtained from a calibration curve prepared for benzo(a)pyrene in octane-cyclohexane. The sample solutions were then diluted and the benzo(a)pyrene concentration in each was determined by the standard addition method.

Using this method Monarca et al²²² found 0.5 ng l⁻¹ benzo(a)pyrene in potable water and between 32 and 38 ng l⁻¹ in river waters. The limit of detection of the method was 0.5 ng l⁻¹ or better using 2.5–5 l samples.

Muel and Lacroix²²⁶ were the first to utilize low temperature spectrofluorimetry to determine the benzo(a)pyrene content of potable water samples by using the standard addition method but this compound was undetectable in the small volume of water samples examined. Jager and Kassovitzova²²⁷ determined the concentration of benzo(a)pyrene in potable water down to a concentration of 3 ng ml⁻¹ with a relative error of 40 per cent and found that the accuracy was greatly influenced by the presence of other organic compounds.

Gas chromatography

Grimmer et al²²⁸ used capillary gas chromatography for the fingerprint analysis of PAHs in potable water samples. Following extraction with cyclohexane (after addition of an internal standard) and clean-up using Sephadex LH 20, the extract is subjected to gas chromatography with a flame ionization detector. The ratio of peak heights to that of the internal standard is used to calculate the amounts of polyaromatic hydrocarbons present in the extract. The limit of detection is about 0.1 ng l⁻¹, less than 1 l of drinking water being required for the analysis.

Thin layer chromatography

Grimmer et al²²⁹ described a semiquantitative test for the detection of PAHs in potable water. A total of 395 West German potable water samples were analysed and only 22 were found to contain more than half the permitted limit of 250 ng l⁻¹ (expressed as organic carbon) for the sum of six individual PAH compounds. A method was devised for distinguishing the heavily contamination samples (more than 125 ng l⁻¹) from the remainder, which involves high performance thin layer chromatography on prepared RP-18 plates of a cyclohexane extract. The chromatogram is developed by acetonitrile:methylene chloride-water (9:1:1) and assessed by visual observation under a UV lamp. The method was capable of distinguishing samples containing more than 50 ng PAH compounds per litre.

Kunte²³⁰ investigated the interference effects of 44 PAHs on a thin layer chromatographic method for determining fluoranthene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, benzo(ghi)perylene and indeno (1,2,3-cd) pyrene according to the West German potable water regulations. Overlapping occurred but these overlaps did not interfere with the determination of these six compounds, nor was quantitative determination of the six compounds influenced by the addition of a soil extract or a mixture of 18 PAHs occurring in the environment.

Harrison et al²³¹ examined the effects of water chlorination upon levels of some PAHs in water including a study of the effects of pH, temperature, contact time and chlorinating agent. Thieleman²⁶¹ investigated by thin layer chromatography the action of chlorine dioxide on acenaphthalene, anthracene, carbazole, chrysene, phenanthrene and pyrene.

Polarography

Nelson et al²³² used phospholipid coated mercury electrodes to determine polyaromatic hydrocarbons in potable water. The electrodes gave a characteristic response for 3-, 4-, and 5-ring polyaromatic compounds.

High performance liquid chromatography

Lewis²³³ gave comprehensive details of a method using counter-current extraction and high performance liquid chromatography with fluorimetric detection for estimating polyaromatic hydrocarbons in water.

Sorrell et al²³⁴ have listed 15 polyaromatic hydrocarbons commonly found in water (Table 23) and have described a high performance liquid chromatographic method for determining 13 trace compounds. Limits of detection are as low as 1 ng l⁻¹ well below the collective limit of 200 ng l⁻¹ for six polyaromatic hydrocarbons recommended by the World Health Organization.

In later work Sorrell and Reding²³⁵ present an extension of this technique, for analysing 1–3 ng l⁻¹ amounts of 15 polynuclear aromatic hydrocarbons in environmental water samples using high pressure liquid chromatography, preceded by a clean-up using alumina, with ultraviolet monitoring and fluorescence emission excitation spectra for identification.

A comparison of the hplc chromatogram of an extract of potable water with that of an extract of spiked tap water eluted through alumina showed the effectiveness of the clean-up in removing uv absorbing interferences. The alumina also fractionated 17 polyaromatic hydrocarbons into three fractions. The two early-eluting fractions, which were discarded, may contain hydrocarbons, benzene, naphthalene, alkyl-substituted benzenes and naphthalenes and other low-molecular weight compounds.

The hplc chromatograms of the three retained fractions from the standard polyaromatic hydrocarbons taken through the analytical procedure are presented in figs 19(a)–(c). The chromatography was performed isocratically and the column temperature was controlled. This permitted specific polyaromatic hydrocarbons to be initially identified from their retention times (which varied less than 2 per cent over a 9 month period), and eliminated the need for column re-equilibration. Although some coeluting polyaromatic hydrocarbons (e.g. anthracene and phenanthrene) had been placed into different fractions, it was clear that no single UV wavelength was capable of resolving all of the polyaromatic hydrocarbons within a fraction. However, instead of further manipulating the chromatography, the sensitivity and resolution of the analysis were optimized by selecting the available UV wavelengths so as to minimize the response of the interferences near a relative absorption maximum of the polyaromatic hydrocarbon of interest. Concentrations of the polyaromatic hydrocarbons were determined from their UV responses. The sensitivity of the UV detectors, defined as a signal to noise ratio of 2, ranged from 0.25 to 1 ng l⁻¹.

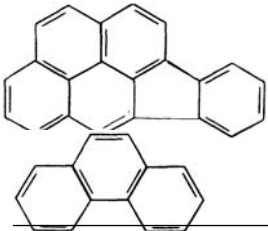
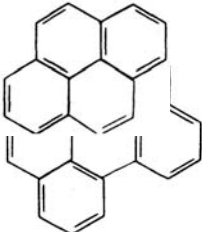
All but two (1-methyl phenanthrene and 2-methyl phenanthrene) of the 17 polyaromatic hydrocarbons could be sufficiently resolved from coeluting polyaromatic hydrocarbons and other interfering compounds by using the variable wavelength and the two fixed wavelength (254 and 280 nm) detectors. In addition, despite the alumina clean-up, some interferences with a 254 nm response coeluted with these polyaromatic hydrocarbons and with 1-methyl phenanthrene. Analysis by gas chromatography-mass spectrometry showed that the di-*n*-octyl adipate and phthalate esters were in this group of interferences. However, since neither the interferences nor 1-methyl phenanthrene or 2-methyl phenanthrene had a significant response at 340 nm, the concentrations of fluorene, pyrene and 1-methyl phenanthrene could be measured (fig. 19(a)). Since no selective wavelength could be found for 1-methyl phenanthrene and 2-methyl phenanthrene they were not qualified by Sorrell and Reding²³⁵.

Fluorescence as a detection system, has the advantage of greater sensitivity and less susceptibility to interferences, since fewer compounds are fluorescent than are UV absorbent. Given the capability to scan both emission and excitation wavelengths, fluorescence provided more unique spectra for PAHs than mass spectrometry and greatly augmented the preliminary identification of polyaromatic hydrocarbons via retention time.

Measurements of the recoveries of eleven polyaromatic hydrocarbons from seven raw or finished water samples over a 9 month period ranged from 53 to 116 per cent and averaged 86±12 per cent.

In a further study, Sorrell and Reding²³⁵ spiked similar concentrations of pyrene, fluoranthene, 1-methylphenanthrene, perylene, benzo(a)pyrene and benzo(ghi)pyrene into four samples of unextracted potable water and the

TABLE 23
Polyaromatic hydrocarbons

Structure	IUPAC name	Mol. wt.	Relative carcinogenicity	Abbreviation
	Benzo(ghi)perylene	276	—	B(ghi)P
	Chrysene	228	—	Ch
	Fluoranthene	202	—	Fl
	Indeno(1,2,3-cd)pyrene	276	+	IP
	Phenanthrene	178	?	Ph
	Perylene	252	—	Per
	Pyrene	202	—	Pyr
Structure	IUPAC name	Mol. wt.	Relative carcinogenicity	Abbreviation
	Anthracene	178	?	An
	Benzo(a)anthracene	228	+	B(a)A
	Benzo(b)fluoranthene	252	++	B(b)F
	Benzo(j)fluoranthene	252	++	B(j)F
	Benzo(k)fluoranthene	252	—	B(k)F
	Benzo(a)pyrene	252	+++	B(a)P
	Benzo(e)pyrene	252	+	B(e)P

+++; active; ++, moderate; +, weak; ?, unknown; —, inactive.

recoveries were determined by analysing the extracts directly (i.e. without alumina clean-up). Corresponding unspiked potable water samples were also extracted and analysed directly to determine the background concentration of the polyaromatic hydrocarbons. After correcting for this background, the recoveries were calculated and ranged from 78 to 99 per cent averaging 88 per cent. The average recovery (for all the polyaromatic hydrocarbons) from these three series of experiments was about 85 per cent.

While the recovery efficiencies allowed quantification of polyaromatic hydrocarbons concentrations at the time of extraction the relevance of those values to the actual concentration at the time of sampling may be less certain. A preliminary experiment showed a complete loss of seven polyaromatic and stored at 5°C for 18 days. The identical water with no chlorine residual hydrocarbons when spiked (about 27 ng l⁻¹ each) into Cincinnati potable water (excess sodium sulphite added) showed only a small loss for five of the polyaromatic hydrocarbons and a somewhat larger loss for benzo(a)pyrene and perylene. A similar 8 day study of the same potable water source looked at only the four polyaromatic hydrocarbons which did not occur naturally. The results showed total and partial losses of the polyaromatic hydrocarbons in the presence and absence of a chlorine residual, respectively. Again, benzo(a)pyrene and perylene showed greater losses than the other polyaromatic hydrocarbons.

Hunt et al²³⁶ have shown that all six representative polyaromatic hydrocarbons tested in the World Health Organisation standards for potable water, (i.e. fluoranthene, 3,4-benzfluoranthene, benzo(b)fluoranthene), 11,12-benzofluoranthene (benzo(k)fluoranthene), 3,4-benzpyrene (benz(a)pyrene), 1,12-benzperylene

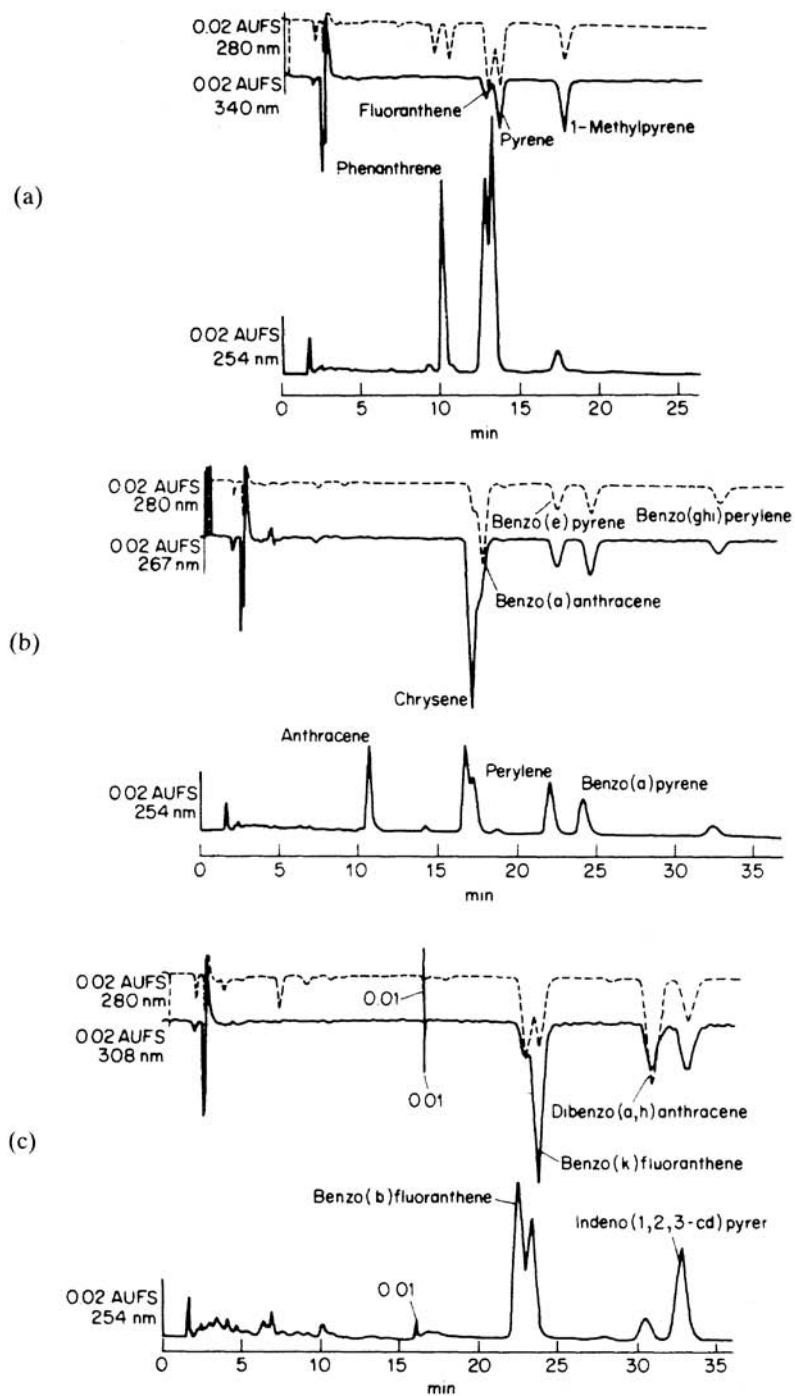


Fig. 19. High performance liquid chromatography of PAH fractions ex alumina column. (a) HPLC analysis of fraction III from alumina column (ca. 10 ng of standards); (b) HPLC analysis of fraction IV from alumina column (ca. 10 ng of standards); (c) HPLC analysis of fraction V from alumina column (ca. 10 ng of standards).

(benzo(ghi)perylene) and indeno(1,2,3-cd)pyrene), can be separated successfully by high performance liquid chromatography, using as a packing material, phthalimidopropyltrichlorosilane bonded to microparticulate silica gel with a non-polar mobile phase of toluene-hexane. They used a non-polar phase of toluene-hexane (1:10) and achieved good separations.

The Environmental Protection Agency has issued a protocol for the determination of the six regulated polyaromatic hydrocarbons²³⁷. The World Health Organization has recommended that the total concentration of six specific polyaromatic hydrocarbon compounds should not exceed 200 ng dm^{-3} , (l^{-1}) in domestic water²³⁸.

Workers at Perkin Elmer²³⁹ have studied the high speed separation of polyaromatic hydrocarbons using a C_{18} bonded phase packing ($5 \mu\text{m}$ particles) using both isocratic and gradient elution. Fig. 20 shows the analysis of several standards using the $5 \mu\text{m}$ bonded phase column with gradient elution from 60 to 100 per cent acetonitrile in 5 min at a flow rate of 4 ml min^{-1} . Although not completely resolving all of the components, this method offers a rapid analysis which is adequate for many of these compounds. These high speed columns can also be used in a very high resolution mode. At the expense of analysis time, very high resolution can be attained by connecting two columns in series. Where two $3 \mu\text{m}$ columns are coupled an efficiency of about 28000 plates was obtained under isocratic conditions. These workers utilized these coupled columns, in this case, with gradient elution, to analyse the same polyaromatic hydrocarbons standards. The analysis time is increased to 26 min but the extremely high resolution achieved is quite apparent. This very high resolution is extremely useful in analysing complex samples containing many components.

Preconcentration

PRECONCENTRATION XAD-2 RESINS: Benoit et al²⁴⁰ have investigated the use of macroporous resins, particularly Amberlite XAD-2 resin, in the preconcentration of Ottawa potable water samples prior to the determination of 50 different polyaromatic hydrocarbons by gas chromatography-mass spectrometry in amounts down to 0.05 ng l^{-1} .

To test the effectiveness of their method of analysis for polyaromatic hydrocarbons in potable water Benoit et al²⁴⁰ prepared and analysed a control blank and carried out a recovery study of 32 selected polyaromatic hydrocarbons from XAD-2 resin. An average recovery of 84 per cent was observed, with recoveries ranging from 57 per cent to 100 per cent. The fate of the unrecovered material was not established although, based on the results of the control blank, it is not likely that these materials were carried away by the effluent water.

Ottawa potable water samples were analysed in order to obtain some indication of whether the results are representative of the general background level of anthropogenic contamination. Aliquots of the reference standard solution (50 polyaromatic hydrocarbons and 5 oxygenated aromatic hydrocarbons) and the concentrated extracts from XAD-2 resin were analysed consecutively by gas chromatography—mass spectrometry under identical operating conditions.

Mass chromatograms were reconstructed from selected ion-currents rather than the total ion-current. Mass chromatograms for selected ions that were characteristic of the compound of interest were obtained by searching the accumulated data for the ion of interest and recording the abundance of this ion as a function of retention times. As an example, the mass chromatograms of three ions— m/e 128, m/e 142 and m/e 154 are superimposed in fig. 21. The location of the peaks corresponding to the compounds of interest are indicated by asterisks in each chromatogram. For m/e 128 the asterisked peak corresponds to the molecular ion of naphthalene, for m/e 142 to the molecular ions of 2-methylnaphthalene and 1-methylnaphthalene,

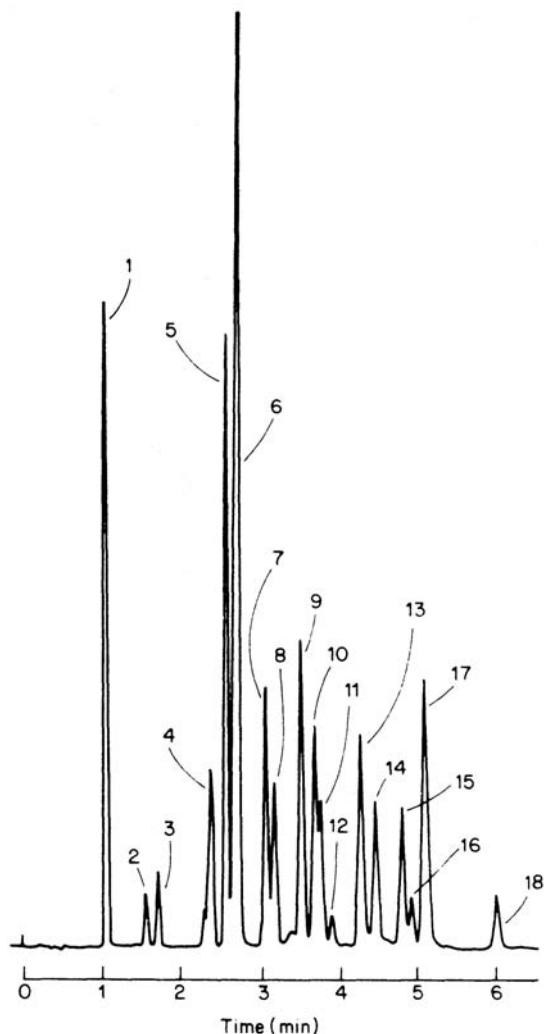


Fig. 20. Analysis of polyaromatic hydrocarbons. Column: 125×4.6 mm i.d. C₁₈ bonded phase packing; 5 μm particles. Mobile phase: acetonitrile-water. linear gradient from 60 to 100 per cent acetonitrile in 5 min, at 4ml min⁻¹; inlet pressures: 3700 psig (25.5 MPa) initial, 2200 psig (15.2 MPa) final; ambient temperature; UV detector at 254 nm. Peaks: 1, benzene; 2, impurity; 3, naphthalene; 4, fluorene+acenaphthalene; 5, phenanthrene; 6, anthracene; 7, fluoranthene; 8, pyrene; 9, benzo(b)fluoranthene; 10, chrysene; 11, benzo(a)anthracene; 12, impurity; 13, benzo(e)pyrene+perylene; 14, benzo(a)pyrene; 15, dibenz(ah)anthracene; 16, dibenz(ac)anthracene; 17, benzo(ghi)perylene+indeno(1,2,3-cd)pyrene; 18, coronene.

respectively, in orders of increasing retention time and for *m/e* 154 to the molecular ions of biphenyl, 2-vinylnaphthalene and acenaphthalene, respectively, in order of increasing retention times. The retention times for each standard were established by analysis of the reference standard solution and the data from the XAD-2 extracts were then searched for the ion of interest within the appropriate time region. In all instances, the molecular ion and the next most abundant ion were selected as the characteristic ions which are listed in Tables 24(a) and (b).

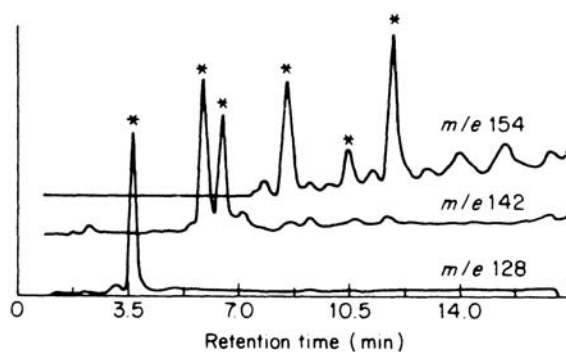


Fig. 21. Reconstructed mass chromatogram for ions m/e 128, m/e 142 and m/e 154 from Ottawa potable water Amberlite XAD-2 resin extract.

A compound was considered identified if the two characteristics of the compound of interest were found to elute from the column within the retention time window (± 0.1 min) of the reference standard and to be in the relative abundance ratio (± 20 per cent) observed in the mass spectrum of the pure compound. For most, but not all, compounds screened unique identification

TABLE 24

(a) Polycyclic aromatic hydrocarbons detected in Ottawa potable water sampled in January (2) and February (1) 1978

Compound	Ions monitored		Rel. ret. time ^a	Concentration (ng l ⁻¹)	
	1	2		1	2
Naphthalene	128	102	1.00	6.8	4.8
2-Methylnaphthalene	142	141	1.59	2.4	4.6
1-Methylnaphthalene	142	141	1.75	1.0	2.0
Azulene	128	102	1.90	n.d.	n.d.
2-Ethyl-naphthalene	156	141	2.26	>0.70	2.1
2,6-Dimethylnaphthalene	156	141	2.32		
Biphenyl	154	153	2.30	0.70	1.1
1,3-Dimethylnaphthalene	156	141	2.51	1.9	1.1
2-Vinylnaphthalene	154	153	2.68	n.d.	n.d.
2,3-Dimethylnaphthalene	156	141	2.69	>0.68	14
1, 4-Dimethylnaphthalene	156	141	2.69		
3-Phenyltoluene	168	167	2.74	0.20	1.5
Diphenylmethane	168	91	2.88	1.4	2.8
4-Phenyltoluene	168	167	2.94	0.20	3.7
Acenaphthylene	152	151	3.00	0.05	n.d.
Acenaphthene	154	153	3.25	0.20	1.8
Bibenzyl	182	91	3.41	1.9	1.5
1,1-Diphenylethylene	180	179	3.48	>7.4	n.d.
<i>cis</i> -Stilbene	180	179	3.59		

(a) Polycyclic aromatic hydrocarbons detected in Ottawa potable water sampled in January (2) and February (1) 1978

Compound	Ions monitored		Rel. ret. time ^a	Concentration (ng l ⁻¹)	
	1	2		1	2
2,2-Diphenylpropane	196	181	3.62	n.d.	n.d.
2,3,5-Trimethylnaphthalene	170	155	3.71	0.65	5.2
3,3-Dimethylbiphenyl	182	167	4.03	0.31	5.2

Compound	Ions monitored		Rel ret. time ^a	Concentration (ng l ⁻¹)	
	1	2		1	2
Fluorene	166	165	4.15	0.15	2.2
4,4'-Dimethylbiphenyl	182	167	4.18	0.57	7.0
4-Vinylbiphenyl	180	178	4.56	n.d.	n.d.
Diphenylacetylene	178	89	4.90	0.05	n.d.
9,10-Dihydroanthracene	180	179	5.03	0.66	n.d.
<i>trans</i> -Stilbene	180	179	5.20	>0.47	9.2
9,10-Dihydrophenanthrene	180	179	5.29		
10,11-Dihydro-5 <i>H</i> -dibenzo(a, d) cycloheptane	194	179	6.03	0.40	n.d.
Phenanthrene	178	89	6.08		
Anthracene	178	89	6.14	>0.52	2.2
1-Phenylnaphthalene	204	203	6.77	n.d.	n.d.
1-Methylphenanthrene	192	191	7.06	n.d.	11
2-Methylphenanthrene	192	191	7.25	0.51	0.70
9-Methylanthracene	192	191	7.59	n.d.	0.70
9-Vinylnanthracene	204	203	7.82	n.d.	n.d.
Triphenylmethane	244	167	8.04	n.d.	n.d.
Fluoranthene	202	101	8.41	0.55	1.9
Pyrene	202	101	8.90	0.53	1.7
9,10-Dimethylanthracene	206	191	8.99	0.19	n.d.
Triphenylethylene	256	178	9.25	0.08	n.d.
<i>p</i> -Terphenyl	230	115	9.44	n.d.	n.d.
1,2-Benzfluorene	216	108	9.64	n.d.	n.d.
2,3-Benzfluorene	216	108	9.73	n.d.	n.d.
Benzylbiphenyl	244	167	9.75	n.d.	n.d.
1,1'-Binaphthyl	254	126	10.95	n.d.	n.d.
Triphenylene	228	114	11.5		
Benz(a)anthracene	228	114	11.6	>8.1	3.3
Chrysene	228	114	11.8		

(b) Oxygenated polycyclic aromatic hydrocarbons detected in Ottawa potable water sampled in January (2) and February (1) 1978

Compound	Ions monitored	Rel. ret. time ^a	Concentration (ng l ⁻¹)
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Compound	Ions monitored		Rel ret. time ^a	Concentration (ng l ⁻¹)	
1	2				
1	2				
Xanthene	182	181	4.83	0.20	0.10
9-Fluorenone	180	152	5.93	0.90	1.5
Perinaphthenone	180	152	7.70	0.28	0.15
Anthrone	194	165	7.90	1.4	n.d.
Anthraquinone	208	180	8.11	2.4	1.8
Naphthalene	128	102	1.00		

^a Retention times are relative to the retention time of naphthalene (3.81 min).

was possible. In some instances however, eluting isomers yielding similar mass spectra could not be resolved sufficiently to allow unequivocal identification.

Because of the large number of compounds contained in the field sample extract, it was not possible to eliminate entirely from all the ion peaks of interest, contributions from possible interfering species. This was particularly true for methyl substituted polyaromatic hydrocarbons for which numerous positional isomers may elute within a narrow time window. In many cases only a small number of the possible positional isomers were available commercially and could be included in the reference standard. Hence, unequivocal identification of positional isomers was often not possible.

Quantitative estimates of the detectable polyaromatic hydrocarbons and oxygenated polyaromatic hydrocarbons in Ottawa potable water were obtained by comparison of the areas of the two characteristic ion peaks (Tables 24(a) and (b)), in the mass chromatograms of the reference standard and the field sample, respectively. The average of the concentrations for the two ions is presented in Table 24(a) (polyaromatic hydrocarbons) and 24(b) (oxygenated polyaromatic hydrocarbons) for the two water samples analysed. No corrections were made for incomplete recovery. Of the 50 polyaromatic hydrocarbons in the standard used by Benoit et al²⁴⁰ 38 were detected in at least one of the two potable water samples tested. In sample 1 (February 1978) 16 polyaromatic hydrocarbons ranging in concentration from 0.05 to 8.1 ng l⁻¹ and in sample 2 (January 1978) 30 polyaromatic hydrocarbons (Table 24(a)) ranging in concentration from 0.05 to 14 ng l⁻¹ were detected.

Of the five oxygenated polyaromatic hydrocarbons in the standard, all five, ranging in concentration from 0.20 to 2.4 ng l⁻¹ were detected in sample 1 and four, ranging in concentration from 0.10 to 1.8 ng l⁻¹ are detected in sample 2 (Table 24(b)). The mean concentrations and total weights of detected oxygenated polyaromatic hydrocarbons in the two samples were 1.0 and 5.2 ng l⁻¹ for sample 1 and 0.91 and 3.7 ng l⁻¹ for sample 2 respectively. It is noteworthy that for three of the oxygenated compounds (anthrone, anthraquinone, and 9-fluorenone) detected, the parent compound is also detected in the potable water sample. Thus, the oxygenated species could possibly originate from the oxidation of the parent compound in the aqueous media.

PRECONCENTRATION ON POLYURETHANE FOAM: Saxena et al²⁴¹ used polyurethane foams to concentrate trace quantities of six representatives of polynuclear aromatic hydrocarbons (fluoranthene, benzo(k)fluoranthene, benzo(j)fluoranthene, benzo(a)pyrene, benzo(ghi)perylene, and indeno(1,2,3-cd)pyrene) prior to regular screening of these compounds in US raw and potable waters. In this method, the polyaromatic hydrocarbons are collected by passing water through a polyurethane foam plug. Water is heated to 62±2°C prior to passage and flow rate is maintained at approximately 250 ml min⁻¹ to obtain

quantitative recoveries. The collection is followed by elution of foam plugs with organic solvent, purification by partitioning with solvents and column chromatography on Florisil, and analysis by two-dimensional thin layer chromatography on cellulose-acetate-alumina plates followed by fluorimetry and gas-liquid chromatography using flame ionization detection.

In further work Saxena et al²⁴² and Basu and Saxena²⁴³ showed that the polyurethane foam plug method had an extraction efficiency for polyaromatic hydrocarbons of at least 88 per cent from treated waters and 72 per cent from raw water. Polyurethane foam plugs under suitable conditions not only effectively concentrate benzo(a)pyrene but other polyaromatic hydrocarbons as well. Foam plugs concentrated polyaromatic hydrocarbon almost quantitatively from finished water at lower concentrations also. The high polyaromatic hydrocarbon retention efficiencies were also maintained with heavily polluted surface waters.

Detection limits of the six polyaromatic hydrocarbons using the polyurethane foam preconcentration method ranged from 3–5 mg l⁻¹ (gas chromatography with a flame ionization detector) to 0.1–2 ng l⁻¹ (thin layer chromatography—fluorimetric analysis).

PRECONCENTRATION ON ALUMINIUM POTASSIUM SILICATE: Cannavacino et al²⁴⁴ in an attempt to improve analytical sensitivity evaluated a sorbent material for preconcentrating polyaromatic hydrocarbons from potable water. The material is a natural aluminium potassium silicate, thermally treated to increase its surface area and processed with silicone oil to make it hydrophobic, which also makes the sorption process a partition one. High pressure liquid chromatography was used to analyse samples passed through a 5 cm bed of the material. Samples containing 5 µg l⁻¹ polyaromatic hydrocarbons were eluted with *n*-pentane as follows.

Aliquots (200 cm³) of samples after percolation through the column were extracted with three equal portions (3×20 ml) of *n*-pentane in a separating funnel. Each *n*-pentane eluate was dried by passing through a column of granular anhydrous sodium sulphate (2 g). Then the sodium sulphate columns were washed with *n*-pentane (5 ml). The combined eluates were then evaporated, after adding the internal standard (4-methylpyrene) with a rotary evaporator (1 ml). Chromatography was carried out by the EPA method 14 on a column of octadecylsilone (Michrosorb RP-18 Merck) using absolute methanol as mobile phase. Detection was achieved using a photometric detector set at 254 nm.

Fluoranthrene is the compound least retained by the sorption column (62 per cent recovery). The sorbent efficiency is extremely dependent on the pollution present in the water samples. For waters containing surfactants, the use of aluminium potassium silicate absorbent is not possible.

PRECONCENTRATION ON ACTIVE CARBON: Active carbon has been used to preconcentrate polyaromatic hydrocarbons²⁴⁵. The preconcentration of polyaromatic hydrocarbons is also discussed in section 1.5.30 (multiorganic analysis).

Oxygen containing compounds

1.5.3

Anionic detergents

Spectrophotometric methods

Began et al²⁴⁶ have described a spectrophotometric method for the determination of anionics based on benzene extraction of a detergent Rhodamine B complex.

Janeva and Borissova-Pangarova²⁴⁷ pointed out that in the spectrophotometric determination of anionic detergents there are many difficulties, because of strong interference of other anionics (chloride, nitrate, bicarbonate, phosphate) which are present in much higher concentrations than the surfactants. These interferences can be decreased by using suitable dyes added in small quantities. They investigated 19 cationic dyes of the Remacryl, Maxilon, Astrazon, Basacryl and Diorlin types as analytical reagents. Remacrylblau B and Remacrylrot 2BL were found to be the most suitable. They proposed routine procedures for the extractational spectrophotometric determination of anionic surfactants in waters by use of these two cationic dyes.

In acid medium anionic surfactants form blue (with Remacrylblau B) and red (with Remacrylrot 2BL) complexes which can be extracted with chloroform under conditions in which the dye remains in the water phase.

The absorption maximum of the complex of lauryl sulphate with Remacrylblau B is at 623 nm and that of the complex with Remacrylrot 2BL at 538 nm. It is found that 0.25 ml of the Remacrylrot B solution (0.50 ml of Remacrylrot 2BL solution) is enough for complete bonding of 40 μg of lauryl sulphate when 0.04 per cent solutions of the dyes are used. It was found that only 5 min are necessary for extraction of the complexes and a single extraction gives about 95 per cent recovery. The reaction in the water phase occurs immediately and a delay of 20 min before extraction is without effect. The absorbance of the organic phase can be measured immediately after the extraction and remains constant for an hour. There is a large pH range over which the absorbance remains constant (pH 1–4 for Remacrylblau B, pH 1–5 for Remacrylrot 2BL). In alkaline medium Remacrylblau B is extracted along with its lauryl sulphate complex. This effect is negligible with Remacrylrot 2BL and the determination can be carried out with it in weakly alkaline medium. This is an important advantage of Remacrylrot 2BL in spite of the lower sensitivity, because waters can be analysed without preliminary treatment.

Janeva and Borissova-Pangarova²⁴⁷ investigated the effect of several ions (calcium, magnesium, sodium, potassium, chlorine, nitrate, bicarbonate and sulphate). They found that the degree of interference depends on the quantity of dye used.

Preconcentration

Anionic detergents have been preconcentrated on active cations prior to their determination.^{248–252}

1.5.4

Phenols

Trace amounts ($<1 \text{ mg l}^{-1}$) of phenolic compounds can have significant detrimental effects on water quality. Phenols are toxic to aquatic life and mammals and can impart objectional tastes and odours to water and fish. The US Environmental Protection Agency²⁵³ recommends a maximum of $1 \mu\text{g l}^{-1}$ for total phenolic compounds in potable water supplies. Various methods have been used to determine traces of phenols in water samples. The earlier methods were usually spectrophotometric or colorimetric. A number of sensitive colorimetric methods have been developed for determining phenols in water based on the reactions with various chromogenic reagents including 4-aminoantipyrine (4-amino-phenazone) in the presence of potassium ferricyanide (at various pHs), *p*-amino-*N,N*-diethylaniline in the presence of potassium ferricyanide (indophenol blue method), 2,6-dibromoquinone chlorimide (Gibbs reagent), pyrimidone (i.e. dimethylaminoantipyrine or aminopyrine) in the presence of potassium ferricyanide, nitroaniline diazotization and 3-methyl-2-benzothiazoline hydrazone. Although these methods are sensitive they cannot

differentiate between substituted phenols and are used primarily for determining total phenol concentrations. Also, the colour forming reagents will not react completely with most para-substituted phenols and thus results obtained for total phenol concentrations may be significantly in error. For this reason, alternative, more specific techniques such as gas chromatography have been investigated in recent years.

Workers at the Water Research Association²⁵⁴ have investigated the applicability of these various methods to the determination of phenols in water at levels down to 0.001 mg l⁻¹. None of the methods was completely satisfactory in that they were less sensitive than desirable and did not respond to all types of phenolic compounds.

These workers did not investigate the 3-methyl-2-benzothiazoline hydrazone method which had only just been introduced at the time their work was carried out.

As a result of their work Cheeseman and Wilson²⁵⁵ recommended that the best spectrophotometric method for the determination of phenol in unchlorinated water samples was the 4-aminoantipyrine method operated at pH 10 as described in the American Public Health Association method²⁵⁶⁻²⁵⁸. For chlorinated water supplied they recommended the 4-aminoantipyrine method operated at pH 7.9 as described below, as this method has an appreciably greater sensitivity towards chlorinated phenols. This reagent reacts with the phenolic group on each molecule but, due to steric considerations, not with equal sensitivity. It is, for example, relatively insensitive to some parasubstituted forms. Lack of selectivity and variable sensitivity is a serious drawback to this method because the many diverse sources with different types of phenols can cause the total phenol concentration of natural waters to appear to vary considerably.

Caution has to be exercised when using the 4-aminoantipyrine method for the determination of certain types of phenols. Thus recovery of phenols in the distillation stage ranged from near 100 per cent (phenol, 2-chlorophenol) to below 30 per cent (catechol, resorcinol, and other polyhydric phenols). Precision in the pH 10 method as measured within batch standard deviation is 0.5 µg phenol l⁻¹ at the zero phenol concentration level and 1.1 µg l⁻¹ at the 50 ng l⁻¹ level (without distillation decreasing to 0.6 µg l⁻¹ at the 50 µg l⁻¹ level with distillation).

The analysis of surface waters gives less precise results than for distilled water solutions. In the range 3–63 µg l⁻¹ the standard deviation for surface waters was not dependent on concentration and had an estimated value of 2.5 µg l⁻¹, i.e. a relative s.d. of 10 per cent at a concentration of 25 µg phenol l⁻¹.

As the method involves a distillation stage, no interference is to be expected from inorganic impurities in the sample. Distillable organic impurities in the sample are, of course, always a potential source of interference.

Raman spectroscopy

Haverbeke and Herman²⁵⁹ used laser excited resonance Raman spectroscopy to determine phenolic compounds at the 20–100 µg l⁻¹ level in potable water. The phenols were first converted to derivatives by reaction with the diazonium salt of 4-nitroaniline.

Haverbeke and Herman²⁵⁹ used a closed-loop flow-through set up in their experiments. In this set up, a large volume of the sample solution, usually 650 ml, was continuously flowed through the laser beam. Since the individual dye molecules are only momentarily exposed to the laser beam, any decomposition occurring will be reduced to a minimum, thus assuring more accurate measurements.

There is a definite contribution from a fluorescence band of dye, on which the resonance Raman spectrum is superimposed. The individual resonance Raman bands are, however, clearly observed. The broad, weak band around 1640 cm⁻¹ is due to deformation vibration of the water solvent molecules.

When decreasing the concentration of phenol, some changes in the spectrum are noticed. Obviously the 1640 cm^{-1} water band becomes relatively more intense. Secondly, the bands around 1120, 1180, 1340 and 1590 cm^{-1} decrease much less in relative intensity than the remaining bands.

This effect can be explained by a contribution to this spectrum by the Raman spectra of the added reagents. Indeed the components of the buffer solution that is added, sodium carbonate and EDTA, are present in non-neglectable concentrations.

To obtain the spectrum of the dye, the spectra of the sample solution and of the background have to be subtracted from one another. With a single beam instrument this can be done only by additional data manipulation. The data of the two spectra are digitized and the background spectrum is subtracted from the sample spectrum, based on equal intensity of the 1640 cm^{-1} water band in both spectra.

Using this spectra substitution procedure, concentration of phenols down to $20\text{ }\mu\text{g l}^{-1}$ could be detected and identified.

Gas chromatography

Gas chromatography has been applied to the determination of phenols²⁶⁰.

Thin layer chromatography

Thielemann²⁶¹ has used thin layer chromatography to study the effect of chloride dioxide on 1- and 2-naphthols in potable water. The coloured products obtained are thought to be condensation products of chloroderivatives of 1,2- or 2,6-naphthaquinone. Thielemann applied paper chromatography to a study of the reaction products of polyhydric phenols with chlorine dioxide.

High performance liquid chromatography has been applied to the determination of 4-aminophenol in potable water²⁶².

Preconcentration

See [section 1.5.30](#).

1.5.5

Phthalate esters

High performance liquid chromatography has been applied to the determination of phthalic acid esters in potable water²⁶³.

1.5.6

Carboxylic acids

Preconcentration

See [section 1.5.30](#).

1.5.7

Alcohols, glycols, dioxans, ethers

Diglycidyl ether in amounts down to $1 \mu\text{g l}^{-1}$ has been determined in potable water by high performance liquid chromatography on C18 bonded silica using 1:1 methanol: dichloromethane, then 1:3 methanol: dichloromethane as eluants²⁶⁴.

Preconcentration

See [section 1.5.30](#).

1.5.8

Aldehydes and ketones

Daignault et al²⁶⁵ have described a purge and trap method for the determination of isobutyraldehyde, isovaleraldehyde and 2-methyl butyraldehyde in potable water in the concentration range 0.5–100 $\mu\text{g l}^{-1}$.

Preconcentration

The preconcentration of ketones is discussed in [section 1.5.30](#).

Halogen containing organic compounds

1.5.9

*Chlorophenols**Gas chromatography*

Chriswell and Cheng²⁶⁶ have showed that chlorophenols and alkylphenols in the mg l^{-1} to $\mu\text{g l}^{-1}$ range in potable water can be determined by sorption on macroporous A-26 anion-exchange resin, elution with acetone and measurement by gas chromatography. These workers describe techniques preventing phenol losses caused by chlorination, oxidation, and other reactions during their determination. Common inorganic ions and many organic substances cause no interference; neutral organics that are retained by the resin can be removed by a methanol wash. Phenols are effectively retained from water when samples of water containing low concentrations of phenols are made basic and passed through a column containing an anion-exchange resin.

A number of neutral organic compounds (aliphatic alcohols, 2-phenoxyethanol, methyl cellosolve, naphthalene, C_4 – C_8 aliphatic acids) are retained by A-26 resin. However, none of these compounds affected recovery of phenols. They are eluted from a resin by basic methanol prior to elution of phenols and thus do not interfere with the gas chromatographic determination of phenols. Carboxylic acids also cause no interference with the recovery of phenols using the procedure but can interfere with the gas chromatographic determinations of phenols on OV-17 columns by overlapping the phenol and cresol peaks. When a Tenax-GC column is used, acids eluate well before phenols.

Morgade et al²⁶⁷ have described an electron capture gas chromatographic method for the determination of polyhalogenated phenols in chlorinated and unchlorinated potable water. The particular phenols studied

were: 2,4-dichlorophenol (2,4-DCP); 2,3,5-trichlorophenol (2,3,5-TCP); 2,4,5-trichlorophenol (2,4,5-TCP); 2,4,6-trichlorophenol (2,4,6-TCP); 2,5-dichloro-4-bromophenol (2,5-DC-4-BP); 2,3,4,5-tetrachlorophenol (2,3,4,5-TTCP); 2,3,4,6-tetrachlorophenol (2,3,4,6-TTCP); and pentachlorophenol (PCP).

Using this method Morgade et al²⁶⁷ found levels of pentachlorophenol between less than 0.14 mg l⁻¹ and 340 µg l⁻¹ in Florida potable water and 0.14 mg l⁻¹ and 0.1 µg l⁻¹ in well water. No other chlorophenols were found.

Ashiya et al²⁶⁸ combine the phenols in the water with bromine, and measure the concentration of phenols and chlorophenols by electron capture detection gas chromatography, obtaining their concentrations separately to the extent of 1 µg l⁻¹.

Sithole et al²⁶⁹ used selected ion gas chromatography mass spectrometry to determine halogenated phenols in raw and potable water. They compared two derivatization procedures, in situ acetylation and the formation of pentafluorobenzyl derivative for determining chlorophenols and bromophenols in raw and potable water. Some problems which prevented the use of the pentafluorobenzyl derivative are discussed. Using in situ acetylation, gas chromatography with electron capture detection was compared with gas chromatography—mass spectrometry with selective ion monitoring. The sensitivity of electron capture detection could not be fully exploited because of background response. The selective ion monitoring technique was less susceptible to interference and more sensitive to phenol and monohalogenated phenols. Recoveries of phenols from water samples were generally more than 80 per cent. Treated water samples showed a variety of halogenated phenols which were not present in the raw water indicating these compounds had been formed in the treatment process.

High performance liquid chromatography

This technique has been applied to the determination of pentachlorophenol in potable water²⁷⁰.

1.5.10

Vinyl chloride

Gas chromatography-mass spectrometry

Fujii²⁷¹ has combined mass spectrometry with gas chromatography for the direct determination of sub µg l⁻¹ amounts of vinyl chloride in potable and river waters. The method is based on mass fragmentography followed by chromatography-mass spectrometry by simultaneously recording m/e 62 and 64.

Rivera et al²⁷² have also described a direct mass spectrometric method for determining volatile chlorinated hydrocarbons, including vinyl chloride, in potable water. They give details of a highly sensitive technique for the determination of aliphatic chlorinated hydrocarbons, based on concentration by adsorption by stripping on a charcoal filter and quantitation by a mass spectrometric integrated ion-current procedure, with desorption from the charcoal inside a temperature programmed inlet probe.

Workers at the National Environment Research Centre, US Environmental Protection Agency²⁷³ have described a method for determining vinyl chloride at the µg l⁻¹ level in water. An inert gas is bubbled through the sample to transfer vinyl chloride to the gas phase, and the vinyl chloride is then concentrated on a silica gel or Carbosieve-B cartridge under non-cryogenic conditions and determined by gas chromatography with a halogen specific detector. Gas chromatography-mass spectrometric methods were used to provide confirmatory identification of vinyl chloride. A quantitative recovery of vinyl chloride was obtained on silica gel and Carbosorb B with purge volumes of 150–400 ml at 20 ml min⁻¹.

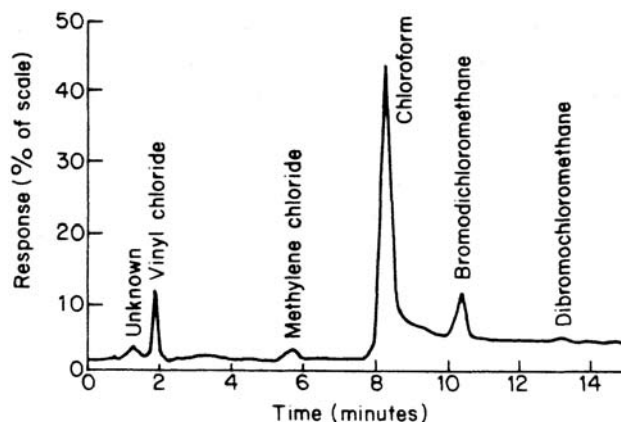


Fig. 22. Microcoulometric gas chromatogram of organohalides recovered from potable water dosed with vinyl chloride (sensitivity 150 ohms).

Fig. 22 represents a typical gas chromatogram obtained from chlorinated potable water which has been dosed with vinyl chloride. The chloroform, bromodichloromethane, and dibromochloromethane are common to chlorinated drinking waters and result from the chlorination process. Low levels of methylene chloride are often observed in samples analysed by this technique. These are attributed to methods background.

Bellar et al²⁷³ used a computer to scan the data and construct a selected ion current profile consisting of peaks that produce a m/e 62 ion. Other compounds likely to be present in the water sample which produce m/e 62 ions are easily resolved using the gas chromatographic conditions recommended by these workers, so, in this sense, the method is specific for vinyl chloride.

Miscellaneous

Ando and Sayato²⁷⁴ carried out studies on the migration of vinyl chloride migrating into potable water from PVC pipes.

1.5.11

Miscellaneous halogenated aliphatic and aromatic compounds

Gas chromatography-mass spectrometry

Dowty et al²⁷⁵ used gas chromatography-mass spectrometry to identify halogenated aliphatic hydrocarbons and aromatics in potable waters. About 70 compounds were identified.

Closed loop stripping-gas chromatography

Unexpected peaks appearing in the gas chromatograms of potable water samples following the addition of bromoalkanes as interval standards have been shown to be chloroalkanes of the same carbon number produced by conversion of bromoalkanes by free chlorine in the sample²⁷⁶.

High performance liquid chromatography

This method has been used to determine non-volatile chlorinated hydrocarbons in potable water²⁷⁷.

High performance liquid chromatography is also discussed in [section 1.5.30](#) (multiorganic analysis).

Preconcentration

Active carbon has been used to preconcentrate chlorinated hydrocarbons from potable and waste waters prior to analysis^{278,279}.

The preconcentration of chlorinated hydrocarbons is also discussed in [section 1.5.30](#).

Chlorinated polyaromatic hydrocarbons

HIGH PERFORMANCE LIQUID CHROMATOGRAPHY: Oyler et al²⁸⁰ have determined aqueous chlorination reaction products of polyaromatic hydrocarbons in amounts down to $\mu\text{g l}^{-1}$ using reversed phase high performance liquid chromatography-gas chromatography. The method involves filtration through a glass microfibre filter and concentration on a high performance liquid chromatography column. The polyaromatic hydrocarbons material is then eluted using an acetonitrile-water gradient elution technique. The fractions are injected separately on to a gas chromatographic column equipped with a photoionization detector.

Hexachlorocyclopentadiene

GAS CHROMATOGRAPHY: Benoit and Williams²⁸¹ give details of a solvent extraction procedure for concentration of trace amounts of hexachlorocyclopentadiene from potable water prior to determination by gas chromatography.

Miscellaneous chloro acids etc.

Uden and Miller²⁸² reported a qualitative and quantitative investigation of some non-volatile chlorinated organics found in chlorinated potable waters. Concentrations of di- and tri-chloroacetic acids were in the range 30–160 $\mu\text{g l}^{-1}$ while those of chloral were lower by an order of magnitude. The concentrations of these compounds were readily measurable using a microwave emission plasma detector. All compounds identified were also formed during the laboratory chlorination of soil fulvic acids.

Stachel et al²⁸³ determined halogenated organic compounds in potable water using mineralization at high temperature in a stream of oxygen. The procedure is carried out in a pyrolysis tube in which the sample is injected into a stream of carbon dioxide carrier gas. The carrier gas is passed through a superheated steam zone at 700°C and a pre-oxidation and cracking zone at 1100°C, in a stream of oxygen. The sample, carrier gas and oxygen are mixed in a pyrolysis chamber at 850°C and passed through a second 850°C heating zone before cooling and titration. The mineralization achieved was about 100 per cent for polychlorinated biphenyl and hexachlorobenzol and 91 per cent for dichloroacetic acid.

1.5.12 *Haloforms*

Numerous articles have appeared referring to the presence of carcinogens in water and questioning the safety of chlorine when used as a disinfectant of water supplies^{284–286}. The impetus for this relatively sudden development was the release of a study by the Environmental Protection Agency (EPA) of the presence of potentially toxic organic substances in the New Orleans Water Supply²⁸⁷ and an epidemiological study of the implications of cancer causing substances in the Mississippi river water by the Environmental Defence Fund²⁸⁸. This latter document is of some importance in that it suggests a relationship between the above average incidence of cancer in certain communities and the Mississippi derived water supply. Subsequent to the passage of the Safe Drinking Act (PL93–523 (in 1974 the United States Government Environmental Protection Agency sponsored two finished water studies, the National Organics Reconnaissance Survey (NORS) and the National Organics Monitoring Survey (NOMS)). These studies confirmed the widespread occurrence of chloroform as well as the other trihalomethanes, bromodichloromethane (CHB_2Cl_2), chlorodibromomethane (CHBr_2Cl) and bromoform (CHBr_3). Since this work, there have been numerous other reports of the presence of chlorinated and brominated haloforms in river and potable Water.^{289–311}

As well as chlorohydrocarbons a wide range of bromohydrocarbons and bromochlorohydrocarbons such as bromoform, bromodichloromethane, and dibromochloromethane have been identified in water supplies. Luong et al²⁹⁰ have recently drawn attention to the role of bromide in water supplies in the formation of brominated trihalomethanes with reference to its interaction during the chlorination process with humic material present in natural waters. Changes during water treatment were examined and subsequent trihalomethane formation, on chlorination of those waters evaluated. For bromide levels in lowland waters of up to $120 \mu\text{g l}^{-1}$ brominated trihalomethanes were shown to account for up to 54 per cent of the total trihalomethanes formed on treatment.

Chloroform apparently results from reaction between hypochlorite and any of several types of organic precursors in the chlorinated raw water. The brominated and mixed brominated/chlorinated trihalomethanes are presumed to be formed from the reaction of hypobromite and hypochlorite with the same precursors; the hypobromite is formed from the oxidation of bromide by hypochlorite. If iodide salts are also present in the water being chlorinated, an analogous reaction with hypochlorite results in trihalomethanes containing iodine.

Fam and Stenstrom³¹⁰ investigated the percussions of non-volatile chlorination products in potable water.

De Leer³¹¹ investigated the nature and mechanism of formation of chlorinated products produced during chlorination of aqueous solutions of humic acid. Techniques for the identification of aryl chlorinated aromatic acids and their intermediates leading to the formation of chloroform and 4-carbon dicarboxylic acids are discussed.

Quimby et al³⁰⁴ used gas chromatography with microwave emission detection to identify the aqueous chlorination and bromination products of fulvic and humic acids in water.

Bunn et al²⁹¹ detected all ten possible mixed and single halogen containing trihalomethanes of chlorine, bromine and iodine when salts containing fluoride, bromide and iodide were added to a river water sample before chlorination (no fluorinated trihalomethanes were detected), Glaze et al²⁹² identified seven trihalomethanes containing chlorine, bromine and iodine in potable water samples. Also found in potable water but not necessarily formed during the chlorination process, are compounds such as methylene chloride, dichlorobenzene, hexachlorobutadiene²⁹³, tetrachloroethylene²⁹⁴, trichloroethylene^{293,294}, carbon tetrachloride²⁹⁵ and 1,2-dichloroethane^{294,295} and ethylene dibromide²⁹⁶.

The formation of volatile organohalogen compounds by the chlorination of waters containing organic contaminants²⁹⁷ has received wide attention^{298–300}. Investigation carried out by Tardiff and Dunzer³⁰⁰

confirmed the presence of six halogenated compounds (viz. chloroform, bromoform, bromodichloromethane, dibromochloromethane, tetrachloromethane and 1,2-dichloroethane) in potable waters with concentrations varying up to $100 \mu\text{g l}^{-1}$ whilst Tabor³⁰¹ identified 3-(2-chloroethoxy) 1,2-dichloropropene.

As a consequence of the concern regarding possible adverse effects of minute quantities of trihalomethanes in potable water the US Environment Protection Agency^{302,303} in 1978 drew up an amendment to US National Interim Primary Drinking Water Regulations designed to protect the public from exposure to undesirable amounts of trihalomethanes (including chloroform) in potable water.

A maximum contaminant level of 0.10 mg l^{-1} has been prescribed for total trihalomethanes, applicable initially to community water supplies for populations as part of the treatment process.

Gas chromatography

Numerous methods based on gas chromatography have been described for the determination of haloforms in potable waters:

- (a) Direct injection of aqueous sample into gas chromatograph, summarized in [Table 25\(a\)](#).
- (b) Gas chromatography on conventional columns of organic solvent extract of water sample, summarized in [Table 25\(b\)](#).

TABLE 25
Determination of haloforms in potable water direct injection and solvent extraction conventional gas chromatographic methods

Extraction solvent	GC detector	GC column	Substances named	Detection limit ($\mu\text{g l}^{-1}$)	Recovery %	Ref.
(a) Direct injection GC methods						
None	EC	—	—	100	—	305
	GC-MS	—	—	5	—	306
None	—	—	Chloroform	—	—	307
			Bromoform			
			Bromodichloromethane			
None	EC	Chromosorb 101	Bromochloromethane	1	—	308
		Chloroform	3	—		
			1,1-dichloroethane	90	—	

Extraction solvent	GC detector	GC column	Substances named	Detection limit ($\mu\text{g l}^{-1}$)	Recovery %	Ref.
			1,2-dichloroethane	150	—	
			Carbon tetrachloride	3	—	
			Dibromomethane	0.6	—	
			1,2-dichloropropane	60	—	
			Tetrachloroethylene	8.0	—	
			Chlorodibromomethane	5	—	
			Bromoform	2	—	
			Tetrachloroethane	7	—	
			<i>p</i> -Dichlorobenzene	500	—	
			<i>o</i> -Dichlorobenzene	500	—	
None	—	Packed	Chloroform	—	—	312
			Carbon tetrachloride	—	—	
			Bromodichloromethane	—	—	
(b) Solvent extraction GC methods						
Petroleum ether	EC	5% FFAP on Chromosorb HPW	Chloroform	0.05	83–96	309
		Bromodichloromethane	0.02			

Extraction solvent	GC detector	GC column	Substances named	Detection limit ($\mu\text{g l}^{-1}$)	Recovery %	Ref.
Hexane	EC	15% OV 225 on Chromosorb W AW	Dibromochloromethane	0.02		
			Bromof orm	0.05		
			Tetrachloromethane	0.1	100–111	313
			Chloroform	0.1	60–78	
			Dichloroethane	10	100–104	
	EC	10% squalane on chromosorb W-AW	Tetrachloroethylene	0.13	100–102	
			Bromodichloromethane	0.15	64–90	
			Chlorodibromomethane	0.2	79–97	
			Bromof orm	0.2	100	
			Chloroform	0.2	85–88	314
cyclohexane		Dichlorobromomethane	0.2	83–83	315	
hexane		Dibromochloromethane	0.4	85–94		
Isooctane	EC	10% squalane on chromosorb W-AW	Bromof orm	0.8	90–94	
			Chloroform	0.1	73	314

Extraction solvent	GC detector	GC column	Substances named	Detection limit ($\mu\text{g l}^{-1}$)	Recovery %	Ref.
		Dichlorobromethane	0-1	76	316	
		Dibromochloromethane	0-2	74		
			Bromoforn	0-5	78	
Pentane	EC	10% squalane on Chromosorb W-AW	Chloroforn	0-1	80	314
		Dichlorobromethane	0-1	82	316	
		Dibromochloromethane	0-2	87		
			Bromoforn	0-5	93	
Pentane	EC	10% squalane on Chromosorb W-AW	Chloroforn	0-1	72	314
		Dichlorobromethane	0-1	73	317	
		Dibromochloromethane	0-2	78		
			Bromoforn	0-5	83	
Extraction solvent	GC detector	GC column	Substances named	Detection limit ($\mu\text{g l}^{-1}$)	Recovery %	Ref.
Pentane (or hexane) or methylcyclohexane	EC	3% SP-1000 on Supelport or 10%	Chloroforn	—	106–110	318

Extraction solvent	GC detector	GC column	Substances named	Detection limit ($\mu\text{g l}^{-1}$)	Recovery %	Ref.
e (iso-octane)		squalene on Chromosorb W-AW				
		Bromodichloromethane	108-125	339		
		Chlorodibromomethane	74-94			
Pentane		Bromoforn	76-114			
	EC	10% Carbowax 20 M on Chromosorb W-HP	Chloroforn	0.1	—	320
		Chlorodibromomethane	0.1	—		
		Dibromodichloromethane	10	—		
Petroleum ether EC		Bromoforn	0.17	—		
			Chloroforn	0.1	—	321
		Bromodichloromethane	0.1	—		
			Dibromodichloromethane	0.1	—	
(c) Solvent extraction/capillary column GC methods						
<i>n</i> -Pentane	EC	GE-20 and Carbowax 20M	Chloroforn	0.001	82	322
		Bromodichloromethane	0.0002	89	323	

Extraction solvent	GC detector	GC column	Substances named	Detection limit ($\mu\text{g l}^{-1}$)	Recovery %	Ref.
<i>n</i> -Pentane	EC	OV-101	Chlorodibromomethane	0.0002	84	
			Dichloromethane		0.05	
			Carbon tetrachloride		0.0001	
			Chloroform		0.0005	
			Tetrachloroethylene		0.0002	
			Bromoform		0.001	
			Chloroform			
			Dichlorobromomethane			
			Dibromochloromethane	0.1–1	—	324
			Bromoform			
Trihalomethanes				325		

(c) Capillary column gas chromatography of organic solvent extract of water sample, summarized in [Table 25 \(c\)](#).

(d) Static head space analysis techniques.

(e) Purge and trap analyses techniques (dynamic head space analysis).

(f) Adsorption of haloforms on resins and subsequent gas chromatography of resin extract.

(g) Gas chromatography-mass spectrometry

(h) High performance liquid chromatography.

(a) Direct injection of aqueous samples. This technique^{322,326} has poor detection limits which are incapable of meeting the detection limits targets of $100 \mu\text{g l}^{-1}$ or lower for potable water as recommended by various authorities^{302,303}.

(b) Gas chromatography (conventional) of solvent extracts. These methods are reviewed in [Table 25](#) from which it is seen that detection limits down to $0.1 \mu\text{g l}^{-1}$ are achievable for most of the haloforms tested. Unfortunately, recoveries are low for several of the haloforms tested.

Inoko et al³²⁷ carried out experiments to assess the feasibility of using xylene as an alternative extraction solvent to determine trace amounts of lower halogenated hydrocarbons in potable water, particularly trichloromethane, dichlorobromomethane, dibromochloromethane, tribromomethane, trichloroethylene,

tetrachloromethane and tetrachloroethylene. The xylene extraction method described is a suitable technique for determining $\mu\text{g l}^{-1}$ levels of lower halogenated hydrocarbons in potable water.

Simmonds and Kerns³²⁸ used a permaselective membrane of perfluorosulphonic acid polymeric material to remove water from aqueous samples by injecting them into a length of tubing made from the material, positioned ahead of a gas chromatographic column. The method allows direct injection of aqueous samples without altering column performance. The method was demonstrated in the analysis of trace amounts of halocarbons in potable water samples by direct electron capture gas chromatography. The water removal technique was also used in conjunction with head space analysis.

Norin and Renberg³²⁹ give details of a rapid solvent extraction procedure for the isolation of trihalomethanes from potable water prior to determination by gas chromatography.

Mehran et al³³⁰ have developed a liquid-liquid extraction procedure to determine trihalomethanes, which avoided opening sample bottles during extraction. The rapid, simple method consisted of extracting trihalomethanes from aqueous samples into an organic solvent, followed by gas chromatography using a Hall electrolytic conductivity detector operated in the halogen mode. The method was directly applicable to aqueous samples and could be guaranteed at low $\mu\text{g l}^{-1}$ concentrations. Recovery ranged from 88.0 to 98.6 per cent.

Reichert and Lochtmann³³¹ studied the determination of haloforms in potable water.

Since some of the halogenated methanes are volatile, a loss in concentration between sampling and analysis could be expected. However, there is increasing evidence that an increase can occur in practice. The increase is due, at least in part, to excess chlorine reacting with organic material (humic acids) in the sample. In practice, therefore, when taking samples of chlorinated treated water, it is important to bear in mind that the reaction producing the halogenated methanes could be incomplete. The addition of ascorbic acid (7 mg l^{-1}) has been reported to stabilize the levels of halogenated methanes³¹⁶. Fielding et al³⁰⁹ showed that addition of ascorbic acid (about 7 mg l^{-1}) at the time of sampling reduced the further formation of halogenated methanes.

(c) Capillary column gas chromatography of organic extracts. Use of a capillary column in the place of a conventional packed column improves resolution in the separation of halomethanes (Table 25(c)).

Trussell et al³²⁴ used glass capillary gas chromatography for the precise and rapid analysis of trihalomethanes in n-pentane extracts of potable water. These workers claim that the use of glass capillary gas chromatography has several advantages over conventional gas chromatography. First, the glass capillary column provides better resolution of individual components; the typical packed column has 2000–10000 theoretical plates whereas capillary columns range from 15 000 to 50 000 theoretical plates. Second, the high quality resolution allows shorter gas chromatographic runs without overlapping peaks and thus brings about time savings. Finally the trihalomethanes can be resolved well on general usage liquid phases, which gave versatility in analytical capability in that a wider range of types of organic compounds can be analysed without requiring time-consuming column changes.

The chromatogram obtained from the analysis of a water sample spiked with 14 volatile organic compounds is shown in fig. 23. Only two of these compounds were not well resolved on the glass capillary column. 1,2-dichloroethane appears as a shoulder on the 1,1,1-trichloroethane peak and trichloroethylene is masked by the dichlorobromomethane peak. Trussell et al³²⁴ point out that although capillary gas chromatography appears to offer no significant advantage in terms of precision and accuracy, there are several ways in which it is superior. The sharp resolution and improved separation resolve low molecular weight, volatile halogenated compounds that might ordinarily appear as a single peak, e.g. dichlorobromomethane and 1,2-dichloropropane. If the raw water itself contains interfering compounds, these are more easily resolved as separate peaks by capillary gas chromatography. On occasion, water

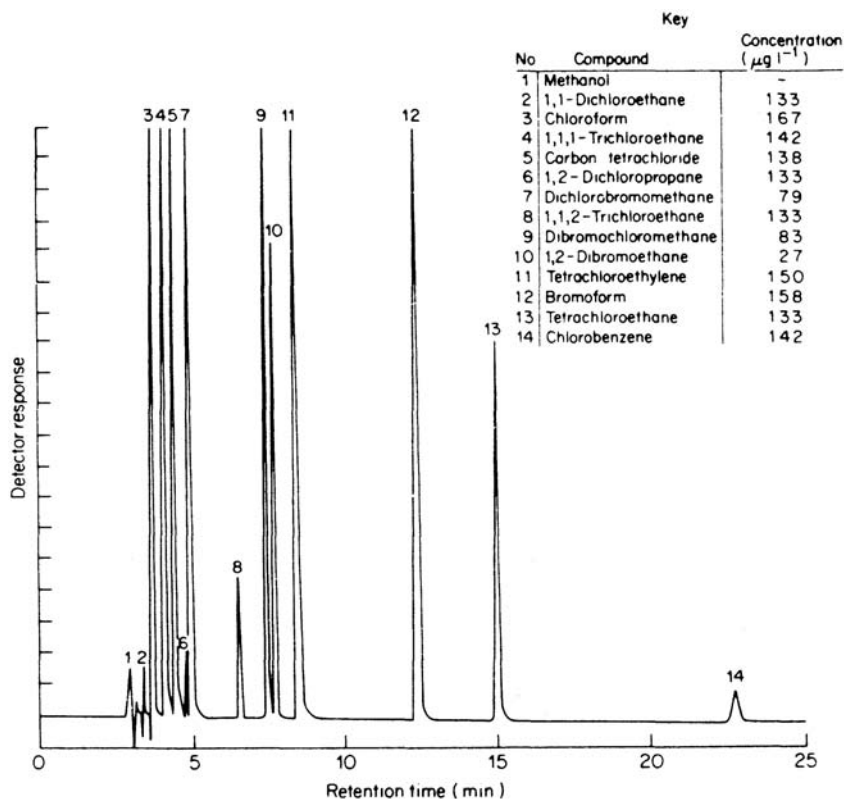


Fig. 23. Resolution of halogenated organics by glass capillary chromatograph.

samples that have shown only the four trihalomethanes on a packed column showed 20 or more compounds on a glass capillary column. The narrow peak widths, the accurately reproducible retention times, the separation of interfering raw water compounds, and the resolution of chlorinated compounds similar to the trihalomethanes all contribute to making more positive identification. This is important because the electron capture detector utilized in liquid-liquid extraction techniques is relatively non-specific, responding to many electron capturing materials in addition to the halogen.

Nicolson et al³³² analysed potable water samples containing trihalomethanes by extraction with methylcyclohexane and analysis by gas chromatography using a short capillary column and electron capture detection. Rate of extraction, extraction efficiencies, effect of temperature on extraction efficiency, detection limits and reproducibility were examined. Ascorbic acid was shown to be a more effective sample preservative than sodium thiosulphate. Detection limits of $1 \mu\text{g l}^{-1}$ were achieved using 100 ml samples and 2 ml of solvent.

Peruzzi and Griffini³³³ studied the efficiency of hydrogen peroxide as a reducing agent for volatile halogenated hydrocarbons and as a dechlorinating agent for chlorinated river water. Trihalomethane removal was measured by gas chromatography with electron capture detection on fused silica capillary columns with split-splitless injection on n-pentane extracts.

Simultaneous flow ionization and electron detection have been used³³⁴ as detectors in the capillary gas chromatography of trace levels of haloforms in potable water.

(d) Static head space analysis. The static head space method is based on the fact that when a water sample that contains organic compounds is sealed in a vial, organics will equilibrate between the water and vial head space. Distribution of compounds between the two phases depends on temperature, vapour pressure for each compound, sample matrix influences on compound activity coefficients and ratio of head space to liquid volume in the vial. A major advantage of this method is that only relatively volatile water-insoluble compounds tend to partition into the head space; therefore, a form of sample clean-up is provided. Also, since only gaseous samples are injected into the gas chromatograph, column and detector contamination are prevented and chromatographic interferences are minimized.

Head space gas chromatography has been used to determine $0.1 \mu\text{g}$ to 1 mg l^{-1} chloroform, carbon tetrachloride, trichloroethylene and tetrachloroethylene in potable waters²⁸⁹. These workers carried out a systematic study of the parameters affecting the accuracy and precision of results obtained by this technique.

Dietz and Singley³³⁵ observed that analytical accuracy is influenced by the effects of sample matrices on chromatographic responses. Several matrix conditions were examined experimentally. The presence of organics in the water sample might upset halocarbon phase equilibration. However, no effects (2 per cent r.s.d.) from either methanol or acetone were observed up to a 2 per cent (v/v) concentration. Methanol is observed in the gas chromatograms at a 2 min retention time but does not interfere in the halocarbon analyses. Sample pH also does not affect (2 per cent r.s.d.) chromatographic results. Sodium chloride concentrations greater than 1 per cent will significantly increase chromatographic responses. These increased responses reflect an increase in halocarbon activity coefficients (salting out).

Otson et al³³⁶ have compared dynamic head space, solvent (hexane) extraction, and static head space techniques utilizing Tenax gas chromatographic columns, a ^{63}Ni electron capture detector and a Hall electrolytic conductivity detector for the determination of trihalomethanes in water. The dynamic head space or gas sparging technique entails purging of a water sample with inert gas, collection of purged trihalomethanes on an adsorbent (e.g. Tenax GC) followed by thermal desorption. The static head space technique, involving equilibration of trihalomethanes between the water sample and air space in a closed vessel, allows an aliquot of the air space to be analysed for trihalomethanes. The relative standard deviation between trihalomethane values obtained by the three techniques ranged 9–10 per cent for chloroform, 3–24 per cent for dichlorobromomethane and 13–61 per cent for dibromochloromethane. Although the dynamic head space technique was the most sensitive, the solvent extraction technique gave comparable precision while the static head space technique showed relatively poor precision and sensitivity. The solvent extraction technique is recommended for routine monitoring since it requires no special equipment and allows more analyses per hour than the dynamic head space technique.

Otson et al³³⁶ found that improved sensitivity for trihalomethanes was achieved by operating the Hall detector in the pyrolytic mode. As expected, the electron capture detector gave considerably lower method detection limits than the Hall detector. The precision of the gas sparging and solvent extraction techniques was comparable to the static head space technique.

Otson et al³³⁶ also studied the effects on reported results of delays of up to 30 hours between taking the sample and carrying out the analysis. Bulk aqueous solutions containing $20\text{--}120 \mu\text{g l}^{-1}$ chloroform, $1.6\text{--}9.9 \mu\text{g l}^{-1}$ dichlorobromomethane and $0.4\text{--}2.4 \mu\text{g l}^{-1}$ bromochloromethane showed respectively concentration losses of 12 ± 3 , 16 ± 5 and 21 ± 4 per cent. Otson et al³³⁶ concluded that the three analytical techniques gave comparable trihalomethane values for potable water samples. Although the gas sparging technique was the most sensitive, the solvent extraction technique gave comparable precision. The static head space technique showed relatively poor precision and inferior sensitivity. The sensitivity of the static head space and solvent extraction techniques can be improved by increasing the volume of the aliquot injected into the gas chromatograph, but overloading of the electron capture detector by organohalides must be avoided.

Varma et al³³⁷ carried out a comparative study of the determination of trihalomethanes in water. They compared the results of chloroform extraction using six liquid-liquid extraction solvents (pentane, methylcyclohexane, isooctane, hexane, *n*-heptane and *n*-nonane) with the vapour space extraction method. The vapour space method yielded the poorer results.

Friant³³⁸ has described a direct head gas analysis procedure for the isolation of chloroform from aqueous environmental samples. The technique included gas chromatography and mass spectrometry. This worker carried out fundamental studies of the partitioning of organic compounds between the aqueous and vapour phases and systematically examined effects of variation in operating parameters. Possible errors and limitations of this method are discussed.

Gomella and Belle³³⁹ studied the determinations of volatile organohalogen compounds in water by the head space technique.

Montiel³⁴⁰ applied the head space analysis technique to the determination of the halomethane content of chlorinated water samples. He considered the effects of operating variables on the sensitivity of the method and the impact of a number of interfering substances (surface active agents and soluble salts). Particular attention is paid to the operation of the electron capture detector system.

Suffet and Radziul³⁴¹ applied various techniques including head space analysis and solvent extraction to the screening of volatile organics including chloroform and bis(2-chloroethyl) ether in water supplies.

Bush et al³⁴² developed a method for the determination of halogen containing organic compounds using measurement of peaks in head space vapour with an electron capture detector and a chromatograph system. The method was used in a screening survey of New York State potable water with the objectives of determining significant seasonal variations in halo-organic concentrations of the compounds in chlorinated ground water and surface water, and the frequency of occurrence of halo-organic compounds in chlorinated water. It is shown that chloroform and bromodichloromethane occur most frequently in chlorinated water.

Dynamic head space techniques for the determination of trihalomethanes have been studied by Symons et al³⁴³, Keith³⁴⁴ and workers of the Health and Welfare Department, Canada³⁴⁵ and static head space techniques have been studied by Keith³⁴⁴, Bush et al³⁴⁶ and Morris and Johnson³⁴⁷.

Castello et al³⁴⁸ evaluated the gas chromatographic sensitivity and linearity of the nickel-63 asymmetric type electron capture detector for trihalomethanes and other haloalkanes using headspace and liquid-liquid extraction techniques for mixed column gas chromatographic separation. Each extraction method showed a wide linearity range, allowing simplified calibration techniques and automation.

Croll et al³⁴⁹ determined trihalomethanes in potable water using gas syringe injection of head space vapours and electron capture gas chromatography. Head space vapours were withdrawn from a sample container, which had been equilibrated at ambient temperature, by a gas tight syringe with a valved needle. The samples were injected into a gas chromatograph with electron capture detector. The use of sealed vials minimized contamination. The method was simple and insensitive to sample volume, natural salt concentration and minor vapour loss during sampling. The relative standard deviation was less than 2 per cent and the results were comparable with liquid-liquid extraction. The limit of detection of trihalomethane was less than $1 \mu\text{g l}^{-1}$.

Castello et al³⁵⁰ determine trihalomethanes using a polar and a non-polar column mounted in series connected to a Ni-63 electron capture detector to separate the trihalomethanes and any other halocarbons present, using temperature programming. The series arrangements enabled the analysis of each head space sample to be completed in less than 30 min.

Static head space analysis has been used to determine methyl bromide in potable waters³⁵¹. The technique used to determine traces of methyl bromide involved addition of sodium iodide to convert methyl bromide

to methyl iodide which was then determined by gas chromatography. The detection limit was approximately 5 ng l^{-1} .

(e) Purge and trap techniques (dynamic head space analysis). In one gas purging method the volatile compounds are extracted from the water sample by passing pure gas (e.g. nitrogen) through the water sample and collecting the volatile compounds on a small adsorption column. The compounds are introduced into a chromatograph by heating the adsorption column. The determination is carried out by temperature programmed gas chromatography using a halogen specific detector (Electrical Conductivity Detector) or a more generalized detector (flame ionization or mass spectrometry). This technique is quite sensitive ($>0.5 \mu\text{g l}^{-1}$).

Dressman et al³¹⁴ are of the opinion that purge and trap methods are very amenable to gas chromatographic mass spectrometric confirmation of the identity of volatile compounds and at levels lower than can be obtained with liquid-liquid extraction methods. The lower minimum detectable concentrations are attainable because virtually all of the trihalomethanes purged from the sample are transferred to the gas chromatographic column and the detector—without the relatively non-volatile interferences coextracted by liquid-liquid extraction methods and without introducing solvent-related interference.

The liquid-liquid extraction methods rarely provide a compound sufficiently concentrated for gas chromatography-mass spectrometry and it may be necessary to resort to a solvent enrichment technique. Enriching the solvent by evaporation commonly results in interference from concentrated solvent impurities to the extent that mass-spectral analysis cannot be performed, or in loss of the more volatile components such that actual enrichment is not achieved.

Quimby and Delaney³⁵² and Quimby et al³⁵³ determined trihalomethanes in potable water by gas chromatography with an atmospheric pressure microwave emission detector. The organics are isolated by a purge and trap technique. This detector, in addition to being very sensitive, is also element selective, distinguishing between chlorine, bromine and iodine.

The water sample is contained in a 6 in long glass tube. Helium or nitrogen purge gas, which has passed through a trap containing silver oxide is heated at 200°C to oxidize any organic contaminants bubbled into the water sample.

The organics purged from the water sample are desorbed from the Tenax GC trap into the gas chromatograph by attaching the end of the trap to a helium line and inserting the entire length of the trap into the injection port of the gas chromatograph.

Carrier gas is then purged through the heated Tenax GC trap on to the gas chromatographic column. For 5 ml water samples, detection limits of ca. $0.1 \mu\text{g l}^{-1}$ are obtained for the four bromine and chlorine containing trihalomethanes, and the linear range extends to above the $100 \mu\text{g l}^{-1}$ level. Similar results are also obtained for the other organohalides. Chlorine-, bromine-, and iodine-selective chromatograms for a standard aqueous solution containing several organohalides at the $25\text{--}30 \mu\text{g l}^{-1}$ level are given in [fig. 24](#).

Kromer³⁵⁴ has described a microprocessor controlled gas chromatograph monitoring system for determining purgeable carbon tetrachloride, haloforms, and halomethane at concentrations of $0.1 \mu\text{g l}^{-1}$ in river water. Chloroform was found in 70 per cent of the samples analysed; other chlorinated solvents found regularly were trichloroethane, trichloroethylene, tetrachloroethylene, methylene chloride, and carbon tetrachloride.

Kirschen³⁵⁵ has investigated the Environmental Protection Agency standard purge and trap method 601³⁵⁶, for determining trihalomethane and other halogenated volatiles in water. Kirschen³⁵⁵ used a Varian Model 3700 gas chromatograph with Model 700A Hall Electrolytic Conductivity Detector VISTA 401 Chromatography Data System. The column comprised $200 \text{ cm} \times 2 \text{ cm}$ glass columns containing 1 per cent Sp.1000 on Carbopack-B (60–80 mesh). This method was used to check the concentrations of four

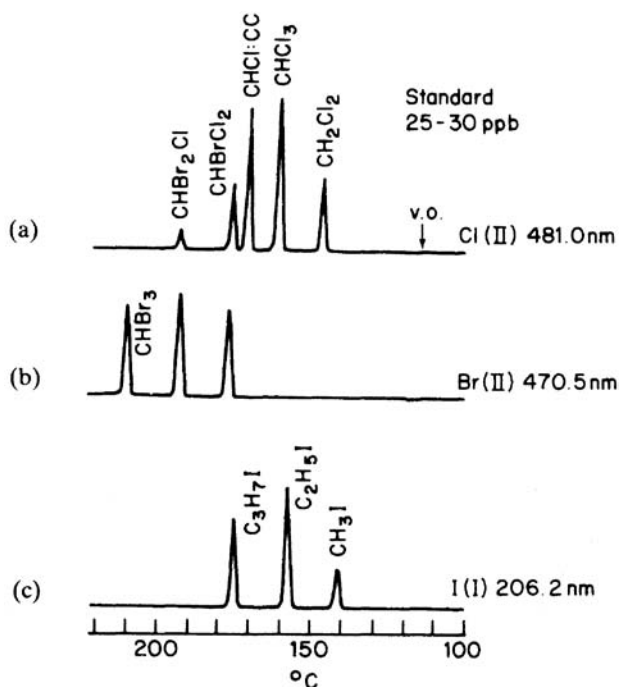


Fig. 24. Element selective chromatograms from sparged standard solution. (a) Cl channel, (b) Br channel, (c) I channel.

halomethanes, chloroform, bromoform, dichlorobromomethane and dibromochloromethane in potable water samples. Relative percentage standard deviations were normally below 5 per cent.

A purging method has been described for the specific determination of low levels of methyl bromide fumigant in water³⁵⁷. The analysis was performed with a Packard Purgatrat, mounted on a P.T.C. (packed trap capillary) MDSS module, with two electron capture detectors. The module was used in a Packard Model 433 gas chromatograph.

Nicolson et al³⁵⁸ have described a convenient easily automated method for the analysis of haloforms and some other volatile organohalides in potable water. This direct aqueous injection method has a detection limit at or below $1 \mu\text{g l}^{-1}$ for haloforms. Simultaneous analysis of finished water samples with direct aqueous injection and the gas sparging method revealed hitherto unknown aspects of water treatment chemistry. While the gas sparging technique measures only the free haloforms present in the potable water, they showed that the direct aqueous injection method quantitates the total potential haloforms that can form after chlorination.

Comparison of determinations of haloforms, particularly chloroform, in potable water revealed that direct aqueous injection results were consistently higher than those obtained by gas sparging. A similar trend was shown for chlorodibromomethane. In general, the direct aqueous injection method indicated chloroform and bromodichloromethane concentrations 1.5 and 2.2 times higher respectively, than the values obtained by gas sparging.

These results suggested to Nicholson et al³⁵⁸ that actual chlorinated natural water samples, as opposed to synthetic standards, contain non-volatile haloform precursors which are injected in determinations by direct injection but not by gas sparging. If the additional quantities of haloforms observed by the direct aqueous

injection method are produced during analysis from non-volatile halogenated organic compounds, then in a given sample the difference should be measurable by analysing prepurged samples by direct aqueous injection.

Pfaender et al³⁵⁹ have also compared purge and trap and direct injection gas chromatographic techniques for the determination of chloroform in potable water and found evidence for the presence of non-volatile precursors. The direct aqueous injection technique employing a bypass valve to vent water and electron capture detector, gave consistently higher values for chloroform than the purge method. Comparable results were obtained if the direct injection value after a 30 min purge was subtracted from the before-purged value. The nature of the residual measured by direct injection after purging was investigated and shown to be due to non-purgeable intermediates that decompose within the injection port of the gas chromatograph to chloroform. The residual varied depending on the source of the water sample examined and the specific configuration of the chromatograph employed. The results indicated the need for caution in the interpretation of chloroform and other trihalomethane values, especially haloform potentials, generated by direct aqueous injection.

Pfaender³⁵⁹ was unable to identify the chloroform precursor in potable water samples. He did conclude that the size of the residual measured by direct aqueous injection depends on the materials and configuration of the injection port of the chromatograph used. This raises doubts as to the usefulness of the residual haloforms measured by direct aqueous injection as an estimate of haloform formation potential. The relationship of the potential as determined by direct aqueous injection and the haloforms formed during distribution of a finished drinking water is still largely unknown.

Dressman et al³¹⁴ compared determinations of haloforms by methods involving extraction with methylcyclohexane³¹⁵, iso-octane³¹⁶ and pentane³¹⁷ with results obtained by a purge and trap method involving purging the sample with nitrogen and adsorption on a Tenax GC trap, followed by thermal desorption from the trap and gas chromatography.

For comparison the average percentage recovery of the trihalomethanes obtained by the purge and trap method in the 1–200 mg l⁻¹ range was 75–95 per cent much the same as in the liquid-liquid extraction methods. The US Environmental Protection Agency has published two methods for trihalomethane analysis³¹⁸; methods 501.1³¹⁹ and 501.2³⁶⁰. Method 501.1 is a procedure for the analysis by the purge and trap technique: method 501.2 is a liquid-liquid extraction technique and also discusses the determination of trihalomethane precursors.

Brass³⁶¹ has compared purge and trap and solvent extraction methods for the determination of halomethanes. He claims similar results are obtained by both methods.

Kirschen³⁶² discussed the determination of 17 halogenated organic compounds by purge and trap capillary gas chromatography. Ammonia has been shown to be a major interferent in the gas chromatographic analysis of trihalomethanes and other organohalogens in water, using the purge and trap technique³²¹. The ammonia must be removed prior to analysis.

Miller and Uden³⁶⁴ have studied the effects of chlorination parameters, such as reaction time, chlorine/carbon ratio, pH and source of humic material, on the formation of nonvolatile organic chlorine compounds during the chlorination process. The process was followed both qualitatively and quantitatively. The quantitation procedure for haloforms in the chlorine/fulvic acid reaction consists of air-tight sampling vials, purge and trap techniques and gas chromatography with a microwave plasma emission detector. Chlorine-selection fingerprint studies were undertaken to follow the formation of 17 major chlorinated products. Detailed data are presented on the formation of chloroform, dichloroacetic acid, trichloroacetic acid and chloral hydrate.

Chiba and Haraguchi³⁶⁵ determined trihalomethanes in $\mu\text{g l}^{-1}$ amounts in potable water by gas chromatography-atmospheric pressure helium microwave induced plasma emission spectrometry with a heated discharge tube for pyrolysis. The trihalomethanes are collected on a Tenax GC column by a gas purge and trap method.

Pierce et al³⁶⁶ describe the use of the purge and trap method with an electrolytic conductivity detector for the determination of volatile halogenated organics including the trihalomethanes. Purge closed loop gas chromatography has been used³⁶⁷ to determine trihalomethane in potable water. This method combines the technique of gas stripping and static head space sampling. Recovery efficiencies of between 81 and 100 per cent are obtained. Better quality chromatograms with faster handling were achieved using the purge closed loop method than by the purge and trap technique.

Marshall and Wampler³⁶⁸ purged haloforms from potable water using a liquid nitrogen cryogenic refocuser interlaced with a capillary column gas chromatograph to determine sub $\mu\text{g l}^{-1}$ quantities of these substances.

(f) Resin adsorption-gas chromatography. Two approaches to this analysis are possible. In one, the water³⁶⁹ sample is purged with purified nitrogen or helium and the purged trihaloforms are trapped on a column of macroporous resin such as Amberlite XAD-2 or XAD-4. The trapped trihaloforms are then desorbed from the column with a small column of a polar solvent prior to gas chromatography. In the second approach the water sample is contacted directly with the resin and then the trihaloforms desorbed as before. Alternatively the resin can be injected directly into the gas chromatograph injection port. Both methods provide a very useful built-in concentration factor which improves method sensitivity.

Renberg³⁷⁰ has reported a resin adsorption method for the determination of trihalomethanes and chloroethanes and dichloroethane in water. In this method halogenated hydrocarbons are determined by adsorption on to XAD-4 polystyrene resin and eluted with ethanol. The extract is analysed by gas chromatography and is sufficiently enriched in hydrocarbon to be suitable for other chemical analysis or biological tests. Volatile hydrocarbons yielded recoveries of 60–95 per cent. By using two series connected columns Renberg was able to study the degree of adsorption and the chloroethanes were found to be more strongly adsorbed than the haloalkanes.

Kissinger³⁷¹ has reported a high resolution capillary column gas chromatographic procedure for the determination of trihaloforms in potable water. The trihaloforms were determined by sorption on to columns of acetylated XAD-2 resin after the removal of the pyridine solvent. Detection limits for the four chloro- and bromo-compounds of the haloform type in a 100 ml sample of water were below $1 \mu\text{g l}^{-1}$.

Various other workers have discussed resin adsorption methods for the determination of trihaloforms in water^{363–378}. Kissinger and Fritz³⁷⁹ have described a method based on adsorption of trihaloforms on acetylated XAD-2 resins followed by elution with pyridine.

Libbey³⁸⁰ used Amberlite XAD-4 resin to extract ethylene dibromide from water for determination by gas chromatography and electron capture detection. Samples spiked with $1 \mu\text{g l}^{-1}$ ethylene dibromide exhibited a mean of $0.98 \mu\text{g l}^{-1}$ and a standard deviation of $0.105 \mu\text{g l}^{-1}$.

(g) Gas chromatography-mass spectrometry. Fujii^{381–383} has carried out extensive work on the application of direct aqueous injection-mass fragmentography-gas chromatography-mass spectrometry to the analysis of various organohalogen compounds including trihaloforms in water at concentrations below $1 \mu\text{g l}^{-1}$. In one method³⁸³ a sample volume of $100 \mu\text{l}$ was injected into a precolumn with diglycerol as stationary phase, on which water is retained. The halogenated compounds, which are not retained by the precolumn, are separated by a packed analytical column. The standard deviation of the method at a $1 \mu\text{g l}^{-1}$ concentration of dichlorobromomethane was 0.14 and the coefficient of variation 4.2 per cent.

In further work, Fujii^{382,383} applied direct injection gas chromatography-mass spectrometry with single ion detection to the determination of 1– 100 $\mu\text{g l}^{-1}$ of chloroform, bromodichloromethane, dibromochloromethane, bromoform and carbon tetrachloride in chlorinated water supplies. This method uses a liquid diglycerol phase to make the organic peaks appear before the large waterpeak.

Gas chromatography-mass spectrometry has been used to study the reaction products and rates of disappearance of 1,2-dibromopropane and 1,2-dibromoethane in water³⁸⁴ and to analyse mutagenic extracts of aqueous chlorinated humic acid^{385,386}, and to study the degradation of chloroform by photo-assisted heterogeneous catalysis in dilute aqueous suspensions of titanium dioxide³⁸⁷.

Miscellaneous

Reichert and Lochtman³⁸⁸ studied the appearance of haloforms in raw water and their formation during potable water treatment, as well as their elimination and the prevention of their formation. Techniques for the determination of organohalogen compounds are discussed, in particular, the extractive organic halogens and adsorbed organic halogens; methods are described and compared. A combination of these methods has been used to analyse surface waters in West Germany. The adsorbed organic halogens are first determined by adsorption on activated carbon, followed by pyrolysis and microcoulometry. Parallel to these determinations the extractive organic halogens are determined according to the DIN regulation, which involves extraction with pentane/diisopropyl ether, pyrolysis and determination of halogens in a condenser, by coulometry or nephelometry.

Okumura et al³⁸⁹ give details of a procedure for the spectrophotometric determination of trace amounts of chloroform in water; it is based on the fact that chloroform produces a blue fluorophore when heated with nicotinamide and concentrated sodium hydroxide solution.

Oake and Anderson³⁹⁰ studied the adsorption of trihalomethanes from water onto carbon.

Reunanen and Kronfeld³⁹¹ describe a method for determination of volatile hydrocarbons in, amongst others, raw water and drinking water. The sample is extracted with petroleum ether and without further purification, analysed by high performance liquid chromatography with electron capture detection. The levels of ten volatile halocarbons in potable water were determined. Levels of trichloromethane in potable water were over 40 times higher than in the river water samples.

High performance liquid chromatography

The high performance liquid chromatography of down to 1 $\mu\text{g l}^{-1}$ of haloforms has been discussed³⁹².

Preconcentration

Haloforms in potable water have been preconcentrated on a minicolumn of active carbon³⁹³. The preconcentration of haloforms is also discussed in [section 1.5.30](#).

1.5.13

*Chlorinated insecticides**Gas chromatography*

Sackmauereva et al³⁹⁴ have described the method, given below, for the determination of chlorinated insecticides (BHC isomers, DDE, DDT and hexachlorobenzene) in potable waters.

The water sample (1–3 l) is extracted with three portions of petroleum ether (boiling point 30–40°C). The petroleum ether layer is then concentrated to a volume of about 0.5 ml using a vacuum and purified on an alumina column (Woelm, neutral, activated by heating at 300°C for 3 hours and deactivated by adding 11 per cent water). Thereafter, insecticides were eluted with 15 per cent dichloromethane in petroleum ether. The eluate was concentrated in a vacuum rotary evaporator to a volume of 1 ml and then used for gas liquid chromatography.

The insecticide concentration is in linear proportion to the peak height over the following range:

–BHC	0.03–0.12 mg l ⁻¹
–BHC	0.15–0.60 mg l ⁻¹
–BHC	0.04–0.18 mg l ⁻¹
–BHC	0.03–0.12 mg l ⁻¹
<i>p,p'</i> -DDE	0.15–0.60 mg l ⁻¹
<i>o,p'</i> -DDT	0.30–1.2 mg l ⁻¹
<i>p,p'</i> -DDD	0.30–1.2 mg l ⁻¹
<i>p,p'</i> -DDT	0.30–1.2 mg l ⁻¹

When the individual insecticides are present in the solution in such a concentration range, the electron capture responds nearly uniformly to all insecticides. A column filled with 1.5 per cent silicone OV-17 plus silicone oil (fluoroalkylsiloxane) on Chromosorb W (80–100 mesh) is used for separation of the BHC, alpha, beta, gamma and delta isomers (hexachlorocyclohexane), *o,p'*-DDT, *p,p'*-DDE, *p,p'*-DDD and *p,p'*-DDT, –BHC and hexachlorobenzene (HCB) have a common peak. They can be separated on a column filled with 2.5 per cent Silicone Oil XE-60 (–cyanoethyl-methylsilicone) on Chromosorb W (80–100 mesh).

Using the gas chromatography methods Sackmauereva et al³⁹⁴ obtained from spiked samples the four BHC isomers at 93–103.5 per cent recovery. Recoveries of DDT and DDE were 85.6–94 per cent from water. Purification on a Florisil column was used in determining chlorinated insecticides unstable at low pH (aldrin, dieldrin). The type and activity of Florisil influence the yield and accuracy of the method. Therefore, the activity of this adsorbent had to be verified and adjusted. From the results of the analyses of 92 potable water samples the average content of –BHC was 0.069 µg l⁻¹, that of –BHC was 0.023 µg l⁻¹ and that of the other isomers (+) of BHC+HCB (hexachlorobenzene) 0.018 µg l⁻¹. The average content of DDE in potable water was 0.022 µg l⁻¹ and that of DDT 0.042 µg l⁻¹.

The Department of the Environment (UK)³⁹⁵ has used a tentative method for the determination of organochloride insecticides and PCBs in potable and natural waters. The first part of this method is concerned with the extraction and determination of the amounts of individual substances present; the second part is concerned with methods for verifying the identity of the various substances quantified in the first part. Representative data are presented for a number of typical insecticides using different chromatographic stationary phases.

Ronsen³⁹⁶ has discussed a systematic analytical scheme for the determination of organic pollutants including toxaphene insecticide and polychlorinated biphenyls in potable water. The pollutants are divided into volatile and extractable compounds, and the extraction further divided into acid and base extractables and into those capable of flame ionization or electron capture detection. The pesticides, toxaphenes and arochlors are combined into one category.

Thin-layer chromatography

Mosinska³⁹⁷ has described a semiquantitative thin-layer chromatographic method for the determination of trichlorphon in potable water. The sample is extracted with redistilled chloroform. The extract is dried with sodium sulphate, reduced in volume to 4 ml in vacuo and then evaporated to dryness in a stream of air. The residue is dissolved in acetone and chromatographed on chloride-free silica gel G plates (activated at 100°C for 1 hour) with benzenemethanol (17:3) as solvent. The spots, revealed with ammoniacal silver nitrate in acetone, are compared with those of standards for semiquantitative determination. The detection limit is 0.02 mg l⁻¹ and the efficiency of extraction is 70 per cent.

Sackmauereva et al³⁹⁴ used thin layer chromatography on silica plates to confirm the identity of chlorinated insecticides previously identified by gas chromatography. The compounds can be separated by single or repeated one-dimensional development in n-heptane or in n-heptane containing 0.3 per cent ethanol. The plate is dried at 65°C for 10 min and detected by spraying with a solution of silver nitrate plus 2-phenoxyethanol. Thereafter, the plate was dried at 65°C for 10 min and illuminated with an ultraviolet light (254 nm) until spots representing the smallest amounts of standards were visible (10–15 min). The pesticide residues may be evaluated semiquantitatively by simple visual evaluation of the size and of the intensity of spot coloration and by comparing extracts with standard solutions.

Sherma and Slobodien³⁹⁸ determined chloropyrifos insecticide and its metabolite 3,5,6-trichloro-2-pyridinol in potable water at 5 µg l⁻¹ by thin layer chromatography. Preadsorbent silica gel layers were used for resolution and silver nitrate for detection prior to reflectance scanning. Recovery of 3,5,6-trichloro-2,2-pyridinol from water was 84.0 per cent. Recovery of chloropyrifos from potable water was 87.5 per cent.

Preconcentration

The preconcentration of chlorinated insecticides is discussed in [section 1.5.30](#).

1.5.14

Polychlorinated biphenyls

Gas chromatography

Albro and Fishbein³⁹⁹ in 1972 carried out early work on the quantitative and qualitative analysis of PCBs using gas chromatography with flame ionization detection. Webb and McCall⁴⁰⁰ studied the question of quantitative PCB standards for electron capture gas chromatography.

Polychlorinated biphenyls are often extracted from water by solvent extraction. However, the relatively small sample size, ca. 1–21, that can be handled restricts the quantitation limits of PCB analyses. Charcoal (Chriswell et al⁴⁰¹), polyurethane foams (Musty and Nickless⁴⁰²), Carbowax-undecane on Chromosorb W (Musty and Nickless⁴⁰³), as well as macroreticular resins (Chriswell et al⁴⁰¹, Musty and Nickless⁴⁰³, Lawrence and Tosine⁴⁰⁴, Coburn et al⁴⁰⁵) have been used to isolate PCBs from water. Amberlite XAD-2 and XAD-4

macroreticular resins have been used by several workers (Chriswell et al⁴⁰¹, Musty and Nickless^{402,403}, Coburn et al⁴⁰⁵) to analyse PCBs from a variety of water sources but on relatively small sample size (1–21) and recovery studies were carried out at relatively high fortification levels (ca. 250 ng l⁻¹). However, Coburn et al⁴⁰⁵ suggested that the XAD-2 method could be used to sample large volumes of water to decrease the quantitation limits for PCB analysis. Following from this suggestion Le'Bel and Williams⁴⁰⁶ described a method for determining PCBs in water in which they obtained a concentrate by passing the water sample through Amberlite XAD-2 macro-reticular resin cartridges. Following clean-up on a Florisil column the extract was gas chromatographed using an electron capture detector. In potable well water samples interference was minimal and the detection limits was about 0.04 ng l⁻¹ for Aroclors 1016, 1232, 1242 and 1254. In potable water from a river source, interference in the chromatogram from other organic compounds made quantitative detection difficult at the 1 ng l⁻¹ level. Aroclor 1254 was detectable at this level but 1232, 1016 and 1242 were only detectable at 10 ng l⁻¹.

Le'Bel and Williams⁴⁰⁶ found that low procedural blank values, equivalent to 0.04 ng l⁻¹ for a 2001 potable water sample were attainable only by using doubly distilled solvents and by exhaustive washing of all reagents and glassware with these solvents.

Gas chromatographic analysis of concentrated extracts of potable water samples without Florisil column clean-up gave off-scale peaks at instrument settings suitable for low ng l⁻¹ PCB analysis. However, fractionation of the extract by Florisil column chromatography gave a PCB fraction sufficiently clear of interfering organics to permit PCB analysis at 1–10 ng l⁻¹. The gas chromatographic analyses were done on a relatively short (11m) capillary column, thus providing a compromise of short analysis time and good resolution with minimum interferences from other substances present in the water extract. Recoveries of Aroclors 1232, 1016, 1242 and 1254 from water samples fortified at the equivalent of 1 and 10 ng l⁻¹ for a 2001 sample ranged from 86 to 99 per cent at the 10 µg l⁻¹ level and from 91 to 110 per cent at the 1 µg l⁻¹ level.

The detection limit was estimated to be ca. 0.04 ng l⁻¹ of Aroclor 1016 from this source of water with Aroclors 1232, 1242 and 1254 having similar levels of detection. When the method was applied to potable water from a river source, the interference in the gas chromatogram from other organic compounds present in the sample made quantitation difficult at the 1 ng l⁻¹ level. Aroclor 1254 would still be detectable at the 1 ng l⁻¹ level but 1 ng l⁻¹ levels of Aroclors 1232, 1016 and 1242 would not have been distinguishable from the background peaks. However, at the 10 ng l⁻¹ level, it was possible to distinguish peaks due to Aroclor 1232, Aroclor 1242 and Aroclor 1016 from the background chromatogram due to other organics. It is concluded that the XAD-2 macroreticular resin method can be used to analyse large volumes of potable water for low ng l⁻¹ levels of PCBs. The detection limits, however, are limited by the interference from other organics in the water sample but are typically in the 1–10 ng l⁻¹ range.

Preconcentration

The preconcentration of PCBs is discussed in [section 1.5.30](#).

1.5.15 Dioxins

Preconcentration

The preconcentration of dioxins is discussed in [section 1.5.30](#).

1.5.16 *Herbicides*

Polarography

Glyphosate (*N*-phosphon-methylglycine) herbicide is manufactured by Monsanto, and marketed under the name 'Round up'. Bronstad and Friestad⁴⁰⁷ have described a method for determining glyphosate residues in potable waters based on the polarography of the *N*-nitroso derivative.

High performance liquid chromatography

This technique has been applied to the determination of Aldicarb⁴⁰⁸ using a C18 Sep-pak separation column.

Preconcentration

In a method 409 for the preconcentration of paraquat and diquat from potable water the sample is passed through an ion-exchange column, followed by desorption, reduction with sodium dithionite and measurement of the reduced forms at 390 μm for paraquat and 379 μm for diquat.

The preconcentration of herbicides is also discussed in [section 1.5.30](#).

Nitrogen containing organic compounds

1.5.17 *Amines*

Gas chromatography-mass spectrometry

Avery and Junk⁴¹⁰ converted trace levels of primary aliphatic amines in aqueous solutions to imine derivatives using pentafluorobenzaldehyde. The derivatives were extracted into hexane and measured by combined high-resolution gas chromatography/mass spectrometry using multiple ion monitoring. The method was successfully applied to the analysis of primary amines in potable water and river water down to a detection limit of 10 $\mu\text{g l}^{-1}$ for 0.5 ml samples.

Preconcentration

See [section 1.5.30](#).

1.5.18 *Nitrocompounds*

Gas chromatography

Patil⁴¹¹ determined nitrobenzene and 2,4-dinitro-phenol in potable water by gas chromatography.

High performance liquid chromatography

This technique has been used to determine traces of ethylene glycol dinitrate in potable water⁴¹².

Preconcentration

See [section 1.5.30](#).

*1.5.19**Nitriles**Preconcentration*

See [section 1.5.30](#).

*1.5.20**Acrylamide**Titration methods*

Ortubia and Mateous⁴¹³ determined polyacrylic acid by conductimetric titration with *N*-cetyl pyridinium chloride.

Spectrophotometric methods

Cationic polyelectrolytes have been determined in water⁴¹⁴ using a method based on changes in light absorbance resulting from the formation of an insoluble change complex with ponceau 5 dye.

Gas chromatography

Croll^{415,416} described an extraction gas chromatographic method for the determination of down to 100 mg l⁻¹ acrylamide in acrylamide polymer polyelectrolytes. Thin layer chromatography and infrared spectroscopy both confirmed conclusions reached by gas chromatography.

High performance liquid chromatography

Acrylamide has been determined in potable water by high performance liquid chromatography with ultraviolet detection⁴¹⁷.

The high performance liquid chromatography of polyacrylamide is also discussed in [section 1.5.30](#) (multiorganic analysis).

1.5.21

*Urea and substituted ureas**Spectrophotometric method*

Nehring⁴¹⁸ has described an enzyme method, based on the use of urease for the determination of traces of urea in potable water. McCarthy⁴¹⁹ has described a urease method for the determination of the microgram amounts of urea. Urea and ammonia in natural waters have been determined⁴²⁰ in amounts down to $0.2 \mu\text{g N l}^{-1}$ by a method based on reaction with phenol and sodium hypochlorite followed by spectrophotometric determination at 454 nm (urea) and 630 nm (ammonia). Tyrosine is the only amino acid which interferes in this procedure.

1.5.22

*Nitrosamines**Gas chromatography*

Fine et al⁴²¹ have described a gas chromatographic method for the determination of *N*-nitroso compounds in potable water.

A gas chromatograph equipped with a flame ionization detector and a 3.6 m \times 3 mm stainless steel column packed with 10 per cent diethyleneglycol succinate on 80–100 mesh Chromosorb W (H.O.) were used.

Recoveries obtained by this procedure were 77 per cent or higher and were particularly good for nitrosamine levels of about $10 \mu\text{g l}^{-1}$.

Richardson et al⁴²² have applied gas chromatography with a chemiluminescent detection system to the determination of microgram levels of nitrosamines (*N*-nitrosodimethylamine, *N*-nitrosodiethylamine, *N*-nitrosomorpholine and *N*-nitrosodiethanolamine, *N*-nitrosopyrrolidine, *N*-nitrosopiperidine and *N*-nitroso-5-methyl-1,3-oxazolidine) in potable water supplies. Nitrosamines may be removed from aqueous media by solvent extraction and subsequently concentrated by evaporation of the solvent, in order to detect levels as low as $0.01 \mu\text{g l}^{-1}$.

For the estimation of volatile dialkyl nitrosamines and *N*-nitrosopiperidine, *N*-nitrosopyrrolidine and *N*-nitrosomorpholine, 10N sulphuric acid was added to the sample which was then extracted with redistilled dichloromethane. 1.5 M sodium hydroxide was added to the combined extract. After separation, the organic layer was dried over sodium sulphate and evaporated to 2.5 ml at 46°C on a water bath. Hexane was added, and evaporation continued to about 250 μl . 5 μl aliquots were analysed for volatile nitrosamines using gas chromatography.

In the chemiluminescent procedure, which detects all nitrosamines amenable to gas chromatography, effluent from a chromatograph passes into a catalytic chamber whereupon the nitrosamine is fragmented to give rise to nitric oxide. This interacts with ozone and results in a chemiluminescent emission in the near infrared, which is detected with a photomultiplier tube. Interferences are minimized by placing a cold trap between the catalyst and ozone chamber, and by incorporating an optical filter in front of the photomultiplier.

The presence and amounts of nitrosamines were confirmed in some of the samples using the gas chromatograph coupled to an AEI MS902 mass spectrometer. The nitrosamines were detected by parent ion monitoring using peak matching, in the manner described by Gough and Webb⁴²³. The detection limit was $0.1 \mu\text{g l}^{-1}$ for each of the nitrosamines. While measurement of the nitric oxide fragment by mass spectrometry is applicable to all nitrosamines, it results in a significantly poorer detection limit. Further, the mass

spectrometer will respond to any compound giving rise to NO^+ , including *C*- and *N*-nitroso compounds, nitro compounds and nitramines.

The upper limits of *N*-nitrosodimethylamine, *N*-nitrosodiethylamine, *N*-nitrosomorpholine and *N*-nitrosodiethanolamine detected were 0.2, 2.0, 100 and 60 $\mu\text{g l}^{-1}$ respectively.

Fine et al⁴²⁴ used gas chromatography to analyse volatile *N*-nitroso compounds at the $\mu\text{g l}^{-1}$ level in American potable water supplies. Two different concentration and extraction procedures were used by these workers; one based on liquid-liquid extraction and the other based on the adsorption of the organic fraction on carbon and its subsequent extraction with chloroform and alcohol. In both cases, final quantitative analysis and identification were carried out on a single column gas chromatograph equipped with *N*-nitroso compound specific thermal energy analyser.

Fig. 25(a) is a chromatograph of 10 μl of the mixture containing seven *N*-nitroso compounds that were added to the water. Fig. 25(b) is the chromatogram of 10 μl of the final dichloromethane extract following concentration on the Kuderna-Danish evaporator. At approximately 0.200 $\mu\text{g l}^{-1}$ concentration level the recovery efficiency is 30 per cent for dimethylnitrosamine, increasing to about 90 per cent for the less volatile species.

Detection limits ranged from 0.001 $\mu\text{g l}^{-1}$ (solvent extraction) to 10 $\mu\text{g l}^{-1}$ (carbon adsorption).

Preconcentration

Absorption on Ambersorb XE-34 cation exchange resin and active carbon⁴²⁶ have been used to preconcentrate nitrosamines from natural water prior to gas chromatography. The preconcentration of nitrosamines is also discussed in section 1.5.30.

1.5.23

Nitriloacetic acid

Polarography

Fayyad⁴²⁷ described an indirect determination of nitrilotriacetic acid in potable waters using the bismuth nitriloacetic acid complex with potentiometric stripping analysis. Spiked samples containing 6–255 $\mu\text{g l}^{-1}$ of nitriloacetic acid were adjusted to pH 2–2.3 (hydrochloric acid), a solution of known bismuth III concentration was added to give a final concentration which exceeded that of nitriloacetic acid by 1.5–2.3 times, then 58 μM of free bismuth III and 0.42 μM of potassium dichromate (oxidant) were added. The electrode system (mercury on glass carbon) was immersed in the solution after stirring for 10 min and voltage stripping time curves recorded. Two subsequent time curves were obtained by adding 50 μl of bismuth III (10 mg l^{-1}) solution. Each time nitriloacetic acid concentrations were calculated from the difference between concentrations of added bismuth III and that of free bismuth determined by potentiometric stripping analysis.

Gas chromatography

Reichert and Linckens⁴²⁸ have reviewed gas chromatographic methods for the determination of nitriloacetic acid in potable waters. They point out that the esterification of the nitriloacetic acid is required to enable it to be volatilized in the gas liquid chromatographic column, and they compared a range of esterification reagents and conditions for simplicity and speed of operation. The method chosen involved treatment of a

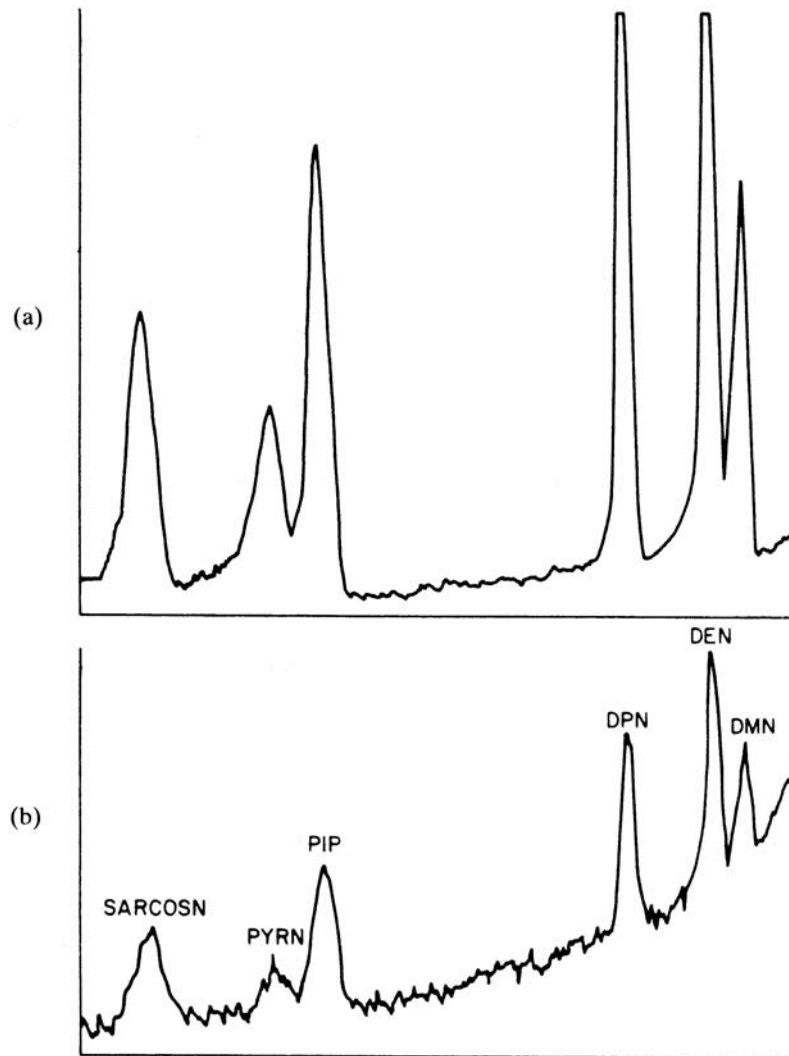


Fig. 25. Gas chromatography of *N*-nitroso compounds in water, dimethylnitrosamine (DMN), diethylnitrosamine (DEN), dipropylnitrosamine (DPN), *N*-nitrosopiperidine (PIP), *N*-nitrosopyrrolidine (PYRN) and *N*-nitrosoarcosinate (SARCOSN). (a) g.c. TEA spiking solution, (b) recovery from water at 0.010 $\mu\text{g l}^{-1}$ level.

concentrated sample with a mixture of *n*-propanol-acetyl chloride (10:1) and the resulting nitriloacetic acid-propyl ester injected into the column, which was fitted with a nitrogen sensitive detector. The detection limit for nitriloacetic acid in potable water is about 1 $\mu\text{g l}^{-1}$.

Williams et al⁴²⁹ applied a nitrogen specific detector to a survey of the levels of nitriloacetic acid as its tri-*n*-butyl ester in US potable water supplies at concentrations approaching 1 $\mu\text{g l}^{-1}$.

1.5.24

*Phosphorus containing compounds**Trihaloalkyl, trialkyl and triaryl phosphates*

Williams and Le Bel⁴³⁰ examined potable waters for 29 cities in Canada, for tri(haloalkyl), trialkyl and triaryl phosphate. A comparison of triaryl phosphate levels with raw-water sources indicated that higher levels were found in potable water from rivers than lakes and ground waters had very low levels. The three central drainage basins of St Lawrence river, Great Lakes and Winnipeg lake had relatively high levels of triaryl phosphate. The fraction of triaryl phosphate values over 10 ng l^{-1} was very small, but about 75 per cent of the tributoxyethyl phosphate values were over 10 ng l^{-1} possibly through contamination from the rubber gasket industry. Trace levels of triaryl phosphate appear to be present in Canadian potable water supplies sampled at the 29 water treatment plants.

Organophosphorus insecticides

The preconcentration of organophosphorus insecticides is discussed in [section 1.5.30](#).

1.5.25

*Sulphur containing compounds**High performance liquid chromatography*

This technique has been applied to the determination of thiafluron in potable water⁴³¹. Separation was achieved on a C18 Seppak column and a fluorescence and electrochemical detector were used to determine $\mu\text{g l}^{-1}$ quantities of this compound.

Miscellaneous organic compounds

1.5.26

Geosmin (trans 1, 10-dimethyl-trans decanol) and other water flavouring chemicals

This is a compound with a musty odour that is a metabolite of some kinds of Actinomyces.

Kikuchi et al⁴³² identified geosmin in water supplies using chromatographymass spectrometry. The water was chlorinated, treated with aluminium sulphate, and filtered through a layer of sand; it was then passed through a column of activated charcoal to adsorb odoriferous compounds. The charcoal was extracted several times with dichloromethane and the oily material recovered from the extract was distilled with water, the distillate was extracted with dichloromethane and the solvent was removed by evaporation. The residue was purified by chromatography on silica gel, with pentane and pentane-ethyl ether (99:1) as solvents. The eluate, which contained a musty smelling oil, was subjected to gas chromatography at 150°C on a stainless steel column (2 m \times 3 mm) packed with 15 per cent of Reoplex 400 on Chromosorb WN AW with nitrogen as carrier gas (30 ml min^{-1}) and flame ionization detection. The identity of geosmin was confirmed by mass spectrometry and by further gas chromatography at 115°C on a glass column (1.5 m \times 2 mm) packed with 25 per cent of PEG 2I M Chromosorb W with helium as carrier gas (2 kg cm^{-2}).

Otsuhara and Suwa⁴³³ conducted studies on odorous compounds in reservoir water, filtration plant water and broth cultivated with actinomycetes and algae by gas chromatographic-mass spectrometric analysis. Odorous compounds were isolated from water by adsorption and extraction methods and identified as geosmin and 12-methylisoborneol. Geosmin and 12-methylisoborneol were found in the surface water of a Japanese reservoir and *Micromonospora* isolated from a filtration plant produced 12-methylisoborneol. It was suggested algae were much concerned in the production of odorous compounds.

Hwang et al⁴³⁴ have described a method for the determination in potable waters of geosmin and other earthy musty odorants (2-isopropyl-3-methoxypyrazine, 2-isobutyl-3-methoxypyrazine, 2-methylisoborneol and 2,3,6-trichloroanisole). These workers used closed loop stripping coupled with gas chromatography and mass spectrometry to determine down to $0.8 \mu\text{g l}^{-1}$ of these compounds. Increasing the ionic strength of the samples by adding sodium sulphate increased both the stripping rate and the sensitivity of the method.

Krasner⁴³⁵ has reviewed methods for the determination of geosmin in potable water.

Preconcentration

See [section 1.5.30](#).

1.5.27

Pyrethrins

Gas chromatography

Down to $0.2 \mu\text{g}$ pyrethrine can be determined in water by gas chromatography⁴³⁶. A hexane extract of the sample is washed with aqueous sodium chloride solution then follows an elaborate working up procedure, it is gas chromatographed on a helical glass column (4 ft \times 0.25 in) packed with 5 per cent of SE-30 on AW-DMCS Chromosorb W (60–80 mesh) and operated at 190°C with nitrogen (40 ml min^{-1}) as carrier gas and flame ionization detection. This permits the simultaneous determination of pyrethrin (linear response range 0.2 – $2.2 \mu\text{g}$) and of the synergistic piperonyl butoxide (range 0.6 – $5.6 \mu\text{g}$) and *N*-(2-ethylhexyl)-norborn-5-ene-2,3-dicarboximide (range 0.6 – $1.8 \mu\text{g}$). Recoveries averaged 93–94 per cent.

1.5.28

Humic acids

Polarography

Farrah et al⁴³⁷ showed that membrane filtration concentrated a material resembling humic acid from tap water samples with an efficiency of about 50 per cent.

Sohr and Wienhold⁴³⁸ have described a d.c. polarographic method for the determination of trace amounts of humic substances in potable waters. The method is based on the extent to which the inhibitory effect of a tri-*n*-butylphosphate layer on the dropping electrode employed to trace the polarographic wave of copper II ions is modified in the presence of humic substances. Humic acids, fulvic acids and lignosulphonic acids react similarly, and hence cannot be determined together, but amines, polypeptides and polyhydroxy compounds do not interfere. The sensitivity of the method is in the $\mu\text{g l}^{-1}$ range. Samples of potable water

from various parts of East Germany were shown to contain humic acid in amounts ranging from $100 \mu\text{g l}^{-1}$ to 2.6 mg l^{-1} .

1.5.29

Ozonolysis products

Miscellaneous

Since the detection of halogenated organics in potable water much research effort has been directed toward finding water treatment processes to remove such organics or their precursors and toward finding disinfectants other than chlorine. Great interest has been focused upon ozonation because both disinfection and organic removal can be accomplished with this process. As ozonated end-products will occur in water produced by such processes and these could be potentially toxic and would accumulate in waste water after repeated cycles of use it is necessary to ascertain what end-products occur in water that has been ozonated and subsequently chlorinated.

Kuo et al^{439,440} have studied the response of solutions of 2-propanol, acetic acid and oxalic acid to ozonation, with and without ultraviolet irradiation, in the laboratory. The effect of ultraviolet irradiation was to enhance the rate of oxidation of these organic compounds; the products of the reaction were identified by gas chromatography and the rate of decomposition determined in each case. Methylene chloride, chloroform, carbon tetrachloride and corresponding bromosubstituted derivatives were identified in the products of chlorination but not in those of ozonation, which appeared to convert the residual organic materials (humic and fulvic acids) to harmless products, alcohols, ketones, formaldehyde, lower fatty acids, oxalic acid, glyoxylic acid, pyruvic acid and keto malonic acid, leading to formation of carbon dioxide.

Glaze et al⁴⁴¹ analysed ozonation by products produced before and after chlorination in potable water and waste water using size exclusion chromatography and halogen specific microcoulometry. Gas chromatography with an electron capture detector and gas chromatography-mass spectrometry was also used.

Jolly et al⁴⁴² have conducted a study into the non-volatile products produced during the chlorination, ozonation and ultraviolet irradiation of supply water and water produced in waste water treatment plants. High performance liquid chromatography and mass spectrometry were used to separate organic constituents from concentrates of samples before and after treatment. Chromatographic profiles reveal differences due to disinfection of the treated sample. High performance liquid chromatographic analysis of chlorinated, ozonated, and UV irradiated secondary effluents indicates that both chlorination and ozonation destroy chromatographic constituents and also produce chromatographic constituents. Ultraviolet irradiation at disinfection levels appears to have little chemical effect on the non-volatile organic constituents separated by high performance liquid chromatography.

Yamada and Samiya⁴⁴³ have reported the quantitative determination of aldehydes and organic acids produced by ozonation of some model compounds in potable water. Aldehydes and ketones were determined by gas chromatography, oxoacids were converted to their methyl esters by diazomethane and then determined by gas chromatography, and dicarbonyl compounds were measured by a spectrophotometric method in alcoholic alkaline solution.

1.5.30

*Multiorganic analysis of potable water**Gas chromatography-mass spectrometry*

A tremendous amount of material has been published on this subject which is beyond the reach of this book to publish in detail. This work is concerned solely with the application of gas chromatography combined with mass spectrometry to the identification and determination of mixtures of organic substances in potable water.

In Table 26 are listed in date order some of the more important papers on the subject which, it is hoped, will assist the reader in tracking down any information he requires.

Perhaps some idea of the power of the gas chromatography-mass spectrometry approach to the analysis of organic micropollutants can be gauged by the work of Coleman et al⁴⁵⁶, on mutagenic extracts of potable water. 400 gallon samples of the water were concentrated to a small volume using reverse osmosis and lyophilization. The concentrates were then fractionated by sequential extraction with petroleum ether, diethyl ether and acetone. Most of the mutagenic activity was found in the diethyl ether extract and this was subjected to the gas chromatography-mass spectrometry technique. Fig. 26 shows the total ion chromatogram obtained following separation on an SP 1000 gas chromatographic column. This figure indicates several organic substances that were positively identified in this extract.

Garrison and Pellizzani⁴⁶⁸ applied the Environmental Protection Agency Master Analytical Scheme to the comprehensive analysis of trace polar organics in potable water.

TABLE 26

Published work on the application of gas chromatography mass spectrometry to multiorganic analysis of potable water

Year of publication	Paper title	Ref.
1975	Identification of volatile organic contaminants in Washington DC municipal water	444
1976	Organic micropollutants in air and water. Sampling, gas chromatographic-mass spectrometric analysis and computer identification	445
1976	Recent advances in the identification and analysis of organic pollutants in water	446
1977	Guidelines for qualitative and quantitative screening of organic pollutants in water supplies	447
1977	Quantitative analysis of volatile organic compounds by GC-MS	448
1977	Trace organics in water	449
1978	An overview of the analysis of trace organics in water	450
1978	GC-MS analysis of volatile organic compounds in water	451
1979	Organic pollution profiles in drinking water	452
1979	Some applications of gas chromatography-mass spectrometry in the water industry	453
1980	GC-MS identification of trace organics in Philadelphia drinking waters during a 2-year period	454
1980	Quantitative aspects of the determination of organic micro pollutants in raw and potable water	455
1980	Identification of organic compounds in a mutagenic extract of a surface drinking water by a computerized gas chromatography-mass spectrometry system	456
1981	Identification and determination of trace organic substances in tap water by computerized gas chromatography-mass spectrometry and mass fragmentography	457

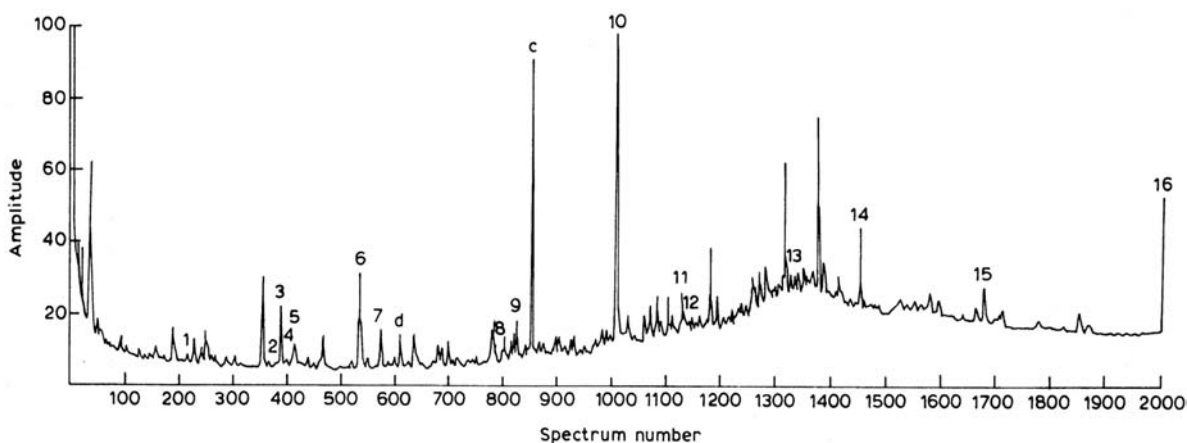
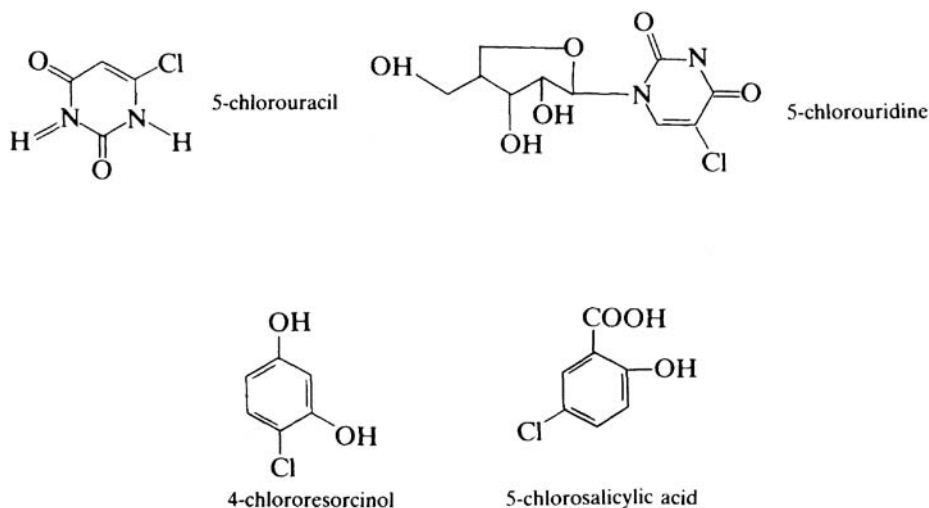


Fig. 26. Total-ion chromatogram of the unpartitioned diethyl ether extract (CE) chromatographed on SP 1000. Numbers identify the following GC peaks: (1) methylpyridine isomer; (2) benzyl chloride; (3) 4-methyl-2-pentanol; (4) ethyl chloroacetate; (5) *N,N*-dimethylformamide; (6) cyclohexanol; (7) cyclohexanone; (8) isophorone; (9) 2-(2-ethoxyethoxy)ethanol; (10) 1-(2-butoxyethoxy)ethanol; (11) benzothiazole; (12) *N*-acetylmorpholine; (13) tetramethylene sulphone; (14) diethylphthalate; (15) diisobutyl phthalate; (16) dibutyl phthalate.

Year of publication	Paper title	Ref.
1981	Determination of organic contaminants by the Grob closed-loop stripping technique	458
1982	Analysis of organic micropollutants in water. Proceedings of 2nd European Symposium held in Killarney, Ireland, November 17–19 (1981)	459
1982	Trace organic contaminants in water—problems of analysis and legal requirements	460
1983	Investigation of a comprehensive approach for trace analysis of dissolved organic substances in water	461
1983	Sampling techniques for analysis of trace organics	462
1983	Application of gas chromatography-mass spectrometry and field desorption mass spectrometry to the identification of organic compounds leached from epoxy resin lined water mains	463
1983	Organic contaminants in the aquatic environment IV Analytical techniques	464
1984	Combination of continuous liquid-liquid extraction and coupled GC-MS for analysis of pesticides in water	465
1986	Precision and accuracy of concurrent multicomponent multiclass analysis of drinking water extracts by GC-MS	466
1986	A study of the trace organics profile of raw and potable water systems	467

High performance liquid chromatography mass spectrometry

Crathorne et al⁴⁶⁹ have described a procedure for solvent extracting, separating and identifying trace levels of non-volatile organic compounds in potable water. A method was developed for analysing four selected chlorine containing compounds and this was then extended using high performance liquid chromatography



linked to mass spectrometry for the analysis of a wider range of non-volatile organics. These workers showed that either vacuum evaporation or freeze drying can be successfully used to isolate and concentrate non-volatile organic matter from potable water.

This technique was applied to several potable water samples. A typical chromatogram is shown in [fig. 27\(a\)](#). The numbers on the chromatograms in [fig. 27\(b\)](#) correspond to the major components in the extract which were examined further by mass spectrometry (see [Table 27](#)). Also included in [Table 27](#) are details of the analysis of the two other samples examined. Concentrations found were in the 5–25 $\mu\text{g l}^{-1}$ range.

It is noteworthy that the chromatograms shown in [fig. 27\(a\)](#) only demonstrate those compounds which absorb at 254 and 280 nm so the extract undoubtedly is of greater complexity than indicated. This was confirmed by mass spectrometric analysis of liquid chromatographic fractions, which generally indicates the presence of a mixture of components when only a single peak is shown by UV absorption. The large peak at the start of the chromatogram was always observed when analysing potable water extracts. This peak is essentially unretained and probably is comprised of the high molecular weight organic compounds which are not partitioned and are eluted as an excluded peak.

Crathorne et al⁴⁶⁹ used the above technique to identify and determine the following four non-volatile chlorinated organic compounds in potable water.

TABLE 27

Major components present in treated water extracts as indicated by UV absorption on HPLC. Initial identities from MS data. Some confirmed by comparison of MS and HPLC data with those of authentic compounds. Approximate levels were based on UV absorption from HPLC chromatogram by comparison with authentic compounds

Fraction	HPLC retention time (min)	Sample site	Identity	Identification	Confirmation	Approximate level ($\mu\text{g l}^{-1}$)
1	4.2	E, I	Multi-halogenated	EI-MS	—	—
2	9.5	E, I	—	—	—	—

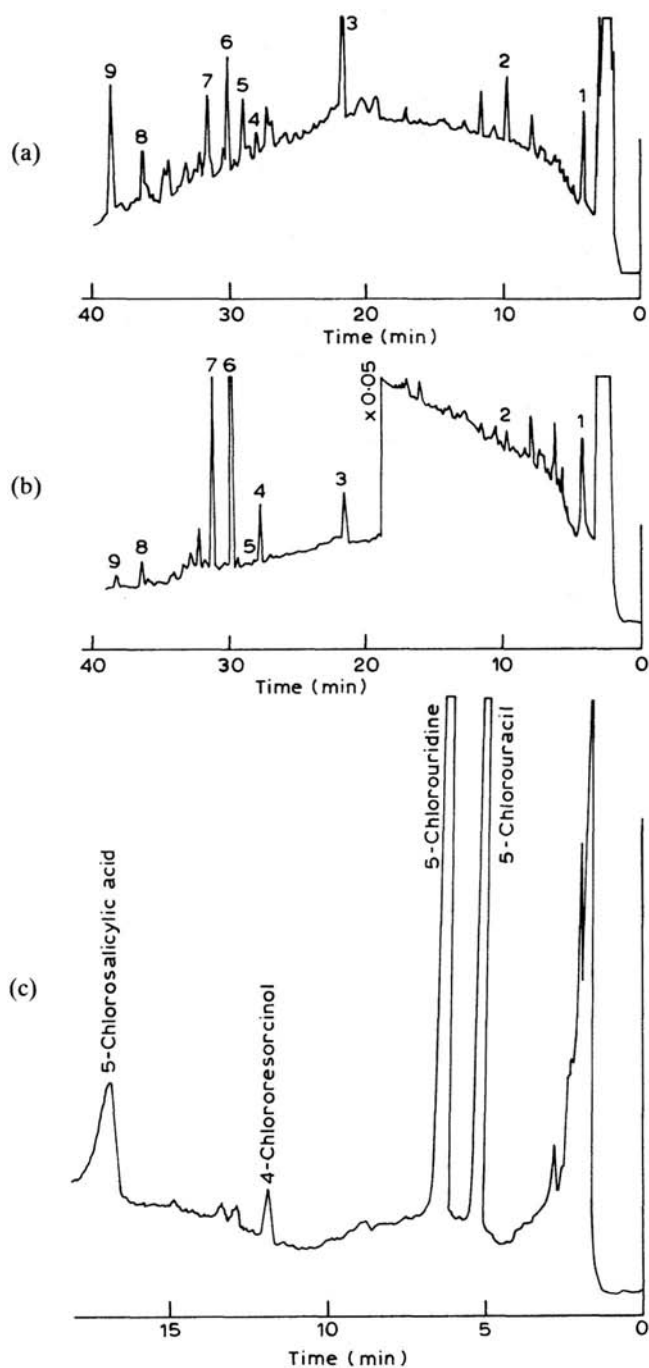


Fig. 27. Separation of a potable water extract (sample site E) monitored at 254 nm (a) and 280 nm (b). Column: 20 cm \times 7 mm i.d. (c) Chromatogram for the analysis of a potable water extract for the four specified compounds. Conditions (200 ng each component). Column 15 cm \times 7 mm i.d.; packing, 5 μ m Spherisorb ODS. Diluent, linear gradient from 1 per cent methanol in 0.1 per cent aqueous acetic acid to 90 per cent methanol in 0.1 per cent aqueous acetic acid over 30 min. Detection: UV 315 nm for 5-chlorosalicylic acid.

Fraction	HPLC retention time (min)	Sample site	Identity	Identification	Confirmation	Approximate level ($\mu\text{g l}^{-1}$)
3	21.5	B, E, I	2-Hydroxybenzothiazole	EI-MS	HPLC, EI-MS, FI-MS	5–25
4	27.5	B, E, I	Partly 2,4,6-trichlorophenol	EI-MS	HPLC	<1
5	28.5	E	—	—	—	—
6	29.5	B, E, I	Dimethylacridan	—	—	—
7	34.0	B, E, I	<i>p</i> -Isopropylidiphenylamine	EI-MS	HPLC, EI-MS	10–15
8	35.8	E, I	—	EI-MS	—	—
9	38.0	B, E, I	di- <i>n</i> -Octyl phthalate	EI-MS, FI-MS	HPLC, EI-MS, FI-MS	10

A modified procedure was used in this case to extract the compounds from the water sample. The four non-volatile compounds were isolated from water samples (11) by rotary evaporation to dryness in vacuo at 35°C. The solid residue was extracted with methanol (3×25 ml). The methanol extract was then concentrated to ca. 2 ml by rotary evaporation and finally to 0.5 ml under a stream of nitrogen. For preparative scale HPLC separations, water (0.5 ml) was added at this stage and the extract was then re-concentrated to 0.5 ml under a stream of nitrogen.

In [fig. 27\(b\)](#) is shown a high performance liquid chromatogram obtained for the four compounds present in a sample of potable water. The large peak at the start of each chromatogram is essentially unretained and is probably equivalent to an excluded peak containing much of the higher molecular weight material. A large peak in this position was always observed when analysing potable water extracts. Monitoring the four compounds was carried out using UV detection at two wavelengths. The absolute detection limit is defined as the amount injected onto the column which results in a signal to noise ratio of 2:1.

Preconcentration

SOLVENT EXTRACTION PROCEDURES: Murray⁴⁷⁰ has described a rapid micro extraction procedure for preconcentration and analysis of trace amounts of organic compounds in water and compared the results obtained with those obtained by macro extraction methods. Final analysis of the solvent extract was carried out by gas chromatography. The method using a flask with a side arm and fitted with a capillary tube involved shaking 980 ml of water with 200 μl of hexane. By carefully adding water through the side arm the solvent layer was displaced into the capillary tube after tilting the flask. About 50 μl were recovered and were suitable for direct analysis by gas chromatography. This method gave as good a recovery and was much more rapid than macro extraction or continuous extraction.

Potable water samples spiked with ng l^{-1} concentrations of selected pesticides and $\mu\text{g l}^{-1}$ concentrations of hydrocarbons (C_{10} , Cl_2 , Cl_4 and C_{16}) were extracted successively with 200 μl of hexane and analysed by gas chromatography using electron capture and flame ionization detectors, respectively. There was a mean recovery of 58.3 per cent in the first 200 μl extract and 94.3 per cent in three 200 μl extracts. The standard deviations for the first extract range from 2.9 to 10.3 per cent with the higher values at the $\mu\text{g l}^{-1}$ level.

Distilled water was extracted in a similar way and analysed for phthalate esters using a flame ionization detector and showed comparable results. The identity of these phthalate esters was confirmed by gas chromatography-mass spectrometry. The typical m/e peak at 149 showed the presence of the phthalate residue and the $M+1$ peaks at 279 and 337 using the chemical ionization mode, identified the parent compounds.

River water was analysed with a single 200 μl extraction using an electron capture detector and several peaks in the pesticide group as well as phthalate esters were found.

When 11 of potable water was extracted with 200 μl of solvent, only about 50 μl were recovered because of losses due to solubility and evaporation. Thus, a concentration factor of $\times 20\,000$ was achieved. But since the extraction efficiency was only about 50 per cent in the first extract, the true concentration factor was $\times 10\,000$. Preconcentration factors of 20 000 for traces of organics in potable water samples have been achieved by extraction using diethyl ether and petroleum ether (pH30–40°C)⁴⁷¹. One portion of the extract was reduced to a volume suitable for analysis by gas chromatography-mass spectrometry. The other portion was reacted with diazomethane, which converted some components to methyl derivatives which were then amenable to analysis by a computerized gas chromatography-mass spectrometry system. In order to check for possible procedural contamination two solvent blanks (one for each solvent) were processed in the same way as the extracts.

High resolution glass capillary (porous layer open tubular-PLOT) columns were used for the gas chromatographic separation and each concentrated solvent extraction and blank was run on two different columns, one of which had OV-1 (a methyl silicone gum) as a stationary phase, while the other had FFAP (Carbowax 20 M treated with 2-nitroterephthalic acid) as stationary phase.

Generally, 1000–1250 mass spectra were acquired during each GC-MS run. The initial data interpretation step involved an inspection, usually on a visual display unit, of the computer reconstructed total ion current chromatogram and the mass spectra obtained for each obvious peak in the chromatogram was examined. If necessary a background subtraction was performed. If the mass spectrum of a compound of interest was not visually recognized as a known compound, reference was made either to the Eight Peak Index of Mass Spectra, or the EPA/NTH Mass Spectral Data Base⁴⁷². If a suitable spectral match was not obtained from either of these sources, the fragmentation pattern of the spectrum of interest was examined and an attempt made to deduce the structure of the compound giving rise to the spectrum. Identifications made either from reference data or from an examination of the mass spectrum produced were considered to be tentative until a pure sample of a known compound gave a suitable match for the mass spectrum and gas chromatographic retention time. Mass chromatography was used to search for compounds of interest which did not appear as obvious peaks on the TIC chromatogram.

Ibrahim and Suffet⁴⁷³ used Freon FC-113 as an alternative solvent to methylene chloride for the liquid-liquid extraction of trace organics from water. The use of freon minimized the interference from solvent artefacts arising from the reaction of cyclohexane (preservation in methylene chloride) with residual free chlorine present in potable water samples.

Adsorption on XAD-4 resin

Ryan and Fitz⁴⁷⁴ used thermal desorption of the organics on a resin directly into the gas chromatograph. In this method a small water sample (20–250 ml) is passed through a small tube containing XAD-4 resin; this effectively retains the organic impurities present in the water. This tube is connected to the permanent apparatus and the sorbed organics are thermally transferred to a small Tenex pre-column while the water vapor is vented. The pre-column is closed off, preheated at 275–280°C and then a valve is opened to plug inject

the vaporized sample into a gas chromatograph. The recoveries are generally quite good at both 10 and 1 $\mu\text{g l}^{-1}$ levels in water although there is some apparent loss of the halocarbons tested at the lower concentration level. The recovery of high boiling compounds was found to be dependent on desorption time and temperature. The reason for this is not entirely clear.

The efficiency of the thermal desorption procedure was determined for several of the model compounds. This was done by comparing the peaks of compounds in standards taken through the entire procedure with peaks of the same compounds in standards injected directly into the gas chromatograph.

The recovery efficiencies of all compounds tested are quite good. Thus for quantitative analysis of actual water samples, the results could be compared with standards injected directly into the gas chromatograph or with water standards passed through the XAD-4 tube.

Tateda and Fritz⁴⁷⁵ used carbon disulphide or acetone extraction, rather than a thermal method to desorb adsorbed organics from XAD resins. These workers used a mini column 1.2–1.8 mm \times 25 mm containing XAD-4 resin or Spherocarb to adsorb organic contaminants from a 50–100ml potable water sample. The sorbed organics are eluted by 50–100 μl of an organic solvent and the organic solutes separated by gas chromatography. The procedure is simple, it requires no evaporation step and gives excellent recoveries of model organic compounds added to water.

Tateda and Fritz⁴⁷⁵ studied the adsorption and acetone desorption of thirty different organic compounds on Mini columns of XAD-4 resin. The recovery of model compounds by using XAD-4 at concentrations of 2–10 $\mu\text{g l}^{-1}$ and 100 $\mu\text{g l}^{-1}$ was 89 per cent and 83 per cent respectively. The average standard deviation is 6.3 per cent. Errors other than sorption and desorption would be included, like evaporation losses from the sample, decomposition, sorption on glassware, calibration of eluate volume and errors in the GC determination.

Tateda and Fritz⁴⁷⁵ compared the adsorptive properties of XAD-4 resin with those of a spherical carbon molecular sieve of large surface area (Spherocarb). It was found that 100 μl carbon disulphide will elute most organic compounds tested with Spherocarb except for phenols and some strongly sorbed compounds like naphthalene. At the 100 $\mu\text{g l}^{-1}$ concentration level average recoveries with Spherocarb are 77 per cent from both water and from 10 per cent methanol. Under similar conditions the average recovery with XAD-4 was 79 per cent from water and 76 per cent from 10 per cent methanol. The average standard deviation was 5.1 per cent for Spherocarb and 4.0 per cent for XAD-4.

Spherocarb has one major advantage over XAD-4 for analytical use, namely a stronger retention of low molecular weight polar organic compounds.

Often compounds that have been preconcentrated on XAD-4 resin include, alcohols, esters, aldehydes, alkyl benzenes, polyaromatic hydrocarbons, chlorocompounds⁴⁷⁶ and alkanes, alkylbenzenes, chloro compounds, alcohols, ketones, esters and bromocompounds⁴⁷⁷.

Adsorption on XAD-2 resin

Chang and Fritz⁴⁷⁸ pointed out that the XAD-2 resin sorption method is a reliable and tested method for determining trace organic pollutants in potable water. However, the solvent evaporation step in this procedure results in a partial or complete loss of volatile compounds.

To avoid these drawbacks a procedure was developed by them in which organic compounds that are sorbed on a resin are thermally desorbed directly onto a gas chromatographic column for analysis. They desorbed the organics onto a Tenax tube from a tube containing XAD-2. This eliminates virtually all of the water entrained in the XAD-2 tube. Then the organics are thermally desorbed from the Tenax tube directly on to the gas chromatographic column.

Recoveries were 88–90 per cent (alkanes), 90–97 per cent (alkyl benzenes), 70–80 per cent (ethers), 86–95 per cent (esters), 87–95 per cent (haloforms), 97–98 per cent (polyaromatic hydrocarbons), 82–90 per cent (chlorobenzenes), 55–92 per cent (ketones), 40–85 per cent (alcohols) and 4–90 per cent (phenols).

Workers at the Water Research Centre, UK⁴⁷⁹ passed up to 5 l of potable water samples through a column of XAD-2 resin and removed the adsorbed organics with 40 μ l of diethyl ether. The ether extract was then concentrated 2500 times and examined by gas chromatography-mass spectrometry. Several hundred organic compounds were examined in this survey, many of which were identified in potable water samples.

Vartiainen et al⁴⁸⁰ compared solvent extraction and resin adsorption techniques for the isolation of multigenic compounds from chlorinated potable water. Both methods gave comparable results.

Adsorption on Sep Pak C₁₈ bonded silica

This material has been used for the preconcentration of various organic substances in water. Pyrazone herbicide in natural water was adsorbed from a large volume of water then desorbed into a small volume of methylene dichloride prior to analysis by high performance liquid chromatography⁴⁸¹. Polyaromatic hydrocarbons in potable water were adsorbed on a C₁₈ reverse phase column, then desorbed with methanol⁴⁸².

Absorption on carbon

Rivera et al⁴⁸³ used activated carbon to preconcentrate organics from the Barcelona water supply. Organics were desorbed with methylene chloride, evaporated to dryness and dissolved in diethyl ether and fractionated. Ether soluble fractions were analysed by gas chromatography-mass spectrometry and ether insoluble fractions were analysed by high performance liquid chromatography with diode array detection followed by fast ion bombardment.

Preconcentration by gas stripping techniques

The gas stripping technique—a large volume of aqueous sample is purged with an inert gas and the effluent containing volatilized organics swept through a trapping medium such as active carbon. The organics are then desorbed from the carbon with a volume of pure solvent which is relatively small compared to the volume of original water sample. Very large preconcentrations of organics in the sample can thereby be achieved.

Piet⁴⁸⁴ described a gas stripping technique for concentrating organic substances in potable water samples and followed this by adsorption on to carbon, desorption from carbon by a solvent and examination of the extract by high resolution gas chromatography in stainless steel capillary columns coupled with an on-line mass spectrometer computer system. The procedure was applied to the identification of microorganic constituents in potable water before and after ozonization.

Westendorf⁴⁸⁵ has described a commercially available gas stripping apparatus, the Tekman CLS-1 instrument, for the semi-automatic determination of traces of organics in water. This instrument can accommodate any sample size up to 4l. More than 90 compounds are present in each sample.

Many of the compounds present in the potable water are chlorinated organics, very few of which were present in the raw water. Raw water, however, included a much higher degree of substituted aromatic compounds.

Analysis of fuels in water by this technique can provide an excellent fingerprint of the sample.

Diesel fuel does not lend itself well to any other concentration technique. The detection limit obtainable by closed loop stripping analysis is even less than $1 \mu\text{g l}^{-1}$ which is 3–4 orders of magnitude more sensitive than any other technique. Detection limits for other fuels, such as gasoline, kerosene, or jet fuel, are even lower.

Duffy et al⁴⁸⁶ applied purge and trap capillary gas chromatography to the analysis of $\mu\text{g l}^{-1}$ levels of organics in water.

Preconcentration by head space analysis techniques

This technique differs from purge and trap techniques in the following respect. In purge and trap, the water sample is purged with a gas and the organics removed and adsorbed on to a solid, usually active carbon. The adsorbed organics are then desorbed in a small volume of an organic solvent, usually chloroform or carbon disulphide which is subsequently analysed by gas chromatography. Although capable of achieving very high concentration factors a disadvantage of this technique is that the organic solvent and impurities therein can cause difficulties at the gas chromatographic stage of the analysis. Head space analysis is solventless in that the aqueous sample is heated say to 30°C in the presence, usually, of inorganic salts which help to drive the organics into the inert gas fitted head space above the sample. Portions of the head space gas are then withdrawn by syringe for gas chromatographic analysis. This head space analysis unlike purge and trap, is a static method. By attention to detail in the design of the apparatus and operating conditions, it is possible by this technique to obtain concentration factors of up to 100 for the organics in the original water sample.

Thus, Friant and Suffet⁴⁸⁷ obtained 66 fold enrichment factors by

- (i) increasing the temperature of the water sample from 30 to 50°C
- (ii) saturating the water sample with sodium sulphate
- (iii) adjusting the pH of the original sample to 7.7 .

The detection limits ranged from $50 \mu\text{g l}^{-1}$ for methyl ethyl ketone to $740 \mu\text{g l}^{-1}$ for dioxane.

The general 'screening' procedure for qualitative analysis with semi-quantitative evaluation has been utilized for taste and odour profiling of water. A primary reason for the investigation of head space analysis was to subsequently develop a method that would isolate volatile organics causing taste and odour in potable water. Isolation of possible taste and odour organics under the enhanced conditions allows determination of the initial water phase concentrations. These concentrations can then be used to determine the vapour phase concentrations of the organic compounds presented to the consumer of drinking water. All that is needed is the partition coefficients of the organic compound at the enhanced and potable water conditions, respectively.

Application of the method of head space analysis as described above was utilized for gas chromatography-mass spectrometry of a potable water sample in Philadelphia. The results of mass spectral identification of the compounds found in the potable water showed the presence of toluene, two C-2 benzene isomers, chloroform, chlorodibromomethane, dichlorobromoethane and 1,1,2,2-tetrachloroethane. The analysis was completed in a 125 ml bottle containing 100 ml of potable water. A $50 \mu\text{l}$ gas sample was injected onto the gas chromatograph using a ^{63}Ni electron capture detector.

Reverse osmosis

Reverse osmosis is a membrane process developed almost entirely in the past 20–25 years. The process is based on the fact that if two solutions of different concentrations are separated by a semipermeable membrane, water will move across the membrane in the direction of higher concentration. The driving force is provided by this difference in concentration: Since many of the dissolved substances will not pass through the membrane, the passage of water will eventually cease when the solutions on both sides reach the same concentration. This process of osmosis can be reversed by applying pressure to the more concentrated solution. The concentration of dissolved substances will then tend to increase on that side of the membrane.

Although the process was initially developed for the purposes of desalination of water, the rejection of organics has also been extensively studied. Reverse osmosis is a promising technique for removing refractory (non-volatile) organics of intermediate to higher molecular weight from water⁴⁸⁸. More study is needed to predict rejections of organics by reverse osmosis; it appears, however, rejection is related to the distribution coefficient of a given compound between the aqueous solution and the hydrated membrane. Obviously, this is complicated by the concentration of inorganic ions that continuously change the solubility of the organic compounds in solution and by the fact that a high salt concentration can affect the degree of hydration of the membrane.

In the scheme used by Kopfler et al⁴⁸⁹ for isolating organics from water 400 gallons of potable water is collected into a covered 500 gallon stainless steel tank over a 2-day period. Soon after collection is begun, 140 mg of silver nitrate is added to retard bacterial growth. The collected water is adjusted to pH 5.5 with hydrochloric acid. This pH is in the optimum range for stability of cellulose acetate membranes.

The water is subjected to reverse osmosis with an Osmonics Model 3319–558C unit containing a spiral wound cellulose acetate membrane. The final concentrate is extracted with pentane.

Reverse osmosis has been used for the determination in potable water of traces of organochlorine and organophosphorus insecticides^{490,493,494} and pentaerythritol, bis(2-chloroethyl)ether, bis(2-chloroisopropyl) ether, urea, triethylene glycol, dipropylamine, chlorobenzene, propylbenzene and benzonitrile⁴⁹¹.

Chian et al⁴⁹⁰ studied two types of reverse osmosis membranes—cellulose acetate and cross-linked polyethylenimine. With each membrane the rejection of pesticides was better than 99 per cent. Deinzer⁴⁹¹ used cellulose acetate membranes.

Klein et al⁴⁹² used cellulose acetate and ethyl cellulose membranes and showed that the retention of a particular organic solute in potable water by a polymer membrane is related not only to the physical interactions such as size but also is dependent upon attractive forces which are normally included in the solubility of the solute in the membrane phase. These workers used solubility parameters for projections of class and specific separations with the two membranes studied.

1.6 Organometallic compounds

1.6.1 *Mercury*

Atomic absorption spectrometry

Jackson and Dellar⁴⁹⁵ have described a photolysis-cold vapour flameless atomic absorption method for determining down to 0.1 mg l⁻¹ total mercury in potable and natural waters. Photolysis converts organomercury compounds to the inorganic state and these workers showed the advantages of this approach over chemical oxidation methods, for converting organic mercury to inorganic mercury.

At the 0.33 µg l⁻¹ level the 95 per cent confidence interval is approximately 0.10 µg l⁻¹. The limit of detection based on the variation of results when estimating low levels is 0.1 µg l⁻¹ for a single estimation. Hence levels above 0.1 µg l⁻¹ may be estimated for 95 per cent confidence intervals to the nearest 0.1 µg l⁻¹ up to 0.5 µg l⁻¹ and over this figure to the nearest 20 per cent.

Jackson and Dellar⁴⁹⁵ emphasize that to obtain results for concentrations of mercury present in water at the sampling time the container and water itself must be stabilized to avoid loss or gain of mercury. Acidic potassium dichromate is believed to be the best preservative⁴⁹⁶. Any particulate matter present in water is likely to adsorb dissolved mercury. Before analysis a decision must be made whether total or dissolved mercury concentration is required.

Radiochemical method

Stary and Prasilova^{497,498} have described a very selective radiochemical determination of phenylmercury and methylmercury^{499,500}. These analytical methods are based in the isotope exchange reactions with the excess of inorganic mercury-203 or on the exchange reactions between phenylmercury and methylmercury chloride in the organic phase and sodium iodide-131 in the aqueous phase. The sensitivity of the methods (0.5–1 µg l⁻¹ in 5 ml sample) is not sufficient to determine organomercurials in natural waters. Subsequently Stary et al⁵⁰¹ developed a preconcentration radioanalytical method for determining down to 0.01 µg l⁻¹ of methyl- and phenylmercury and inorganic mercury using 100–500 ml samples of potable or river water. Extraction chromatography and dithizone extraction were the most promising methods for the concentration of organomercurials in the concentration range 0.01–2 µg l⁻¹. The dithizone extraction was used for the preconcentration of inorganic mercury.

16.2 *Tin*

Fluorimetric method

Fluorimetry has been used to determine triphenyltin compounds in potable water⁵⁰². Triphenyltin compounds in water at concentrations of 0.004–2 mg l⁻¹ are readily extracted into toluene and can be determined by spectrofluorimetric measurements of the triphenyltin-3-hydroxyflavone complex.

Tri-, di-, and monobutyl and di- and monomethyltin compounds did not fluoresce under the conditions used for the determination of triphenyltin. However, trimethyltin compounds react in a similar manner with 3-hydroxyflavone, and although the emission maximum is at approximately 510 nm, this is not sufficiently different from the emission maximum of triphenyltin compounds (approximately 495 nm) for these compounds to be determined in the presence of each other.

Spiking recoveries by the above procedure carried out on standard solutions of triphenyltin chloride in various types of water ranged from 74 per cent at the $4 \mu\text{g l}^{-1}$ tin level (r. s.d. 8.9 per cent) to 93.6 per cent at the 2 mg l^{-1} level (r. s.d. 4.2 per cent).

Gas chromatography

Maguire and Huneault⁵⁰³ developed a gas chromatographic method with flame photometric detection for the determination of bis(tri-*n*-butyl tin) oxide and some of its possible dialkylation products in potable and natural waters. This method involves extraction of bis(tri-*n*-butyltin) oxide, $\text{Bu}_2\text{Sn}^{2+}$, BuSn^{3+} and Sn^{4+} from the water sample with 1 per cent tropolone in benzene, derivatization with a pentyl Grignard reagent to form the various $\text{Bu}_n\text{pentyl}(4-n)$ Sn species followed by analysis of these by flame photometric gas chromatography-mass spectrometry. The pentyl derivatives are all sufficiently non-volatile compared with benzene that none are lost in solvent 'stripping' yet they are volatile enough to be analysed by gas chromatography.

1.7

Dissolved gases

1.7.1

Chlorine, free, total and combined

Titration methods

The relative proportions of chlorine, hypochlorous acid and hypochlorite ion in potable water, vary markedly with pH and have been calculated by Wong⁵⁰⁴ over the pH range 0–14 for chlorine (1 mg l^{-1}) in 0.55 M sodium chloride, using the thermodynamic data given by Garrels and Christ⁵⁰⁵. The concentration of hypochlorous acid is at a maximum at pH 5; at low pH, chlorine is dominant and at high pH, hypochlorite ion is dominant. Hypochlorous acid solutions slowly disproportionate irreversibly into oxygen and hydrochloric acid, with a consequent fall in residual chlorine.

The British Standards Institution⁵⁰⁶ have described a titrimetric method using *N,N*-diethyl-1,4-phenylenediamine for the determination of 0.03–5 mg l^{-1} of free chlorine and total chlorine in potable water.

Spectrometric-colorimetric methods

N,N-DIETHYL,1,4-PHENYLENE DIAMINE (PALINS METHOD): Various workers have used this reagent for the spectrophotometric determination of free, total and combined residual available chlorine in potable water^{507–512}. Various wavelengths have been used for the spectrophotometric evaluation including 540 nm ⁵⁰⁷, 530 nm ⁵¹¹ and $490\text{--}530 \text{ nm}$ ⁵¹².

In the original Palin method⁵¹² for determining free chlorine, a measured volume of sample is treated with a solution of *N,N*-diethyl 1,4-phenylene diamine or 4-amino-*N,N*-diethylanilinium sulphate in sulphuric acid and EDTA. The solution is then buffered to pH 6–7. The intensity of the resulting red-violet colour (after diluting the solution to 10 ml) is determined either by photometry in the range 490–530 nm or by using a colour comparator. Chloroamine, dichloroamine and nitrogen trichloride can also be determined after the sequential addition of appropriate amounts of potassium iodide to the coloured solution. Calibration may be effected with standard potassium iodide solution as an alternative to the relatively unstable aqueous chlorine.

Palin^{513,514} in a modification to this procedure, introduced the use of thioacetamide added after the *N,N*-diethyl 1,4-phenylene diamine to ensure accurate measurement of free chlorine under extreme conditions. Particularly, this reagent overcomes interference by high levels of monochloroamines and nitrogen trichloride in potable water^{510,514}. The addition of 0.5 ml of a 0.25 per cent w/v solution of thioacetamide is sufficient to counteract the effect of at least 10 mg chloramine per litre (in terms of chlorine); larger amounts may be added if required as the compound has no effect on the colour developments of the DPD reagent.

Determination of chloramines is, of course, not possible after using thioacetamide so it is necessary to repeat the procedure with a fresh portion of sample adding both *N,N*-diethyl 1,4-phenylene diamine and potassium iodide (using 0.05–0.1 mg potassium iodide to 10 ml sample) but no thioacetamide. The total reading is then corrected by subtracting the free available chlorine reading. Thoroughly rinse both tube and cap after using potassium iodide.

Other residual disinfecting agents that, if present, will appear in the free available chlorine fraction include chlorine dioxide, bromine, iodine and ozone.

Differential methods employing *N,N*-diethyl 1,4-phenylene diamine are available^{515–517} for the analysis of such mixtures in potable water.

The interference by oxidized manganese in the chlorine test utilizing *N,N*-diethyl 1,4-phenylene diamine appears as a colour in the thioacetamide fraction and is usually corrected by the sodium arsenite technique described in Standard Methods⁵¹⁸.

Roeske⁵¹⁹ has described a continuous analyser, based on the Palin reactions, for the determination of residual chlorine in potable water. The apparatus is standardized using the diethylphenyldiamine reaction with either a colorimeter or a photometer. The sample water is passed at about 35 litres per hour over a platinum/copper electrode assembly. The presence of chlorine causes almost complete polarization of the electrode and the weak residual current is proportional to the chlorine content. The sensitivity is about 0.01 mg chlorine l⁻¹ and the precision about 5 per cent.

Overath and Oberam⁵²⁰ applied Palin's method to the determination of chlorine, chlorine dioxide and chloride in potable water and reported detection limits for these three determinations.

The limits of detection of chlorine, chloride dioxide and chlorite were determined separately and in the presence of one or more of the others. Palin's procedure was employed as published except that chlorine was reacted with Weil's reagent (potassium bromide/sodium formate) instead of glycine. A single analysis could be used to detect 0.10 mg l⁻¹ chlorite in the presence of chlorine dioxide and/or chlorine with 99 per cent confidence limits.

Strupler and Rouault⁵¹¹ studied interferences in the determination of free and combined chlorine by Palin's method and by the syringaldehyde spectrophotometric method discussed in the next section. The interference of chloramines was investigated for both methods while the influence of a number of additional substances, including copper, manganese, chromium and nitrite on the Palin method, employing *N,N*-

diethyl 1,4-phenylene diamine was also examined. Trichloramine, but not mono- or dichloramine, was shown to react instantaneously with syringaldehyde in dilute aqueous solution.

SYRINGALDEHYDE: Syringaldazine (bis(4-hydroxy-3,5-dimethoxybenzylidene)hydrazine) reacts with hypochlorous acid or hypochlorite with 1:1 stoichiometry but does not react with chloramines. Optimum conditions for the determination of hypochlorous acid or hypochlorite with syringaldehyde are pH 7 and 530 nm. The calibration graph is rectilinear for up to 1 mg l⁻¹ chlorine if the concentration of syringaldehyde is about 10 μM⁵²¹.

Cooper et al⁵²² evaluated the accuracy of four field kits employing stabilized arsenite, *N,N*-ethyl-*p*-phenylenediamine and syringaldazine for the determination of free available chlorine over the range 0.0–10.0 mg l⁻¹. Interference from monochloramine, dichloramine, divalent manganese and nitrite was evaluated. Modifications of the stabilized neutral orthotolidine, *N,N*diethyl 1,4-phenylenediamine and syringaldazine procedures were also evaluated. Syringaldazine was shown to be most specific for free available chlorine and details of its use are given for the determination of free and available chlorine.

Lieberman et al⁵²³ modified the syringaldehyde spectrophotometric procedure for the determination of free available chlorine to determine total available chlorine in potable water over the range 0.2–10 mg l⁻¹ total available chlorine with a detection limit of 0.02 mg l⁻¹.

PYRIDINE-PYRAZOLONE: Kanno et al⁵²⁴ determined total and combined chlorine in potable water using a pyridine pyrazolone reagent. The method is based on conversion of total chlorine to cyanogen chloride with potassium cyanide, the amount of which was then determined by the pyridine-pyrazolone method. Combined chloride could also be determined by adding sodium arsenite to the sample to eliminate free chlorine, before conversion of combined chlorine to cyanogen chloride. Free chlorine could be calculated from the difference between total and combined chlorine.

Flow injection analysis

Trojanowicz et al⁵²⁵ give details of equipment and procedure for determination of residual chlorine in water by a flow injection potentiometric system using silver iodide and platinum electrodes for detection. Between 40 and 60 samples per hour can be analysed by this procedure. Results obtained by this method are compared with those obtained by spectrophotometry; differences between the two methods are attributed to the presence of various organic compounds.

The system is based on stoichiometric oxidation of iodide to iodine by free and combined residual chlorine. The potentials of the platinum electrode and of the silver iodide electrode are expressed, respectively by

$$E_1 = E_{I_2, I^-}^0 - RT(2F)^{-1} \ln [I_2]/[I^-]^2 \quad \text{and} \quad E_2 = E_{Ag, AgI}^0 - RTF^{-1} \ln [I^-]$$

Thus the EMF of the cell is $E = \text{Const.} + RT(2F)^{-1} \ln [I_2]$ which permits evaluation of the residual chlorine content in the sample introduced.

Results obtained by this procedure were considerably higher (50–100 per cent) than those obtained by various spectrophotometric methods for residual chlorine. Potable waters, especially after chlorination, contain not only simple chloramines but also more complex chloro-organic compounds. Many of them do not react with o-tolidine, but react with iodide, so that the colorimetric method gives lower values. Potable water contains small amounts of organic compounds (e.g. humic substances) which may reduce residual chlorine. The compounds present in potable water samples are in equilibrium with residual chlorine, but the addition of standard chlorine water would displace the equilibrium and involve further consumption of added chlorine. This gives incomplete recovery of chlorine, the error decreasing with progressive dilution of fresh tap water. It seems that the results of this potentiometric determination of total residual chlorine can

be considered as reliable, although as the procedure involves an arbitrary indication of a level of oxidants with various redox potentials, these results may differ from the results obtained by standard colorimetric procedures. Difference in the kinetic characteristics of redox processes in natural waters as well as processes in the actual measurements may also influence the results of both procedures.

Zenki et al⁵²⁶ described a flow injection spectrometric method for determining residual chlorine based on the redox reaction between chlorine and 4,4, tetramethyldiaminothiobenzophenone at pH 3.5 and measurements of the absorbance of the blue quinoidal product at 640 nm. Linear calibration was achieved in the range 0.2–1.0 $\mu\text{g l}^{-1}$ residual chlorine.

Continuous flow analysis

Isacsson and Wettermark⁵²⁷ have described a continuous flow technique for simultaneous analysis of chlorine and chlorine dioxide based on measurements (at two positions) of the intensity of light emitted following reaction with luminol (5-amino-2,3-dihydro-1,4-phthalazinedione) in aqueous solution. The pH dependence of the reaction was investigated and the response of hypochlorite was distinguishable from that of chlorine dioxide; by using a solution buffered to pH 9.7 at predetermined flow rates it was possible to ensure that the intensity of light emission at each of the two arbitrarily chosen sampling points was a function of the concentration of one of the two chemical species.

Aoki and Munemori⁵²⁸ have discussed a technique for the continuous flow measurement of free chlorine in water which uses a double-tube system, consisting of an inner tube of microporous poly(tetrafluoroethylene) and an outer tube of poly(tetrafluoroethylene) and a UV detector. The sample is mixed with 1 N hydrochloric acid in the outer tube and the molecular chlorine produced permeates the microporous poly(tetrafluoroethylene) and changes to the hypochlorite ion, as it dissolves in the 0.1 N sodium hydroxide in the inner tube. The inner tube solution, containing the hypochlorite flows into the UV detector where it is measured spectrophotometrically at 290 nm. UV signals are proportional to concentrations of free chlorine from 10^{-5} to 10^{-2} M. The lower limit of detection of free chlorine is 2×10^{-6} M. The time required for a 98 per cent response is 3 min. Free chlorine is selectively measured even in the presence of permanganate and chromate, combined chlorine and heavy metals.

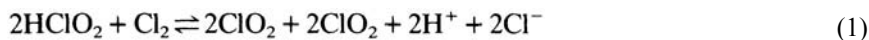
The UV signals are proportional to the concentrations of free chlorine from 10^{-5} to 10^{-2} M. The relative standard deviations ($n=4$) were 1.7 per cent at 6×10^{-5} M and 0.8 per cent at 1.0×10^{-3} M. The detection limit was 2×10^{-6} M

Both chromate and permanganate absorb in the ultraviolet region at 290 nm, at which their molar absorptivities are 1.32×10^3 and 4.96×10^2 $\text{l mol}^{-1} \text{cm}^{-1}$ respectively. These values are larger than that of hypochlorite, 3.58×10^2 $\text{l mol}^{-1} \text{cm}^{-1}$. Therefore, the determination of hypochlorite in their presence cannot be performed directly by UV measurements.

Gallic acid and pyrogallol absorb at 290 nm and are naturally occurring organic compounds. They had no direct effect on the signal because they do not permeate the microporous poly(tetrafluoroethylene) but added to the sample, they reduced the signal of free chlorine.

Free chlorine reacts with them. So only the remaining free chlorine, if any, after reaction with these compounds could be measured by this method.

Among the oxo acids of chlorine, chlorate and perchlorate did not interfere, but chlorite, did negatively. At pH 0 the standard oxidation-reduction potential of the $\text{ClO}_2\text{--HClO}_2$ and $\text{Cl}_2\text{--Cl}^-$ systems are 1.27 and 1.37 V (vs. NHE) respectively. Hence, there is a possibility that chlorine reacts with chlorous acid according to the following equation.



The formation of chlorine according to the following side reaction (2) caused the observed full chlorine recoveries to be higher than those expected.



In acidic solution, chlorine reacts stoichiometrically with bromide and iodide. Hence, free chlorine was not expected to be recovered in their presence. However, there appeared to be significant recoveries.

This fact suggests that the method of Aoki and Muemori⁵²⁸ can also be applied to the determination of free bromine and free iodine. Calibration curves for these species were linear over a wide range, like that of free chlorine. The slopes of the gradients relative to that of free chlorine were 0.143 for bromine and 0.405 for iodine. However, these ratios are slightly different from those of the molar absorptivities of standard hypochlorite, hypobromite and hypoiodite measured at 290 nm. This difference may be explained by the fact that bromine and iodine are partially converted to BrCl⁻ and I₂Cl⁻ in the presence of excess chloride ion and these anions do not permeate microporous poly (tetrafluoroethylene).

Free chlorine is known to react with ammonia in a molar ratio of 2:1 to give dichloramine. However the dichloramine produced did not interfere with this method. Monochloramine, one of the other reaction products, permeates the microporous poly(tetrafluoroethylene) but does not interfere, because its absorption spectrum ($\lambda_{\text{max}}=243$ nm) does not overlap with that of hypochlorite. Determinations of free chlorine in potable water obtained by the continuous flow method of Aoki and Munemori⁵²⁸ and by the Palin spectrophotometric method give comparable results.

Chemiluminescence methods

Marino and Ingle⁵²⁹ have developed chemiluminescence methods for free chlorine based on the hydrogen peroxide-hypochlorite singlet oxygen chemiluminescence reaction and the luminol-hypochlorite chemiluminescence reaction⁵³⁰. The former method⁵²⁹ is capable of detecting down to $4 \mu\text{g l}^{-1}$ of free chlorine, is relatively free from interferences including chloramine, and gives results for potable water which are comparable to those obtained by Palin's *N,N*-diethyl 1,4-phenylene diamine spectrophotometric method. The latter method⁵³⁰ has a detection limit of $0.2 \mu\text{g l}^{-1}$ is relatively free from interference and agrees well with Palin's method.

The species that could most likely cause interference is chlorine dioxide.

Chemiluminescence reaction with luminol⁵³⁰

Optimized conditions for this reaction were a pH of 10.0 and a luminol cell concentration of 1.8×10^{-3} M.

Addition of a pH 10.0 buffer to the hypochlorite sample prior to luminol injection resulted in poor reproducibility of the chemiluminescence signal due to the finite and somewhat variable time between buffer addition and luminol injection. Injection of luminol and buffer together served to reduce the relative standard deviation in the chemiluminescence signal from 11 to 1 per cent at the $2 \mu\text{g l}^{-1}$ level. At the higher hypochlorite concentrations normally found in potable water, the rate of decomposition is much lower.

The chemiluminescence peak height is proportional to the hypochlorite concentration from the limit of detection ($0.2 \mu\text{g l}^{-1}$) up to $500 \mu\text{g l}^{-1}$ at which point the calibration curve starts to level off. This is primarily a chemical effect. Species that could possibly cause interference are iron III, monochloramine, chlorite, iron II, magnesium, calcium and permanganate. Iron II would only be present in reducing waters and destroy the hypochlorite. For some transition metals and calcium and magnesium the interference effect is depressive. Since no chemiluminescence reaction with luminol was observed in the absence of hypochlorite these metal ions probably decompose some of the hypochlorite. In real samples, this would

occur naturally before the analysis so the hypochlorite procedure would still measure the desired remaining free chlorine. The chemiluminescence activation by iron III may be due to iron II contamination since the detection limit for iron II is so much lower.

Thus, overall there are few interferences to the chemiluminescence technique. This is especially true for potable water analysis for two reasons. First, a 1–10 dilution of a potable sample is required to bring the hypochlorite concentration (typically 0.5–1.0 mg l⁻¹) onto the linear portion of the calibration curve although alternatively a 0.1 ml instead of 1.0 ml sample size could be used. This will reduce the typical concentrations of iron III, calcium and magnesium below their interference levels. Second, the interference levels indicate the effect on a hypochlorite determination at the detection limit of hypochlorite, while an actual determination in potable water is made at hypochlorite levels about 1000 times greater than the detection limit. Hypochlorite is not often used in water chlorination due to the problems of on-site generation incurred with this gas. Monochloramine, however, is present in most natural waters and does interfere in the absence of hypochlorite, although its detection limit is 30 times higher than that of hypochlorite. In the presence of hypochlorite however, it is not a serious interferent. The luminol technique is suitable for the routine determination of hypochlorite in potable water and it gives results comparable to the standard Palin method in terms of accuracy and freedom from major interferences but is more precise and has a detection limit of over 2 orders of magnitude lower. Equal chloramine and hypochlorite levels lead to only a ca. 1 per cent error in both methods.

Ion selective electrodes

Johnson et al⁵³¹ designed a hypochlorous and membrane electrode for the determination of un-ionized hypochlorite in solution. The unit uses a microporous polythene or teflon membrane in solution contact with a platinum or gold cathode; the electrode provides a measure of the concentration of hypochlorous acid in solution, irrespective of the hypochlorite ion and thus provides a true measure of the disinfection capacity of potable water.

Tang and Gordon⁵³² described an improved analytical procedure to determine the stoichiometry of the reaction between the chlorite ion and hypochlorous acid at pH 5, at various reagent ratios. The procedure involved the combination of ion selective electrode and iodometry, using the former to determine chlorides, chlorates and total chlorine and the latter to determine the oxychlorine species in terms of redox properties. The stoichiometry varied with the initial reagent concentration ratio. The yield of chlorine dioxide varied with this ratio and contact time between reagents. Molecular oxygen is thought to be formed as a byproduct.

Computer automation used in conjunction with a residual chlorine electrode has been used to assay $\pm 2 \mu\text{g l}^{-1}$ of chlorine in the 3–100 $\mu\text{g l}^{-1}$ concentration range in potable water.

Electrochemical methods

Voltammetry has been used to determine combined chlorine in potable waters^{533,534}. The sample is adjusted to contain 0.1 N sulphuric acid⁵³³ and the voltammetric curve is recorded between +0.8 and -0.1 V with the graphite electrode vs. the SCE, the peak current being proportional to the concentration of chlorine except at very low concentrations.

Evans⁵³⁴ followed the kinetics of the aqueous reactions of free chlorine and excess ammonia to form chloramines voltammetrically in the range of pH 3–12. Molar ratios of ammonia to hypochlorite vary from 1.3 to 6.3. The predominant chloramine species at each pH was confirmed by UV spectrometry.

Amperometry

Portable and continuous analysers have been described for the measurement of chlorine as hypochlorite or hypochlorous acid in potable water. Canelli⁵³⁵ gives details of a portable bore electrode amperometric analyser for the direct determination of 0.1–0.3 mg l⁻¹ free chlorine in potable water and water from swimming baths. Bromine, triiodide ion and manganese VII generated signals were stoichiometrically equivalent to that of hypochlorite but manganese dioxide suspensions (1.5, 5.0 or 15 mg l⁻¹) did not produce detectable amperometric signals.

Analysis of solutions of hypochlorite with ammonium chloride or selected organic nitrogen compounds indicated that various *N*-chloro compounds may interfere. In the presence of *N*-chloroglycine (2.70 mg l⁻¹ chlorine) the amperometric signal was about 5 per cent of that for the equivalent concentration of hypochlorite, but higher relative responses were obtained with monochloramine, dichloramine or nitrogen trichloride (19.42 and 70 per cent at 2.60, 1.20 or 1.00 mg l⁻¹ chlorine respectively). Chlorinated urea (2.2 mg l⁻¹ N, 2.90 mg l⁻¹ chlorine), chlorinated bovine albumin (10 mg l⁻¹ albumin), (2.00 mg l⁻¹ chlorine) or monochloroisocyanurate (1.30 mg l⁻¹ chlorine) produced amperometric signals (76, 5 and 50 per cent respectively) which are lower than those obtained by the *N,N*-diethyl-*p*-phenylenediamine method (100, 12 and 92 per cent). The advantages of this simple procedure must be weighed against possible inaccurate results in the presence of mono- and dichloramines and nitrogen trichloride. Statistical analysis showed no significant differences between the results obtained by this method and by the Palin *N,N*-diethyl 1,4-phenylene-diamine spectrophotometric method.

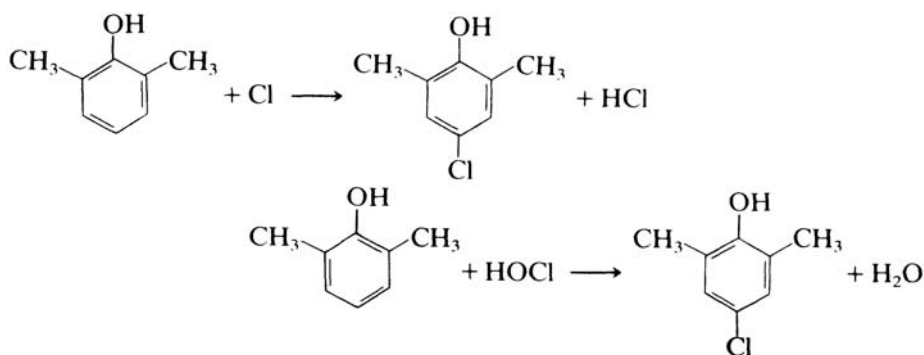
Saunier and Regnier⁵³⁶ describe an apparatus for plant use which gives 'an accurate and reliable measurement of free chlorine in water, even in the presence of an excess of combined chlorine. Two amperometric analysers operate in parallel; the first measures total chlorine in untreated water, while the second measures combined chlorine in water to which nitrite has been added as a reducing agent, the free chlorine being calculated by difference. By coupling the analysers with a pH meter and a temperature probe, the concentration of hypochlorous acid can be determined. The measurements are carried out in the presence of potassium iodide and a buffer to pH 4.0 to avoid polarization of the electrodes.

Gas chromatography

Derivatization with 2,6-dimethylphenol and gas chromatographic separation has been used⁵³⁷ to determine residual chlorine in potable water. The chlorine is converted to 4-chloro-2,6-dimethylphenol, at pH 1–3, and extracted with *n*-hexane. The dried extract is warmed with bis-(trimethylsilyl)-trifluoroacetamide and the chlorinated phenol is measured by gas chromatography. The method is rapid and simple. With a flame-ionization detector concentrations as low as 0.01 mg l⁻¹ can be determined with chlorine recovery higher than 99 per cent and a precision of about 0.6 per cent. The method is highly selective and free from interference from oxidizing agents. 2,6-dimethylphenol can be chlorinated by chlorine and by hypochlorous acid to give 4-chloro-2,6-dimethylphenol. In either case, one mole of the chlorine species is equivalent to one mole of the mono-chlorinated phenol.

Chlorine recoveries were 99.2–101.4 per cent with relative standard deviations of 0.36–1.1 per cent. When the f.i.d. detector is used, the limiting lower concentration of chlorine which can be measured is determined by the gas chromatographic peak for the 4-chloro-2,6-dimethylphenol being superimposed on the much larger peak of the 2,6-dimethylphenol.

The presence of manganese dioxide, copper II ion, iodate or nitrite (20 mg l⁻¹) did not alter the chlorine recovery. However, when nitrite was present, an additional peak ($t_r=6$ min 50 s) appeared in the gas chromatogram. The peak was due to 4-nitroso-2,6-dimethylphenol and did not interfere with the peak area



measurements of the 4-chloro and 4-bromo derivatives. Unlike colorimetric methods, this method is unaffected by the presence of coloured impurities in the aqueous chlorine solution.

Miscellaneous

Kutt and Vohra⁵³⁸ described an apparatus designed on the principle that the electrochemical generation of iodine is exactly the same as the chemical generation of iodine from buffered potassium iodide by its stoichiometric reaction with total residual chlorine in the sample. A digital meter provides a direct readout of the analyte concentration of chlorine in potable water in mg l^{-1} or $\mu\text{g l}^{-1}$.

Morrow and Martin⁵³⁹ review terminology pertaining to disinfection with chlorine, including definitions of free chlorine residual, combined chlorine residual, total chlorine residual and breakpoint chlorination, and consider methods for the determination and monitoring of residual chlorine, to be used in conjunction with manual or automatic chlorination equipment. It is recommended that the concentration of residual chlorine in treated water or waste waters should always be controlled, and suitable automatic chlorination equipment is described.

Comparison of methods for determining chlorine

Cooper et al⁵⁴⁰ evaluated two membrane electrodes, a potentiometric electrode and a total chlorine analyser for determining chlorine residuals in water. The results show that the order of precision was total chlorine analyser, amperometric titration, potentiometric electrode. There was no statistical difference between results obtained with the amperometric titrator and those of the potentiometric electrode, nor, in three out of four samples between the results from the total chlorine analyser and the potentiometric electrode. There was a significant difference between results from the total chlorine analyser and those from the amperometric titrator. The total chlorine analyser was shown to be operator-independent and provided online, continuous measurement. The potentiometric electrode is easy to operate but results vary from operator to operator. The results from the amperometric membrane electrodes were too variable to form firm conclusions about its application.

Tsuchigashi⁵⁴¹ determined residual available chlorine in potable water by the ortho-tolidine method and the *N,N*-diethyl 1,4-phenylenediamine spectrophotometric methods.

Cooper et al⁵⁴² organized a trial between 16 laboratories of methods for determining free chlorine by three different methods, the *N,N*-diethyl-*p*-phenyl-enediamine method, the free available chlorine test with

syringaldazine method and the amperometric titration procedures. Results obtained by the syringaldehyde method were equivalent to those obtained by the other two methods.

Piccardi et al⁵⁴³ carried out a critical comparison between spectrophotometric and electrochemical methods, for determining chlorine and hypochlorite in potable water. These workers showed that the *o*-tolidine spectrophotometric method was neither reproducible nor specific. They recommend an acid chrome violet method for determining chlorine dioxide.

Gordon et al⁵⁴⁴ has reviewed methods for the determination of free chlorine, combined chlorine, chloramines, chlorine dioxide, chlorite, chlorate and ozone in potable water.

TABLE 28
Individual methods for determining chlorine

Method	
Ion selective electrode potentiometric method (Pt/ iodide sensing electrode)	Not specific for chlorine. Gives a Nernstian response with all oxidizing agents that are stoichiometrically able to release iodine from an iodide solution
Amperometric titration with phenylarsenic oxide (Cu/Pt electrodes for chlorine and chlorine-dioxide) (Ag Pt electrodes for chloramines)	Direct titration at pH 7 after conversion of chlorine dioxide to chlorite and chlorate in an alkaline medium, yields free chlorine. The same titration with the addition of potassium iodide yields free chlorine +monochloramine. If chlorine is not destroyed, the titration at pH 7 in the presence of potassium iodide gives chlorine+ monochloramine+1 equivalent (0.2 mole) of chlorine dioxide. Finally, adding sulphuric acid to lower the pH to 2, it is possible to develop iodine, by adding potassium iodide, from all available chlorine and that is, from free chlorine monochloramine, chlorine dioxide (5 equivalents mole ⁻¹) and chlorite (4 equivalents mole ⁻¹)

Comments on individual methods for determining chlorine made by Piccardi et al⁵⁴³ are summarized in Table 28.

Tribromamine (spectrophotometric method)

Madec et al⁵⁴⁵ investigated the influence of chloride ions in the spectrophotometric determination of tribromamine in potable water.

Monochloramine

Valentine and Jafvert⁵⁴⁶ have studied the disproportionation of monochloramine in the presence of sulphate and phosphate. They showed that the disproportionation of monochloramine to form dichloramine involved a general acid-catalysed reaction pathway.

1.7.2 Ozone

Spectrophotometric methods

Earlier spectrophotometric methods for the determination of ozone in potable water involve reaction with methyl red⁵⁴⁷, indigo⁵⁴⁸ formation of manganese III pyrophosphate complex^{549,550} and spectrophotometric evaluation of iodide^{551,552} produced upon reaction with potassiumiodide. Gilbert⁵⁵³ has described a modification to the iodine method based on the use of *N,N*-diethyl-*p*-phenylenediamine. The ozone is allowed to oxidize iodide to iodine which reacts with *N,N*-diethyl-*o*-phenylenediamine to form a reddish complex, the absorption of which is measured at 500 or 550 nm. A linear calibration curve is obtained over the ozone concentration range of 0.02–2.5 mg l⁻¹. Owing to the instability of the coloured complex, measurement of the absorption intensity must be performed within 5 min of the completion of the reaction.

Liebermann et al⁵⁵⁴ described a spectrophotometric method using syringaldehyde as chromogenic reagent for the determination of ozone in potable water in the concentration range 0.2–5 mg l⁻¹ with a detection limit of 0.2 mg l⁻¹.

Agreement with Beer's law was excellent and allowed determination of ozone concentrations from 0.17 to 4.5 mg l⁻¹. Higher ozone concentrations could be determined by dilution of samples; however, ozone concentrations greater than this are rarely encountered in water treatment.

Tomiyasu and Gordon⁵⁵⁵ have recently described a promising spectrophotometric method for determining down to 50 µg l⁻¹ ozone based on the reaction between ozone and bis(terpyridine) iron II in dilute hydrochloric acid. Ozone concentrations down to 0.05 mg l⁻¹ could be determined with a precision of plus or minus 3 per cent, which compared well with that of the indigo method of Bader and Hoigne^{556,557} and uv spectrophotometric measurements. The reaction is not affected by interference from hydrogen peroxide or chlorine, for example, and provides the basis for a rapid comparative laboratory method for ozone analysis.

Ultraviolet spectroscopy

Gubelin^{558,559} has described a continuous plant monitoring instrument for ozone based on ultraviolet measurements at 254 nm. The high reliability of this system makes it useful for the automatic control of ozone water purification systems.

Amperometry

Amperometric methods for determining ozone in potable water have been described based on the use of a nickel oxidized silver electrode⁵⁶⁰ and on a gold cathode coated with a Teflon membrane-double junction reference electrode⁵⁶¹. The latter procedure gives a detection limit of 50–100 µg l⁻¹ ozone and is free from interference from a number of halogen derivative oxidizing agents such as bromine, hypobromous acid, chlorine dioxide, hydrogen peroxide, trichloramine and hypochlorous acid.

Differential pulse polarography

OZONE AND RESIDUAL CHLORINE: Smart et al⁵⁶² have investigated the use of differential pulse polarography of phenylarsine oxide for the indirect determination of ozone and residual chlorine. This

method has very attractive limits of detection; $2.5 \mu\text{g l}^{-1}$ for ozone and $3.3 \mu\text{g l}^{-1}$ and $1.6 \mu\text{g l}^{-1}$ respectively for free chlorine (pH 7) and for total chlorine (pH 4). These methods are based not on direct manual titration of ozone and free chlorine by phenyl arsine oxide which constitute the current standard methods, but on the addition of an excess of standard phenylarsine oxide to the sample followed by back titration of excess phenylarsine oxide with standard iodine solution at dual platinum electrodes. Smart et al⁵⁶² showed that the differential pulse technique compares very well with the standard methods for both ozone and chlorine. The direct measurement of phenylarsine oxide by differential pulse polarography offers the advantage of fixing and storing samples for free chlorine and ozone, while this cannot be accomplished using conventional standard methods.

The measurement of $\mu\text{g l}^{-1}$ for total chlorine, ozone, and free chlorine using differential pulse polarography are substantially better than the conventional standard methods. This excellent sensitivity is achieved with samples as small as 5 ml, as compared to the 0.2–11 samples required for the standard procedures. The small sample volume offers the additional advantage of using less reagent. The analysis time and precision of the differential pulse technique are comparable to the standard methods.

Potentiometric method

Vodzinskii and Platnikova⁵⁶³ have described a method for determining ozone based on direct potentiometry.

Chemiluminescent method

Aoki⁵⁶⁴ described a continuous flow determination of residual ozone using a PTFE membrane separation and chemiluminescent detection.

1.7.3

Chlorine dioxide

Titration procedure

Titration with standard ferrous ammonium sulphate to the *N,N*-diethylamine-*p*-phenylenediamine end-point (i.e. Palin's method) has been used to estimate chlorine dioxide and chlorite in potable water⁵⁶⁵⁻⁵⁶⁷. In these methods malonic acid has been used to suppress interference by free chlorine.

In its reactions with potassium iodide only one-fifth of the available chlorine content of chlorine dioxide responds in neutral solution, corresponding to the first stage reduction to chlorite. The remaining four-fifths is released after acidification and corresponds to the second stage reduction of chlorite to chloride.

A similar behaviour occurs in the *N,N*-diethylamine-*p*-phenylenediamine methods and has formed the basis for their use in the determination of chlorine dioxide separate from free and combined chlorine and from any chlorite originally present as such in the water^{568,569}. Accurate determination of such chlorite is also important since it may be present in significant amounts as a potentially toxic by-product of chlorine dioxide treatment⁵⁷⁰. Certain difficulties have been experienced because the reaction of chlorite with *N,N*-diethylamine-*p*-phenylenediamine appears to be catalysed by the ferric ions derived from reduction of the ferrous ammonium sulphate titrant, resulting in slow colour development in neutral solution which makes the end points less distinct. The effect can be minimized by using additional EDTA.

Two further modifications to the titrimetric procedure have been discussed by Palin and Darrall⁵⁶⁶ for use in the above circumstances. First, is the use of thioacetamide⁵⁷¹, the addition of which after the first reaction between *N,N*-diethylamine-*p*-phenylenediamine and chlorine dioxide eliminates the chlorite immediately so preventing colour drift back at the end points. Second is the omission of the two minute standing period before titration of the combined chlorine fraction. This period was introduced to ensure complete reaction with high levels of dichloramine. In the differential determinations described by Palin⁵¹⁷ no error should arise by omitting it in view of the finding of Adams et al⁵⁷² that the two species, chlorine dioxide and dichloramine, interact causing the elimination of one of them, i.e. it is not possible to have both of these compounds present in one solution. The modified method using thioacetamide is applicable to the determination of mixtures of free and combined chlorine, chlorine dioxide, and chlorite in water. A particular advantage of the modified method lies in its ability to determine chloride in the presence of high levels of residual chlorine and chlorine dioxide.

Valenta⁵⁷³ has described titration and UV methods for the determination of chlorine, chlorine dioxide and related anions in concentrated solutions of chlorine dioxide used for water dosing.

Spectrophotometric methods

Harp et al⁵⁷⁴ have discussed a method for the determination of 0.05–1 mg l⁻¹ chlorine dioxide based on the oxidation of chlorophenol red, and spectrophotometric measurement of the decrease in absorbance at 570 nm. The reaction is very specific, and no interference is caused by hypochlorite, chlorite, chlorate, chromate, permanganate, ferric iron, chloramines, turbidity or temperature.

Hartung and Quentin⁵⁷⁵ have also discussed a method for determining chlorine dioxide and chlorite in potable water which involves determination at 350 nm of iodine liberated by reaction of chlorine dioxide with iodide at pH 7 or pH 2.5. This procedure was effective at chlorine dioxide concentrations down to 0.001 mg l⁻¹. Interfering chlorine could be removed beforehand, while chlorite only interfered at pH 2.5. Preconcentration and isolation of chlorine dioxide could be performed by nitrogen stripping or hexane extraction. Quantities of chlorite down to 0.001 mg l⁻¹ could be determined photometrically after stripping out any chlorine dioxide, preconcentration and oxidation by sodium persulphate to chlorine dioxide.

Flow injection analysis

The chemiluminescent reactions of chlorine dioxide and the reagents luminol and hydrogen peroxide have been evaluated for the selective determination of chlorine dioxide in water. The luminol reaction was optimized with respect to pH effects by using phosphate and borate buffer solutions. A novel chemiluminescence flow-through detector cell has been used⁵⁷⁶ for measurement of chlorine dioxide concentrations as a function of chemiluminescence intensity. An automated method employing luminol, as sole chemiluminescence reagent, and gas-diffusion flow injection analysis provided greater selectivity for chlorine dioxide versus chlorine or other interfering substances such as chlorite and chlorate ions, iron and manganese.

The detection limit for chlorine dioxide was 5 µg l⁻¹.

Ion-selective electrodes

Orion Model 97–70 residual chlorine electrodes have been used^{577,578} to determine down to 0.1 µ mole l⁻¹ of chlorine dioxide in potable water. The electrode records the potential difference between iodide and

iodine liberated by chlorine dioxide at pH 7 and by chlorous acid at pH 2.5. The amounts of each are calculated with the aid of a calibration curve. Since free chlorine in solution also liberates iodine, it can be determined by difference following its removal by addition of potassium bromide and sodium formate.

Chemiluminescence

Smart⁵⁷⁹ has designed a membrane flow cell which uses a homogeneous polymeric membrane for the separation of the luminol peroxide reagent from chlorine dioxide, in chemiluminescent determinations of the latter, and to act as a barrier to possible interference. They showed that concentrations of less than 1 mg l⁻¹ could be measured and that dissolved electrolytes as well as bacteria and colloidal particles are isolated from the reagent solution.

1.8 Radioactive substances

1.8.1 Iodine-131

A specific method has been described^{580,581} for iodine-131 in potable water which involves addition of sodium iodide carrier to the sample, treatment with nitrous acid, extraction of total iodine with carbon tetrachloride and back extraction of iodine from the carbon tetrachloride with 0.05 M sodium sulphate. This solution is then passed through a Dowex 2×5 film to adsorb iodide ions which are then subject to low level -counting. The chemical yield of iodine-131 was 99 per cent and the limit of detection 0.6 pCi.

1.8.2 Radium-226 and radium-228

Various workers have discussed the determination of radium-226⁵⁸²⁻⁵⁸⁵ and radium-228^{586,587} in potable waters.

Higuchi et al⁵⁸³ determined radium-226 by liquid scintillation counting after preconcentration with ion-exchange resin. The procedure requires 2 hours and the detection limit 0.03 pCi l⁻¹.

In a further method applicable to potable and rain water⁵⁸⁴ the radium fraction in potable waters is coprecipitated with barium and filtered through a membrane. Boiling the sample then removed radon and carbon dioxide. Actinides were precipitated by addition of ferric iron. Ammonium hydroxide induced the coprecipitation of ferric iron and actinides. Both fractions were measured with a gas-flow proportional counter. The isotopic radium composition was obtained by measuring at two or three different times the alpha activity from the radium fraction. Friedmann and Hernegger⁵⁸⁵ conducted a systematic survey of the concentration of radium-226 in bottled Austrian mineral waters. Complicating factors due to the presence of radon of geological origins are discussed. Only in respect of one sample was the WHO recommended limit of 3.3 pCi l⁻¹ substantially exceeded.

Baratta and Lumsden⁵⁸⁶ have described a method for the rapid determination of radium-228 in food and water by measuring its decay product actinium-228. It is based on a solvent extraction/ion-exchange technique and lanthanum is used as coprecipitant. The method is sensitive to less than 1 pCi l⁻¹ of water.

Mills et al⁵⁸⁷ monitored radium-228 in potable water supplies. They comment that in the view of the US Environmental Protection Agency radium-228 need only be measured on the rare occasions when

radium-226 exceeds 3.0 pCi l⁻¹. They argue that radium-228 rarely exceeds radium-226 and the costs of mandatory monitoring of the former radionuclide would not be justified.

1.8.3

Radon-222

Pritchard and Gesell⁵⁸⁸ give details of a procedure for measuring concentrations of radon-222 as low as 10 pCi l⁻¹ in water. Measurements are carried out by a 40 min count of a 10 ml sample, using a commercial liquid scintillation counter.

Countess⁵⁸⁹ has described a simple, rapid method for determining the concentration of radon in water based on a gamma-counting method. The method is calibrated by using an aliquot of a standard solution of radium-226. The method was applied to measurement of the radon concentration in water samples from houses within a 50 mile radius of New York. Levels ranged from zero to 2000 pCi l⁻¹.

Countess⁵⁸⁹ noted one disadvantage of this method. The simplicity and convenience of an integrated gamma count is somewhat offset by the lack of specificity; other gamma-emitting nuclides in water samples could be mistaken for radon. In cases of doubt, the detailed gamma energy spectrum can be examined or the sample can be recounted after several days to confirm the expected half-life of ²²²Rn of 3.8 days. Radium itself could be the source of part or all of the observed radon, but radium concentrations in water are normally much lower than the limit of detection.

Samples of water stored in the Marinelli beakers for a week show that there is no loss of radon, except by radioactive decay, presumably because of the 0.3 cm thickness of the polyethylene. However, since radon does dissolve slowly in the plastic, it may possibly increase the background of the beaker. To minimize this effect, avoid storing the samples in the beakers for longer than necessary. If the dissolved radon does increase the background of the beaker, it will be necessary to let the beaker stand before re-use (usually for several weeks) until all the radon has been eliminated by radioactive decay.

1.8.4

Technetium-99

Technetium-99 has been recovered⁵⁹⁰ from flocs formed during coagulation at water works. The analytical method used was an adapted radiochemical technique involving oxidation, extraction into tributylphosphate, back-extraction with sodium hydroxide and electroplating. Yields varied from 7.0 to 63 per cent. The recovered radionuclide was determined using a gas flow proportional counter with two shielded detectors. The method enabled the authors to analyse 1 g of dry floc representing a high volume of water. A typical value was 0.56 plus or minus 0.26 mBq per g.

1.8.5

Gross alpha and gross beta activity

Measurement of these activities in potable water supplies has been reviewed⁵⁹¹ together with results obtained in an interlaboratory study of measurements carried out in the USA.

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Chapter 2

WASTE WATERS

2.1 Anions

2.1.1 *Chloride*

Titration methods

Barrera and Martinez¹ have compared two methods, the Mohr procedure based on precipitation of silver chloride with a chromate indicator and the mercuric nitrate method based on the formation of soluble, slightly ionized mercuric chloride, for the volumetric determination of chlorides in waste waters. Results are in agreement. The mercuric nitrate method is preferred because the end-point is sharper, a magnetic stirrer is not required, the range of concentrations is 0–700 mg l⁻¹ (against 5–300 mg l⁻¹) and it is less expensive for both high and low chloride concentrations.

Ion chromatography

The determination of chloride in waste waters is discussed in [section 2.1.17](#) (multianion mixtures).

2.1.2 *Iodide or iodine*

Titration method

Erdey and Kozmutza² used xenon difluoride as a reagent for the determination of mg l⁻¹ quantities of iodide and iodine in nuclear reactor cooling waters. The test solution is made 1 N in sulphuric acid and excess solid xenon difluoride added to convert iodide to periodate which is then determined by standard iodometric procedures.

2.1.3 Fluoride

Microdiffusion method

Microdiffusion has been applied³ to the determination of down to $50 \mu\text{g l}^{-1}$ fluoride in waste waters, also effluents and river waters. The sample is placed in the outer compartment of a polypropylene Conway-type diffusion cell containing 1 ml of 0.5 N sodium hydroxide in a polystyrene cup in the inner compartment, then 1 ml of 70 per cent (v/v) sulphuric acid is rapidly added to the sample and a polystyrene lid, greased with silicone, is placed on the cell, which is then heated in an oven at 65°C for 5 hours. To the dried residue in the centre cup is added 1 drop of phenolphthalein solution and the contents are washed with water into a volumetric flask. Fluoride is then determined by the lanthanum complexan or spectrophotometric procedure^{4,5}.

Ion chromatography

The chromatography of fluoride in waste waters is discussed in [section 2.1.17](#) (multianion analysis).

2.1.4 Free cyanide

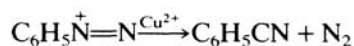
Spectrophotometric methods

Nagashima and Ozawa⁶ have given details for the determination of cyanide in aqueous samples by spectrophotometry, using isonicotinic acid and barbituric acid as reagents. Cyanide reacts with chloramine-T, and then the reagent is added to form a soluble violet-blue product, which is measured at 600 nm. Maximum absorbance is achieved in 15 min at 25°C and remains constant for about 30 min. This method is applicable to water samples containing $0\text{--}5 \text{ mg l}^{-1}$ cyanide. Results obtained on several plating waste waters are reported and show good agreement with those obtained by the conventional pyridine-pyrazolone method⁷.

Fu-Sheng et al⁸ applied the copper-cation 2B-Triton A-100 system to the spectrophotometric determination of micro amounts of free cyanide in waste water.

Gas chromatography

Funazo et al⁹ have described a method for the determination of cyanide in water in which the cyanide ion is converted into benzonitrile by reaction with aniline, sodium nitrite and cupric sulphate. The benzonitrile is extracted into chloroform and determined by gas chromatography with a flame ionization detector. The detection limit for potassium cyanide is 3 mg l^{-1} . Lead, zinc and sulphide ion interfere at 100 mg l^{-1} but not at 10 mg l^{-1} .



More recently, Funazo et al¹⁰ have described a more sensitive gas chromatographic procedure capable of determining down to $3 \mu\text{g l}^{-1}$ total cyanide in waste waters. The method is based on the derivatization of

cyanide to benzonitrile, which is extracted with benzene and determined by flame thermionic gas chromatography. In the derivatization reaction, aqueous cyanide reacts with aniline and sodium nitrite in the presence of copper II sulphate and forms benzonitrile.

Funazo et al¹⁰ tested this method in the presence of several ions normally found in environmental samples. The peak area of benzonitrile derivatized from the standard cyanide solution (0.5 mg l^{-1}) was arbitrarily assigned a value of 100.

None of the ions except thiocyanate, cyanate and sulphide interfered at a concentration of 500 mg l^{-1} . At this concentration, thiocyanate interferes negatively and cyanate positively. However, these interferences are not observed at the 100 mg l^{-1} level. Sulphide ion interferes at relatively low concentrations, even at 0.1 mg l^{-1} , a negative interference is observed. Similar interferences of sulphide are well known in the pyridine pyrazolone method and in the method using a cyanide ion selective electrode. However, sulphide can be removed from the sample solution by treating the alkaline sample at pH 11.0 with small amounts of powdered lead carbonate¹¹.

Funazo et al¹⁰ analysed several wastewater samples from various factories using cyanide, such as metal refining and plating factories by the gas chromatographic and by the spectrophotometric pyridine pyrazolone methods⁷. Instantly after collection, sodium hydroxide was added to the samples and the solution was adjusted to pH 12–13 in order to prevent the evolution of hydrogen cyanide. The results show that the values measured by the two methods agree well.

Cyanide-selective electrodes

REMARKS ON ION-SELECTIVE ELECTRODE FINISH: Ion-selective potentiometry in alkaline solution provides a suitable finish for the determination of cyanide^{11–14}. Sulphide ion is an interferent, a cadmium nitrate treatment has been found to remove sulphide without influencing the response of the silver iodide-silver sulphide electrode. If both the precipitate and solution from this treatment are colourless (sulphide absent) filtration of the mixture before the potentiometric measurement is unnecessary. Since the electrode response of the electrode is pH dependent, standards and samples must be brought to the same pH. It is noteworthy that the silver/silver sulphide electrode (e.g. Orion 94–16) is more sensitive to cyanide than the silver iodide-silver sulphide one^{13,15}, but the response is affected by cadmium ion.

Fraut et al¹⁵ have described an electrode indicator technique for the determination of low levels of free cyanide in waste waters. Concentrations of cyanide down to $30 \mu\text{g l}^{-1}$ are determined with the use of the Ag^+ selective electrode and $10 \mu\text{M}$ as indicator solution. The pH of the sample is adjusted to between 11 and 12 and an addition procedure is used, the concentration of cyanide in the sample being obtained by use of a Gran plot; samples containing more than 260 mg l^{-1} of cyanide must be diluted initially. Copper and nickel are masked with EDTA and any sulphide removed by addition of lead ions in slight excess. Ammonia does not interfere even in a 1000 fold excess.

Chronopotentiometry

Procopio et al¹⁶ carried out an indirect determination of cyanide in waste waters by this technique. Cyanide was determined by measuring the displacement of the quarter wave potential of the chronopotentiometric graph of formaldehyde. After separation of the cyanide by distillation into alkaline media, formaldehyde solution was added and the resultant solution transferred to the cell of a constant current coulostat. A constant potential of -1.4 V was applied for 5 min while nitrogen flowed through continuously. The potential was removed and the solution allowed to become quiescent, before applying a constant current to

the working gold electrode. A transition time of 30 s was obtained. From the displacement of the formaldehyde curve with and without cyanide present, a detection limit of $10 \mu\text{g l}^{-1}$ cyanide was obtained with a relative error of less than 2 per cent and a relative standard deviation of 1 per cent.

2.1.5

Total cyanide

Total cyanide includes free cyanide ions plus complexed metal cyanides, e.g. ferrocyanides. The methods discussed in the previous section determine only free uncomplexed cyanide. To determine uncomplexed plus complexed cyanide, i.e. total cyanide, it is necessary prior to analysis to decompose the complexed cyanides to free cyanide.

Overbach¹⁷ discussed problems encountered in the determination of low concentrations of cyanide in photographic processing waste waters. Determination of both total and free cyanide in the same sample differentiates between the toxic free cyanide and the complexed ferrocyanide. Because of possible instability of the cyanide, he recommended that samples should be analysed on site, for instance by the microdiffusion technique.

A spectrophotometric method has been described for the determination in waste waters of total cyanide, including free cyanide, complex cyanides and thiocyanates¹⁸. Thiocyanates, together with simple and complex cyanides, are reacted with acid cuprous chloride and the hydrogen cyanide formed is absorbed in a sodium hydroxide solution which is then made slightly acidic, to prevent hydrolysis to cyanate, chloramine-T is added to produce cyanogen chloride, a pyridine/pyrazolone reagent is added, and the optical absorbance of the resulting blue dye is measured at 620 nm. Volatile aldehydes and ketones interfere in the final colour development.

Csikai and Barnard¹⁹ used EDTA at pH 4 to displace cyanide from metal complexes and to avoid converting thiocyanate to free cyanide where oxidants are present. Sulphamic acid is added to prevent nitrite interference, sulphides are removed from the sample with calcium carbonate and from distillates with cadmium nitrate. Evolved cyanide is determined by pyridine-barbiturate photometry or potentiometrically with ion-selective electrodes.

Czikai and Barnard¹⁹ evaluated their procedure by adding both free cyanide and complex metal cyanides to both deionized water solutions and wastewater samples containing or spiked with nitrate and thiocyanate. The recovery of cyanide was virtually complete.

For the cyanide complexes of chromium, copper, iron, and nickel, the recovery of cyanide was usually greater than 95 per cent. As mentioned previously, the failure to disrupt hexacyanocobaltate III due to its kinetic inertness, is a limitation of most total cyanide procedures.

Ion-selective electrode

A procedure has been developed for determination of cyanide²⁰ in concentrations down to 2 mg l^{-1} by manual or automated potentiometry using a cyanide ion-selective electrode. Distinction is made between simple and complex cyanides by irradiation with ultraviolet light.

Flow injection analysis

Zhu and Fang²¹ have described a spectrophotometric determination of total cyanide in waste waters in a flow injection system with a gas diffusion separation. The method is based on the formation of the unstable

red intermediate product of the reaction of cyanide with isonicotinic acid and pyrazolone. A detection limit of $0.6 \mu\text{g l}^{-1}$ was achieved. Cobalt interfered in this method.

Gas chromatography

Complex cyanides have been determined gas chromatographically in amounts down to $100 \mu\text{g l}^{-1}$ ²². The complex cyanides are broken down by ultraviolet radiation, reacted with bromine water and the cyanogen bromide formed is separated and determined selectively by means of an electron capture detector.

Atomic absorption spectroscopy

Rameyer and Janauer²³ have described a method using reactive ion exchange for the determination of complex iron cyanides in water in the mg l^{-1} range. The cyanide complexes are preconcentrated on shallow beds of sulphonated cation-exchange resin in the copper II form by precipitation as copper hexacyanoferrate II or copper hexacyanoferrate III. Other cations, including contaminant iron species, are eluted with hydrochloric acid. Aqueous ammonia relatively releases and elutes the hexacyanoferrate by the formation of the copper amine complex. Finally the complex cyanides are determined as iron by atomic absorption spectrometry.

Miscellaneous

Pohlandt et al²⁴ have critically evaluated 92 methods applicable to the separate determination of free cyanides and complex cyanides in waste waters and process streams. These include titrimetric, spectrophotometric, potentiometric, amperometric, polarographic, voltammetric, ion-selective electrodes, indirect atomic absorption spectrometric, gas chromatographic and automated techniques. From this work it appears that most titrimetric, colorimetric and electrochemical methods (including potentiometry and the use of cyanideselective electrodes) for the determination of ionic cyanide are liable to interference from ionizable metal cyanide complexes, e.g. . These methods can therefore be employed only if such complexes are known to be absent. Potentially accurate methods for the determination of ionic cyanide include ion chromatography (because of its ability to effect separations) and indirect atomic absorption spectrophotometry based on the selective formation of $(\text{Ag}(\text{CN})_2)^-$.

Similarly, none of the methods mentioned gives a reliable result for the total amount of cyanide present in a sample. The decomposition of stable complexes and the separation from interfering substances by distillation is therefore necessary. However, most distillation procedures cannot effect the decomposition of all the metal cyanide complexes and they suffer from interferences. The most useful distillation procedure appears to be the ligand displacement technique²⁴. With this method, interference from sulphide and thiocyanate can be avoided and all the ionic and coordinated cyanide—except cyanide from $(\text{Co}(\text{CN})_4)^{3-}$ —present in a sample can be distilled out.

Because of the speed in decomposing cyanide complexes, irradiation with ultraviolet light warrants further attention. A combination of this method with the separation, by ion chromatography, of interfering species might result in a fast method for the determination of total cyanide.

2.1.6 *Nitrite*

Spectrophotometric methods

Various spectrophotometric procedures have been described for the determination of nitrite in waste waters^{25–27}. In the spectrophotometric method²⁵ based on the reaction between Griess Romijn reagent (i.e. the reaction of nitrite with a primary aromatic amine to form a diazonium salt, which is then coupled with another aromatic compound to form an azo dye whose absorbance is measured) and nitrite, interference by iodide, sulphide, thiosulphate, sulphite or tetrathionate is avoided by the addition of mercuric chloride solution.

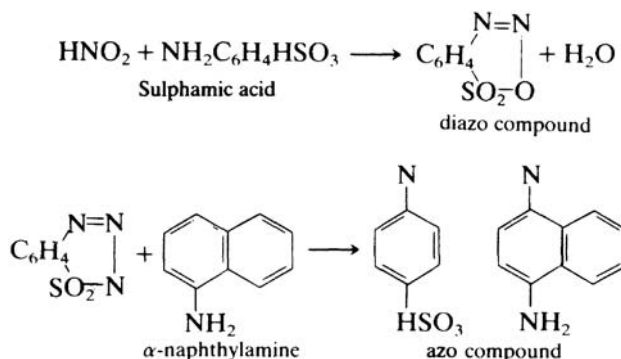
Nakamura and Mazuka²⁶ extracted nitrite in an ethyl acetate solution of 4,5-dihydroxycoumarin. Beer's law was obeyed up to 0.75 mg l⁻¹. Only iodide, sulphide, iron III and chromium V ions interfered seriously at the 10 µg level. Results agreed well with those obtained using the diazotizing coupling method.

Koupparis et al²⁷ have described procedures for the determination of nitrite using an automatic microprocessor-based stopped-flow analyser. The reaction is based on diazotization of sulphanilamide, the product being coupled with *N*-(1-naphthyl)ethylenediamine dihydrochloride to form a coloured azo dye which is measured at 540 nm. The analysis should be carried out on fresh samples, to avoid bacterial conversion of nitrite to nitrate or ammonia; however, samples can be preserved for 1–2 days, either by freezing at -20°C or by addition of mercuric chloride and storage at 4°C. The methods are fast, sensitive, accurate and precise, and without serious interference. The sample throughput for routine analysis can be up to 360 samples per hour in the range 0.025–2.00 mg l⁻¹ of nitrite nitrogen. The automated microprocessor-based stopped flow analyser has been described by Koupparis et al²⁸.

An average recovery of 98.6 per cent was obtained for the analysis of samples. Major interference is caused by reducing or oxidizing ions. The low results caused by copper II ion because of its catalysis of the decomposition of the diazonium salt in methods with long reaction times are avoided in this method. The serious sulphite interference is also almost eliminated in this method. The sulphide interference can be eliminated by adding excess of cadmium ions and filtering. Addition of 200 mg l⁻¹ of Cd²⁺ to a waste water sample containing 1 mg l⁻¹ of and 50 mg l⁻¹ of sulphide eliminated the error.

Raman spectroscopy

Furuya et al²⁹ have developed a method for the determination of nitrite in amounts down to 0.5 µg l⁻¹ in waste and treated waters, by resonance Raman spectrometry after conversion of nitrite to coloured azo dyes. Nitrate can also be determined simultaneously by this method.



In resonance Raman spectrometry, due to the resonance effect, the intensities of spectra often become five or six orders of magnitude larger than those of usual Raman spectra. Therefore, Furaya et al²⁹ attempted to determine nitrite by use of resonance Raman spectrometry. This method, however, can be applied only to coloured compounds and aqueous solutions of are completely colourless. Therefore, nitrite was converted to a coloured product by diazotization and after that the resonance Raman spectrum was measured.

Furaya et al²⁹ investigated the simultaneous determination of nitrite and nitrate using resonance Raman spectroscopy.

Sample solutions which contain much larger quantities of nitrate relative to those of nitrite can be measured. The spectrum demonstrates that the key band of nitrate can be measured almost independently of the adjacent band of the coloured product corresponding to nitrite. This result shows clearly the possibility of the simultaneous determination of nitrite and nitrate and also proves the excellent selectivity of the Raman spectrometry.

2.1.7

Nitrate

Raman spectroscopy

As mentioned in the previous section Furaya et al²⁹ have used resonance Raman spectroscopy to determine nitrite in waste waters. They also proposed a method for simultaneous determination of nitrite and nitrate. These workers³⁰ have also discussed a laser Raman spectroscopic method for the determination of down to mg l⁻¹ nitrate in waste waters.

In the case of waste and treated waters, the detection limit becomes about an order of magnitude higher than that in the case of pure water because of the strong luminescence of water samples. Furaya et al³⁰ demonstrated that the addition of potassium iodide as a quencher makes the background markedly smaller. By this procedure, the sensitivity becomes comparable to that in the case of pure water samples.

Spectrophotometric method

Nitrates have been determined³¹ in waste water in the presence of nitrites by a spectrophotometric method using salicylane as the chromogenic agent. Nitrites interfere in the determination of nitrates using the salicylane method but can be removed by amido sulphonic acid. The spectrophotometric method with

salicylane may be used for determining nitrate levels of up to 20 mg l⁻¹ nitrate-nitrogen in the presence of equimolar concentrations of nitritenitrogen.

Ion chromatography

The ion chromatography of nitrate in waste waters is discussed in [section 2.1.17](#) (multianion analysis).

2.1.8

Phosphate

Recently, eutrophication in lakes and reservoirs has become an important problem. Phosphorus is a critical nutrient aiding the eutrophication process. The principal sources of phosphorus in environmental waters are agricultural effluents, municipal waste waters, industrial waste waters, etc. The determination of phosphorus is important.

Ultraviolet spectroscopy

The automated ultraviolet spectrophotometric method³² for the determination of ortho and ortho plus hydrolysable or total phosphate involves the use of two independent flow systems, which are flow-charted, concurrently allowing these phosphates to be measured colorimetrically as orthophosphate. Features of the method include compensation of the bias effect of turbidity during orthophosphate determination, and the elimination of the need to neutralize acidified samples in hydrolysable and total phosphate determinations prior to colour development. The method and equipment both allow continuous operation for up to 24 hours.

Standard deviations over the ranges 0–3 mg of l⁻¹ phosphate and 3–30 mg l⁻¹ phosphate were 0.03 and 0.2 respectively. Up to 100 mg of silicate, iron or nitrate⁻¹ did not interfere in the determination of 30 mg l⁻¹ phosphate.

Spectrophotometric method

Buchanan and Easty³³ showed that the official methods^{34,35} for determining orthophosphate and total phosphorus (i.e. phosphate after digestion with persulphate) in waste water as reduced molybdophosphate are subject to interference when applied to waste samples. Thus sulphide interferes in the determination of orthophosphate but not in that of total phosphorus because they are oxidized by the persulphate. Ligninsulphonates interfere in the determination of total phosphorus and somewhat less in the determination of orthophosphate. Addition of excess of aqueous bromine to the sample prevents interference from sulphide and greatly reduces that from ligninsulphonates; in the determination of orthophosphate the unconsumed bromine is removed by a stream of air before further steps in the determination. It is also shown that the precipitation of alkali lignin and other substances which occurs when the solution, after the persulphate oxidation is neutralized according to the official procedure, can be eliminated by, instead, filtering the solution while it is still acidic (the amount of acid used in the reagent solution being reduced to compensate for that already present).

Atomic absorption spectrometry

In the atomic absorption inhibition titration method³⁶ the phosphate in the sample is treated with incremental amounts of magnesium solution and magnesium determined by atomic absorption spectrometry. The end-point is indicated by a sharp rise in the magnesium absorption; features of the titration curve after the end-point are related to species formed in the flame. Some observations on polyphosphate titrations are presented, and the method was applied to the determination of phosphate in surface and waste waters.

Condensed phosphate is a generic title for all phosphates which are formed by the removal of one or more water molecules from orthophosphoric acid, which may be represented as $3\text{H}_2\text{O}\cdot\text{P}_2\text{O}_5$. These include metaphosphoric acid ($\text{H}_2\text{O}\cdot\text{P}_2\text{O}_5$), pyrophosphoric acid ($2\text{H}_2\text{O}\cdot\text{P}_2\text{O}_5$), ultraphosphoric acid (general formula $m\text{H}_2\text{O}\cdot\text{P}_2\text{O}_5$) where $0 < m < 1$), and polyphosphoric acid (general formula $m\text{H}_3\text{O}\cdot\text{P}_4(m-1)\text{H}_2\text{O}$ where $1 < m < \infty$). The most common condensed phosphates are pyro- and tripolyphosphate which have dissociable protons and behave as typical polyprotic acids. The pyrophosphate and tripolyphosphate each occur in three forms

pyrophosphates ($\text{H}_3\text{P}_2\text{O}_7^-$, $\text{H}_2\text{P}_2\text{O}_7^{2-}$ and $\text{HP}_2\text{O}_7^{3-}$)

tripolyphosphates ($\text{H}_3\text{P}_3\text{O}_{10}^{2-}$, $\text{H}_2\text{P}_3\text{O}_{10}^{3-}$ and $\text{HP}_3\text{O}_{10}^{4-}$)

A number of factors affect the rate at which condensed and organic phosphates undergo hydrolytic degradation in aqueous solution. The major environmental factors in decreasing order of effectiveness are listed in Table 29. Consideration of Table 29 indicates that pH is one of the factors which exerts a considerable influence on the rate of hydrolysis.

TABLE 29

Major environmental factors affecting the hydrolytic degradation of condensed phosphates

Factor	Approximate effect on rate
Temperature	10^5 – 10^6 faster from freezing to boiling
pH	10^3 – 10^4 slower from strong acid to base
Enzymes	As much as 10^5 – 10^6 faster
Colloidal gels	As much as 10^4 – 10^5 faster
Complexing cations	Very many-fold faster in most cases
Concentration	Roughly proportional
Ionic environment in the solution	Several-fold change

In a domestic waste water, all these factors may influence the hydrolysis of condensed phosphate to orthophosphate. Thus if the sample is not analysed immediately, changes in the concentrations of condensed and orthophosphates will occur. If the forms of phosphate are to be determined rather than total phosphate, hydrolysis must be prevented.

Sample preservation

Rossin and Lester³⁷ evaluated some of the methods available for the preservation of condensed phosphates in samples of domestic waste waters, i.e. the prevention of the hydrolysis of condensed phosphate to orthophosphate. They showed that mercuric chloride at 40 mg l^{-1} at normal pH is the most effective preservative of those examined for samples stored at 20°C for 6 days. Samples should be filtered as soon as possible after they have been taken. Mercuric chloride at high pH was not a satisfactory preservative.

Addition of sodium hydroxide to raise the pH increases phosphatase activity but lowers the rate of spontaneous hydrolysis and on balance, is not a satisfactory treatment. Formaldehyde at elevated pH was less efficient than mercuric chloride at normal pH.

The samples treated with mercuric chloride at normal pH presented the smallest difference from the mean with a range between -0.07 and $+0.06$. When formaldehyde was used at high pH, the range was between -0.16 and 0.00 . The samples containing mercuric chloride at pH 10 showed a range from -0.15 to $+0.21$. A variation between -0.21 and $+0.35$ was found when pH was increased in the filtered samples. The use of formaldehyde at normal pH resulted in a variation from -0.25 to $+0.34$.

Ion chromatography

The ion chromatography of phosphates in waste waters is discussed in [Section 2.1.17](#) (multianion analysis).

Ion exclusion chromatography

Tanaka and Ishizuka²⁸⁹ have investigated the possibility of determining orthophosphate in waste waters by ion exclusion chromatography on a cation exchange resin in the H^+ form by elution with acetone water. They discuss optimal conditions for the separation of phosphate from chloride, sulphate, carbonate, etc. which are always present in waste water and sewage samples.

[Fig. 28](#) shows the chromatogram of a mixture of 10 mg l^{-1} of chloride sulphate, nitrate, phosphate and carbonate obtained with the flow colorimetric detector by elution with 60 per cent acetone water. As can be seen from [fig. 28](#) phosphate could be separated from the strong acid anions and carbonate. The R_s value between the strong acid anions and phosphate was about 1.7. This R_s value suffices for the quantitation of phosphate by the peak area measurement with a computing integrator.

In [fig. 28](#) an unknown peak was observed between phosphate and carbonate. This peak was due to water in the sample solution introduced into the chromatograph. However, the peak did not interfere with the quantitation of phosphate.

2.1.9

Silicate

Atomic absorption spectrometry

Looyenga and Huber³⁸ used atomic absorption inhibition titration to determine silicate in waste water. The method is based on the strong inhibition by silicate of the absorption of magnesium ions which is measured continuously during titration. The sample solution (pH 3–4) is first passed through Amberlite IR-120 resin (H^+ form) to remove magnesium and other interfering cations and the percolate is then titrated with a standard solution ($100\text{--}200\text{ mg l}^{-1}$); the titrated solution is simultaneously aspirated into the hydrogen air flame for measurement of the absorption at 285.2 nm . The end point is detected by a sharp increase in the magnesium signal. The detection limit is 0.1 mg l^{-1} and there is no interference from phosphate or sulphate.

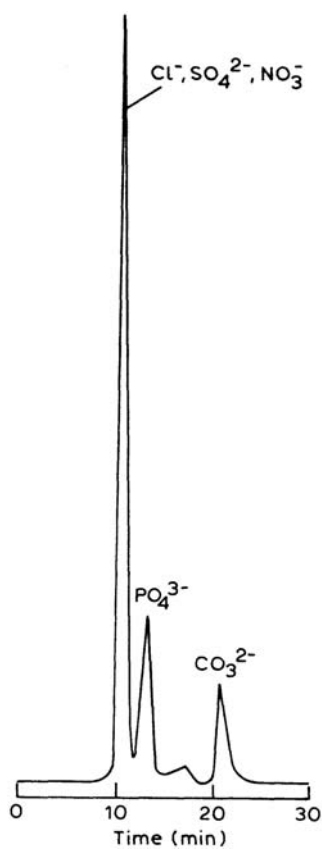


Fig. 28. Ion-exclusion chromatogram of mixture of 10 mg l^{-1} each of Cl^- , SO_4^{2-} , and NO_3^- , and obtained by elution with 60 per cent acetone-water. Detected with FCD (100 mV full scale).

2.1.10

Chlorite, nitrate, nitrite and ammonia

Miscellaneous

Canelli³⁹ has described an autoanalyser based procedure for the simultaneous determination of these ions in waste water.

Jenkins⁴⁰ has discussed the determination of nitrogen forms, including nitrite and nitrate in waste water.

2.1.11 *Sulphate*

Ion-selective membranes

Srivastava and Jain⁴¹ investigated the performance of a sulphate ion-selective membrane electrode prepared from hydrous thorium oxide gel with polystyrene as binder. The membrane showed good selectivity for sulphate ions in the range 0.1–100 μM and there was practically no interference from a large number of anions and cations. The electrode could be used at pH 6–10 and could be used in partially non-aqueous systems. This electrode was used to determine sulphate in waste waters from the pulp and paper and leather processing industries.

Liquid chromatography

This technique has been used⁴² to determine sulphate in waste water. A post column solid phase reaction detector was employed in conjunction with an anion-exchange separation column to determine 5–40 mg l^{-1} sulphate.

Ion chromatography

The ion chromatography of sulphate in waste waters is discussed in [section 2.1.17](#) (multianion analysis).

2.1.12 *Sulphite*

Ion chromatography

The ion chromatography of sulphite is discussed in [section 2.1.17](#) (multianion analysis).

2.1.13 *Sulphide*

Ion-selective electrode

Both sulphide⁴³ and iodide-selective⁴⁴ electrodes have been used to determine sulphide in waste water. Papp and Havas⁴³ used a sulphide ion-selective electrode as an indicator electrode in the potentiometric titration of sulphide with mercuric chloride. Novkirishka et al⁴⁴ used an iodide-selective electrode in an indirect potentiometric titration procedure to determine sulphide in industrial waste waters. Sulphide is first precipitated as cadmium sulphide by addition of cadmium acetate in an alkaline medium. The isolated cadmium sulphide is dissolved in excess standard iodine solution and excess iodine estimated by potentiometric titration using the iodide-selective electrode.

Rama Bhat et al⁴⁵ have described spectrophotometric methods for the determination of sulphides, sulphites and sulphates in waste waters.

Ion chromatography

The ion chromatography of sulphide in wastewaters is discussed in [section 2.1.17](#) (multianion analysis).

*2.1.14**Thiosulphate, sulphite, sulphate, polysulphide**Anodic stripping voltammetry*

Differential pulse anodic stripping voltammetry has been used⁴⁶ to detect thiosulphate, a potential substrate for sulphuric acid forming thiobacilli. The method was selective for thiosulphate in the presence of hydrogen sulphide, sulphite, polysulphide and elemental sulphur. Reproducible results were obtained for thiosulphate concentrations of 5 mg l⁻¹ to 3 mg l⁻¹.

Sulphide, thiosulphate, sulphite, sulphate and polysulphide have been determined in paper mill waste waters⁴⁷ using a sulphide ion-selective electrode. The electrode is used as an indicator electrode in potentiometric titration with mercuric chloride. In 0.1 N sodium hydroxide medium, sulphide and polysulphides are titrated to form mercuric sulphide (and HgS_x). Mercuric ions, thiosulphate and sulphite can also be converted into thiosulphate and can be titrated; sulphite can be decomposed with formaldehyde and so thiosulphate can be titrated alone.

Spectrophotometric method

Bhat et al⁴⁸ reported methods for the determination of low levels of sulphides, sulphites and sulphates in waste waters. The method for sulphite and sulphide involves the reduction of the bis-2,9-dimethyl-1-10-phenanthroline copper II ion by sulphide in the presence of formaldehyde and by sulphite in its absence. In the method for sulphate, stannous chloride in hydrochloric acid is used to reduce sulphate ions to hydrogen sulphide which is reacted with bis-2,9-dimethyl-1-10-phenanthroline copper II ion.

All analyses are completed by measuring the absorbances due to the coloured copper I complex formed by chemical reduction. Whilst the methods are less than ideal from the point of view of sensitivity, simplicity and freedom from interferences, the colours formed are stable and the sulphate reduction system can be used repeatedly.

Ion chromatography

The ion chromatography of thiosulphate is discussed in [section 2.1.17](#) (multianion analysis).

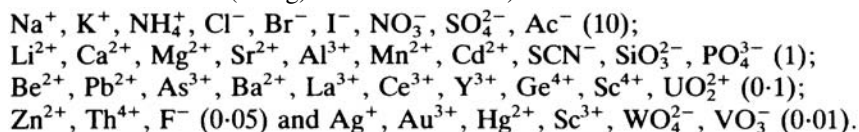
*2.1.15**Chromate**Spectrophotometric methods*

O-tolidine⁴⁹, *o*-nitrophenyl fluorone acid⁵⁰, 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol⁵¹ have been used as chromogenic reagents in the determination of hexavalent chromium (chromate) in waste waters. Qi and Zhu⁵⁰ reacted chromium VI with *o*-nitrophenyl fluorene in the presence of acetyltrimethyl ammonium bromide to form a purple red complex at pH 4.7–6.6 by heating at 50°C for 10 min. The wavelength of

maximal absorbance was 582 nm. Beer's law is obeyed up to $0.2 \mu\text{g l}^{-1}$ chromium VI. Interference due to copper II, iron III and aluminium III was eliminated by the addition of a masking agent containing potassium fluoride, trans 1,2-diaminocyclohexane tetraacetic acid and potassium sodium tartrate.

Wei et al⁵¹ described a spectrophotometric method for the determination of chromium VI in electroplating waste waters and total chromium (III, VI) in industrial waste waters using 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol. This was found to be the most sensitive reagent for chromium. The complex formed was very stable.

The effect of foreign ions on the determination of $10 \mu\text{g}$ of chromium III was examined. The following ions (when present in the amounts (in mg) shown in brackets) do not interfere:



Equal amounts of Fe^{3+} , Cu^{2+} , Co^{2+} , Ni^{2+} , Ga^{3+} , In^{3+} and Tl^{3+} produce positive errors.

Atomic absorption spectroscopy

Martin and Riley⁵² used this technique to determine hexavalent chromium in waste waters.

Differential pulse polarography

Harzdorf and Janser⁵³ applied this technique to waste water samples and investigated interference by other cations.

Miscellaneous

Pavel et al⁵⁴ examined the behaviour and persistence of trace amounts of chromium VI in waste water samples as a function of pH, container material, initial concentration and temperature. Based on these results they devised a method for preserving the hexavalent form of chromium; following adjustment to pH 7–8, addition of 10 per cent v/v of a solution containing 0.5 M sodium bicarbonate and 0.1 M EDTA (disodium salt) reduced losses of chromium VI to less than 20 per cent after 7 days, compared with a 60–80 per cent loss in unprotected samples.

2.1.16

Thiocyanate, cyanate and cyanide

Spectrophotometric method

Luthy et al⁵⁵ have described a spectrophotometric method for the determination of thiocyanate and cyanide in coal gasification waste waters. They showed that the copper pyridine method with pre-extraction was applicable but that high concentrations of carbonate and sulphide must first be removed from the sample.

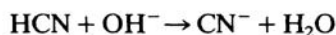
Botto et al⁵⁶ used *p*-phenylenediamine as the chromogenic reagent in the spectrophotometric determination of thiocyanate and uncomplexed cyanide in waste water.

Miscellaneous

Thieleman⁵⁷ attempted the separation of thiocyanate, cyanate and cyanide ions by thin layer and paper chromatography. Thin layer chromatography was not successful but these three ions were successfully separated by paper chromatography with the solvent methanol-pyridine-dioxan (7:2:1) in 7–8 hours. Cyanide and cyanate were identified by means of bromocresol purple and thiocyanate by 15 per cent ferric chloride solution, as spray reagent. Carbonate ions have the same R_F value as cyanide and cyanate.

Cyanide and cyanate in waste water have also been separated by paper chromatography⁵⁸. Separation is achieved by use of isopropyl alcoholethanol-water (9:4:3) as solvent with Filtrak FN 8 paper. After drying, the paper is sprayed with bromocresol green solution. On a green background the ions appear as clear blue spots (R_F values: cyanide, 0.04, cyanate 0.29). The spots may also be located by treating the paper with silver nitrate solution and exposing it to hydrogen sulphide.

Thiocyanate has been determined in waste water using a cyanide selective electrode⁵⁹. In this method thiocyanate is first converted to cyanogen bromide using bromine water. Excess bromine is removed by the addition of phenol. The cyanogen bromide is then converted to cyanide by the addition of sulphurous acid and then sodium hydroxide added. Cyanide was then estimated using the cyanide-selective electrode.

*Ion chromatography*

The ion chromatography of thiocyanate in wastewater is discussed in [section 2.1.17](#) (multianion analysis).

2.1.17

Multianion analysis

Ion chromatography has been applied to the analysis of mixtures of chloride and sulphite,^{60,61} fluoride, chloride, phosphate and sulphate⁶¹ and halides, nitrate, sulphate, sulphite, thiosulphate and thiocyanate⁶².

2.2**Cations**

2.2.1

Aluminium

The determination of aluminium is discussed in [section 2.2.32](#) (multication analysis).

2.2.2 Ammonium

Ion-selective electrodes

Ion-selective electrodes have been used for the determination of ammonium in waste waters⁶³⁻⁶⁶.

Evans and Partridge⁶⁴ used an ammonia probe for laboratory measurements of discrete free and saline ammoniacal nitrogen in a variety of waters, such as surface water, effluents, and sewage. The probe consisted of a glass pH electrode surrounded with a filling solution of ammonium chloride in contact with a gas-permeable hydrophobic membrane. The probe was tested on a number of samples of various origins, and the data obtained are compared with those obtained using existing methods for the determination of ammonia. The results indicate that determination should be possible with a precision of 4 per cent for levels greater than 0.4 mg l⁻¹ of ammoniacal nitrogen. The calculated lower limit of detection was 0.03 mg l⁻¹.

Ip and Pilkington⁶⁵ have discussed the development of a method for determining ammonium in waste water using a gas sensing electrode. In this method one ml of 10 M sodium hydroxide is added to 100 ml of the waste water sample and the equilibrium potential, E_1 , is measured. Next, 2.00 ml of 1000 mg l⁻¹ ammonium nitrogen solution are added to the solution and the new equilibrium potential E_2 , is measured. Thus the change in potential caused by the standard addition is known.

The ammonium nitrogen concentration in the water can be calculated, using the following equation or by using a nomogram. Because the nomogram has been developed specifically for this procedure, it is important that this procedure be followed carefully.

Let the concentration of ammonium nitrogen in the unknown solution be 'C'. The initial electrode potential, E_1 after the addition of 1 ml of 10 M sodium hydroxide to 100 ml of sample, may be represented

$$E_1 = E_0 - S \log_{10} \frac{C \times 100}{101}$$

where S is the electrode slope.

After the addition of 2.00 ml of 1000 mg l⁻¹ ammonium nitrogen solution, the electrode potential E_2 is given by:

$$E_2 = E_0 - S \log_{10} \left\{ \frac{(C \times 100) + (2 \times 1000)}{103} \right\}$$

Thus

$$-\Delta E = -(E_2 - E_1) = S \log \left[\frac{\frac{100C + 2000}{103}}{\frac{100C}{101}} \right]$$

where

$$C = \frac{20}{\left[\frac{103}{101} \times 10^{-\Delta E/S} - 1 \right]}$$

In this derivation of the equation, it is assumed that there is no change in the activity coefficient of the ammonium nitrogen when the standard addition is carried out and also that there is no complexing of the ammonia, either before or after the standard addition. In cases where complexing is suspected, ethylenediamine tetraacetic acid may be added to the 10 M sodium hydroxide solution.

Stark microwave cavity resonator

This technique has been applied to the determination of ammonium in petrochemical industry waste waters⁶⁶. The sample is first made strongly alkaline with sodium hydroxide and ammonia collected in a dialyser.

Hall and Dawes⁶⁷ have described an automated procedure for the determination of ammonia and total kjeldahl nitrogen in waste water.

2.2.3

Antimony

A method for determining antimony in industrial waste involves reaction of antimony III with iodide in sulphuric acid (1–4M) and extraction of iodo complex with amidines into chloroform for spectroscopic evaluation in amounts down to $0.2 \mu\text{g l}^{-1}$ ⁶⁸.

The analysed antimony in waste water is also discussed in [section 2.2.32](#) (multication analysis).

2.2.4

Arsenic

Non-dispersive atomic fluorescence spectrometry

Non-dispersive atomic fluorescence spectrometry after hydride generation has been used to determine down to 0.5 ng arsenic in waste waters⁶⁹. In this method, reductions are performed using either sodium borohydride⁷⁰ or zinc/stannous chloride/potassium iodide⁷¹.

Arsine generated by reduction for 60 and 80 s in the sodium borohydride method or the zinc-stannous chloride-potassium iodide method respectively, is introduced into the premixed argon (entrained air)-hydrogen flame (hydrogen, 4.01 min^{-1} ; argon carrier gas, 4.01 min^{-1} ; argon auxiliary gas, 2.01 min^{-1}) and is atomized in the flame. Fluorescence, excited with an arsenic electrodeless discharge lamp, is detected at right angles to the axis of the optical path with a 'solar blind' photomultiplier (R-166, Hamamatsu TV Co.) and recorded simultaneously on a pen recorder and a digital integrator for peak height and peak area measurements, respectively.

The effects of 1000 fold amounts of diverse elements on the fluorescence signal of 500 ng of arsenic are shown in [Table 30](#). [Table 30](#) also compares the result of the interference study for the zinc reduction method with those for the sodium borohydride method.

The determination of arsenic is also discussed in [section 2.2.32](#) (multication analysis).

2.2.5

Barium

Graphite furnace atomic absorption spectrometry

Graphite furnace atomic absorption spectroscopy has been used to determine barium in paper mill waste waters⁷².

The determination of barium is also discussed in [section 2.2.32](#) (multication analysis).

TABLE 30
Effect of diverse elements on the a.f.s. of arsenic

Element	Compound added	Relative atomic fluorescence signal		
NaBH ₄ method		Zn-SnCl ₂ -KI method		
		Peak height ⁷¹		
Peak height	Peak area			
Au	HAuCl ₄	0.01	0.01	1.01
Co	CoCl ₂	0.28	0.28	0.89
Fe	FeCl ₃	0.49	0.56	0.88
Ni	NiCl ₂	0.06	0.05	0.88
Pd	PdCl ₂	0.00	0.01	0.05
Pt	H ₂ PtCl	0.00	0.01	0.07
Bi	Bi(NO ₃) ₃	5.89	6.95	0.84
Sb	SbCl ₃	0.40	0.57	0.51
Se	SeO ₂	0.51	0.44	0.76
Sn	SnCl ₂	0.30	0.35	—
Te	metal in HCl	0.19	0.20	0.41

No interference in the NaBH₄ method: Ag^b, Al^c, B^c, Ba^d, Be^c, Ca^c, Cd^c, Ce^b, Cr^d, Cs^b, Cu^b, Ga^b, Hg^d, In^b, K^b, La^c, Li^d, Mg^b, Mn^b, Na^b, Pb^b, Rb^b, Si^b, Sr^b, Tl^c, V^b, W^b, Y^b and Zn^b.

^a Relative atomic fluorescence signal of 0.9–1.1.

^b No interference in the Zn-SnCl₂-KI method.

^c Relative atomic fluorescence signal of 0.8–0.9 except for boron which gives a relative atomic fluorescence signal of 1.15 in the Zn-SnCl₂-KI method⁷¹.

^d Relative atomic fluorescence signal of 0.3–0.8 in the Zn-SnCl₂-KI method⁷¹.

2.2.6

Beryllium

The determination of beryllium is discussed in [section 2.2.32](#) (multication analysis).

227

Bismuth

The determination of bismuth is discussed in [section 2.2.32](#) (multication analysis).

2.2.8

Boron

The determination of boron is discussed in [section 2.2.32](#) (multication analysis).

2.2.9 *Calcium*

Flow injection analysis

Hansen et al⁷³ investigated the use of automated flow injection analysis for the determination of calcium in waste water.

Spectrophotometric (i.e. total calcium as *o*-cresolphthalein complexone) and calcium-selective electrodes (uncomplexed calcium) were investigated as detectors for calcium.

The flow cell⁷⁴⁻⁷⁷ housed an indicator electrode and a saturated calomel reference electrode (Radiometer K401). The electrode signals were monitored with a digital pH meter connected to a recorder furnished with an 500 mV interface (Radiometer). Additionally an interface unit was inserted between the pH meter and the recorder, this allows the peak maximum value to be locked automatically on the meter and read to within 0.1 mV while the recorder was still continuously registering the actual potential output⁷⁷.

The membrane of the calcium electrode, based on the calcium salt of di-(*n*-octylphenyl)phosphoric acid dissolved in dioctylphenylphosphonate and incorporated into PVC⁷⁸ was mounted on a PVC tube of the type used in the standard Radiometer Selectrode (F 2002) which comprises an internal silver-silver chloride reference electrode. The inner reference solution was 1×10^{-2} M calcium chloride. The procedure gives satisfactory results for waste water samples.

Very good agreement was found between the values obtained with the calcium electrode and those recorded by spectrophotometry and atomic absorption titration.

The determination of calcium is also discussed in [section 2.2.32](#) (multication analysis).

2.2.10 *Cadmium*

Spectrophotometric method

Chung-gin et al⁷⁹ have described a spectrophotometric method utilizing Cadion (*p*-nitrobenzene diazaminobenzene-*p*-azobenzene) reagent for the determination of microgram amounts of cadmium in waste waters. Triton X100 is used as a solubilizing agent, and a mixture of ascorbic acid. Rochelle salt, potassium cyanide and potassium fluoride are used to mask interfering ions. The cadmium-cyanide complex is demasked by addition of excess formalin, and the coloured complex formed with Cadion is measured directly at 480 nm without separation.

The effect of foreign ions on the determination of cadmium by this procedure is listed in [Table 31](#).

Miscellaneous

Malz and Reichert⁸⁰ have reviewed the determination of cadmium in waste waters.

The determination of cadmium is also discussed in [section 2.2.32](#) (multication analysis).

Effect of cations on determination of 4 μg of Cd

Cation (mg)	Cation/Cd (w/w)		Cd found (μg)	Error (μg)	Anion (mg)	Anion/Cd (w/w)		Cd found (μg)	Error (μg)
Cu(II)	4.0	1000	4.11	+0.11	Dichromate	1.2	300	4.17	+0.17
Fe(II)	1.6	400	4.10	+0.41	Nitrate	10.0	2 500	3.94	-0.06
Ni(II)	3.2	800	3.99	-0.01	Chloride	10.0	2 500	3.91	-0.09
Co(II)	0.5	125	4.05	+0.05	Sulphate	10.0	2 500	3.82	-0.18
Zn(II)	10.0	2500	3.97 ^a	-0.03	Phosphate	10.0	2500	3.96	-0.04
	0.4	100	4.09	+0.09	Pyrophosphate	10.0	2500	4.07	+0.07
Ca(II)	5.0	1250	4.03	+0.03	Carbonate	10.0	2 500	3.95	-0.05
Mg(II)	5.0	1250	3.85 ^b	-0.15	Oxalate	10.0	2500	4.00	0.00
	0.3	75	4.01	+0.01	Fluoride	10.0	2500	3.99	-0.01
Cr(III)	0.8	200	4.20	+0.20	Cyanide	10.0	2500	3.92	-0.08
Ag(I)	0.4	100	4.09 ^c	+0.09	Sulphide	0.01	2.5	4.12	+0.12
Pb(II)	10.0	2500	3.97	-0.03		1.0	250	3.92 ^d	-0.08
Hg(II)	0.04	10	3.92	-0.08	Arsenate	10.0	2500	4.01	-0.01
NH ₄ (I)	10.0	2500	3.82	-0.18	Citrate	10.0	2500	3.94	-0.06
Ti(IV)	0.08	20	4.01	+0.01	Tartrate	10.0	2500	3.93	-0.07
Al(III)	2.0	500	3.94	-0.06	Nitrilotriacetate	0.5	125	4.00	0.07
Sb(III)	1.0	250	4.00	0.00	Ethylenediaminetetraacetate	0.03	7.5	4.01	+0.01
Sn(IV)	0.8	200	3.99	-0.01		1.0	250	3.94 ^d	-0.06
Sn(II)	1.0	250	4.19	+0.19					
K(I)	10.0	2 500	3.94	-0.06					
Na(I)	10.0	2500	3.91	-0.09					
Bi(III)	0.6	150	3.95	-0.05					
Ba(II)	5.0	1250	4.19	+0.19					
Mn(II)	1.0	250	4.17	+0.17					

^a Concentration of KOH 0.4 M.

^b Addition of KF, stood for 30 min, then filtered and washed with small amount of water.

^c KOH and KCN were added together.

^d Digested with H₂SO₄-HNO₃ mixture before the determination.

2.2.11 Chromium

Titration

Wendl⁸¹ has described a titration method for determining down to 5 $\mu\text{g l}^{-1}$ chromium in dipworks and tanning waste waters.

Spectrophotometric method

Yanagisawa et al⁸² have described a method for the determination of trivalent (and hexavalent) chromium in waste waters.

In this method an aliquot of the sample containing up to 40 μg of chromium as chromium VI and chromium III is adjusted to pH 4 by addition of acetate buffer solution and treated with 2 per cent sodium diethyldithiocarbamate solution. The resulting chromium VI complex is extracted with isobutyl methyl ketone and the atomic absorption is measured at 357.9 nm (air-nitrous oxide) or, preferably, air-acetylene flame). Another aliquot of solution is adjusted to pH 6 with acetate buffer solution and treated with 1 per cent ethanolic 8-hydroxyquinoline (or 2-thenoyltrifluoroacetone) on a steam bath for 5 min. The chromium III complex is extracted into isobutyl methyl ketone and the absorption of the solution is measured as above. The determination of 25 μg of chromium was unaffected by the presence of 1 mg of iron, copper, aluminium, vanadium or molybdenum.

Chemiluminescence method

Dubovenko et al⁸³ determined chromium in waste waters by a chemiluminescence method using 4-diethylaminophthalhydrazide in potassium hydroxide. Total chromium, i.e. chromium III plus chromate, was determined by first reducing chromate to chromium III with hydrogen peroxide and measuring the chemiluminescence due to chromium III. Chromate ion was determined by difference between initial and final chromium III concentrations.

The determination of chromium is also discussed in [section 2.2.32](#) (multication analysis).

2.2.12

Cobalt

See [section 2.2.32](#) (multication analysis).

High performance liquid chromatography

See [section 2.2.32](#) (multication analysis).

2.2.13

Copper

See [section 2.2.32](#) (multication analysis).

High performance liquid chromatography

See [section 2.2.32](#) (multication analysis).

2.2.14

*Iron**Polarography*

Tackett and Wieselmann⁸⁴ used polarography to simultaneously determine iron II and iron III in coal mine waste waters. In this method, 10 ml sample of water is mixed with 15 ml of supporting electrolyte (0.5 M in sodium carbonate and in oxalic acid) and polarograms are recorded from 0.1 to -0.9 V vs the SCE at 30°C and pH 3. Diffusion currents for iron II and iron III are found by subtracting the residual current value from the diffusion current values at 0.1 V and at -0.6 V respectively. Calibration graphs for both species are rectilinear up to 500 mg l⁻¹. For a mixture containing 125 mg l⁻¹ of each species the coefficient of variation is 0.96 per cent for iron II and 1.36 per cent for iron III.

The determination of iron is also discussed in [section 2.2.32](#) (multication analysis).

2.2.15

Lead

See [section 2.2.32](#) (multication analysis).

High performance liquid chromatography

See [section 2.2.32](#) (multication analysis).

2.2.16

*Lithium**Atomic absorption spectrometry*

Thompson and Cummins⁸⁵ determined lithium in waste waters by atomic absorption spectrometry using an air/acetylene flame. The technique is prone to chemical interference. Using the hotter dinitrogen oxide/acetylene flame minimizes interference. To achieve acceptable precision of a relative standard deviation of less than 1 per cent, an intense lithium source must be used.

The lithium tracer technique is frequently employed in the water industry to determine the flow of raw or waste waters in open channels or pipes. The results are often used for the calibration of flow meters.

In the dinitrogen oxide/acetylene flame the lithium response was virtually independent of potassium concentration over the range 500–200 µg ml⁻¹ of potassium. This indicated a negligible chemical interference effect in this hotter flame.

The determination of lithium is also discussed in [section 2.2.32](#) (multication analysis).

2.2.17

Magnesium

See [section 2.2.32](#) (multication analysis).

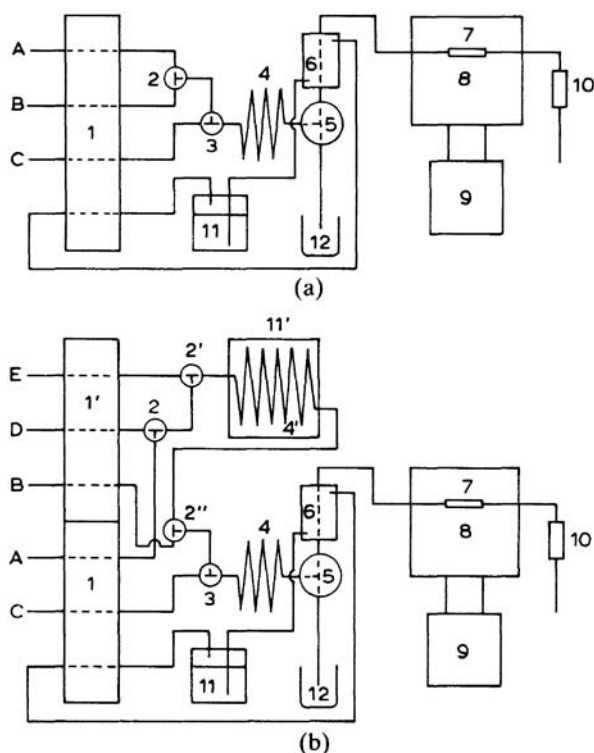


Fig. 29. Schematic diagrams of the continuous monitoring system for inorganic (a) and total mercury (b) in water. (1,1') Peristaltic pump; (2, 2', 2'') mixing joints for sample and reagents; (3) mixing joint for air and mixed solution; (4) reaction coil for sample reduction and mercury vapour extraction (polyethylene tubing 60 cm×1 mm i.d.); (4') reaction coil for sample digestion (teflon tubing, 10 m x 1 mm i.d.); (5) gas liquid separator; (6) condenser; (7) flow cell (8 μ l); (8) UV photometer (253.7 nm); (9) recorder; (10) mercury vapour absorbent; (11) water bath (0°C); (11) water bath (80°C); (12) waste reservoir, A, B, C, D and E are inlets for sample reducing reagent, air, acid reagent and oxidizing reagent respectively.

2.2.18 Manganese

See [section 2.2.32](#) (multication analysis).

2.2.19 Mercury

Atomic absorption spectroscopy

Goto et al⁸⁶ have given details of an automated system for continuous monitoring of down to 0.1 μ g l⁻¹ total and inorganic mercury in water and waste waters by cold vapour atomic absorption spectrometry.

[Fig. 29](#) shows schematic diagrams of the apparatus for continuous monitoring of inorganic and total mercury. One or two peristaltic pumps were used for feeding sample, air, cold water and three reagents.

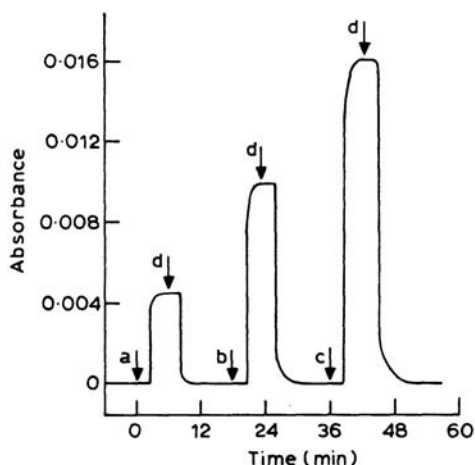


Fig. 30. Typical response for the determination of total mercury. Concentration of sample pumped (mg l^{-1}); (a) 2.0; (b) 4.0; (c) 6.0; (d) 0. Flow rates (ml min^{-1}); sample 3, 2, air 3, 5 acid reagent 0.5, oxidizing reagent 0.5, reducing reagent 0.5.

The three reagents comprised are potassium phenoxysulphate (to convert organic mercury to inorganic mercury), and 5 per cent sulphuric acid and stannous chloride (to convert inorganic mercury to elemental mercury). A UV photometer with a gas flow cell (1 mm i.d. 10 mm long with quartz end windows) and a pen recorder (Rika Denki, model R-20) was used for measuring and recording the absorbance based on mercury vapour.

Fig. 30 shows a typical response for the determination of total mercury. The different standard samples and the blank solution were pumped alternately. The concentrations of the samples pumped were in the range 2.0–6.0 $\mu\text{g l}^{-1}$. With the flow rates used the response time was about 5 min.

Flow injection analysis

Birnie⁸⁷ has applied automated flow injection analysis coupled with coldvapour atomic absorption spectrometry to the determination of inorganic mercury and total mercury in waste water.

Comparison of methods

Lugowska and Rubel^{88,89} compared potentiometric, dithizone, spectrophotometric and atomic absorption (253.7 nm) methods for the determination of mercury in waste waters. Potentiometric titration with dithio-oxamide has adequate sensitivity and selectivity. The potentiometric titration procedure with dithio-oxamide is preceded by preliminary separation of mercury by reduction^{89,90}.

Silver, even in a significant excess compared to mercury does not affect the determination whereas copper significantly decreases the results. The positive error in the presence of iodide and bromide results from their oxidation to bromine and iodine by potassium permanganate.

Extraction with dithizone in sulphuric acid medium is suitable for determinations of above 0.005 mg l^{-1} mercury; the relative standard deviation ($n=7$) varying from 0.005 to 0.03 mg l^{-1} Hg to 0.1 to 0.005 mg l^{-1} Hg. Interference from many metal ions occurring in water and wastes are few, but copper and silver are

coextracted with mercury. In the presence of these two ions, satisfactory results were obtained when modifications were applied.

- (a) Extraction from 0.02 M acetate buffered medium in presence of EDTA and thiocyanate as masking agents, coupled with back-extraction of silver in the aqueous phase by shaking the dithizone extract with acidified sodium chloride solution.
- (b) Determination of mercury as in the absence of copper and silver, after its preliminary separation by the reduction method⁹⁰.

Application of the extraction separation from acetate buffered medium as in modification (a) makes it possible to determine mercury even in the presence of 1000 fold amounts of copper and 100 fold amounts of silver so that this method is suitable in the analysis of industrial waters and wastes. Modification (b) gives selective separation of mercury from other ions, including copper and silver, but for satisfactory mercury results, it is necessary to wait for 2 hours after reduction of excess of permanganate before extraction. Otherwise the results show positive errors and irreproducibility.

The three methods were applied to waste water samples rich in organics. Just after sampling, the samples were stabilized by nitric acid (20 ml l⁻¹ of waste) or sulphuric acid (5 ml l⁻¹) plus permanganate to give a stable colour. Prior to analysis the sample was mineralized by adding 3 ml concentrated sulphuric acid and 3 ml concentrated nitric acid per 25 ml sample, and potassium permanganate to give a stable colour. The mixture was then heated for 2 hours at 120–130°C and excess permanganate decomposed by 30 per cent hydrogen peroxide. Results obtained by the three procedures are tabulated in Table 32.

The potentiometric titration of mercury with dithiooxamide, especially combined with preliminary separation of mercury by reduction, is applicable in the analysis of different types of industrial wastes. In comparison to the atomic absorption spectrometric and spectrophotometric methods, the potentiometric determination has a worse detection limit, though it is adequate for waste analysis, and is more time-consuming. Nevertheless, it has significant advantages of simplicity and economy. The apparatus is simple, and the reagents are easy to prepare and stable and do not require special purification. The selectivity is similar to that of the dithizone method. When interfering ions are present, the preliminary reduction separation of mercury increases the time required by only 20 min. Titrations can be done directly after reduction of the excess of permanganate in the absorbing solution.

This preliminary separation provides limits of determination similar to those of the other two methods.

TABLE 32
Comparison of the results of mercury determination in industrial waste samples by three different methods

	Potentiometric titration	Dithizone method	A.a.S.
Waste I			
Hg found (mg l ⁻¹)	0.161	0.137	0.161
<i>n</i>	7	7	7
<i>s</i>	0.014	0.007	0.004
<i>s_r</i>	0.089	0.048	0.024
μ^a	0.161±0.013	0.137±0.007	0.161±0.04
Waste II			
Hg found (mg l ⁻¹)	8.40	8.30	8.40
<i>n</i>	9	7	7

	Potentiometric titration	Dithizone method	A.a .S.
s	0	0.10	0.28
s_r	0	0.01	0.03
μ	8.40±0.00	8.30±0.01	8.40±0.26
Waste III			
Hg found (mg l ⁻¹)	2.48	2.46	2.36
n	5	5	5
s	0.03	0.15	0.13
s_r	0.01	0.06	0.06
μ	2.48±0.03	2.46±0.19	2.36±0.17
waste IV			
Hg found (mg l ⁻¹)	5.07	5.54	5.86
n	6	6	6
s	0.12	0.06	0.09
s_r	0.02	0.01	0.01
μ	5.07±0.13	5.54±0.07	5.86±0.11

^a Mean result±standard deviation (95 per cent confidence limit).

Miscellaneous

Malz and Reichert⁹¹ have reviewed the determination of mercury in waste waters.

Preconcentration

Bhattacharyya⁹² used a liquid chelating exchange, a beta-keto derivative of Versatic-10, to extract mercury selectively from waste waters prior to its determination by cold-vapour atomic absorption spectrometry.

2.2.20

Molybdenum

Spectrophotometric method

Bilikhova⁹³ has described a spectrophotometric procedure utilizing dithiol (3,4-toluene dithiol) for the determination of down to 0.01 $\mu\text{g l}^{-1}$ molybdenum in waste waters.

Dithiol in a strongly acid medium of sulphuric acid forms a green coloured complex, which after separation into carbon tetrachloride, or chloroform, is determined spectrophotometrically at an absorption maximum of 682 nm against the blank. This technique is only applicable to samples which are free from copper II and which do not contain more than 0.5 mg of iron III or other metals in the sample volume taken for analysis.

If after the preliminary extraction the sample is still coloured, it is necessary to repeat the extraction with petroleum ether and this step must be included in the calibration procedure. If the sample contains copper II then the procedure is modified as follows: add to the 1100 ml of sample, 2 ml 1+1 sulphuric acid, 3 ml of ducpral, mix and leave to react for 10 min. Then add 10 ml of petroleum ether and extract for 10 min. If

necessary repeat the petroleum ether extractions until the sample is free from colour. Separate the phases and to 11 of the water layer, add 3 ml dithiol reagent. After 10 min, extract the water phase with 10 ml carbon tetrachloride and evaluate at 682 nm. Dicapral reacts with copper II forming a yellow brown complex compound, meanwhile mercury II, silver I, selenium IV and cerium IV get bound into colourless complexes. Those components are removed by extraction with petroleum ether together with organic coloured substances.

The determination of molybdenum is also discussed in [section 2.2.32](#) (multication analysis).

2.2.21

Nickel

See [section 2.2.32](#) (multication analysis).

High performance liquid chromatography,

See [section 2.2.32](#).

2.2.22

Selenium

Atomic absorption spectrometry

In this method⁹⁴ a nitric perchloric acid digest of the sample is injected onto a carbon rod and evaluated at 196 nm. Iron, molybdenum, aluminium, chromium, copper, manganese, nickel, and zinc are tolerated at 1000 fold excess and bismuth, lead and vanadium in 150 fold excess.

Krivan et al⁹⁵ carried out a radioactive tracer diagnostic investigation of the determination of selenium in waste water by hydride generation atomic absorption spectrometry. This procedure involved preliminary treatment of the sample with hydrogen peroxide and hydrochloric acid. Apparent losses of selenium were attributed to chlorine induced back oxidation of selenium IV to selenium VI.

The determination of selenium is also discussed in [section 2.2.32](#) (multication analysis).

2.2.23

Sodium

Miscellaneous

Ranzen and Solov'eva⁹⁶ determined sodium concentrations in waste waters by measuring pNa values. The determination was performed potentiometrically with use of a sodium responsive glass electrode. For solutions containing up to 20 m equiv. of sodium salts the instrument can be calibrated with solutions of known concentration but for more concentrated solutions the calibration must be carried out with solutions of known activity. Measurements obtained on the scale (pNa) are converted into concentration by use of activity coefficient calculated from the Debye-Huckel equation.

The determination of sodium is also discussed in [section 2.2.32](#) (multication analysis).

2.2.24

Strontium

See [section 2.2.32](#) (multication analysis).

2.2.25

Tantalum

See [section 2.2.32](#) (multication analysis).

2.2.26

Tellurium

See [section 2.2.32](#) (multication analysis).

2.2.27

*Thallium**Spectrophotometric method*

Raikova et al⁹⁷ determined thallium in waste water by a spectrophotometric method using methyl violet as the chromogenic reagent and extraction of the coloured complex into benzene. For 2.2 mg l⁻¹ M thallium the standard deviation was 80 µg l⁻¹ and the coefficient of variation was 3.6 per cent. The sensitivity was 0.2 mg l⁻¹ and there was no interference from antimony or gold.

The determination of thallium is also discussed in [section 2.2.32](#) (multication analysis).

2.2.28

Tungsten

See [section 2.2.32](#) (multication analysis).

2.2.29

*Uranium**Flow injection analysis*

Attalah et al⁹⁸ described a continuous flow solvent extraction system for the determination of traces of uranium in nuclear plant reprocessing solutions. Methyl-isobutyl ketone was used as the extraction solvent and 2-(5-bromo-2-pyridylazo)-5-(diethylamino) phenol in methanol as the chromogenic reagent.

The determination of uranium is also discussed in [section 2.2.32](#) (multication analysis).

2.2.30 Vanadium

Spectrophotometric method

A spectrophotometric method has been described for the determination of vanadium in waste water. The determination of vanadium in waste water is also discussed in [section 2.2.32](#) (multication analysis).

2.2.31 Zinc

Differential pulse polarography

Zinc has been determined in waste water by differential pulse polarography¹⁰⁰.

The determination of zinc in waste water is also discussed in [section 2.2.32](#) (multication analysis).

High performance liquid chromatography

See [section 2.2.32](#) (multication analysis).

2.2.32 Multication analysis

Atomic absorption spectrometry

Applications of atomic absorption spectrometry to waste water analysis have been reviewed by Ediger¹⁰¹ and Fisher¹⁰².

Ediger¹⁰¹ discusses the determination by graphite furnace atomic absorption spectrometry of calcium, magnesium, cadmium, mercury, nickel, selenium, antimony, thallium and zinc, in paper mill waste waters.

Okuso et al¹⁰³ successfully established conditions for the determination of cadmium, zinc, copper and lead in waste water by atomic absorption spectrometry. They examined the effect of various mineral acids on depressant effects in the determinations of these elements in waste waters and concluded that these effects did not occur in samples containing up to 0.1 N nitric acid, hydrochloric acid, acetic acid or perchloric acid. They also discuss enhancement and interelement effects and the avoidance of these.

Hicks et al¹⁰⁴ discuss the effects of low concentrations of miscible organic solvents on the determination of cobalt, chromium, copper, iron, cadmium, beryllium, sodium and calcium in waste waters. They observed no effect when concentrations of ethyl alcohol, acetone, ethyl acetate and acetic acid were less than 0.1 per cent although enhancements occurred with all these metals when the sample contained 5 per cent of organic solvent.

Ediger¹⁰¹ determined low levels of arsenic, selenium, bismuth and antimony in waste waters using hydride generation atomic absorption spectrometry.

Hwang et al¹⁰⁵ applied this technique to the determination of arsenic, selenium, antimony and mercury in waste waters. Antimony, selenium and arsenic were determined at 217.7, 196.0 and 193.7 nm respectively with corresponding sensitivities of 30, 5 and 4 ng. Coefficients of variation were 2.6, 3.0 and 2.8 per cent

for arsenic ($0.2 \mu\text{g}$), selenium ($0.2 \mu\text{g}$) and antimony ($1 \mu\text{g}$) respectively. For the determination of 5 ng of mercury the coefficient of variation was 4 per cent.

Zeeman atomic absorption spectrometry

The heavy matrix component of many waste water samples makes analysis of them by conventional atomic absorption techniques difficult. In such circumstances, Zeeman effect background correction is mandatory. If a sample in a graphite furnace atomizer is volatilized into an atmosphere in thermal equilibrium, peak area integration can eliminate variations in the atomization rate caused by distinct properties of different compounds of the same element within sample and reference solutions. This means that integrating over the signal (peak area) instead of measuring peak height can be used to eliminate condensed phase interferences in a stabilized temperature platform furnace.

Vollkopf et al¹⁰⁶ used a stabilized temperature platform with Zeeman effect background correction for the determination of cadmium, lead and chromium in waste water.

If phosphoric acid or ammonium is added as modifier in the determination of lead the maximum pretreatment temperature is about 850°C , the optimum atomization temperature 1700°C .

The advantage of peak area integration was demonstrated in the determination of chromium in waste water. Fifty μg of magnesium nitrate was added to each sample aliquot ($20 \mu\text{l}$) as matrix modifier. A thermal pretreatment temperature of 1600°C and an atomization temperature of 2500°C were used in the determination of chromium.

As matrix modifier, $100 \mu\text{g}$ ammonium dihydrogen phosphate was added to each sample aliquot in the graphite tube in the determination of cadmium. The addition of $5 \mu\text{g}$ magnesium nitrate caused almost no correction problem. A thermal pretreatment temperature of 800°C could be used. Higher pretreatment temperatures led to analysis element losses. In the presence of $10 \mu\text{g}$ and $20 \mu\text{g}$ magnesium nitrate, cadmium is thermally more stable and therefore a pretreatment temperature of 900°C may be applied but an overcorrection becomes visible. This means that magnesium nitrate has in combination with ammonium phosphate an additional stabilizing effect on cadmium. But this mixed modifier cannot be recommended when a spectrometer with continuum source background correction is used. If the Perkin Elmer Zeeman 5000 System is used, the thermal pretreatment temperature may be increased to about 1000°C when a matrix modifier containing $100 \mu\text{g}$ ammonium dihydrogen phosphate and $20 \mu\text{g}$ magnesium nitrate is added to the sample.

Without matrix modification the maximum thermal pretreatment temperature is about 300°C . The addition of $500 \mu\text{g}$ ammonium dihydrogen phosphate permits thermal pretreatment temperatures of up to 750°C . The addition of a mixed modifier containing magnesium nitrate and ammonium dihydrogen phosphate allows maximum pretreatment temperatures of up to 1000°C . The same stabilizing effect is achieved when small amounts of sodium chloride (about $25 \mu\text{g}$) are added to the ammonium phosphate. However, sodium chloride itself produces background and therefore, magnesium nitrate is generally preferred.

Fig. 31 shows the addition curve for cadmium in the waste water sample shown earlier in comparison to the analytical curve. Using the mixed modifier, $100 \mu\text{g}$ ammonium dihydrogen phosphate plus $20 \mu\text{g}$ magnesium nitrate, a direct determination of cadmium in this waste water is possible. The characteristic mass for cadmium was calculated to be $0.35 \text{ pg}/0.0044 \text{ A s}$.

Drying of the sample aliquot within two program steps is recommended. It permits proper sample drying even for more viscous matrices. The additional thermal pretreatment step (step 4) ensures that there is no more cool inert gas streaming into the tube from the inlets when the atomization cycle starts. Step 7 is an

additional cool-down step which is necessary to cool down the platform to ambient temperature. The matrix modifier is typically pipetted automatically by the AS-40 autosampler using the alternate volume position. In general, a modifier volume equal to the sample volume (10 μl in this example) is used. If the added modifier volume is too small and a viscous sample was pipetted prior to the modifier, reproducibility problems may occur. They are caused by a rolloff of the modifier from the sample.

Inductively coupled plasma atomic emission spectrometry

Klok et al¹⁰⁷ applied this technique to the determination of boron, molybdenum, zirconium, tantalum and tungsten in waste waters and surface waters. The method can be used in conjunction with the hydride technique, allowing much lower detection limits in the cases of arsenic, selenium, bismuth, antimony, tellurium and lead. The precision is better than 3 per cent at concentrations over 100 times the detection limits. A 3 ml sample containing 40 elements can be determined in less than 1 min.

To optimize inductively coupled plasma working conditions, spectral interferences and the carrier gas flow were examined by Delijska and Zadgorska¹⁰⁸. The influence of high salt content or sulphuric acid were eliminated by using a peristaltic pump, dilution or internal standardization.

A method for the determination of aluminium, calcium, cadmium, copper, iron, magnesium, manganese, nickel, lead and zinc in waste waters and industrial solution was developed. Relative standard deviations were 0.5–5.0 per cent.

Blakemore et al¹⁰⁹ simultaneously determined ten elements in waste water by inductively coupled plasma emission spectrometry with electrothermal atomization.

X-ray fluorescence spectrometry has been applied¹¹⁰ to the determination of seven priority pollutants in waste water. 100–500 ml sample solution is formed filter paper. All of the measured X-ray lines, except Pb L α are the K α lines of the analysed ions.

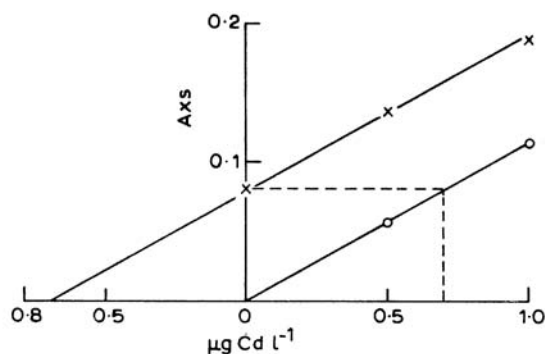
transferred into a beaker and 5 ml of 10 wt-per cent sodium acetate solution and 5 ml of the sodium diethyl dithiocarbamate solution added. The pH is adjusted to 6.0 ± 0.1 then the solution transferred into a separating funnel, and 10 ml of diisobutyl ketone added accurately. The separating funnel is shaken vigorously for 1 min and allowed to stand for about 5 min. 100 μl of the solvent phase is loaded on the centre of the formed filter paper, which is then air-dried at room temperature. Measure the X-ray fluorescence intensity for 100 s by using a cylindrical sample holder. Measure background intensity on the blank

In [fig. 32](#) are shown metal recoveries as a function of sample pH. The recovery of cobalt II, nickel II, copper II and lead was almost 100 per cent in the pH range 4–8 when a standard $200 \mu\text{g l}^{-1}$ solution of each metal ion was examined. The recovery of manganese II, iron III and zinc II decreased at pH values below 5. The manganese DDTC compound was unstable in the diisobutylketone phase and 10–20 per cent of its decomposition occurred during 15 min of the standing time after the extraction. The decomposition was negligible within 5 min after the extraction. The recommended pH is 6.7 ± 0.1 .

Precisions achieved in this method ranged from 1 to 9 per cent in the concentration range $1\text{--}100 \mu\text{g l}^{-1}$. Detection limits are in the range $8\text{--}40 \mu\text{g l}^{-1}$ for the seven elements studied.

Murata et al^{111–113} used an ion exchanger epoxy resin pelletization method to preconcentrate waste water samples for X-ray fluorescence analysis. The method was applied to the micro analysis of manganese, iron, nickel, copper, zinc, strontium, barium, lead and bismuth ions in industrial waste water. Detection limits of these metals ions based on a 500 ml sample solution are 5, 12, 5, 8, 4, 9, 300, 17 and $20 \mu\text{g l}^{-1}$ respectively.

Hellmann and Griffatong¹¹⁴ determined the optimum conditions for the determination by X-ray fluorescence of zinc, copper, nickel, lead, cobalt, manganese, iron and chromium in waste water. The sample (101) was filtered through a bed of Amberlite IR-120 ion-exchange resin in the sodium form to



Furnace Parameters for Direct Determination of Cd in Wastewater

Wavelength	228.8 nm						
Light source	EDL						
Graphite tube	Pyrocoated						
Platform	Yes						
Matrix modifier	500 μg $\text{NH}_4\text{H}_2\text{PO}_4$ + 10 μg $\text{Mg}(\text{NO}_3)_2$						
Sample volume	10 μl						
Alt. volume	10 μl						
HGA Program							
Step	1	2	3	4	5	6	7
Temp ($^{\circ}\text{C}$)	90	150	900	900	1700	2600	20
Ramp (s)	1	15	20	1	0	1	1
Hold (s)	15	15	30	4	3	5	9
Read					×		
Rec.					-3		
Int. flow (ml/min)				Gas stop	Gas stop		

Fig. 31. Cadmium in waste water; graphic evaluation of analyte addition technique; 100 μg $\text{NH}_4\text{H}_2\text{PO}_4$ +20 μg $\text{Mg}(\text{NO}_3)_2$ as matrix modifier. pre-concentrate the metals. The metals were then eluted with sodium chloride solution and converted to their diethyl dithiocarbamates prior to embedding the precipitate in a cellulose disc for X-ray analysis.

Differential pulse voltammetry

Clark et al¹¹⁵ described a system combining differential pulse anodic stripping voltammetry and differential pulse polarography in an on-line automatic analysis of trace metals in waste water. Chromium, nickel, zinc, cadmium, lead and copper were studied.

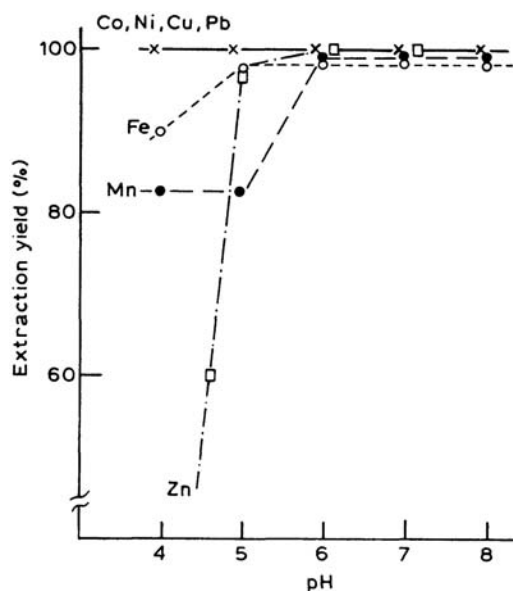


Fig. 32. Extraction yield of metal ions with DDTC-DIBK as a function of pH. Amount of metal ion: 100 μg .

High performance liquid chromatography

The most common detector used in the separation of metals by high performance liquid chromatography is based on monitoring the column effluent with a variable wavelength spectrometer operating in the ultraviolet or visible region. To make the metals visible before they enter the detector, they must be complexed with an organic reagent to produce complexes which absorb in the above regions of the spectrum and which, incidentally, improve the sensitivity of detection of the metals. Various metal complexing agents have been studied including 4-(2-pyridylazo) resorcinol (PAR), dithizone, sodium diethyldithiocarbamate, bis(*n*-butyl-2)-naphthyl methyl (dithiocarbamate) zinc II. Since 1982 various investigators have studied the application of high performance liquid chromatography to the determination of very low concentrations of metals in water samples.

Some investigators have produced organic chelate complexes from the metals after they have been separated in the inorganic form on the column, but before entry into the detector, i.e. post column derivatization, whilst other investigators form the organic complexes before the sample is applied to the separation column, i.e. pre-column derivatization.

Post column derivatization methods

NICKEL, COBALT, COPPER, ZINC AND LEAD: Cassidy and Elchuk^{116,117} carried out trace enrichments and high performance liquid chromatography of solutions of nickel, cobalt, copper, zinc and lead in the low $\mu\text{g l}^{-1}$ range. The metal ions were enriched on a short bonded phase ion exchanger and then separated on a 13 μm styrene divinylbenzene resin. The eluted metal ions were detected with a variable wavelength UV/visible detector after a post column reaction with 4-(2-pyridylazo) resorcinol monosodium salt.

Recovery data for 21 samples of the test metal ions in the low picogram ml^{-1} range are shown in fig. 33. For each metal ion the solid line represents 100 per cent recovery and not the best fit to the actual data

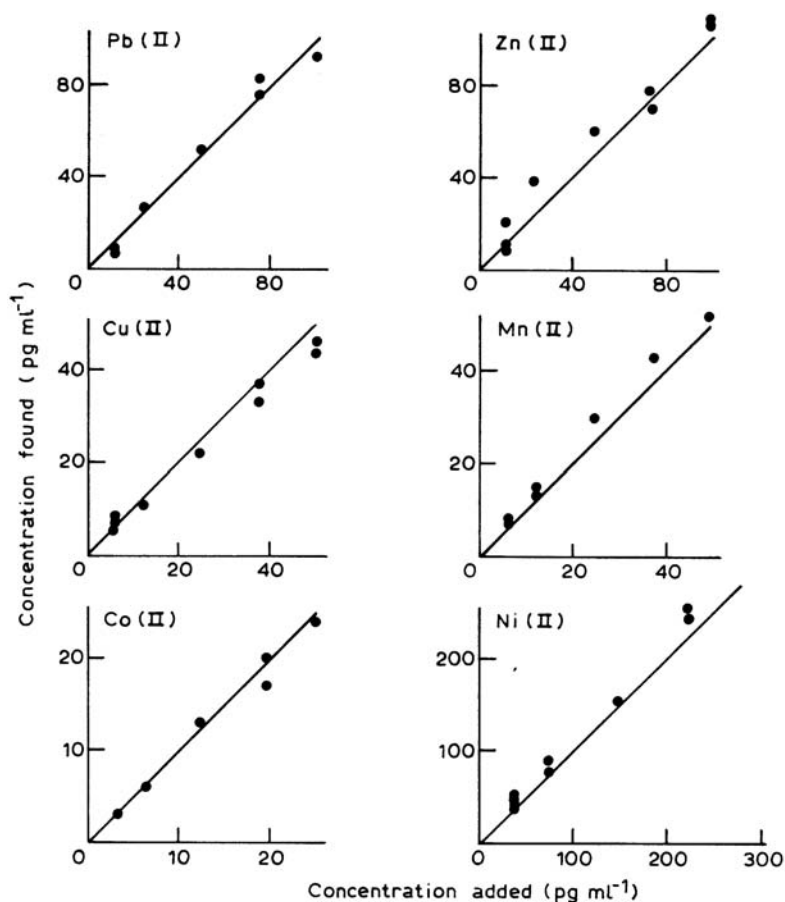


Fig. 33. Calibration curves for test metal ions. Solid lines represent 100 per cent recovery. points shown. All of the concentrations given in [fig. 33](#) were calculated from the linear calibration curves obtained from the direct injection ($20 \mu\text{l}$) of low nanogram to low microgram amounts of the metal ions. In view of the extremely small concentrations used, these results are excellent. The scatter of data, both at single concentration values and about the 100 per cent recovery line, shows that the reproducibility of this method is also good at these low concentrations.

Detection limits for these metal ions, determined under the same experimental conditions used to generate the data in [fig. 33](#) are in the range $0.5 \mu\text{g l}^{-1}$ (cobalt) to $15 \mu\text{g l}^{-1}$ (nickel).

In [fig. 34](#) is shown a chromatogram obtained by this technique for two waste water samples. Excellent resolution is obtained for all elements examined.

COBALT, COPPER, MERCURY AND NICKEL: High performance liquid chromatography has been applied to the determination of these elements as the ammonium-bis(2-hydroxyethyl) dithiocarbonates in plating wastewaters¹¹⁸.

AMMONIUM: Chau and Farquharson¹¹⁹ have described a procedure for the determination of trace amounts of ammonium (and amines) in waste water. The usual detectors do not respond well to these substances. This problem has been overcome by converting them to their *m*-toluyl derivatives and extracting the derivatives with dichloromethane prior to chromatography.

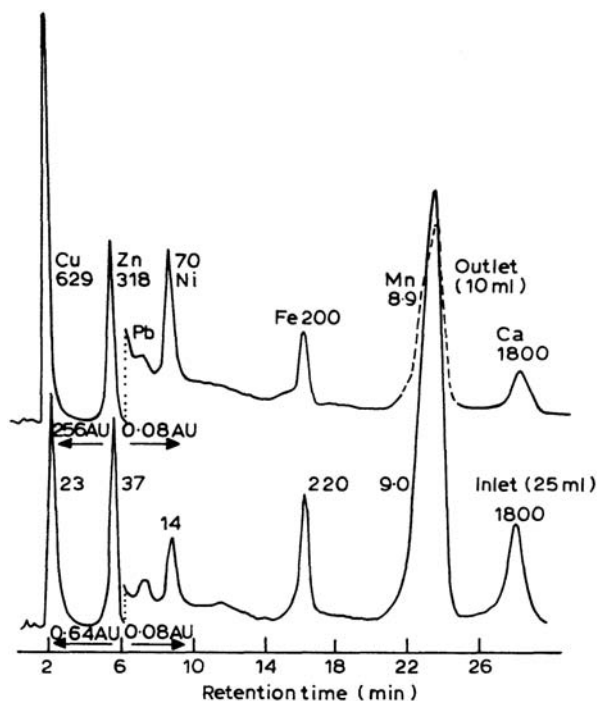


Fig. 34. HPLC analysis of fresh water coolant. Experimental conditions: samples were made $0.0001 \text{ mol l}^{-1}$ in citrate (pH 4.5) and allowed to sit for 2–3 days.

2.3

Elemental analysis

2.3.1

Chlorine

Miscellaneous

Jager and Hagenmaier¹²⁰ have described a simple method for the determination of the total extractable organochlorine content of waste water samples. Chlorine is determined by extraction with petroleum ether, followed by reductive hydrolysis using elemental sodium and isopropanol, and determination of the liberated chloride ions either by titration (Mohr's method) or by amperometric procedures. Volatile and non-volatile organochlorine compounds can be determined, the detection limit being 0.1 mg chlorine by titration against silver nitrate, or 0.01 mg l^{-1} chlorine using a coulometer. Recoveries are between 95 per cent and nil, depending on the type of organochlorine compound being investigated. Interference due to sulphide ions can be eliminated by addition of hydrogen peroxide.

Nulton et al¹²¹ have described a rapid and sensitive procedure for the determination of total organohalogen in environmental samples, using a short gas chromatography column and a Hall electrolytic conductivity detector.

Kaj and Solyom¹²² have described a method for the determination of adsorbable organic halogens (AOX) in waste waters.

2.3.2

Iodine

Titration method

Erdey and Kozmutza¹²³ have used xenon difluoride as a reagent for the determination of iodine or iodide in cooling waste waters from nuclear reactors. The test solution, made 1 N to sulphuric acid is treated with solid xenon difluoride to convert iodine or iodide to periodate, the solution is then heated to 100°C to remove unconsumed xenon difluoride. Periodate is determined by standard iodometric methods.

2.3.3

Total nitrogen and phosphorus

Kjeldahl digestion

Kei¹²⁴ has described an automated Kjeldahl procedure for the determination of low levels of nitrogen in waste waters.

Inductively coupled plasma atomic emission spectrometry

Ishizuka et al¹²⁵ examined the determination of total phosphorus in waste waters by inductively coupled plasma emission spectrometry. This method includes both organic and inorganic forms of phosphorus such as are found in municipal and industrial waste waters. The detection limits are 20, 40 and 110 $\mu\text{g l}^{-1}$ at the 213-618, 214-914 and 253-585 nm lines respectively. Interferences by other elements are negligible at the concentration levels of these elements in environmental and waste waters, except for the spectral interference of copper on the lines at 213-618 and 214-914 nm. Differences in emission response for various inorganic and organic phosphorus compounds are small.

Good agreement was obtained in the results of phosphorus determinations in real samples by inductively coupled plasma and by the standard persulphate digestion molybdenum blue spectrophotometric method¹²⁶.

Miscellaneous

Various workers¹²⁷⁻¹²⁹ have discussed the determination of total nitrogen and total phosphorus in waste waters. Automated and semi-automated spectro photometric procedures have been employed^{128,129}. Generally nitrogen is decomposed by Kjeldahl digestion¹²⁸⁻¹³⁰ and is determinable in amounts down to 50 $\mu\text{g l}^{-1}$ (as N).

Irie et al¹³⁰ compared a peroxydisulphate digestion method with Kjeldahl digestion for total nitrogen and compared peroxydisulphate digestion for total nitrogen with sulphuric and nitric acid digestion for total phosphorus. Coefficients of correlation were 0.982 (total nitrogen) and 0.995 (total phosphorus) respectively. For waste water samples, the recoveries of total nitrogen and total phosphorus ranged from 95 to 98 per cent, with a coefficient of variation of 5 per cent.

Veillon and Park¹²⁷ used the Salet phenomenon to determine total phosphorus and sulphur in waste waters. When a solution of a sulphur compound is sprayed into a low temperature, fuel rich hydrogen air flame, a blue emission (attributed to molecular S₂) is observed near the surface of a cold object placed in the flame. Similarly phosphorus compounds give rise to a green emission attributed to molecular HPO. A burner with a borosilicate glass sheath was designed to produce such emission spectra from S₂ and HPO with maxima at 384.0 and 526.5 nm respectively.

2.3.4

Boron

Inductively coupled plasma atomic emission spectrometry

Broekaert and Leis¹³¹ carried out the sequential determination of down to 50 µg l⁻¹ boron and several metals (barium, cadmium, copper, iron, manganese, molybdenum, nickel and zinc) by inductively coupled plasma atomic emission spectrometry. This procedure was applied in conjunction with an injection method and the amplified photomultiplier current was used as the analytical signal.

2. 3.5

Total carbon and total organic carbon

Soluble and particulate organic material can be rapidly converted to the gaseous phase in an appropriate high temperature reaction environment and the carbon content of the resultant gases can be quantitatively measured and recorded. The commercial instruments available either oxidize carbon in the water sample to carbon dioxide and subsequently measure the carbon dioxide by infrared analysis or alternatively reduce the carbon to methane and measure the methane by a flame ionization technique. No more than 8 min per single determination is required for previously standardized instruments. Differentiation between organic and inorganic carbon is relatively easy to obtain with available instrumentation. Based on the organic carbon content of a waste water sample, an approximation of the ultimate oxygen demand of the waste water can be estimated based on stoichiometry.

Only very small samples, usually 20–100 µl, are required and sampling error may be a problem. Because of the small bore diameter of most total organic carbon (TOC) injection systems, solids must be precluded or reduced in size prior to injection for most instruments.

Miscellaneous

The determination of total organic carbon in waste water has been reviewed by Busse¹³². Earlier methods^{133,134} for the determination of total organic carbon in waste water involved the use of the Beckmann apparatus in which the sample is evaporated at 900–1000°C. The carbon dioxide produced is measured by infrared spectroscopy. These techniques can detect down to 0.5 mg l⁻¹ carbon. Dobbs et al¹³⁵ established a correlation between the total organic carbon content of waste water and its extinction at 254 nm. High correlation coefficients were obtained for samples that contained sufficient carbon to permit accurate determinations. The procedure is not applicable to turbid samples. Becker¹³⁶ reviewed methods and equipment available for automated determinations of total organic carbon and inorganic carbon in waste waters.

Stover and McCartney¹³⁷ characterized industrial waste waters by evaluating biochemical oxygen demand, chemical oxygen demand and total organic carbon, and evaluated relationships between these parameters for 30 categories of waste water.

Chandler et al¹³⁸ have reported on the feasibility of using measurements of total organic carbon for indirect estimation of biochemical oxygen demand and chemical oxygen demand in waste treatment plants. The results showed a significant correlation between 5 day biochemical oxygen demand and total organic carbon. It is concluded that total organic carbon analyses may be used as alternatives to biochemical oxygen demand and chemical oxygen demand tests once the necessary correlations have been determined.

Power and Langford¹³⁹ have used the thermal lens effect for the thermo-optical determination of dissolved organic matter.

2.4

Miscellaneous determinands

2.4.1

Colour

Allen et al¹⁴⁰ point out that the American Dye Manufacturers Institute have developed a method for assessing the colour of water, which is independent of hue. It is based on examination of a filtered sample, either in a spectrophotometer or a suitable tristimulus colorimeter, to determine the tristimulus values for the sample; from these the corresponding Munsell values are obtained by reference to a set of tables and the ADMI value is then calculated from the Munsell values for the sample and for distilled water. The method is described.

Wagner and Ruck¹⁴¹ and Allen et al¹⁴⁰ have discussed the measurement of the colour of waste waters. Wagner and Ruck propose that the colour of a waste water is quantitatively characterized by the mean value of the spectral absorption coefficient in the spectral range 380–780 nm. It is claimed that this quantity is more easy to measure than the ADMI colour value proposed by the American Dye Manufacturers Association and that some relationships exist between these two measurements.

2.5

Organic substances

2.5.1

Aliphatic hydrocarbons

Miscellaneous

Goretti et al¹⁴² discussed the thin-layer chromatographic determination of the constituents of ether extracts of industrial waste waters. A light petroleum extract of the sample is evaporated and the residue is weighed, dissolved in ethyl ether (5–50 μg) and applied to silica gel in a lane formed by scratching two lines 3 mm apart along the plate and widening them beyond the width of the applied spot at the start. The chromatogram is developed with chloroformbenzene (1:3) for 13 cm at 18°C in 75 min. Separate controls are prepared for various amounts of vegetable oils (mixtures of olive and seed oils) and mineral oils (petroleum hydrocarbons containing 60–70 per cent of naphthenes). The materials are identified by the fact that mineral oils travel

with the solvent front, vegetable oils show an R_f of 0.5 and other compounds (e.g. phenols, acids, and alcohols) remain at the start. For determination of the constituents, the spot lengths are compared with those of the appropriate controls, the relationship between spot length and the amount of applied material being rectilinear up to 8 μg . The materials in the respective spots were analysed and identified by extraction followed by gas chromatography.

Strensom et al¹⁴³ have reviewed and evaluated methods for the quantitative and qualitative determination of hydrocarbons in waste water. Earlier methods used petroleum ether as solvent and required weighing of the extract to obtain oil and grease residue. More recent methods use Freon-113, chloroform, carbon tetrachloride, *n*-heptane, *n*-pentane or *n*-hexane as solvents. The 1985 edition of Standard Methods for the Examination of Waters and Waste Waters¹⁴⁴ had five methods for the determination of oil and grease in water and sludges; partition gravimetric method, partition-infrared method, Soxhlet extraction method, an extraction method for sludge and a method allowing separate analysis of hydrocarbons. Instrumental methods for automated analysis were fluorimetry, light scattering, dye transfer and light transmission. Column chromatography and thin layer chromatography were used to isolate and characterize hydrocarbon fractions. Identification and quantification techniques included gravimetric and infrared spectrophotometry, UV visible spectrophotometry, nuclear magnetic resonance and high pressure liquid chromatography.

Rotteri¹⁴⁵ investigated various methods for the determination of total hydrocarbons in petroleum industry waste waters and concluded that the best results would be obtained by infrared spectroscopy. Any procedure used should include solvent extraction, separation of non-polar material and measurement at three wavelengths.

2.5.2

Aromatic hydrocarbons

Gas chromatography

Stolyarov¹⁴⁶ used head space gas chromatography to determine $\mu\text{g l}^{-1}$ quantities of aromatic hydrocarbons in waste water. Urano et al¹⁴⁷ developed a steam carrier gas chromatographic method for determining aromatics in refinery wastes.

The determination of aromatic hydrocarbons in waste water is also discussed in [section 2.5.27](#) (multicomponent organic analysis).

2.5.3

Polyaromatic hydrocarbons

High performance liquid chromatography

Das and Thomas¹⁴⁸ used fluorescence detection in high performance liquid chromatography to determine nine polyaromatic hydrocarbons in occupational health samples including process waters. The nine compounds studied were, benzo(a)anthracene, benzo(k)fluoranthene, benzo(a)pyrene/fluoranthene, chrysene, benzo(k)fluorene, perylene, benzo(e)pyrene, deibenz(ah)anthracene, and benz(ghi)perylene.

The method involves the use of a deuterium light source and excitation wavelengths below 300 nm. Limits of detection in the 0.5–1.0 pg range were obtained for several polyaromatic hydrocarbons of environmental or toxicological significance. Limits of detection close to subpicogram levels were obtained

(e.g. benzo(a)anthracene, 0.6 pg; benzo(k)fluoranthene, 0.4 pg; benzo(a)pyrene, 1.1 pg). Precision studies gave a relative standard deviation from 0.32 to 2.66 per cent (e.g. benzo(a)anthracene, 0.33 per cent benzo(k)fluoranthene, 0.70 per cent; benzo(a)-pyrene, 0.50 per cent). The system allows the use of dilute solutions, thus eliminating the usual clean-up procedures associated with trace analysis.

H.p.l.c. in reverse phase mode was performed isocratically with 82 per cent acetonitrile in water.

Detection wavelengths of 254 and 280 nm were used and the following three sets of excitation and emission wavelengths conditions were used in fluorescence detection with excitation prefilter Corning 7-54; (a) λ_{ex} 280 nm, λ_{em} >389 nm, (b) λ_{ex} 250 nm, λ_{em} >370 nm, and (c) λ_{ex} 240 nm, λ_{em} >470 nm.

Figs 35(a) and 35(b) show the chromatographic profiles of the polyaromatic hydrocarbon obtained with UV detection at 254 nm and 280 nm respectively. It is seen from the figures that the microparticulate column gives good separation of fluoranthene, dibenz(ah)anthracene and benz(ghi)perylene but fails to resolve either chrysene from benzo(a)anthracene or benzo(k)fluoranthene, benzo(e)pyrene and perylene from each other in the multicomponent mixture.

Das and Thomas¹⁴⁸ discuss in particular difficult separations such as chrysene from benzo(a)anthracene and perylene from benzo(e)pyrene and show how these separations can be achieved.

Between 0.5 and 3.0 pg of polyaromatic hydrocarbons can be detected by this procedure.

2.5.4

Greases and vegetable oils

Solvent extraction methods

The traditional and widely accepted method for determining grease in waste water is based on organic solvent extraction, solvent evaporation and weighing¹⁴⁹. The method is time-consuming, both in the analyst's time and in duration. A rather large sample of waste water is required for the traditional method and it is difficult to manipulate the samples to assure a homogeneous aliquot. Simplification of the methodology is fraught with difficulties because of the extreme complexity of waste water in composition and variability.

Maxcy¹⁵⁰ has described a simpler volumetric procedure, for the determination of grease in waste water.

Cook et al¹⁵¹ have described improved methods for the determination of oil and grease in water. This method utilizes the semi-automatic oil monitoring instrument, the Horiba OCMA-200. These workers compared results obtained by this procedure with those obtained by a US Environmental Protection Agency reference method¹⁵². The Horiba instrument is a very convenient device to use since sample handling and contamination possibilities are almost nil. An acidified, 10 ml oil-in-water sample is injected via a syringe into an extraction chamber with an equal amount of solvent, either Freon or carbon tetrachloride. A vibrating plunger is activated for a given time causing intimate mixing of the sample and solvent. The plunger is deactivated and the solvent and oil mixture is allowed to separate. A valve is then opened, permitting the solvent mixture to flow through a filter into the infrared chamber where the amount of 3.5 μ m light attenuation by the oil in solvent is measured.

Cleverley¹⁵⁶ has carried out a comparison of various lubricating greases by infrared spectroscopy in the 4000–650 cm^{-1} region. This work would be useful in classifying greases originating in extracts of water samples.

Various workers^{153–155} have discussed the volumetric determination of greases in sewage, sludges and industrial wastes.

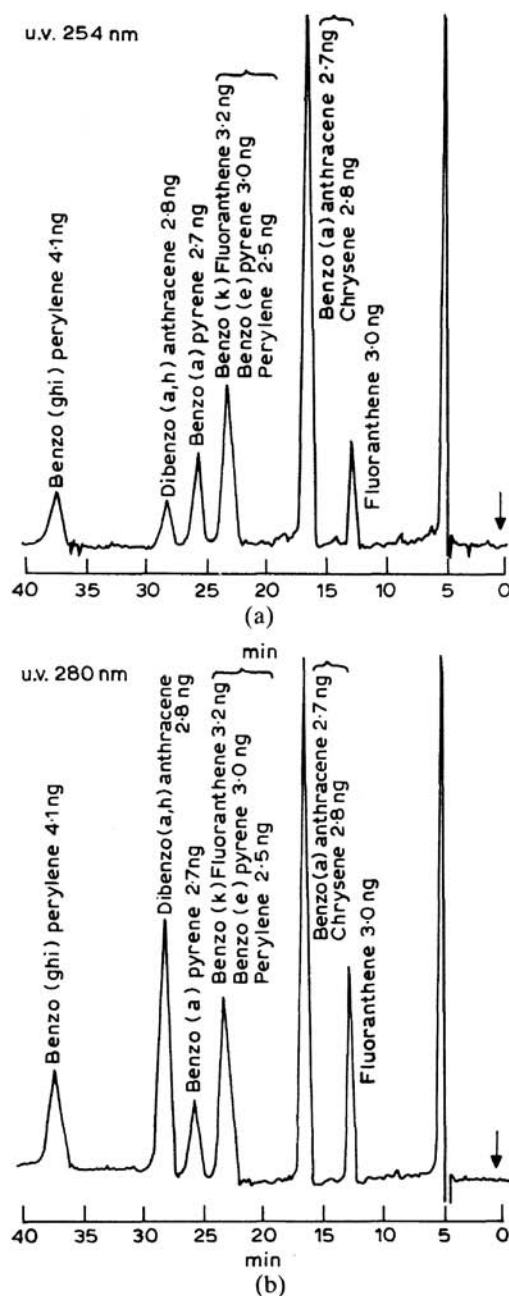


Fig. 35. Liquid chromatogram of a mixture of nine polycyclic aromatic hydrocarbons with UV absorption detection. Chromatographic conditions: two 1 mm i.d. \times 25 cm Zorbax ODS column, 82:18 (v/v) $\text{CH}_3\text{CN}:\text{H}_2\text{O}$, 25°C, 300–500 psi, flow rate 0.3 min^{-1} , 10 μl injection of PAH dissolved in 75 per cent CH_3CH . (a) UV 254 nm at 0.01 AUFS, (b) UV 280 nm at 0.01 AUFS.

Vegetable oils

H.M. Stationery Office (UK)¹⁵⁷ have described a petroleum ether extraction procedure for the determination

of oils and fats in waste water.

2.5.5 *Anionic detergents*

Spectrophotometric methods

Wudzinska and Ponikowska¹⁵⁸ developed automated methods for the determination of anionics in waste water based on the use of methylene blue. The method involves colorimetric determination of the concentration of the products by reaction of the anionic surfactants with methylene blue. These complexes are extracted into chloroform and measurements are made at 650 nm in a flow through cell. Samples of waste water should be diluted with 10 per cent aqueous sodium sulphate to ensure separation of the chloroform extract. The method can be used for determining surfactants in concentrations equivalent to 0.05–1 mg l⁻¹ of sodium hexacosylbenzene sulphonate. For samples containing 1, 0.5 and 0.1 mg l⁻¹ of sodium hexacosylbenzene sulphonate the respective standard deviations were 3.5, 2.5 and 2.5 µg l⁻¹.

Atomic absorption spectrometry

Gallago et al¹⁵⁹ used indirect atomic absorption spectrometry to determine down to 100 µg l⁻¹ anionic detergents in waste water by flow injection continuous liquid liquid extraction. A membrane phase separator designed for the continuous extraction of anionic surfactants is described. The detergent 1,10-phenanthroline copper II ion pair was extracted into methyl isobutyl ketone through two layers of Fluoropore membranes (1.0 µm pore size). The concentration of detergent was determined indirectly by atomic absorption per cent over the range 100–500 µg l⁻¹. The method was highly selective and spectrometric determination of copper. The relative standard deviation was 0.8 showed good agreement with the methylene blue method.

Infrared spectroscopy

Oba et al¹⁶⁰ have described an infrared method for the microanalysis of anionic surfactants in waste waters and sewage.

The surfactants are extracted with chloroform as methylene blue complexes; and sulphate-type surfactants (fatty alcohol sulphate and fatty alcohol ethoxysulphate) are then removed by hydrolysis; residual sulphonate type surfactants are released from the methylene blue complexes by ion exchange and then converted to sulphonyl chloride derivatives for infrared spectroscopy. Sulphate-type surfactants are calculated from the differences in methylene blue active substances before and after hydrolysis. The types of detergents that can be determined by the Oba et al¹⁶⁰ method include linear alkylbenzene sulphate (LAS), branched alkylbenzene sulphonate (ABS), alpha olefin sulphonate (AOS), fatty alcohol sulphate (AS) and fatty alcohol ethoxysulphate (AES). In this method anionic detergents such as LAB, ABS, AOS, AS and AES contained in sewage or river waters were extracted by chloroform as methylene blue complexes. After evaporation of chloroform the residue obtained was hydrolysed to decompose sulphate type surfactant methylene blue complexes. The amount of sulphate type surfactants was calculated from the loss of methylene blue active substances (MBAS) level before and after hydrolysis.

After hydrolysis sulphonate type surfactant methylene blue complexes were first hydrogenated to saturate the AOS, second, ion-exchanged to remove methylene blue and then converted to sulphonyl chloride derivatives for infrared analysis.

The infrared absorption peak at 810 cm^{-1} was observed in infrared spectra of sulphonyl chloride derivatives of hexyl- and octylbenzene sulphonate. This absorption peak was not observed in the cases of alkylbenzene sulphonates having ten or more carbon atoms in their alkyl chain.

Furthermore, in infrared spectra of sulphonyl chloride derivatives of hexyl- and octylbenzene sulphonate, the interfering peak appeared at 524 cm^{-1} which was a key band for alpha-olefin sulphonates. At the same time, the absorption peak at 640 cm^{-1} specific for linear alkyl sulphonate was weakened. Therefore, if these materials exist, the amount of linear alkyl sulphonate could be underestimated and the amount of alpha-olefin sulphonate could be overestimated. It is necessary to make corrections. In the case of analysis of unknown samples which show an absorption peak at 810 cm^{-1} the analytical results should be corrected providing that hexyl- and octylbenzene sulphonates are interfering materials. For convenience, this correction was made with 1:1 mixtures of hexyl- and octylbenzene sulphonate because no difference in molecular extinction coefficients between these two alkylbenzene sulphonates exists. Three kinds of calibration curves with a mixture (1:1) of hexyl- and octylbenzene sulphonate were made at 810 cm^{-1} and at 524 and 610 cm^{-1} . The correction for unknown samples was carried out as follows. If the absorption peak at 810 cm^{-1} appeared, the absorption intensity was converted into the concentration of the mixtures of the alkylbenzene sulphonates by the calibration curve at 810 cm^{-1} . First the concentration was changed into the corresponding absorbance by the calibration curve at 524 cm^{-1} , which was converted into the apparently surplus concentration of alpha-olefin sulphonate by the calibration curve made on alpha-olefin sulphonate at 524 cm^{-1} . The net alpha-olefin sulphonate concentration was obtained by subtracting the apparent surplus alpha-olefin sulphonate concentration from the apparent alpha-olefin sulphonate concentration. Second, the concentration was changed into the corresponding absorbance by the calibration curve at 640 cm^{-1} which was then converted into linear alkyl sulphonate concentration by the calibration curve prepared with linear alkyl sulphonate at 640 cm^{-1} .

Gas chromatography

Reubecker¹⁶¹ developed a procedure for the determination of alkyl ethoxylated surfactants in waste water. The method of determination involves concentration of the alkylethoxylated surfactants on an anion-exchange resin, elution with ethanolic hydrochloric acid, hydrolysis of the surfactants to alkylethoxy, which was then extracted from the remaining ionic species and conversion to the corresponding alkyl bromides which were determined by gas chromatography.

2.5.6

Cationic detergents

Flow injection analysis

Rios et al¹⁶² used flow injection analysis to determine this type of detergent in waste waters.

2.5.7

Non-ionic detergents

Zoller and Ramono¹⁶³ have developed procedures for facilitating the application of existing analytical methods for the determination of non-ionic detergents, in waste waters. They determined the ratio between biodegradable and non-biodegradable non-ionics in the sample and correlated the analytical data with the information available on production, formulation and use of non-ionic detergents. Using the hydrophilic cobalthiocyanate method, with certain modifications, average factorized calibration curves were obtained.

Atomic absorption spectrometry

Grasso and Buffalo¹⁶⁴ determined down to 0.1 mg l⁻¹ non-ionic detergents in waste water by atomic absorption spectrometry. This technique was based on the formation of an insoluble calcium surfactant phosphotungstic acid complex in acid media. A high performance liquid chromatographic microfiltration apparatus was used to recover this precipitate before dissolving it in acetone and measuring the cadmium absorbance signal by flame atomic absorption spectroscopy. A calibration curve, plotted using nonyl phenol containing 10 units of ethylene oxide per mol, as standard compound, was used for calculating the amount of non-ionic surfactant in the sample. This amount was expressed as the equivalent amount of the same standard. Strontium chloride was required to overcome the interference of phosphates on calcium absorbance signals.

2.5.8

*Phenols**Spectrophotometric methods*

Goodwin and Marton¹⁶⁵ describe an improved continuous flow method for the determination of phenol in waste water. The colorimetric step uses the 4-aminoantipyrine technique. Interference from chloride ions is countered using a phosphate buffer (pH 10.2). The method analyses ten samples per hour with a detection limit of 5 µg l⁻¹.

Amlather et al¹⁶⁶ have described a spectrophotometric method for determining phenols in waste water involving the formation of a greenish blue indophenol dye by the reaction of phenol, ammonia and *N*-chlorosuccinamide in the presence of sodium nitroprusside catalyst.

Absorbance was measured at 670 µm and the method applicable in the 0.3–2.4 µg l⁻¹ concentration range.

Korenman and Selmanschuk¹⁶⁷ described a method for the determination of phenol in waste water in which the sample is first prehalogenated with hydrochloric acid and the phenol extracted with an organic solvent containing a solvotropic agent. On extraction with 10 µl of active extraction agent from 1 litre of water, followed by re-extraction from 1 litre of alkaline photometric reagent the phenol could be determined spectrophotometrically using diazotized sulphanilic acid.

Thin layer chromatography

Rump¹⁶⁸ has described a cellulose thin layer method for the detection of phenolic acids such as *m*-hydroxybenzoic acid, *m*-hydroxyphenylacetic acid and *m*-hydroxyphenylpropionic acid, in water samples

suspected to be contaminated with liquid manure. The phenolic acid is extracted with ethyl acetate from a volume of acidified sample equalling 1 mg of oxygen consumed (measured with potassium permanganate). The ethyl acetate is evaporated and the residue dissolved in ethanol. After spotting of a 1 μ l aliquot on a cellulose plate the chromatogram is developed by capillary ascent with the solvent *n*-propanol: *n*-butanol: 25 per cent NH₃: water (4:4:4:1) by vol. The solvent front is allowed to advance 10 cm. The air-dried plate is sprayed with a diazotized *p*-nitroaniline reagent to make the phenolic acids visible.

The determination of phenols is also discussed in [section 2.5.28](#) (multiorganic mixtures).

High performance liquid chromatography

See [section 2.5.28](#) (multiorganic mixtures).

Sample preservation

Carter and Huston¹⁶⁹ have compared preservation of phenolic compounds in waste waters using (a) copper sulphate and phosphoric acid, storage at 4°C, with (b) the use of strong acids or bases and storage of samples at 25°C and 4°C. The addition of 2 ml concentrated sulphuric acid with sample storage at 4°C was shown to be effective for 3–4 weeks, while other preservatives were effective for only 8 days. Loss of phenolic compounds occurred rapidly unless the preservative was added immediately after sampling. A correlation found between loss of phenolic compounds and microbial activity suggests that the latter is dominant in determining sample stability.

The stability of phenolics in three different waste waters preserved with copper sulphate-phosphoric acid and stored at 4°C was studied. The most important result of this study was the rapid loss of phenolics from the samples at 4°C with no addition of any chemical preservative. The percentage loss of phenolics within 24 hours for the industrial waste, raw and treated sewage samples was 85, 80 and 40 per cent respectively.

Preconcentration

See [section 2.5.28](#) (multiorganic mixtures).

2.5.9

Alcohols and glycols

Gas chromatography

Nevinnaya and Kofanov¹⁷⁰ have developed a gas chromatographic method for the determination of mono-, di- and triethylene glycols. The glycols were extracted with mixtures of distilled water and organic solvents, such as dioxane or acetone, acetylated with acetic anhydride in the presence of boron trifluoride and subjected to gas chromatography on a nitrile siloxane rubber, using a flame ionization detector. The actual concentration, the determined concentration and the deviance of the results at 95 per cent confidence limit were, respectively: for monoethylene glycol 100, 96.7, 5.2; for diethylene glycol, 10, 9.7, 0.3; for triethylene glycol, 40, 38.2, 1.6.

The determination of alcohols is also discussed in [section 2.5.27](#) (multiorganic mixtures).

Preconcentration

See [section 2.5.28](#) (multiorganic mixtures).

2.5.10

Ketones and aldehydes

See [section 2.5.28](#) (multiorganic mixtures).

Preconcentration

See [section 2.5.28](#) (multiorganic mixtures).

2.5.11

*Organic acids**Gas chromatography*

Pilipenko et al¹⁷¹ quantitatively determined carboxylic acids in waste water by gas chromatography of their methyl esters.

Miscellaneous

Narkis and Henfield-Furie¹⁷² have described a procedure for the determination of volatile organic acids in raw municipal waste water.

Dzidic et al¹⁷³ used fluoride ion chemical ionization mass spectrometry to determine naphthenic acids in refinery wastewaters.

Preconcentration

See [section 2.5.28](#) (multiorganic mixtures).

2.5.12

*Phthalate esters**Polarography*

Total phthalate esters as phthalic acid have been determined¹⁷⁴ using differential pulse polarography. Crude and treated waste water samples were extracted with hexane to remove phthalate esters. Individual esters were hydrolysed by refluxing with 10 M potassium hydroxide to phthalic acid, this being extracted with ethyl acetate. The residue was dissolved in acetic acid and potassium chloride for polarography. The calibration curve was linear over the range 2–100 μM and the detection limit for phthalic acid was 0.5 μM .

The determination of esters is also discussed in [section 2.5.28](#) (multiorganic mixtures).

2.5.13

Aromatic ethers

See [section 2.5.28](#) (multiorganic mixtures).

2.5.14

*Chlorine containing organic compounds**High performance liquid chromatography*

Column chromatographic techniques have been described¹⁷⁵ for the determination of pentachlorophenol and other chlorophenols, but these methods are not suitable for the determination of low levels. The best method for determining pentachlorophenol is conversion into the methyl ether followed by analysis using gas chromatography with an electron capture detector, or gas chromatography coupled with mass spectrometry. Both of these methods require an extensive amount of pretreatment and highly trained personnel for the operation of the equipment.

Ervin and McGinnis¹⁷⁵ attempted to overcome this problem by developing a high performance liquid chromatographic method for determining in water low concentrations of pentachlorophenol and chlorinated impurities that occur in the technical grade material such as 2,3,4,6-tetrachlorophenol, mono-, di- and trichlorophenols, octa- hepta- and hexachlorodibenzo-*p*-dioxins, and a variety of other polychlorinated aromatic compounds.

The method involves chloroform extraction of acidified waste water samples and rotary evaporation without heat. After redissolving in chloroform the samples were analysed directly by high performance liquid chromatography on a microparticulate silica gel column. A number of solvent combinations are possible and cyclohexane: acetic acid (92:2v/v) is preferred. The minimum detectable concentration is 1 mg l⁻¹ (without sample concentration) and the coefficient of variation is 1–2 per cent.

Gas chromatography

Matthew and Elzerman¹⁷⁶ directly acetylated these substituted phenols and determined them by gas chromatography of methylene dichloride extracts. Acetylation was achieved by addition of acetic anhydride to an alkaline aqueous solution of phenols. The results of the analysis of four synthetic mixtures of six phenols spiked into distilled water (at 0.8–40 μg l⁻¹) are given. For dye waste waters, direct acetylation accomplished a considerable although not complete, elimination of co-extractives. The application of direct acetylation to municipal waste waters is considered promising as they contain fewer co-extractives.

Chau and Coburn¹⁷⁷ have described an electron capture gas chromatographic method for the determination of pentachlorophenol in natural waste waters. The phenol is extracted from the sample (1 l) into benzene and subsequently from the latter into 0.1 M potassium carbonate. Addition of acetic anhydride to the aqueous solution gives the acetate derivative, which is extracted into hexane and analysed by gas chromatography with the use of a conventional polar column. The limit of detection is 10 pg l⁻¹ of sample.

Buisson et al¹⁷⁸ determined ng l⁻¹ levels of chlorinated phenols in waste water by capillary gas chromatography with electron capture detection. Derivatization, by alkylation with pentafluorobenzoyl chloride enhanced the response of the electron capture detector, gave stable derivatives, improved selectivity and volatility, reduced background and reagent peaks and provided a simple methodology. Spiked samples showed a mean recovery of 70 per cent and a relative standard deviation of 7–15 per cent.

The American Public Health Authority Standard Method series includes gas chromatographic methods for the determination in waste waters of pentachlorophenol. To determine pentachlorophenol, the sample is acidified (pH3) and pentachlorophenol extracted with an organic solvent, methylated with diazomethane and analysed by electron capture gas chromatography.

Further identification of pentachlorophenol is made with a mass spectrometer.

High performance liquid chromatography

See [section 2.5.28](#) (multiorganic mixtures).

2.5.15

Aliphatic chlorocompounds

Gas chromatography

Lukacovic et al¹⁷⁹ applied head space gas chromatography to the determination down to 0.5 mg l⁻¹ of chlorinated hydrocarbons in waste waters. Sherman et al¹⁸⁰ determined haloethers in industrial and municipal waste waters. Techniques for enrichment and clean-up of the extract were devised, the preferred method consisting of liquid/liquid extraction with methylene chloride, followed by flash evaporation, clean up of the concentrate by column chromatography on Florisil, a further evaporation step and subsequent gas chromatography with an electron capture detector. Two gas chromatographic packings were compared for use with these haloethers, 3 per cent SP-1000 on Supelcoport giving better results than Tenax-GC on account of better peak shape and resolution. The validity of the method was confirmed by application to samples of either municipal or industrial effluents spiked with known amounts of particular haloethers. Pfannhauser and Thaller¹⁸¹ have described a gas chromatographic method for quantitatively estimating traces of 16 different halogenated solvents in waste water. The solvent residues were extracted using *n*-pentane on a column containing a mixture of deactivated Florisil with the ground sample. The elute was injected into a fused silica capillary column and the peaks recorded by electron capture detection (Ni-63). The method could detect as little as 0.01 µl⁻¹ of most halogenated short-chain aliphatic hydrocarbons.

An American Public Health Association method¹⁸² has been published for the determination in waste water of the following aliphatic and aromatic chloro-compounds:

Benzylchloride

Carbon tetrachloride

Chlorobenzene

Chloroform

Epichlorohydrin

Methylene chloride

1,1,2,2-Tetrachloroethane

Tetrachloroethylene

1,2,4-Trichlorobenzene

1,1,2-Trichloroethane

A 3–10 μl aliquot of the sample is injected into the gas chromatograph equipped with a halogenated specific detector. The resulting chromatogram is used to identify and quantitate specific components in the sample. Results are reported in $\mu\text{g l}^{-1}$. Confirmation of qualitative identifications are made using two or more dissimilar columns.

The use of a halogen specific detector minimizes the possibility of interference from compounds not containing chlorine, bromine, or iodine. Compounds containing bromine or iodine will interfere with the determination of organochlorine compounds. The use of two dissimilar chromatographic columns helps to eliminate this interference and, in addition, this procedure helps to verify all qualitative identifications. When concentrations are sufficiently high, unequivocal identification can be made using infrared or mass spectroscopy. Though non-specific, the flame ionization detector may be used for known systems where interferences are not a problem.

The analysis of chlorocompounds is also discussed in [section 2.5.28](#) (multiorganic mixtures).

Preconcentration

Martinsen et al¹⁸³ preconcentrated organochlorine compounds on activated carbon and XAD-4 resin prior to determination by neutron activation analysis, thin-layer and gel permeation chromatography.

2.5.16

Dioxins

Miscellaneous

Peters et al¹⁸⁴ have discussed the determination of 2,3,7,8-tetrachlorobenzo-*p*-dioxin in waste water.

2.5.17

Chlorinated insecticides and polychlorinated biphenyls

A method has been described¹⁸⁵ for the determination of the following PCBs (Aroclors) at the nanogram level in 15:85 methylene chloride-hexane extracts of water and waste water:

PCB-1016

PCB-1221

PCB-1232

PCB-1242

PCB-1248

PCB-1254

PCB-1260

This method is an extension of the method for chlorinated hydrocarbons in water and waste water (described by Georlitz and Law¹⁸⁶). It is designed so that determination of both the PCBs and the following organochlorine insecticides can be made on the same sample.

Aldrin	DDT	Mirex
BHC	Heptachlor	Pentachloronitro benzene
Chlordane	Heptachlor epoxide	Strobane
DDD	Lindane	Toxaphene
DDE	Methoxychlor	Trifluralin

The PCBs and the organochlorine insecticides are coextracted by liquid liquid extraction and, insofar as possible, the two classes of compounds separated from one another prior to gas chromatographic determination. A combination of the standard Florisil column clean-up procedure and a silica gel microcolumn separation procedure are employed. Identification is made from gas chromatographic patterns obtained through the use of two or more unlike columns including SE-30 or OV-1 (3 per cent), OV-17 (1.5 per cent) or OV-210 (1.95 per cent) on Gaschrom Q (100–120 mesh). Detection and measurement is accomplished using an electron capture, microcoulometric or electrolytic conductivity detector. Techniques for confirming qualitative identification are suggested by these workers.

The interferences in industrial effluents are high and varied and pose great difficulty in obtaining accurate and precise measurement of PCBs and organochlorine insecticides. Separation and clean-up procedures are generally required and may result in the loss of certain organochlorine compounds. Therefore, great care should be exercised in the selection and use of methods for eliminating or minimizing interferences. Phthalate esters, certain organophosphorus insecticides and elemental sulphur will interfere when the microcoulometric or electrolytic conductivity detectors are used in the halogen mode. Organochlorine insecticides and other halogenated compounds constitute interferences in the determination of PCBs. Most of these are separated by the method described. However, certain compounds, if present in the sample, will occur with the PCBs. Included are: sulphur, heptachlor, aldrin, DDE, chlordane, mirex. Miller et al¹⁸⁷ have described a gas chromatographic method for the determination of 25 organochlorine insecticides and polychlorinated biphenyls in waste water. Data are presented on extractability, recovery from clean-up columns, and preservation of samples for analysis.

McIntyre et al¹⁸⁸ determined organochlorine pesticides and polychlorinated biphenyls by electron capture gas chromatography. The waste water sample is extracted with hexane and the extract cleaned up on alumina-silver nitrate and silica gel columns prior to electron capture gas chromatography.

Dunn et al¹⁸⁹ used gas chromatographic data to carry out pattern recognition for classification and determination of polychlorinated biphenyls in waste waters and waste dump extracts.

Ericksen et al¹⁹⁰ used high resolution gas chromatography-electron impact mass spectrometry to determine polychlorobiphenyls in halocarbon solvent process and product wastes.

2.5.18

*Aniline and substituted anilines**Gas chromatography*

Aniline and its derivatives have been determined¹⁹¹ in waste water at the low $\mu\text{g l}^{-1}$ level by gas chromatography with thermionic nitrogen-phosphorus detection. Precision is generally 5–15 per cent relative standard deviation and recoveries are generally 75 per cent or better.

High performance liquid chromatography

See [section 2.5.28](#) (multiorganic mixtures).

2.5.19

*Trinitrotoluene**Miscellaneous*

Heller et al¹⁹² have described a semi-quantitative method, using fluorescent ion-exchange resins for the monitoring of trinitrotoluene in munition plant waste waters. Spangord and Suta¹⁹³ characterized various nitrocompounds in waste waters produced during the manufacture of trinitrotoluene.

High performance liquid chromatography

See [section 2.5.28](#) (multiorganic mixtures).

2.5.20

*Nitrosamines**Gas chromatography-mass spectrometry*

Volatile nitrosamines have been determined in ng l^{-1} amounts in waste water¹⁹⁴ by combined capillary gas chromatography-mass spectrometry. Dimethylnitrosamines, diethylnitrosamine and dipropylnitrosamine were determined.

2.5.21

*Miscellaneous nitrogen compounds**Chlorinated amino acids*

GAS CHROMATOGRAPHY-MASS SPECTROMETRY: Chlorinated tyrosine has been determined¹⁹⁵ in municipal waste water by combined gas chromatography-mass spectrometry. Chlorinated amino acids are also discussed in [section 2.5.28](#) (multiorganic mixtures).

Pyridazinones

GAS CHROMATOGRAPHY: Matisova et al¹⁹⁶ have described a specific flame ionization gas chromatographic procedure for determining pyridazinones in waste water.

See also [section 2.5.28](#) (multiorganic mixtures).

Nitriloacetic acid

GAS CHROMATOGRAPHY: Kirk et al¹⁹⁷ determined nitriloacetic acid in waste waters by gas chromatography, differential pulse polarography and spectrophotometry. Gas chromatography gave good results down to $10 \mu\text{g l}^{-1}$. Differential pulse polarography was quicker and was more precise for all sample types, but only down to $100 \mu\text{g l}^{-1}$ nitriloacetic acid could be determined. The detection limit of the spectrophotometric method was $500 \mu\text{g l}^{-1}$.

See also [section 2.5.28](#) (multiorganic mixtures).

Diethanolamine

Nevinnaya and Klyachko¹⁹⁸ developed a process involving extraction with dimethyl-acetamide in the presence of potassium carbonate followed by conversion to the acetyl derivative and gas chromatography to determine down to $5 \mu\text{g l}^{-1}$ diethanolamine in waste water.

Melamine and cyanuric acid

See [section 2.5.28](#) (multiorganic mixtures).

A minophenols

See [section 2.5.28](#) (multiorganic mixtures).

High performance liquid chromatography of miscellaneous nitrogen containing compounds

The high performance liquid chromatography of heterocyclic bases, pyridazinones, substituted guanidines, chloroacetanilides and chloroanilines is discussed in [section 2.5.28](#) (multiorganic mixtures).

2.5.22

*Phosphorus containing organic compounds**Organophosphorus insecticides*

GAS CHROMATOGRAPHY: Gas chromatography has been used¹⁹⁹ to determine the following organophosphorus insecticides at the $\mu\text{g l}^{-1}$ level in water and disolfoton, malathion, parathion-methyl, and parathionethyl. This method is waste water samples: azinphos-methyl, demeten-0, demeton-S, diazinon, claimed to offer several analytical alternatives, dependent on the analysts' assessment of the nature and extent of interferences and the complexity of the pesticide mixtures found. Specifically, the procedure uses

a mixture of 15 per cent v/v methylene chloride in hexane to extract organophosphorus insecticides from the aqueous sample. The method provides, through use of column chromatography and liquid-liquid partition, methods for the elimination of non-pesticide interference and the pre-separation of pesticide mixtures. Identification is made by selective gas chromatographic separations and may be corroborated through the use of two or more unlike columns. Detection and measurement are best accomplished by flame photometric gas chromatography using a phosphorus specific filter. The electron capture detector, though non-specific, may also be used for those compounds to which it responds. Confirmation of the identity of the compounds should be made by gas chromatography-mass spectrometry when a new or undefined sample type is being analysed and the concentration is adequate for such determination. Detailed instructions are given for clean-up of reagents, solvents and glassware to avoid the occurrence of discrete artefacts and/or elevated baselines. Sample clean-up procedures are generally required and may result in the loss of certain organophosphorus insecticides. Therefore, great care should be exercised in the selection and use of methods for eliminating or minimizing interferences. Compounds such as organochlorine insecticides, polychlorinated biphenyls, and phthalate esters interfere with the analysis of organophosphorus insecticides by electron capture gas chromatography. When encountered, these interferences are overcome by the use of the phosphorus specific flame photometric detector. Elemental sulphur will interfere with the determination of organophosphorus insecticides by flame photometric and electron capture gas chromatography. The elimination of elemental sulphur as an interference is discussed in detail.

FIELD DESORPTION MASS SPECTROMETRY: Schulten and Sun²⁰⁰ used field desorption mass spectrometry to identify organophosphorus insecticides in waste water. The characteristic behaviour of four groups of common organophosphorus pesticides (phosphates, phosphorothionates, phosphorothiolates and phosphorodithioates) were investigated. This technique is suitable for identification of traces of these compounds in waste waters and other environmental samples without the need for preliminary separation and purification.

HIGH PERFORMANCE LIQUID CHROMATOGRAPHY: Liquid-liquid extraction or preconcentration adsorption resins have been combined with high performance liquid chromatography to determine organophosphorus insecticides in waste waters²⁰¹.

2.5.23

Miscellaneous organic sulphur compounds

Benethonium salts

SPECTROPHOTOMETRIC METHOD. These compounds have been determined in waste water by a spectrophotometric method based on reaction with tetrabromo-phenolphthalein ethyl ester²⁰².

HIGH PERFORMANCE LIQUID CHROMATOGRAPHY: See [Section 2.5.28](#) (multiorganic mixtures).

2.5.24

Herbicides

Gas chromatography

Onuska and Boos²⁰³ have determined S-alkyl derivatives of *N,N*-dialkyl dithiocarbamates in waste water samples by a gas chromatographic-mass spectrometric method. Separation of the derivatives was carried

out on a column of 10 per cent of Apiezon L on Varaport 80 operated at 250°C with helium as carrier gas and flame ionization detection. Separation was also achieved on a similar column as above, but with the temperature maintained at 190°C for 4-5 min and then programmed at 4°C min⁻¹ to 270°C, the helium flow rate being 28 ml min⁻¹. The effluent from the second column was examined by mass spectrometry-gas chromatography.

Hill et al²⁰⁴ developed a multi-residue gas chromatographic method for the analysis of chlorophenoxy herbicides in waste waters and waste water sludges. The method, however, can only determine the acid form of chlorophenoxy herbicides. It was applicable for six herbicides, including 4-chlorophenoxyacetic acid, 4-chloro-2-methylphenoxyacetic acid, 2,4-D (2,4-dichlorophenoxyacetic acid) and 2,4,5-TP (2,4,5-trichlorophenoxypropionic acid). The degree and reproducibility of the chlorophenoxy herbicide recovery was 5.0 µg l⁻¹ in an 11 ml sewage sample for all the herbicides, except 2,4-dichlorophenoxybutyric acid.

High performance liquid chromatography

See [section 2.5.28](#) (multiorganic mixtures).

2.5.25

Polymeric flocculents

Spectrophotometric method

The levels of cationic and non-ionic polymeric flocculants (used for sludge dewatering in sewage works) in waste water were measured by Hanasaki et al²⁰⁵. Test solution, tannic acid solution and inorganic salt (sodium nitrate or sodium chlorate) solution were incubated for 1 hour at room temperature and the transmittance measured with a spectrophotometer at 554 nm (more sensitive than 830 nm). Transmittance was independent of temperature between 10 and 30°C and was not affected by ferric ion concentrations up to 200 mg l⁻¹. Determinations should be made at pH 7 or less as transmittance decreased rapidly at higher pH values.

25.26

Ozonization products

HPLC and gas chromatography

Jolly et al²⁰⁶ characterized non-volatile organics produced in the ozonation and chlorination of waste water. The treated effluents were analysed by high pressure liquid chromatography and gas liquid chromatography as a means of detecting both non-volatile and volatile organic constituents. While chlorinated primary effluent was repeatedly found to be mutagenic towards a particular strain, neither chlorinated, ozonated nor UV irradiated secondary effluents exhibited mutagenic activity even when tested at 10–20 fold concentration.

2.5.27

*Multicomponent organic analysis**Gas chromatography*

Kuhelka et al²⁰⁷ used a preconcentration technique involving extraction of the sample with organic solvent followed by gas liquid chromatographic determination on a packed column or by mass fragmentography. Using the second technique the detection limit could be lowered by a factor of 10–100. Detailed procedures for analysis of chemical works waste waters by gas chromatography-mass spectrometry techniques are outlined.

Leinster et al²⁰⁸ analysed aqueous volatile organic compounds in waste water by solvent extraction, dynamic head space analysis (gas sparging) and the closed-loop stripping technique and the methods were evaluated. If the volatile organic content is of most importance the purging technique combined with thermal desorption/gas liquid chromatography is recommended.

Austern et al²⁰⁹ described methods for the determination of 11 organic compounds in crude and treated waste water. The compounds selected on the basis of potential hazard to health or degradation of water quality, non-biodegradability and production quantity, were styrene, *p*-xylene, ethylbenzene, nitrobenzene, acetophenone, *o*-anisidine, anethole, trichloroethylene, turpentine, nonylphenol and dimethyl phthalate. Stock solutions of the compounds were added to waste water, extracted with Freon and concentrated in a Kuderna Danish apparatus. The gas chromatographic conditions for analysis of each compound are tabulated. These methods are precise and sensitive to the low $\mu\text{g l}^{-1}$ range.

In this method, sample volumes were 350 ml for concentrations less than 100 $\mu\text{g l}^{-1}$ and 11 for lower concentrations.

Kuo et al²¹⁰ investigated a distillation technique as a means of concentrating in the distillate the low molecular weight volatile polar organic compounds such as alcohols, ketones, and aldehydes in waste waters. The basic principle of this technique is to take advantage of the high volatility of volatile polar organics to enrich them in a small volume of distillate obtained from distilling a large volume of aqueous sample. The volatility of these compounds relative to that of water was found to be a useful parameter in determining the concentration of the respective compounds in the distillate. By injecting directly the distillate onto a gas chromatographic column, low molecular weight volatile polar organics can be determined quantitatively at the $\mu\text{g l}^{-1}$ level. The relative standard deviation for the distillation technique was approximately 5 per cent based on triplicate runs using an internal standard.

The conclusions reached in this study were that for volatile polar organics of molecular weight less than 85, salting out along with the use of an internal standard can improve the recovery and precision of distillation processes using a glass bead packed column. If experimental time is not a limitation and if a large volume of sample (e.g. 11) is available, a two stage distillation technique is recommended, using a micro apparatus for the second stage distillation so as to collect less than 10 ml (e.g. 1.5 ml or less) of distillate for analysis. If time is a limiting factor, collecting the first 10 ml of distillate from a 11 sample with a large apparatus would be the method of choice. If, however, time and sample volume are both limited, 100 ml of sample solution can be distilled with a micro apparatus. In that case, either 10 ml or a smaller amount of distillate (e.g. 1.5 ml or less) can be collected for analysis. The latter approach is recommended, provided that the volume is sufficient for subsequent chemical analysis.

Hornbrook and Ode²¹¹ combined robotics with capillary gas chromatography or chromatography-mass spectrometry to determine acidic, basic and neutral organics in waste water.

Gas chromatography-mass spectrometry

Thomas et al²¹² surveyed proposed US Environmental Protection Agency methods for the analysis of priority pollutants in waste waters by chromatography and gas chromatography-mass spectrometry. Sampling, storage, apparatus, sample preparation, chromatographic and gas chromatography-mass spectrometry analysis, quality control and quality assurance, and data handling as they apply to the proposed methods are discussed.

Bishop has discussed²¹³ the effectiveness of the procedure developed by the US Environmental Protection Agency for the detection of priority trace organic compounds in waste waters by gas chromatography and mass spectrometry. The original procedures failed to detect four of the purgeable pollutants (chloromethane, dichlorodifluoromethane, vinyl chloride, and bromomethane); with the substitution of charcoal for silica gel in the Tenax trap, coupled with purging at 49°C, it was possible to identify all the volatile priority organics. Data from the routine determination of priority pollutants in waste waters by gas chromatography and mass spectrometry using EPA Methods 624 and 625 were analysed statistically to identify the principal sources of error. Random error was the principal cause of inaccuracy in Method 624. Calibration bias was the principal source of error in Method 625. Modifying the calibration procedure reduced calibration bias and random error for Method 625.

Shakelford et al²¹⁴ evaluated automated spectrum matching for survey identification of waste water components by gas chromatography-mass spectrometry. Details are given of the computer system, laboratory procedures and reference libraries involved. The reliability of spectrum matching was enhanced by the use of retention data accumulated in an historical library. An overall reliability of 71 per cent was demonstrated.

Lysyj²¹⁵ described a technique for the direct analysis of organic materials in waste water by pyrolysis and gas chromatography.

Nuclear magnetic resonance spectroscopy

Laude and Wilkins²¹⁶ identified organics in waters by carbon-13 nuclear magnetic resonance spectroscopy.

High performance liquid chromatography

This technique has been applied to the following multiorganic mixtures in waste waters; guanidines, substituted guanidines and s-triazines²¹⁷, pyridazinones²¹⁸, maleic hydrazine, ethoxyquinathiabendazole²¹⁹, ametryne²²⁰, alkylphenols, alkyl-, mono- and diethoxylates²²¹, chlorophenols²²², chloroacetanilides and chloranilines²²³ and phenols, aromatic amines and heterocyclic bases²²⁴.

Nielen et al²²⁵ analysed waste waters by liquid chromatography equipped with a C 18 PRP precolumn and a cation-exchange separation column. Diode array detection was used and multisignal plots were used to obtain preliminary compound identification.

2.5.28

Preconcentration of multiorganic mixtures

Head space analysis

Malten and Vreden²²⁶ applied the gas chromatographic head space analysis technique to the detection of organic volatiles in very small volumes of aqueous samples. Cowen et al²²⁷ have described the construction of a septumless injection device for delivering head space gases into a gas chromatograph.

Distillation techniques have been combined with head space analysis as a means of improving preconcentration factors of up to 100^{228–230}.

Heyndrickx and Peteghem²³¹ identified volatile components in waste waters by combined head space analysis and gas chromatography. Drodz and Novak²³² have shown that low concentrations of volatile organics can be determined in water by the double sampling method of head space gas chromatography using a closed loop strip/trap technique.

XAD-2 resin preconcentration

Phenols, carboxylic acids, aldehydes and ketones have been preconcentrated on columns of XAD-2 resin prior to determination by gas chromatography²³³.

2.6

Organometallic compounds

2.6.1

Arsenic

Spectrophotometric method

Sandhu and Nelson²³⁴ have also studied the interference effects of several metals on the determination of organically bound arsenic at the 0–100 $\mu\text{g l}^{-1}$ range in waste water by the silver diethyldithiocarbamate method. Antimony and mercury interfere specifically, forming complexes with silver diethyl dithiocarbamate at absorbance maxima at 510 and 425 nm respectively. Recovery of arsenic released by digesting solutions was tested and shown to give about 90 per cent recovery of organic arsenic.

2.6.2

Lead

Atomic absorption spectrometry

Aneva²³⁵ has discussed the determination of traces of tetraalkyl-lead compounds in waste waters by graphite furnace atomic absorption spectrometry. Tetraalkyl lead compounds were extracted from water with hexane, converted to water soluble iodides by reaction with iodine in the extract and re-extracted in dilute nitric acid. Determination was by graphite furnace atomic absorption spectrometry against an inorganic lead standard. The mean recovery of lead was 95 per cent and no interference from other metal

and non-metal ions was experienced. The method could be used for samples containing down to $5 \mu\text{g l}^{-1}$ lead.

2.6.3

Mercury

Spectrophotometric method

Itsuki and Komuro²³⁶ determined organomercury compounds in waste water by heating the sample with 2:1 mixture of nitric and hydrochloric acids and 30 per cent hydrogen peroxide at 90°C for one hour followed by the addition of 50 per cent ammonium citrate solution, diaminocyclohexane-tetraacetone in sodium hydroxide and hydroxylamine hydrochloride solution followed by pH adjustment to pH3–4 with aqueous ammonia. The solution is shaken with 1,1,1-trifluoro-4-(2-thienyl)-4-mercaptabuta-3-en-2-one in benzene, the benzene layer washed with 0.1 M borate pH 11 and the solution evaluated spectrophotometrically at 365 nm.

2.7

Oxygen demand parameters

2.7.1

Chemical oxygen demand

The chemical oxygen demand (COD) test is a relatively simple, straightforward wet chemistry method for determining the oxygen equivalent of waste water constituents that are susceptible to oxidation by a strong oxidizing agent. The procedure for determining the oxygen demand of a waste water sample is relatively rapid, requiring about 3 hours and has the advantage of being able to digest colloidal and particulate material. Unfortunately, the COD test will reflect the oxygen equivalent of organic compounds that are not readily biodegradable and does not completely oxidize benzene, toluene, pyridine and similar compounds. However, the COD test is commonly used for monitoring the performance of industrial waste water treatment systems.

COD data cannot be expected to correlate well with BOD data primarily because the two tests are measuring different aspects of the oxidizable constituents of waste water. In addition, the limitations of the BOD test further hamper meaningful correlations. The COD test has been semi-automated for handling large numbers of samples and several modifications have been proposed to shorten the time required to minimize chemical requirements.

Titration methods

The generally used method^{237–245} for estimating the chemical oxygen demand of waste waters involves heating the sample with an excess of acidic potassium dichromate in the presence of silver ions to catalyse the reaction and mercuric ions to prevent or reduce interference from chloride ions. Excess dichromate is then determined by titration with standard ferrous ammonium sulphate to a suitable Redox indicator end-point. The standard UK procedure²⁴⁰ employs both a titrimetric and a spectrophotometric (at 440 nm) finish.

The determination of chemical oxygen demand in waste waters by a sealed tube procedure, using silver nitrate to suppress chloride interference, has been described by Ballinger et al²³⁷. The procedure employed the standard reflux conditions commonly used in Water Authority laboratories. The sealed-tube chemical oxygen demand procedure²⁴¹ offers several advantages over the reflux procedure, notably a saving in bench space and cost of equipment. In spite of these advantages and general comparability with reflux procedures^{237,240} in results, the sealed-tube procedure has not been adopted as a standard method. The Department of the Environment's Standing Committee of Analysts (UK) decided not to endorse a sealed-tube chemical oxygen demand procedure because of safety considerations. Thermal degradation of the tube caps and liners is also found to occur. This creates difficulties in unscrewing caps and occasionally causes contamination of samples, particularly if an oven is used to heat the tubes.

The apparatus described by Lloyd²⁴² overcomes the problems cited above and offers several advantages over the silver nitrate reflux procedure. It is not necessary to use a weaker dichromate solution for chemical oxygen demand levels of 200 mg l⁻¹ or less. The suppression of chloride interference is improved and lower concentrations of silver nitrate are used.

In this procedure²⁴² samples are digested at 150°C in a glass stoppered flask using springs to retain the stopper. The use of sealed flask conditions offers two advantages over reflux conditions; simplified apparatus and experimental procedure and improved suppression of chloride interference. This procedure is similar to the standard procedure in accuracy and reproducibility of results.

Within-batch relative standard deviation in waste water analysis ranged from 2.2 per cent at levels of 60 mg l⁻¹ of COD to 0.8 per cent at 380 mg l⁻¹ of chemical oxygen demand (4 degrees of freedom). Total relative standard deviation in analysis of a 300 mg l⁻¹ chemical oxygen demand potassium hydrogen phthalate solution was 1.0 per cent (8 degrees of freedom). These results did not differ significantly ($p=0.05$) from data obtained using the standard procedure or the silver nitrate reflux procedure.

Ballinger et al²³⁷ have also studied mercury free methods for the determination of the chemical oxygen demand of waste waters.

Automation of the chemical oxygen demand test has been discussed²³⁸. The waste water sample is mixed in the Autoanalyser with an oxidant solution comprising potassium dichromate and sulphuric acid and 75 per cent sulphuric acid. After heating to 145°C the mixture is treated with hydrogen peroxide to produce molecular oxygen, which is measured, after separation of the aqueous phase, and absorption of carbon dioxide by means of a sensor based on a porous catalytic silver electrode. Nitrite and chloride interfere in the procedure.

Akesson and Lind²³⁹ evaluated two simplified methods for the determination of the chemical oxygen demand of waste waters. These methods both used capsules prepared with chemicals in advance and then fed with 2 ml samples. The methods were compared with the standard method. Both the simplified methods had advantages with respect to time, space, safety and ease of handling, but had disadvantages in regard to costs, precision and accuracy. For waste waters with a high chemical oxygen demand (above 100 mg l⁻¹) the capsule methods afforded values about 10 per cent higher than the standard method while in the low chemical oxygen demand range (under 100 mg l⁻¹) the values were lower.

Flow injection analysis

Korenga and Ikatsu²⁴⁵ have described a flow injection analysis technique with an acidic dichromate carrier, for the continuous determination of chemical oxygen demand in waste water samples. The system compares well with other methods and has the advantages of being cheap and simple.

Appleton et al²⁴⁶ also described a flow injection system in which a reagent stream containing potassium dichromate and sulphuric acid was merged with a distilled water carrier into which the sample was injected. The combined stream then flowed through a suitable reactor where the sample was oxidized and hexavalent chromium was reduced to the trivalent state; the absorbance of chromate was measured downstream at 445 nm. Results obtained on several types of waste water by this proposed method and by the standard method are compared. Interference by chloride could be prevented by adding mercuric sulphate.

2.7.2

Total oxygen demand

The total oxygen demand (TOD) technique consists of determining the quantitative amounts of oxygen required to convert the oxidizable constituents in a waste water to end products under near ideal combustion conditions. Again, instrument response time is 2–3 min and detection limits are on the order of 5 mg l⁻¹ for oxygen demanding materials. Acceptable particulate size is dependent on the instrument purchased and most waste waters will require physical disintegration prior to injection. A TOD determination may include the oxygen demand of inorganic materials such as sulphides and ferrous ions. Both TOC and TOD instrumentation can be provided with on-line, semicontinuous determinations of soluble waste water strength.

Total oxygen demand is a parameter which measures the oxygen demand of a water sample by combustion at 900°C of oxidizable matter, at a defined oxygen level, during the combustion process. For the user, there exist three important requirements, viz.:

1. The possibility of measuring total oxygen demand over a wide range of values.
2. The time per measurement should be minimal.
3. Results should be attainable without recourse to a calibration curve, i.e. they should be direct readings.

These requirements impose strict conditions with regard to the design of equipment for measuring total oxygen demand. Since complete combustion of the oxidizable matter must be assured, within a short period of time, the sample volume itself must also be small—typically, 10 μ l (larger volumes tend to generate excessive volumes of water vapour and thus undesirable pressure pulses in the actual measuring system). Hence the quantity of oxygen consumed and measured, will only be a few micrograms.

Furthermore, to avoid possible uncertainties of measuring small differences between two large quantities, the oxygen content of the gas prior to combustion must be low; and for, good reproducibility, it must also be constant. Finally, since large excesses of oxygen can give different levels of oxidation when substances containing nitrogen and sulphur are oxidized, the oxygen concentration should be matched to the probable oxygen demand of any practical sample, and the value can vary by as much as 100.

These requirements are met, for example, by the Philips Total Oxygen Demand Meter. This instrument utilizes two well known electrochemical relationships: Faraday's Law, which relates to the electrochemical transport of elements, and Nernst's Law, which is concerned with electrochemical potentials at boundaries. It is known that, at elevated temperatures and under the influence of an electrical current, oxygen can be transported through specially prepared zirconium oxide and that, in the electrolyte state and in the presence of oxygen zirconium oxide will generate an electrical potential at its surface. Furthermore, when there exists a difference in the oxygen concentration, there will be a measurable potential difference.

In the Philips total oxygen demand meter the zirconium oxide is specially prepared and is in the form of two series connected tubes or cells, through which a nitrogen carrier gas is allowed to flow. Each cell is

provided with two pairs of annular (internal and external) electrodes and the whole assembly is maintained at about 600°C.

One pair of electrodes conduct an electrical current through the zirconium oxide wall, thereby transporting oxygen from the external atmosphere through the cell wall, into the nitrogen carrier gas. The other pair is used to measure the potential difference over the zirconium oxide.

Voorn and Marlow²⁴⁷ applied this technique to waste water samples. They found an excellent correlation with chemical oxygen demand obtained for a range of pure substances containing carbon, hydrogen and oxygen.

Several nitrogen containing substances were tested by Voorn and Marlow²⁴⁷.

Their results strongly suggest that hydrogen and carbon were oxidized and nitrogen was not.

Some oxidation of combined nitrogen to nitric oxide may take place when measurements are made low in a range, so that an excess of oxygen is available for combustion.

Although poorer correlation was obtained with organic substances containing nitrogen, where chemical oxygen demand values are lower than total oxygen demand values (with chemical oxygen demand the combined nitrogen is converted to ammonia and many nitrogen containing substances are not oxidized by the dichromate to the theoretical degree), it is firmly believed that the total oxygen demand value measured by the Philips instrument closely approaches the true oxygen demand due to natural degradation, because nitrogen is the end-product of the natural nitrogen cycle. Sulphur mainly oxidizes to sulphur dioxide.

Marty and Aim²⁴⁸ have described an automatic determination of the total oxygen demand of waste water. The method gives rapid results and correlates well with chemical oxygen demand and biochemical oxygen demand. Measurements of corrections are made for nitrogen compounds which are the principal interferents.

Other workers who have discussed the determination of total oxygen demand include Wells²⁴⁹ and Ravenscroft²⁵⁰.

2.7.3

Oxygen demand index

Spectrophotometric method

The oxygen demand index of²⁵¹ a sample is determined by heating it for 20 min at 100°C with potassium dichromate in the presence of a strong acid to oxidize the organic matter. Silver sulphate is used as a catalyst and mercuric sulphate is added to prevent interference from chloride solution. The extinction of the resulting solution is measured at 600 nm. The test was found to be useful for providing a rapid estimate of the biochemical oxygen demand of waste water provided that enough data were collected at each sampling point. Correlation of results between the oxygen demand index and the five-day dilution biochemical oxygen demand was inferior to that for the biochemical oxygen demand and the standard chemical oxygen demand but was superior to that for the biochemical oxygen demand and total organic carbon.

2.7.4

Oxygen demand parameters

Biochemical oxygen demand tests are historically and routinely used for a great many purposes, including some for which the test is not well suited. In the majority of cases, the test is performed by the dilution (bottle) method, and the incubation time is 5 days. The results are often designated BOD₅. For example, BOD₅ tests are used at waste water treatment plants to assess influent and effluent strength. Loading and

design criteria for biological treatment processes are frequently based on kilograms of BOD₅ per day. Even the quality of the receiving water is often evaluated on this basis, although in this application there is seldom if ever, a rational justification for the 5-day incubation in terms of real-world conditions.

The most serious and obvious limitation of BOD₅ as a parameter for process control or effluent monitoring is its long response time. Good reproducibility in this test is attained only when the sample tested contains a variety of readily biodegradable compounds, mostly of natural origin, or only slightly modified from their natural sources. When the sample contains substantial proportions of natural or synthetic products that require energy input before they become readily degradable, precision suffers seriously. A simple example is acetate. One molecule of adenosine triphosphate is required per molecule of acetate to enter the Krebs cycle. Samples high in acetates usually show a lack of reproducibility in the standard BOD₅ test because of a variable lag period before the onset of rapid oxidation. On the other hand, a sample that contains a preponderance of readily degradable components tends to exhibit a more repeatable course of oxygen utilization and hence a more reproducible value after an arbitrarily fixed time.

There are many cases for which a 5-day BOD value alone has little meaning. A different incubation period, a series of points at various incubation periods (that is, a 'BOD curve'), use of an adapted microbial culture, a technique other than the bottle dilution method or a combination of such modifications is often far more informative. For many kinds of samples, a BOD curve may be needed for intelligent interpretation of a 5-day value.

For monitoring and controlling the operation of waste water treatment plants, other and better tools exist and should be used. Several methods for evaluation of waste water strength are available that can be implemented rapidly for both process control and monitoring purposes.

Sherrard et al²⁵² outline the purposes and requirements of parameters for monitoring and control of waste treatment processes. These authors indicate the limitations of the BOD test and discuss possible alternatives including chemical oxygen demand, total carbon and total organic carbon, total oxygen demand, use of respirometers and comparison between measurement parameters.

It is often assumed that measurements of COD, long term BOD, TOD the stoichiometric equivalent of TOC, and the long term respirometric oxygen requirement for a waste water sample should produce equal results. Because each technique is measuring a different combination of waste water properties, however, identical results and absolute oxygen demand correlations between measurement systems cannot be expected. For example, the chemical techniques do not differentiate between readily biodegradable and refractory organic materials. The rapid biological techniques do not describe the long term oxygen demand that can be exerted by organic material incorporated into aeration basin floc particles. Despite these deficiencies, each measurement provides useful information. The rapid techniques described can aid significantly in effective, efficient, on-line operation of a treatment plant. In addition, their use with batch biological tests can be used to predict plant response to changing influent conditions.

Waite²⁵³ evaluated the usefulness of the conventional biochemical oxygen demand test and considered possible alternatives or replacements for the biochemical oxygen demand determination. The nature of organic contaminants encountered in waste waters, the kinetics of the biochemical oxygen demand determination and the relevance of other methods of estimating the organic fraction are discussed, and the nature and methodology of a range of experimental procedures for water quality estimation are reviewed. A single test such as the biochemical oxygen demand test is not considered completely satisfactory; the total organic carbon test is considered superior in certain circumstances.

As a result of a detailed study of the application of the BOD method to waste water samples, Stover and McCartney²⁵⁴ recommended the following general rules:

Use acclimated seed material with complex waste waters.

Inhibit nitrification when appropriate (run both inhibited and uninhibited BOD₅).

Determine seed demand and dilution water depletions with multiple dilutions.

Apply appropriate correction factors. Dilution water correction can be calculated according to the amount of dilution water used if desired.

Generally, if greater than 200 ml of dilution water is used, the total water correction can be used.

Select seed concentration to yield between 0.2 and 1.0 mg l⁻¹ oxygen demand.

During data interpretation, place greater emphasis on sample volumes with higher total depletion. The influences of water and seed corrections are minimized during the calculation of these BOD values.

Best sample volumes for BOD calculations are those with net depletions between 25 and 75 per cent of the initial DO values.

Place more emphasis on sample volumes with greater than 2.0 mg l⁻¹ net depletion. Do not use sample volumes with final DO values below 1.0 mg l⁻¹.

Plot BOD versus sample volume to determine inhibition. Use sample volumes below the threshold inhibition level for BOD calculations.

Although the BOD test is run as a series of dilutions, the result from each dilution is ordinarily analysed separately from the rest of the series of dilutions. By combining the results observed from each dilution, using appropriate data points and considering the effects of the previously described factors of BOD testing, the variability of BOD testing can be minimized.

Correlations between oxygen demand parameters

Work on the correlation of oxygen demand parameters measured in waste waters, principally chemical oxygen demand, biochemical oxygen demand and total oxygen demand, is summarized in [Table 33](#). A fair assessment of the situation as it is now seen, regarding these correlations is as follows.

Analysis of total organic carbon in plant effluents, receiving waters, and in water and waste water treatment processes is rapidly gaining favour as the most reliable index of waste loading and stream pollution. If the waste is from a single source, or relatively constant in nature, reasonably good correlation is usually found between total organic carbon, biochemical oxygen demand and chemical oxygen demand. If the wastes are highly variable in composition, correlation among the methods is lost. That is not too surprising because there is no inherent correlation between biochemical oxygen demand and chemical oxygen demand. The chemical oxygen demand method does not oxidize certain organics which are measured in the total organic carbon procedure and are biodegraded in the biochemical oxygen demand test. Results in both the biochemical oxygen demand and chemical oxygen demand methods are affected by certain oxidizable inorganic compounds, while total organic carbon measurement is unaffected by those inorganic compounds in concentrations normally found in the waters to be analysed.

Methodology: conventional 5 day BOD

Stover and McCartney²⁵⁴ showed that by making a plot of BOD exerted versus sample volume added to the BOD bottle, the threshold inhibition level of BOD testing can be determined. The threshold inhibition level can be defined

TABLE 33
Correlation of oxygen demand parameters of waste waters

Parameters	Comments	Ref.
COD-BOD	COD subdivided into (a) 5 day BOD portion, (b) sludge COD portion and (c) filtrate COD portion COD, BOD and BOD each have their own significance in the assessment of waste waters. Conventional BOD and 5-day BOD portion (a) parameters cannot be replaced by COD	255
TOD-COD -BOD	Low correlation of TOD with BOD TOD demand correlates well with COD plus BOD measurements if corrections made for nitrogen compounds	256,257, 258

as the lowest concentration or volume that causes a reduction in the carbonaceous biological oxidation rate for carbonaceous BOD inhibition. When the BOD of this waste water was measured, with sample values below 3 ml of a 1–10 waste water dilution, consistent BOD values were determined. This type of depletion indicating inhibition is often observed in many municipal waste waters and overlooked.

It is clear that an understanding of the kinetics and mechanisms of biological growth and respiration are necessary for accurately determining BODs of complex municipal and industrial waste water types. The effects of acclimated versus non-acclimated seed material, nitrification, inhibition, dilution, seed demand and dilution water depletion must be understood by the analyst conducting BOD testing to minimize variability and obtain reliable test results.

Tests on waste water samples have shown²⁵⁹ that intermittent stirring tended to increase the five-day BOD value by about 7 per cent. This increase is of approximately the same order of magnitude as the error inherent in the BOD determination itself and it is therefore concluded that for routine determinations stirring is unnecessary.

Middlebrooks²⁶⁰ has presented a nomogram for solution of the BOD equation. This nomogram solves the ultimate BOD temperature correction, and the rate constant temperature correction.

Parisod and Schroeder²⁶¹ carried out experiments with glucose, glutamic acid, succinic acid, and sorbitol to determine whether plateau BOD values obtained from mixed substrate systems were stoichiometric end-points for the substrate conversion reactions and to investigate the kinetics of the mixed substrate system. It was found that the plateau values resulting from substrate mixtures could be closely predicted by adding the average plateau values for the individual components. It was also shown that the ultimate BOD of a waste water can be determined by adding the plateau BOD and the theoretical BOD of the cells produced up to the plateau.

Damiecki²⁶² has stated that 5-day BOD determinations should be performed in the presence of 0.5 mg l⁻¹ of allylthiourea as a nitrification inhibitor. A comparison of BOD values for effluents from biological treatment plants with a wide range of sludge and volumetric loadings, with and without the addition of allylthiourea is reported. Both for biological filters and for activated sludge plants the values determined without the addition of allylthiourea were markedly higher than those for which nitrification was inhibited. The difference decreased from over 60 per cent at low values of organic sludge loading (200 BOD per m³ day) to about 20 per cent at 750 BOD per m³ day and over.

Ogunrombi and Onuoha²⁶³ present a second order model of the kinetics of the BOD reaction. Composite samples and crude sewage waste water from the inlet to the sewage treatment plant, were analysed for biochemical and chemical oxygen demand; hydraulic flows were estimated by using a throat flume. Values of the deoxygenation rate constant were estimated on the basis of the second order kinetics. The waste

water was of medium strength, with an average BOD₅ of 310 mg l⁻¹ and COD of 491 mg l⁻¹, and an approximately linear relationship existed between BOD and COD.

Washington et al²⁶⁴ determined the amount of nitrogenous oxygen demand as measured in the standard BOD₅ tests associated with different types of sewage waters from various sources. It was found that a substantial BOD was exerted in both completely and partially nitrified sewage and primary and secondary effluents, including chlorinated effluent. Alternative techniques for limiting nitrogenous oxygen demand, to comply with effluent BOD standards, are indicated.

Ademoroti²⁶⁵ studied the effects of copper, zinc, sulphate, nitrate and chloride containments on the BOD of wastewaters. One µg l⁻¹ of copper or zinc, respectively, suppressed BOD by 33 and 16.9 per cent.

Microbial electrodes

Karube et al²⁶⁶ and Strand and Carlson²⁶⁷ have discussed microbial electrode BOD sensors. Karube et al²⁶⁶ evaluated two types of sensor for estimating BOD. The first consisted of a bacteria collagen membrane and oxygen electrode. The current of the electrode decreased to a steady state which had a linear relationship with the BOD of solution when the electrode was inserted in a solution of glucose and glutamic acid. BOD can be estimated in 15 min. The second sensor was a biofuel cell using an immobilized *Clostridium butyricum* platinum electrode. The steady state current was attained in 30–40 min at 37°C and was proportional to BOD. The relative error of the BOD estimation was within plus or minus 10 per cent, and the current output of the biofuel cell was almost constant for 30 days.

Strand and Carlson²⁶⁷ carried out rapid BOD measurements on municipal waste waters using a biofilm electrode. They compared the efficiency of a biofilm electrode with the standard BOD test for samples of crude, settled and biologically treated sewage. Two immobilized membranes (biofilms) were prepared by applying centrifuged cell paste to a nylon net; these were placed on the surface of a dissolved oxygen electrode covered with a teflon membrane and the biofilm was covered with a polycarbonate membrane filter and a protective layer of nylon mesh. The biofilm probe gave a signal within 20 min which was proportional to the conventional 5-day BOD for soluble organic matter in settled and treated sewage but did not respond to the particulate organic matter in crude sewage. The precision of the results obtained was comparable to that of the conventional 5-day BOD test and the electrode remained stable for up to 3 weeks.

Hirata et al²⁶⁸ developed equipment for the rapid determination of biochemical oxygen demand by means of a microbial electrode of immobilized living whole cells of yeast, a porous membrane, and an oxygen electrode. The oxygen electrode current indicated the level of oxygen saturated when air was bubbled through a water sample containing no organic matter; the current decreased when this water was replaced with a sample containing organic matter. Tests were carried out on various domestic and industrial waste waters. Good correlation was obtained between biochemical oxygen demand values determined by this technique and those determined by the conventional BOD₅ method.

Respirometric techniques

Respirometers can be used to determine the oxygen demand of a waste water exerted by a specific biological culture. The test is relatively easy to perform and preliminary data for monitoring purposes can be available in less than 3 hours. If used with rapidly settled influent waste waters and fresh aeration tank solids, respirometric data can be used to predict aeration tank culture responses to changing influent oxygen demands. Commercially available respirometer systems are easy to use and inexpensive to operate. Respiro

metric techniques have the advantage of providing operators with toxicity information when correlated with non-biological tests.

Damaschke²⁶⁹ has described an apparatus for the automatic determination of BOD in undiluted waste water by the continuous measurement of the oxygen consumption. The oxygen consumption is recorded continuously for 6 measuring positions simultaneously and a BOD time curve is plotted, from which the 5 day oxygen consumption can be evaluated.

Tuffy et al²⁷⁰ carried out a critical analysis of Warburg respirometry for biochemical oxygen demand determinations on waste waters. The reliability of the Warburg technique for estimation of biochemical oxygen demand at levels of 10 mg l⁻¹ or less was examined using water samples from a stream receiving discharges of primarily domestic origin. The results indicate that the Warburg method can be used to determine low levels of carbonaceous biochemical oxygen demand but that the variance is an order of magnitude greater than that of the alternative technique employing a BOD bottle and a dissolved oxygen probe. The method is, however, unsuitable for nitrification studies since, although ammonia is oxidized to nitrite under the experimental conditions, the action of Nitrobacter, and the consequent oxidation of nitrite to nitrate, is inhibited by the potassium hydroxide used to absorb carbon dioxide.

Tuffy et al²⁷⁰ used Aminco Warburg respirometers with 125 ml flasks and 50 ml sample volumes, 1 ml of 15 per cent potassium hydroxide was placed in the centre well as a carbon dioxide absorbent. Temperature was maintained at 20°C for the duration of the runs, usually 15–20 days. Standard operating procedure consisted of equilibrating the sample to 20°C and aerating it to saturation. Manometer readings were recorded to the nearest mm and incubation time to the nearest 0.01 days. In order to determine the variances of the conventional and the Warburg biochemical oxygen demand techniques, nitrification inhibited samples, uninhibited samples, and thermo-barometers were incubated. Inhibition was achieved with 0.5 mg l⁻¹ of allylthiourea replenished at 7 day intervals. Inhibited and uninhibited samples were also incubated at 20°C with the biochemical oxygen demand bottle technique. Standard 300 ml biochemical oxygen demand bottles were used and dissolved oxygen was recorded to the nearest 0.02 mg l⁻¹.

The study on nitrification was accomplished by comparing the oxygen demand, change in nitrogen species, and the enumeration of Nitrosomonas and Nitrobacter found in the Warburg sample to that found in a control.

In nitrification, the ammoniacal nitrogen in the system undergoes oxidation by the bacterial species Nitrosomonas to nitrite and then oxidation from nitrite to nitrate by the species, Nitrobacter. These reactions proceed according to the following equations respectively:



and



The associated oxygen consumption would be 3.43 mg oxygen for every 1.0 mg of nitrogen oxidized in eqn (3) and 1.14 mg oxygen for every 1.0 mg of nitrogen oxidized in eqn (4). Experimental results²⁷¹ indicate a slightly lower combined oxygen demand of 4.3 mg l⁻¹ per 1 mg l⁻¹ of ammoniacal nitrogen.

Fig. 36 is a plot of the carbonaceous biochemical oxygen demand data as well as total combined biochemical oxygen demand obtained by the two techniques. The differences between the total combined and the carbonaceous biochemical oxygen demand is that portion of the biochemical oxygen demand due to nitrification. The nitrogenous fraction calculated from the biochemical oxygen demand bottle dissolved oxygen probe technique is 34.22 mg l⁻¹ whilst that from the Warburg data is only 20.33 mg l⁻¹. Some of this difference is due to inaccuracies in measuring the 20 day carbonaceous biochemical oxygen demand

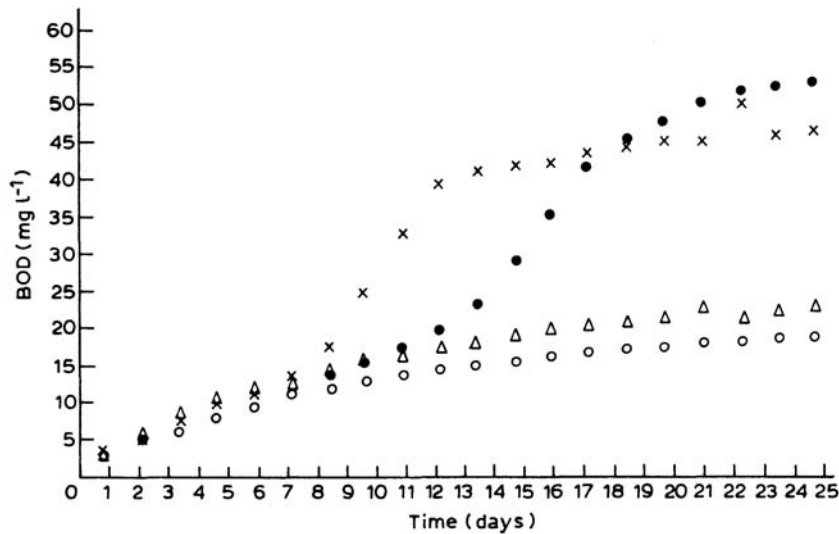


Fig. 36. BOD of Pappsaic River sample with and without nitrification as determined by Warburg and BOD bottle DO probe technique. (●) with nitrification, BOD-DO; (×) with nitrification, Warburg; (○) without nitrification, BOD-DO; (△) without nitrification, Warburg.

but the greatest portion is accounted for in an interference to the normal course of nitrification by the Warburg technique.

The oxygen respirometric method of measuring the oxygen uptake of waste waters has also been discussed by Clark et al²⁷².

Schoenen and Thofern²⁷³ using samples of synthetic waste water made measurements of BOD using an automatic manometric apparatus under various conditions, to investigate factors affecting the results, such as the speed of stirring, size of magnetic stirrer and shape of the measuring flask. Their results indicate the importance of ensuring constant, optimal and reproducible conditions for BOD tests. It is especially indicated that an optimal input of oxygen should be ensured, by a high rate of stirring, to avoid adverse effects on the microbial growth; typical results are given showing the advantages of increasing the rate of stirring from about 350 to about 700 rev per min. The use of oxygen demand curves to assess the toxic effects of a waste water is also considered.

2.8

Dissolved gases

2.8.1

Dissolved oxygen

Winkler titration

The classical method for the determination of dissolved oxygen is the Winkler titration procedure and this remains the most reliable and precise method for analysing dissolved oxygen. Toledo et al²⁷⁴ discuss

experiments carried out to verify the influence on the dissolved oxygen determination, of the following parameters: composition of the fixation reagent acid used to dissolve the formed precipitate, volume of fixation reagent and the time interval between collection and titration of the sample.

Reddy et al²⁷⁵ have described a modification of the Winkler procedure for the titrimetric determination of dissolved oxygen in waste water which eliminates interference from oxidizing or reducing compounds such as ferrous ions or chlorine in solution. The trivalent manganese is reduced with an excess of hydroquinone, the unoxidized fraction of which is estimated by titration with ceric sulphate; the errors due to oxidizable or reducible impurities are compensated for by a blank titration in which the order of addition of reagents is reversed so that the solution remains acidic. Results obtained with the modified procedure were in good agreement with those obtained by the standard Winkler method on clean samples.

Electrode measurements

Lilly et al²⁷⁶ determined dissolved oxygen in waste water chronopotentiometrically using membrane electrodes. In this method a potential of -0.7 V is applied to the electrode and a current time plot prepared. The current is measured 1.2 s after the application of the potential. A rectilinear current-concentration curve is obtained for dissolved oxygen over the range 0.5–15 mg l⁻¹ oxygen.

Wells²⁷⁷ has described a dissolved oxygen sampler for waste water samples.

Kalmaz²⁷⁸ has developed equations for calculating errors in the use of membrane covered probes for the measurement of dissolved oxygen in waste waters.

Hale²⁷⁹ has described the use of an oxygen detecting system as a dissolved oxygen probe in a feedback dissolved oxygen control system for waste water treatment plants. It was found that this system gave accurate results, while requiring neither maintenance nor recalibration throughout the 60 day test period. Innovations include a very low flow rate requirement; a rugged teflon membrane which can be brushed clean; an efficient sealing method between membrane and sensor body and a sensor which is insensitive to dissolved poisons such as hydrogen sulphide.

The feasibility of continuously measuring dissolved oxygen in the field of waste water treatment and the problem of adhesion of pollutants to dissolved oxygen electrodes and their removal have been discussed²⁸⁰. To overcome this problem the adhesion mechanism has been investigated and the effectiveness of an air-bubbling device developed to remove pollutants, has been verified in the aeration tank of an activated sludge process and in coastal waters. The air-bubbling device protects dissolved oxygen electrodes from pollutants and gives more accurate results for longer periods.

2.8.2

Free chlorine

Amperometric titration

Brooks and Sergent²⁸¹ have described an amperometric titration procedure for the determination of down to 0.002 mg l⁻¹ free chlorine in waste waters. The method is applicable in three concentration ranges: 0.002–0.05 mg l⁻¹, 0.1–0.5 mg l⁻¹ and 1–5 mg l⁻¹. This method follows the general procedures described in 'Standard Methods'²⁷¹ with the following modifications.

A three electrode cell, consisting of stationary platinum working and counter electrodes plus a saturated calomel reference electrode, was used. The platinum electrodes were of the leaf and spiral types. The three electrodes were connected to a polarograph. The cell potential was maintained at a constant +0.11 V versus

the saturated calomel electrode. Standardized 0.0028 N phenylarsine oxide was used as the titrant. At this normality 0.001 ml of phenylarsine oxide was equivalent to 0.001 mg l⁻¹ of residual chlorine.

Chlorine-selective electrode

Jenkins and Baird²⁸² reported results obtained in an investigation of an electrode system for measuring total chlorine residual in the field. Laboratory compiled data using both the Orion 97-70 residual chlorine electrode and the phenylarsine oxide back-titration method were compared and it was found that at less than 1 mg l⁻¹ chlorine concentrations, the electrode system was preferred.

The chemistry of the electrode method is based on that outlined in eqn (5). If a known amount of potassium iodide is added to the sample, the electrode is capable of quantitating the ratio (I₂)/(I⁻) which is directly related to the chlorine residual in the original sample.



Jenkins and Baird²⁸² compared chlorine determinations on waste water samples obtained by the selective electrode and the phenylarsine oxide titration procedure²⁸³. The percentage difference between results obtained by the two methods was 0.66–2.2 per cent when chlorine concentrations were greater than 1 mg l⁻¹ and 4.4–25.4 per cent for concentrations less than 1 mg l⁻¹. Hence, it is seen that the agreement between the two methods suffers in the sub mg l⁻¹ range, a result which is probably due to poor precision and accuracy of the phenylarsine oxide method in this range. This latter observation is consistent with the recommendation that the phenylarsine oxide method is not quantitative for chlorine concentrations below 1 mg l⁻¹.

Use of the electrode for measuring chlorine in residuals in waters with a biochemical oxygen demand in excess of 50 mg l⁻¹ oxygen was not possible because of a continuous needle drift toward zero. Presumably, this needle drift is due to the reaction of liberated iodine with organics in the sample.

The precision of the electrode and titration methods are comparable at the 1 mg l⁻¹ level with per cent RSDs of 1.2 and 5.0 respectively. However, at lower chlorine levels the respective per cent RSDs were 2.2 and 50 for electrode and titration methods. A similar trend was observed for accuracy comparisons, i.e. comparable results at the 1 mg l⁻¹ level and poor performance by the titrimetric method at lower levels.

Oxidizing agents such as iodate, bromine, dissolved oxygen, cupric and manganese dioxide produce a positive interference for all iodometric methods. Hence, both the titrimetric and the electrode techniques for chlorine residual are susceptible to these interferences. Because these oxidizing agents are usually present in low concentration in waste waters, resultant analytical errors are most significant for sub-mg l⁻¹ chlorine measurements. Since the electrode has good sensitivity in the sub-mg l⁻¹ range, the most accurate measurements would result if a standard addition technique were employed.

2.8.3

Chlorine dioxide

Voltammetry

Smart and Freeze²⁸⁴ described a rotating voltammetric membrane electrode which they used to measure chlorine dioxide in water and waste water. The apparatus is suitable for continuous automatic monitoring and the detection limit is less than 1 mg l⁻¹ of chlorine dioxide. At a concentration of 0.30 mg l⁻¹ the relative standard deviation is 6.4 per cent. The electrode is very specific, with no interference from

hypochlorite, chlorate, permanganate, ferric iron or sample turbidity. The results agree well with those obtained by the chlorophenol red method but are lower than those obtained by the iodoform technique.

The electrode and the chlorophenol red methods are very specific with no interferences from hypochlorite, chlorite, chlorate, chromate, permanganate, ferric iron or sample turbidity.

2.8.4

Monochloramine

Spectrophotometric method

Figuet²⁸⁵ has studied the interference from other halogens and their compounds on the colorimetric determination of free chlorine in the presence of chloramine, using diphenylene diamine. While the presence of bromides rarely results in an error greater than 10 per cent, iodides at concentrations less than $60 \mu\text{g l}^{-1}$ have a catalytic effect on the colour formation that results in significant errors. To reduce the error, the author proposes the development of the curve of colour formation with respect to time and its extrapolation to zero time. There is little interference from iodates.

2.8.5

Monobromamine

Miscellaneous

Inman and Johnson²⁸⁶ studied the kinetics of monobromamine disproportionation to dibromamine in aqueous ammonia solutions.

2.8.6

Hydrogen sulphide

Miscellaneous

Garber et al²⁸⁷ have compared various techniques for the determination of hydrogen sulphide in waste water. These included spectrophotometric, titrimetric and automated coulometric analysis based on reaction of hydrogen sulphide with electrogenerated bromine. Down to 0.1 mg l^{-1} hydrogen sulphide can be determined by latter procedure.

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Chapter 3

SEWAGE EFFLUENTS

3.1 Anions

3.1.1 *Chloride*

Miscellaneous

Official methods issued by the Department of the Environment UK¹ describe various methods for the determination of chloride in sewage and trade effluents and waters. These methods are silver nitrate titration with chromate indicator (Mohr's method), mercuric nitrate titration with diphenyl-carbazone indicator, potentiometric titration with silver nitrate and an automated mercuric-ferric thiocyanate colorimetric method. With one or other of these methods concentrations from 1 to 1000 mg l⁻¹ chloride may be determined. Brief notes are given in respect of the chloride ion-selective electrode, silver coulometry and ion chromatography, the latter being relevant at very low concentrations down to the $\mu\text{g l}^{-1}$ level.

Hindin² has shown that chloride concentrations in sewage can be determined by the ion-specific electrode method as an alternative to the standard mercuric nitrate method providing the following precautions are taken; the addition of an ionic strength adjusting solution to overcome any effect the ionic strength of the sample or standard may have, and the removal of sulphide ions by a cadmium ion precipitating solution.

3.1.2 *Fluoride*

Spectrophotometric method

Devine and Partington³ have shown that errors in the determination of fluoride in sewage by the SPADNS colorimetric method are due to sulphate carried over during the preliminary distillation step. It is suggested that the colorimetric method should be replaced by the fluoride-ion electrode method following distillation.

3.1.3

Nitrate

Spectrophotometric method

Slicko and Tawfik⁴ have described an automated technicon on-line method for overcoming phosphate interference in the cadmium reduction method for the determination of nitrate. It involved removal of phosphate by precipitation with calcium chloride prior to the sample entering the reduction column.

Ion-selective electrodes

Nitrate levels in sewage in amounts down to 1 mg l^{-1} have been determined by specific ion electrodes^{5,6}. Langmuir & Jacobson⁵ used a non-porous plastic membrane nitrate-selective electrode and compared results obtained with this electrode and those obtained by a standard spectrophotometric method on a sewage works effluent. The results indicate that the selective ion electrode is suitable both for laboratory and plant monitoring purposes. Only chloride and, to a lesser extent, nitrite and bicarbonate interfere in these measurements of nitrate.

3.1.4

Nitrate and nitrite

Spectrophotometric method

Workers at the Water Research Centre UK⁶ have described detailed procedures based on the use of the Technicon Autoanalyser AA11 for the determination of nitrate and nitrite in sewage and sewage effluents. Measurements of nitrate in sewage at the $10\text{--}50 \text{ mg l}^{-1}$ level were made with a within batch standard deviation of 0.1 mg l^{-1} nitrate. Nitrate recoveries at the 12 mg l^{-1} level were in the range $100\text{--}100.7$ per cent. Standard deviations of nitrite determinations were in the range 0.003 (at 0.2 mg l^{-1} nitrite) to 0.010 (at 1 mg l^{-1} nitrite). Nitrite recoveries in the 0.4 mg l^{-1} region were between 98 and 102 per cent.

3.1.5

Phosphate

Spectrophotometric method

The Department of the Environment UK⁷ has issued details of the spectrophotometric methods for the determination of ortho-phosphate in sewage effluents.

These methods are based on reaction with acid molybdate reagent to form a phosphomolybdenum blue complex which is determined at 882 nm . The first method has a range of $0\text{--}0.40 \text{ mg l}^{-1}$ (after dilution of sample if required) and the second is mainly designed for oligotrophic waters with phosphorus contents in the range $0\text{--}25 \mu\text{g l}^{-1}$. In addition, the report discusses various methods for converting other forms of phosphorus to orthophosphate, and the elimination of interference due to arsenic, based on the reduction of arsenate to arsenite.

Bretscher and Gas⁸ discuss reduction reagents for the spectrophotometric determination of phosphate in sewage as the phosphomolybdenum blue complex. They point out that the disadvantage of aqueous stannous chloride reduction reagent is that it oxidizes rapidly and a fresh solution must be prepared daily. Solutions of stannous chloride in glycerol were found to be stable for at least six months.

Flow injection analysis

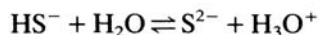
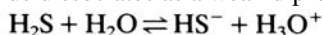
Schulze and Thiele⁹ compared results obtained by flow injection analysis and the standard DIN 38402 method for the determination of orthophosphate.

3.1.6 *Sulphide*

Draeger tube method

Ballinger and Lloyd¹⁰ have described a detailed procedure for the rapid determination of down to 0.06 mg l⁻¹ sulphides in sewage samples. Hydrogen sulphide is brought to solution/vapour equilibrium in a closed flask under controlled conditions. The concentration of hydrogen sulphide vapour is determined by means of Draeger tubes, and related to the concentration in solution by means of a calibration graph.

In aqueous solution, hydrogen sulphide dissociates as a weak diprotic acid:



At a given pH, the degree of dissociation depends upon the temperature and activity of the sulphide species. At pH 5.0, dissolved sulphides are present almost entirely as undissociated hydrogen sulphide. It follows from Henry's law that the vapour pressure of hydrogen sulphide above its aqueous solution is a function of the mole fraction of dissolved hydrogen sulphide. In this method, hydrogen sulphide is brought to solution-vapour equilibrium in a closed flask, and the concentration of hydrogen sulphide vapour in the air space is determined by conventional gas analyser. The pH of the solution is adjusted to 5.0 by means of a buffer solution and the ionic strengths of samples and standards are maintained at a constant level by the strong electrolytes incorporated into this solution. The above method determines undissociated hydrogen sulphides, hydrosulphide and sulphide ions. To determine total sulphide including above plus other compounds liberating hydrogen sulphide from a cold solution containing 0.5 M hydrochloric acid, follow the above procedure using 50 ml acid chloride solution instead of buffer solution.

The comparative freedom of interference from other sulphur-containing anions is of particular note. Sulphite, metabisulphite and thiosulphate do not interfere significantly at 100 fold excess, detergents depress the recovery of sulphide at 100 fold excess but do not interfere significantly at 10 fold excess.

Ion-selective electrode

Glaister et al¹¹ studied three sulphide ion-selective electrodes in cascade flow and flow-through modes to investigate carrier stream, sample size and flow rate parameters in the analysis of sulphide in sewage effluents. Results were compared with those obtained by direct potentiometry. The electrodes were successfully used as detectors of sulphide during flow injection analysis and the presence of ascorbic acid in

the standard antioxidant buffer minimized deleterious effects of hydrogen peroxide in the samples. Both the cascade flow and flow-through modes of electrodes yielded sulphide concentrations similar to those from colorimetric methods.

3.1.7 *Cyanide*

Spectrophotometric method

Kodura and Lada¹² determined cyanide in sewage spectrophotometrically using ferriin. Iron, copper sulphide, acrylonitrile, phenol, methanol, formaldehyde, urea, thiourea, caprolactam or hexamine did not interfere at concentrations up to 1 g l^{-1} . In an indirect atomic absorption procedure¹³ for determining down to $20\ \mu\text{M}$ cyanide the sample is treated with sodium carbonate and a known excess of cupric sulphate to precipitate cupric cyanide. Excess copper in the filtrate is then determined by atomic absorption spectrometry and hence the cyanide content of the sample calculated. Iron III does not interfere except at low cyanide concentrations. Quantitative recovery of cyanide from sewage was obtained by this procedure.

3.1.8 *Borate*

Borate has been determined¹⁴ in amounts down to 0.02 mg l^{-1} in sewage effluents spectrophotometrically by reaction with phenol and carminic acid in concentrated sulphuric acid to produce a coloured compound with an absorption maximum at 610 nm .

3.1.9 *Miscellaneous*

King¹⁵ has discussed the application of the Autoanalyser to the determination of ammonia, phosphate, total phosphorus, total nitrogen, nitrite, nitrate, detergents, chloride, toxic metals, cyanide and phenols in sewage.

3.2 **Cations**

3.2.1 *Ammonium*

Spectrophotometric methods

Autoanalyser techniques have been used extensively for the determination of ammonium ions in sewage^{16,17}. Official methods issued by the Department of the Environment UK¹⁷ describe a spectrophotometric Autoanalyser method for the determination of less than 1 mg l^{-1} ammonium ion in sewage based on the formation of the indophenol blue compound. The within batch standard deviation ranges from 0.2 mg l^{-1} at the 10 mg l^{-1} ammonium level to 0.5 mg l^{-1} at the 50 mg l^{-1} ammonium level. 100 per cent recovery of ammonium was obtained from spiked sewage samples.

Ruider and Spatzierer¹⁸ have described a comparator method for the determination of ammonium and phosphate in sewage works effluent. Results obtained were generally within 15 per cent of those obtained by more reliable Autoanalyser methods but represent a good approximation requiring less time and expense than the standard procedures in circumstances where more sophisticated equipment is not available.

Rechenberg¹⁹ described procedures for the determination of the ammonium content of sewage as a precaution against corrosive attack of concrete. A colorimetric method based on the use of Nessler's solution and an appropriate standard solution (10 mg l⁻¹ ammonium chloride) was adequate to determine whether the ammonium concentration was less than 10 mg l⁻¹ (after distilling off free ammonia and ammonium hydroxide). For amounts greater than this threshold value up to 100 mg l⁻¹ alkaline hydrolysis, absorption of distillate in concentrated sulphuric acid followed by back titration against standard alkali can be employed.

Klasse²⁰ has described a rapid voltammetric method for the determination of ammonia nitrogen in sewage sludge. The method is based on the volume of nitrogen released following oxidation of ammonia by an alkaline solution of hypochlorite.

3.2.2

Aluminium

Atomic absorption spectrometry

This element has been determined in sewage by atomic absorption spectrometry²¹. For electrothermal analyses of aluminium a Perkin-Elmer Model 603 atomic absorption spectrometer was employed in conjunction with a Perkin-Elmer HGA 76 heated graphite atomizer, with argon as the inert gas. The conditions were: sample injected, 20//1; drying, 100°C for 30 s; two stage churning with ramping from 100°C to 400°C in 45 s followed by isothermal ashing at 1200°C for 30 s; atomization at 2770°C for 8 s. The insensitive line at 257.5 nm and a spectral band of 0.2 nm were used for electrothermal analysis.

The sewage sample was acidified to 1 per cent with nitric acid and homogenized.

3.2.3

Calcium

A Department of the Environment (UK) Report discusses the determination of calcium in sewage by atomic absorption spectrometry in the presence of a lanthanum salt as a calcium release agent²².

3.2.4

Cadmium

Hoffmann²³ has reviewed the determination of cadmium in a sewage system.

Ion chromatography

See [section 3.2.14](#) (multication analysis).

Preconcentration

See [section 3.2.14](#) (multication analysis).

3.2.5

*Copper and lead**Polarography*

Cooksey et al²⁴ used dc polarography to determine copper and lead in sewage works effluents at concentrations in the range 1–20 mg l⁻¹. Phosphate and carbonate interfered in the measurements.

Ion chromatography

See [section 3.2.14](#) (multication analysis).

Preconcentration

See [section 3.2.14](#) (multication analysis).

3.2.6

*Chromium**Luminescence and atomic absorption spectrometry*

Low temperature luminescence measurements of the chromium III thicyanate complex²⁵ and atomic absorption spectrometry²⁶ using an air-acetylene flame have been used to determine chromium in sewage. The chemiluminescence method²⁵ is capable of determining down to 0.1 µg l⁻¹ chromium whilst the atomic absorption method determined down to 0.004 µg l⁻¹. In the latter method the sample is concentrated by a factor of five. Interference effects were reduced by working with a flame on the verge of luminosity rather than a distinctly luminous flame. Inter-element effects were considered acceptable.

Preconcentration

See [section 3.2.14](#) (multication analysis).

3.2.7

Iron

See [section 3.2.14](#) (multication analysis).

3.2.8

*Magnesium**Atomic absorption spectrometry*

A Department of the Environment UK²² report discusses the atomic absorption spectrometric determination of magnesium in sewage. Lanthanum is present in the solution which is aspirated in order to release magnesium from refractory compounds. The limit of detection is 0.06 mg l^{-1} .

3.2.9

*Lead**Preconcentration*

See [section 3.2.14](#) (multication analysis).

3.2.10

*Nickel**Miscellaneous*

Cantwell et al²⁷ have described an ion concentration method for the determination of 10^{-6} – 10^{-7} M of nickel in sewage utilizing application of an ionexchange column equilibrium method and EDTA nickel and glycol-1-alanine nickel ligands.

Ion chromatography

See [section 3.2.14](#) (multication analysis).

3.2.11

*Selenium**Fluorescence spectrometry*

Elliott et al²⁸ determined selenium in urban and rural sewage sludges using fluorescence spectrometry of the piaselelol complex with 2,3-diamino naphthalene. The urban sludge contained elemental selenium or selenium II and little or no organic or oxidized selenium. Rural sludge contained a considerable proportion of organic selenium in addition to reduced forms. These results reflect both the origin of the sludges and the treatment they had received.

3.2.12

*Zinc**Ion chromatography*

See [section 3.2.14](#) (multication analysis).

Preconcentration

Zinc in sewage has been preconcentrated on anion-exchange resin prior to desorption with hydrochloric acid and spectrometric determination²⁹.

The preconcentration of zinc is also discussed in [section 3.2.14](#) (multication analysis).

3.2.13

Other elements

These are discussed under section dealing with multication analysis. Elements discussed are: sodium, potassium, rubidium, caesium, lithium, strontium, barium, cobalt, manganese, molybdenum, mercury, arsenic, antimony, vanadium, silver, gold, titanium, tungsten, tantalum, zirconium, hafnium, scandium, cerium, europium, lanthanum, samarium, neodymium and terbium.

3.2.14

*Multication analysis of sewage**Atomic absorption spectrometry*

LEAD, CADMIUM, COPPER, CHROMIUM, NICKEL AND ZINC: Carrondo et al³⁰ analysed homogenized samples of sewage and sewage effluents by a rapid flameless atomic absorption technique. The results obtained for the analysis of lead, copper, cadmium, chromium, nickel and zinc were compared with those obtained by acid digestion and flame atomic absorption. The flameless method was found to be suitable for all metals in all samples and the results were comparable for accuracy with conventional methods.

A Perkin-Elmer model 305 atomic absorption spectrophotometer fitted with a deuterium background corrector and an HGA 72 heated graphite atomizer was used by these workers for all flameless analysis.

Nitric acid (1 per cent), sulphuric acid-nitric acid or nitric acid acid-hydrogen peroxide were used to carry out the initial sample digestion.

The results obtained by flameless procedures using various sample pre treatments are shown in [Table 34](#).

No significant differences between the treatments were detected for the analysis of cadmium, copper, nickel and zinc in all samples. It may therefore be concluded that all three methods are suitable for the analysis of these metals in these samples.

Carrondo et al³⁰ also examined these samples by flame atomic absorption spectrometry and, with some elements at least, they found the results were not as satisfactory as those obtained by flameless techniques. For the analysis of lead, for example, only flameless atomic absorption yielded accurate results, although flame results were of the same order of magnitude. The respective detection limits for the analysis of lead by the two methods are for flame $10 \mu\text{g l}^{-1}$ and for flameless $0.05 \mu\text{g l}^{-1}$. This clearly indicates the value of

the increased detection limits enjoyed by flameless atomic absorption spectro photometry for the analysis of this type of sample.

The rapid flameless procedure can be used advantageously for routine analysis. The time saved is considerable, since homogenization takes only five minutes as opposed to the three to six hours required to undertake a digestion. This more than compensates for the additional time (three minutes) required for flameless analysis as opposed to flame analysis. Moreover, the sensitivities are considerably lowered and so extraction and/or concentration techniques that could be required for some final effluent samples and more generally for lead analysis, may be avoided.

ALUMINIUM, CALCIUM, IRON AND MAGNESIUM: The same workers³¹ also Investigated the application of both flame and flameless electrothermal atomic absorption spectrometry to the determination of these elements in sewage. They present the results of an experiment to compare a rapid electrothermal atomic absorption method of analysis using low-sensitivity lines, and requiring

TABLE 34
Concentrations of lead, cadmium and copper in raw sewage, settled sewage and final effluent determined by three flameless analytical methods

Metal	Sample	Method	Mode	<i>F</i> test level of significance	Mean conc. mg l ⁻¹ (×100)	R.S.D. (%)
Lead	Raw sewage	H ₂ O ₂ /HNO ₃	FL	0.01	10.5	6.7
		Homog	FL		9.9	4.2
		H ₂ SO ₄ /HNO ₃	FL		8.1 ^a	11.0
	Settled sewage	H ₂ O ₂ /HNO ₃	FL	0.01	5.8	3.9
		Homog	FL		5.6	2.7
		H ₂ SO ₄ /HNO ₃	FL		4.4 ^a	10.5
	Final effluent	H ₂ O ₂	FL	0.05	2.8	8.7
		Homog	FL		2.6	4.7
		H ₂ SO ₄ /HNO ₃	FL		2.4 ^b	8.5
Cadmium	Raw sewage	Homog	FL	N.S.	5.9	2.6
	Settled sewage	Homog	FL	N.S.	0.60	15.6
	Final effluent	Homog	FL	N.S.	0.38	15.0
Copper	Raw sewage	Hotmog	FL	N.S.	26.8	3.4
	Settled sewage	Homog	FL	N.S.	10.2	5.6
	Final effluent	Homog	FL	N.S.	5.6	7.5
Chromium	Raw sewage	Homog	FL	N.S.	19.9	2.1
	Settled sewage	Homog	FL	N.S.	18.3	1.5
	Final effluent	Homog	FL	0.5	9.6	2.3
Nickel	Raw sewage	Homog	FL	N.S.	26.3	2.2
	Settled sewage	Homog	FL	N.S.	23.6	2.8
	Final effluent	Homog	FL	N.S.	16.7	3.4
Zinc	Raw sewage	Homog	FL	N.S.	64.5	2.0
	Settled sewage	Homog	FL	N.S.	25.5	4.6
	Final effluent	Homog	FL	N.S.	12.9	3.2

Metal	Sample	Method	Mode	<i>F</i> test level of significance	Mean conc. mg l ⁻¹ (×100)	R.S.D. (%)
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^a Indicates that individual treatment means are different from the others at the 0.01 probability.

^b Indicates that individual treatment means are different from the others at the 0.05 probability.

FL=flameless atomic absorption analysis; H₂O₂/HNO₃=hydrogen peroxide-nitric acid digestion; H₂SO₄/HNO₃=sulphuric acid-nitric acid digestion; Homog= pretreatment by homogenization.

N.S.=not significant at the 0.05 probability.

only homogenization as pre-treatment for samples, with flame atomic absorption analysis of acid-digested samples, using high-sensitivity lines, for determining aluminium, calcium, iron and magnesium in sewages and sewage effluents. They concluded that the rapid electrothermal atomic absorption technique saves considerable time and it is recommended for use in routine analysis.

Flame analysis was undertaken using a Perkin-Elmer Model 603, atomic absorption spectrophotometer equipped with deuterium background correction. In order to remove interferences or suppress ionization, the samples and standards to be analysed for aluminium were made up to 2000 mg l⁻¹ in potassium chloride and those to be analysed for calcium and magnesium were made up to 0.5 per cent in lanthanum.

Electrothermal analyses were undertaken using the same spectrophotometer in conjunction with a Perkin-Elmer HGA-76 heated graphite atomizer. The atomization programme used was identical for all metals and consisted, for the 20 µl samples used, in a drying stage at 100°C for 30 s, a double stage thermal decomposition with temperature ramping from 100 to 400°C in 45s (rate 2), followed by isothermal decomposition at 1200°C for 30 s and atomization at 2770°C for 5 s for all metals except aluminium, for which an 8 s atomization was used. The ramping stage during the thermal decomposition avoided spattering of the sample that would otherwise have occurred if the temperature had been suddenly increased from 100 to 1200°C.

A comparison of the means indicated that the sulphuric acid-nitric acid digestion yielded lower results for the determination of calcium in all samples. Results obtained by flame atomic absorption spectroscopy and the hydrogen peroxide nitric acid digestion procedure and electrothermal atomic absorption spectroscopy in conjunction with homogenization were always in agreement and yielded higher recoveries than the sulphuric acid-nitric acid digestion procedure. For the determination of magnesium in settled sewage and final effluents, the results obtained by the hydrogen peroxide-nitric acid digestion were comparable to those obtained by both of the other methods. However, a statistically significant difference exists between the sulphuric acid-nitric acid digestion followed by flame atomic absorption spectroscopy and homogenization followed by the electrothermal method, the former method yielding lower results than the latter. For unknown reasons, all values seem to be in good statistical agreement for the determination of magnesium in raw sewage. The lower results obtained for the determination of calcium and to a lesser extent magnesium after digestion by the sulphuric acid-nitric acid method are probably due to the formation of insoluble sulphates that were retained in the filter or were not aspirated into the flame.

It is concluded that the rapid electrothermal atomic absorption method compares well with flame atomic absorption spectroscopy in conjunction with digestion methods. Homogenization takes only 5 min as opposed to 3–6 h needed for digestion; this more than compensates for the additional time (2–3 min) required in the electrothermal as opposed to the flame method. The electrothermal method has the further advantage over flame atomic absorption spectroscopy that it dispenses with the need to add interference removal agents to samples and standards prior to analysis. Deuterium background correction is not required for the determination of the metals indicated.

The Standing Committee of Analysts (UK)³² have described an atomic absorption spectrometric method for the determination of lithium, magnesium, calcium, strontium and barium in sewage effluents.

Inductively coupled plasma atomic emission spectrometry

Moselby and Vijan³³ developed inductively coupled plasma excitation sources for use in the simultaneous determination of sixteen elements in sewage effluents. In Table 35 are shown data on control solutions over a three month

TABLE 35

Typical results for selected samples and measurement methods (all concentrations are in mg l⁻¹)

Sample	Quality control A					Quality control B				
	I.c.p.			A.a.s.		I.c.p.			A.a.s.	
Element	Expected	Found ^a	S.d.	Found ^a	S.d.	Expected	Found ^a	S.d.	Found ^a	S.d.
Fe	2.0	2.07	0.17	1.97	0.16	4.0	3.88	0.31	3.89	0.17
Al	2.0	1.87	0.19	1.90	0.23	4.0	3.49	0.35	3.73	0.19
Ca	25.0	24.8	1.89	25.6	1.75	50.0	48.3	3.59	49.0	2.02
Zn	0.4	0.42	0.08	0.37	0.03	0.8	0.78	0.09	0.74	0.03
Cd	0.4	0.40	0.03	0.40	0.03	0.8	0.76	0.06	0.79	0.08
Co	0.5	0.47	0.04	0.46	0.06	1.0	0.89	0.08	0.94	0.06
Mg	10.0	9.77	0.85	10.4	0.57	20.0	18.7	1.52	20.8	2.44
Mn	0.4	0.39	0.03	0.41	0.04	0.8	0.74	0.06	0.08	0.04
Cr	0.5	0.48	0.04	0.47	0.04	1.0	0.91	0.07	0.94	0.07
Cu	0.4	0.41	0.07	0.40	0.05	0.8	0.74	0.10	0.77	0.03
Ni	1.0	1.01	0.08	0.94	0.09	2.0	1.91	0.15	1.88	0.08
Pb	0.5	0.51	0.06	0.50	0.06	1.0	0.98	0.08	0.98	0.07
Mo	0.2	0.21	0.02	0.20	0.02	0.4	0.40	0.03	0.39	0.04
Sr	0.2	0.20	0.02	0.23	0.03	0.4	0.40	0.05	0.46	0.05
Ti	—	—	—	—	—	—	—	—	—	—
V	0.2	0.18	0.02	0.19	0.04	0.4	0.36	0.03	0.39	0.05

^a Average of 20.

period obtained by the inductively coupled plasma technique and by conventional atomic absorption spectrometry.

As shown in Table 35 results appear to be acceptable, although there is a slight bias towards the high concentration for the plasma technique. Statistical evaluation of the plasma and the atomic absorption results obtained on control solutions A and B for the same period is also summarized in Table 35. The calculated accuracy and precision values represent the long-term analytical performance of both systems. The following sample digestion procedure was used by these workers.

Aliquots (2 ml) of each sample were pipetted into test tubes held in the aluminium blocks. Blanks and control solutions were included in each block. The loaded blocks were placed in a forced air oven to dry overnight at 90°C. The dried materials were digested in aqua regia; 4 ml of aqua regia was dispensed into each test tube and the aluminium block was placed on a hot plate at 120°C. Samples were allowed to digest

until brown fumes ceased to evolve and smooth boiling and refluxing ensued. A few drops of nitric acid were added to test tubes showing a dark residue. The volume in each test tube was reduced to approximately 2 ml by vaporation. The aluminium block was allowed to cool to room temperature and the content of each tube was diluted to 25 ml with distilled water. The acid concentration of the prepared solution was 1–1.3 M.

Digestion with a mixture of nitric acid and hydrogen peroxide has also been used to prepare solutions of sewage for analysis by inductively coupled plasma atomic emission spectrometry³⁴.

Neutron activation analysis

Kim et al³⁵ have determined trace inorganic constituents in urban sewage by monostandard neutron activation analysis and have used this method to determine the fluxes and dissolved trace metal through a sewage works³³. The concentration of trace elements in sewage is assessed by an appropriate sampling of effluent; the sewage collected either from the inflow or the outflow of the plant is centrifuged and filtered with a 0.45 µm micropore filter and the filtrate adjusted to pH2 using 14 M ultrapure nitric acid, solid samples were dried at 60°C.

The procedure described by Kim³⁵ provides the opportunity of activating a large volume of water sample for any desired length of time and of direct gamma spectrometric assay in a stable geometry. Such a possibility without chemical elaboration, therefore, increases sensitivity and accuracy. Furthermore, the use of standards is eliminated by introducing the monostandard method which replaces the standards by nuclear data. The method facilitates attaining the high precision of analysis without sacrificing the accuracy.

Irradiation was carried out on 250 ml portions of the liquid samples, adjusted to pH 2 with nitric acid and contained in a quartz volumetric flask.

After irradiation, the sample solution was cooled for 2–7 days depending on its activity intensity and transferred into a counting vessel for gamma spectrometry. The standard wires are dissolved in 6 M hydrochloric acid and diluted to a 250 ml in a counting vessel with just the same geometry as the sample mounting.

Table 36 presents the weighed mean values of each element in the effluents and suspended materials. The concentration of an element in effluent I is the sum of its concentrations in effluent II and suspended material. For silver, gold, mercury, caesium and scandium, the given standard deviations include analytical errors as well as deviations owing to inhomogeneities. Since the elements barium and rubidium are not detected in the suspended materials, both inflow and outflow, their concentrations in effluent I are assumed to be equal to those found in effluent II and they are given in brackets. The analytical results shown in this table indicate the location of trace elements, either in the solution or in the suspended material. Nearly all the silver as well as the mercury is found in the suspended material, whereas other elements are dissolved largely in the solution, except gold which is distributed between both. This characteristic is the same for the inflow and outflow, which can be easily ascertained by comparison of the concentration in effluent I with that in effluent II.

The techniques of inductively coupled plasma atomic emission spectrometry and neutron activation analysis are receiving extensive attention for multielement analysis of sewage samples. The former method is fast and requires a relatively small amount of sample but its sensitivity is still inferior to the

TABLE 36

Distribution of trace elements in effluents and suspended materials of the inflow and outflow

Element	Inflow			Outflow		
	Effluent I ^a ($\mu\text{g l}^{-1}$)	Effluent II ^b ($\mu\text{g l}^{-1}$)	Suspended mat ^c ($\mu\text{g l}^{-1}$)	Effluent I ^a ($\mu\text{g l}^{-1}$)	Effluent II ^b ($\mu\text{g l}^{-1}$)	Suspended mat ^c ($\mu\text{g l}^{-1}$)
Ag	9.05±0.07	0.41±0.02	253±2.1	4.97±0.18	0.78±0.16	346±7
Au	0.041±0.001	0.021±0.001	0.58±0.02	0.032±0.002	0.016±0.002	1.40±0.06
Ba	(20.5±0.7) ^d	20.5±0.7	—	(37.8±3.1)	37.8±3.1	—
Br	128±2	127±2	26.5±0.7	188±11	187±11	52.8±2.7
Co	0.83±0.01	0.78±0.01	1.41±0.06	1.16±0.03	1.09±0.03	5.75±0.20
Cr	12.3±0.1	9.7±0.1	76.5±2.5	9.59±0.28	8.42±0.26	96.7±9.6
CS	0.345±0.002	0.333±0.002	0.345±0.036	0.58±0.06	0.57±0.06	1.02±0.18
Fe	187±5	141±4	1357±63	119±5	100.8±4.9	1496±87
Hg	0.262±0.008	0.045±0.006	6.37±0.18	0.293±0.061	0.19±0.06	8.48±1.08
Na	—	—	2226±82	—	—	5503±826
Rb	(12.6±0.2)	12.6±0.2	—	(13.6±0.55)	13.6±0.55	—
Sb	2.72±0.03	2.62±0.03	2.98±0.13	1.94±0.07	1.87±0.07	5.75±0.53
Sc	0.0072±0.0008	0.0052±0.0008	0.058±0.002	0.0040±0.0006	0.0032±0.0006	0.065±0.003
Se	0.72±0.01	0.643±0.014	2.11±0.10	1.58±0.04	1.54±0.04	3.36±0.27
Zn	96.3±0.7	72.4±0.6	701±13	90.2±3.7	76.2±3.6	1154±65

^a Effluents after centrifugation at 45 000 g, containing suspended materials.

^b Effluents centrifuged and filtered by a 0.45- μm micropore filter.

^c Suspended materials filtered from effluent I by a 0.45 μm micropore filter.

^d Values in () are taken from effluent II.

Effluent I before filtration.

Effluent II after filtration.

neutron activation analysis for many elements. On the other hand, the neutron activation analysis does not provide satisfactory sensitivity for lead and cadmium, barium, calcium, iron, zinc and calcium. A preconcentration technique helps inductively coupled plasma atomic emission spectrometry to improve the sensitivity but the procedure is negated by the possibility of contamination and it is not always quantitative for many elements. The neutron activation analysis involves difficulties in irradiation and counting of voluminous water samples and also in handling of standards in diverse analytical conditions.

Differential pulse anodic scanning voltammetry

This technique has been shown³⁶ to be capable of simultaneous determination of copper, lead, cadmium and zinc in trace amounts in domestic sewage and in the treated effluents. Suspended particulates are filtered off and subjected to ashing or wet digestion prior to the determination, and the aqueous filtrate is subjected to UV irradiation under oxidizing conditions to decompose organic compounds and chelating agents. The influence of UV irradiation conditions on the recovery of the four metals from solution was examined. It was shown that the major proportion of these metals was present in the suspended solids fraction of filtered sewage and suspended water.

Ion chromatography

This technique has been applied to the determination of cobalt, nickel, copper, zinc and cadmium as their EDTA complexes using anion separation and suppressor columns and 0.03 μm sodium bicarbonate – 0.3 μm sodium carbonate³⁷ eluant and a conductive metric detector.

Preconcentration

Morrison³⁸ estimated bioavailable metal uptake from sewage and storm water using dialysis with Chelex-100 resin in the calcium form. The resin was incorporated within the dialysis bag sealed at both ends. The bag was immersed in the sample for 1–4 days before releasing the chelated resin to a separation column. Metals were eluted from the resin with 1 M nitric acid and metal concentrations determined by graphite furnace and flame atomic absorption spectrometry. Zinc, cadmium, lead and copper were studied.

3.3

Elemental analysis

3.3.1

Total organic nitrogen

Kjeldahl digestion

Croll et al³⁹ determined kjeldahl nitrogen in sewage effluents and sludges using a copper-titanium catalyst.

Flow injection analysis

Haga et al⁴⁰ used flow injection analysis for the determination of total nitrogen and total phosphorus in sewage which had been previously pretreated by persulphate oxidation.

3.3.2

Boron

Fluorimetric method

An automated fluorimetric method has been applied to the determination⁴¹ of boron in sewage effluents. It is based on the reaction of 4'-chloro-2-hydroxy-4-methoxybenzophenone with boron in 90 per cent sulphuric acid medium to produce fluorescent species. The method permits the determination of different chemical forms of boron, the limit of detection being 1 $\mu\text{g l}^{-1}$.

3.3.3

*Total organic carbon**Combustion method*

Various workers have reported on the determination of total organic carbon in sewage^{42–45}.

In one method a stream of carbon dioxide, alone or mixed with an inert gas is passed through a bed of carbon, at 450–650°C where a small portion of the carbon dioxide is reduced to carbon monoxide and then into a combustion zone containing a catalyst, e.g. platinum, at 500–1000°C where carbon dioxide reacts with any oxidizable material present in the sample to form carbon monoxide. The increase in carbon monoxide content in the gas stream in the presence of a sample is suitably determined.

Tieman and Wagner⁴³ have described the principles of design and operation of a total organic carbon measuring device with particular emphasis on the need to control the particle size of the suspended solids so as to prevent blockages and false readings. Criteria for the successful performance of a total organic carbon measuring system are outlined, and a system specially developed to meet them and overcome the deficiencies of earlier models is described. The application of this equipment in the operation and process control of activated-sludge plants is described.

Van Steenderen⁴⁵ found that samples for total organic carbon measurement must at all times be stored in all glass sealed containers and analysed immediately upon arrival. Failing this, samples must be preserved with silver sulphate solution and stored at 4°C. If dissolved organic carbon is desired, samples must be filtered through a 0.45 µm membrane filter previously rinsed with distilled water. The practice of acidifying samples to remove inorganic carbon is not recommended.

Van Steenderen⁴⁵ analysed sewage and other samples using the Beckman TOC analyser. This instrument determines organic carbon in water by the difference between total carbon and inorganic carbon. To analyse a sample completely for carbon, two infrared analysers and two automatic sample injectors are necessary since the instrument is equipped with a dual furnace but only one infrared analyser. He found that over a two day period the total organic carbon content of settled sewage samples decreased appreciably whilst the total inorganic content increased. Acidification of the sample prior to analysis also has a profound effect on reported total oxygen demands (Table 37).

Van Steenderen⁴⁵ used factorial analysis to study the interaction of temperature, preservation and container material simultaneously on the organic carbon content of water samples which had been filtered through a porosity glass filter. Three different temperatures (4, 10 and 30°C) were employed, preservation was applied at three different concentrations (unpreserved, 1 ml saturated AgSO₄ ml⁻¹ 4 ml saturated AgSO₄ ml⁻¹ sample).

Temperature and container material were the critical parameters affecting the carbon concentration and not preservation. Plastic containers were found to release organic material into solution and this was especially noticeable on the humus tank effluent sample. On the other hand, preservation was the dominant factor when dealing with a chemically unstable and more concentrated organic carbon sample such as settled sewage where humus tank effluent contained a higher organic carbon content than usual and, as a result,

TABLE 37

The effect of acidification and membrane filtration on the organic content of settled sewage and humus tank effluent. Results in mg l⁻¹

Sample	Settled sewage	Humus tank effluent
Original	86	22

Sample	Settled sewage	Humus tank effluent
Membrane filtered (0.45 μm)	45	18
Membrane filtered then acidified to pH 4	40	11
Acidified to pH 4 then membrane filtered	29	10
Acidified to pH 4	80	14

preservation began to play a major role exceeding the effects of temperature and container material. Acidifying of samples had an immediate effect on the organic carbon present and all volatile organic carbon was removed between a pH of 2 and 4. General conclusions are that: samples must be collected and stored in all-glass sealed containers and that preservation of samples must be carried out with silver sulphate solution combined with storage at 4°C. For the determination of dissolved organic carbon, samples must be filtered through a 0.45 μm membrane filter previously rinsed with distilled water. Lastly, the acidification of samples in order to remove inorganic carbon from solution is not recommended.

3.4

Miscellaneous determinands

3.4.1

Suspended solids

Miscellaneous

Rich and Karr⁴⁶ have described a method for use in estimating the amount of suspended solids in a secondary settlement tank. It consists of an open-ended plexiglass tube that is lowered to the bottom of the tank, sealed and withdrawn. The contents of the tube are then transferred to a container and mixed before determination of suspended solids. Blanket height within the tank can be observed from the solids height in the tube and it is suggested that the solids concentration gradient could also be measured by installation of several valves along the length of the tube, with sampling ports between the valves.

Optically depolarized light from a mercury source is the basis of a method⁴⁷ for measurement of the concentration of suspended solids in sewage. Finger and Strutynski⁴⁸ have described an automated spectrophotometric method for estimating the suspended solids content of sewage. The method is based on the measurement of polysaccharides, which is related to suspended solids content. Results indicate that the method is suitable for continuous measurement of suspended solids and that values obtained are in fair agreement with those obtained by classical gravimetric methods.

Turbidimetry has also been used for estimating suspended solids in sewage⁴⁹.

3.4.2

Particle size distribution

Leschber⁵⁰ has reviewed the use of particle size distribution measurements for the classification of sewage.

3.4.3

Hydrogen peroxide

Spectrophotometric method

Hydrogen peroxide has been used as an oxidizing agent during the purification of sewage. Masschelein et al⁵¹ has described a spectrophotometric method for estimating hydrogen peroxide based on the cobalt-hydrogen peroxide reaction.

3.4.4

Urea

Gas sensing electrode

An ammonia gas sensing electrode has been used⁵² to determine urea nitrogen in raw sewage. Less than 1 mg l⁻¹ urea nitrogen can be determined. Urease activity has been determined spectrophotometrically⁵³.

3.4.5

Flocculation rate and sedimentation rate

This subject has been reviewed by Gregory⁵⁴.

3.4.6

Odour

Koe and Brady⁵⁵ used hydrogen sulphide as a surrogate parameter for sewage works smells, and its concentration is measured with lead acetate tapes. The tapes are exposed to the air for three hours, allowing concentrations in the range to which the human nose is sensitive to be calculated. Strategically placed tapes can thus give useful odour contours.

Air that comes in contact with sewage (in sewers, pump stations and at waste water treatment plants) becomes odorous as it picks up traces of various volatile odorous compounds. Analyses of samples of air collected from waste water transmission systems have identified the principal odorants that are emitted from these facilities including aldehydes, ammonia, alkylamines, dimethyl sulphide, ethylmercaptan, hydrogen sulphide, methylmercaptan and skatole. Typical values range from as high as 1000 $\mu\text{g l}^{-1}$ for hydrogen sulphide down to as low as 20 $\mu\text{g l}^{-1}$ for some organic components such as amines and mercaptans.

3.5 Organic substances

3.5.1 *Aliphatic hydrocarbons*

Miscellaneous

The UK Department of the Environment standard methods⁵⁶ involving carbon tetrachloride extraction for the determination of extractable hydrocarbon oils and greases in sewage have been published. The first method consists of solvent extraction using carbon tetrachloride followed by gravimetric determination of the extractable material. The second method partially fractionates this material according to the type of material using chromatographic techniques. Separation on a silica gel column with an upper layer of Florisil is used to remove aromatic and polar compounds respectively, while the eluate contains the aliphatic hydrocarbon ingredients.

Gas chromatography

Copin et al⁵⁷ determined aliphatic C₁₆ and C₂₆ hydrocarbons present at low vapour pressure in sewage by gas chromatography. Recoveries of 95–102 per cent were achieved for concentrations of 20–30 mg l⁻¹. The levels of the hydrocarbons were 200–500 mg l⁻¹ (dry basis) in urban treatment sludges and less than 150 mg l⁻¹ in the agro-industrial effluent sludge.

Bohne-Mabusall et al⁵⁸ studied problems connected with the determination of emulsified hydrocarbons in domestic sewage. A liquid chromatographic method is described for the separation of anionic and non-ionic detergents, following which the simultaneous determination of hydrocarbons, fats and fatty acids could be accomplished by infrared spectroscopy.

3.5.2 *Polyaromatic hydrocarbons*

Miscellaneous

Stepanova et al⁵⁹ developed a procedure for the quantitative analysis of a mixture of benzo(a)pyrene and other polyaromatic hydrocarbons in sewage and other industrial exhausts, based on preliminary thin-layer chromatographic separation and low temperature spectrofluorimetric quantification.

The analysis of polyaromatic hydrocarbons is also discussed in [section 3.5.30](#) (multiorganic analysis).

High performance liquid chromatography

This technique has been applied to the determination of polyaromatic hydrocarbons in sewage in amounts down to 2 µg l⁻¹^{60,61}

3.5.3 *Anionic detergents*

Spectrophotometric methods

Workers at the Water Research Centre⁶² have described a methylene blue based autoanalysis method for determining 0–1 $\mu\text{g l}^{-1}$ anionic detergents in water and sewage effluents.

The Water Research Centre report describes the method in detail and discusses its precision and accuracy.

Taylor and Williams⁶³ studied the selective determination of anionic surfactants using ionic association compounds of these compounds with iron II chelates. The effects of solution variables including ionic strength, pH and buffer concentration, reagent excesses, solution volume, type of solvent, and the selection of reagents and conditions of extraction and separation are examined, and a method is proposed for the selective determination of homologous surfactants. A method is also proposed for the determination of surfactants of various chain lengths.

Taylor and Waters⁶⁴ studied the extraction constants of association compounds of anionic surfactants with iron II chelates of the ferriin type. The extraction constants of these chelates distributed between water and chloro form were correlated with the structure of the surfactant and the ligand. Taylor et al⁶⁵ also studied the use of iron II chelates of 1,10-phenanthroline and its derivatives, bipyridyl and terpyridyl in the estimation of anionic surfactants in chloroform extracts of water samples. The extent of extraction increases with increasing chain length of surfactants and is characterized by a breakthrough-point (i.e. the chain length above which the surfactant is extracted and below which it is not). This point depends on the choice of iron II chelate and extracting solvent. A selective procedure for determining surfactants in sewage based on experimental control of the 'breakthrough point' and involving spectrophotometric determination of the extracted complexes, is described. The effect of foreign ions is also discussed by the workers.

Differential pulse polarography

Hart et al⁶⁶ have described an indirect polarographic method for determining linear alkylbenzene sulphonates in sewage and potable water. The method is reliable for concentrations of 0.5 $\mu\text{g l}^{-1}$ or more. In this procedure the sample was nitrated with fuming nitric acid, then adjusted to pH 12 and polarographed. All of the sewage samples gave a reduction peak that occurred at the same potential as for the nitro derivative of 4-phenyldodecane sulphonate, i.e. 0.74 V.

The polarographic method was found to be suitable for the determination of linear alkylbenzene sulphonate with reasonable specificity.

In general, the methylene blue spectrophotometric method gave higher results, probably because the methylene blue procedure gives a total anionic surfactant content, the so-called MBAS value (methylene blue active substances), whereas only surfactant species or other organic compounds with a benzene ring would be likely to interfere in the polarographic method. Even then the E_p values of the derivatives of these species would not necessarily coincide with those of linear alkylbenzene sulphonates nitro derivatives.

High performance liquid chromatography

Giger et al⁶⁷ determined alkylbenzene sulphonates and nonylphenolethoxylates in sewage sludge by this procedure.

3.5.4

Non -ionic detergents

Spectrophotometric methods

Dozanska⁶⁸ has described a spectrophotometric method involving reaction with cobalt thiocyanate or tungstophosphoric acid for the determination of non-ionic detergents in sewage. Stephanou and Giger⁶⁹ carried out quantitative determinations of nonylphenoethoxylates and nonylphenol in sewage effluents by capillary gas chromatography.

Waters et al⁷⁰ investigated the scope and limitations of the Wickbold active substances procedure for the determination of non-ionic substances in sewage. The method was found to be unsuitable for sewage which gives low recoveries.

3.5.5

Phenols

Enzyme electrode

Kjellen and Neujahr⁷¹ have discussed an enzyme electrode for the determination of total phenols in sewage works samples. The most sensitive electrodes were obtained by immobilization of the enzyme covalently bound to AH-Sepharose 4B or to nylon nets, as well as by enzyme adsorption on ion-exchangers. Optimal conditions include pH 6.5–9.5, 40°C and incubation in a buffer containing NADPH for a few minutes before addition of the sample in order to make the electrode response independent of the diffusion rate of the substrate. Readout is achieved within 30 s of sample addition and the maximum rate of oxygen consumption is linearly dependent on phenol concentration in the 0.5–50 μM range.

Flow injection analysis

Moller and Martin⁷² described a flow injection analysis method for determining phenols in sewage based on the condensation of phenols with 4-amino antipyrine, subsequent alkaline oxidation and spectrophotometric detection.

Gas chromatography

Extractive alkylation using pentafluorobenzoylation and glass capillary gas chromatography using electron capture detection has been used⁷³ to determine phenols and carboxylic acids in sewage effluents. Excess of alkylating reagent in the combined extraction/alkylation is minimized and there is no need to remove it before the gas chromatography. By suitable selection of the extraction and derivatization conditions byproduct formation can also be minimized. The detection limit is in the range 1–10 $\mu\text{g l}^{-1}$ and can be lowered at the expense of the range of compounds which can be determined.

The analysis of phenols is also discussed in [section 3.5.30](#) (multiorganic analysis).

High performance liquid chromatography

The HPLC of alkyl phenols and alkylphenol mono- and di-ethoxylates on Zorbox NH2 columns in amounts down to 0.2 μg with fluorescence detection has been discussed⁷⁴. The high performance liquid chromatography of phenols is also discussed in [section 3.5.30](#) (multiorganic analysis).

3.5.6

Fatty acids

Gas chromatography

Van Huyssteen⁷⁵ determined C₂–C₆ fatty acids in sewage samples. The samples were centrifuged at 105 000 g for 20 min at 2°C, about 5 ml of the clear supernatant liquid decanted and acidified to pH 1–2 with hydrochloric acid. The acids were identified by their retention times. For the low level fatty acid content, high sensitivity was used and additional peaks, probably alcohol, appeared between the acid peaks. To eliminate ghosting, 10 μl distilled water was injected between samples. Ghosting was observed by injecting 2 μl distilled water after 2 μl 25 mg l⁻¹ C₂–C₆ solution or 1 μl distilled water after 1 μl 750 mg l⁻¹ C₂–C₆ solution.

Narkis and Henfield Furie⁷⁶ have described a direct method for the identification and determination of volatile water soluble C₁–C₂ acids in municipal waste water and raw sewage. The method involves direct injection of the sewage into a gas chromatograph equipped with a Carbowax 20 M on acid-washed Chromosorb W column and a flame ionization detector. Preliminary preparation of the sample is limited to the addition of solid metaphosphoric acid to the sewage and removal of precipitated proteins and suspended solids by centrifuging.

[Table 38](#) summarizes the individual volatile acid concentrations in raw sewage determined by the direct injection procedure of Narkis and Henfield-Furie⁷⁶ and that of Standard Methods⁷⁷. The results were also expressed as acetic acid for comparison with the collective total amount of organic acids determined by the Standard Method⁷⁷. The total amount of organic acids determined according to the Standard Method is higher than that found by the Narkis and Henfield Furie method. On average between 85 and 98 per cent of the organic acids determined by the standard methods procedure were found to be volatile acids by the direct injection method.

Abbatichio et al⁷⁸ have described a procedure for the determination of individual volatile fatty acids in sewage, which overcomes problems associated with direct aqueous injections on a gas chromatograph, such as frequent cleaning, column ageing and flame ionization detection. The chromatographic determination is preceded by steam distillation. The recoveries, for volatile fatty acid concentrations of 50–200 mg l⁻¹ were 97.6–99.0 per cent and almost stoichiometric. The precision and accuracy of the method are good.

Salicylic acid has been determined in sewage works effluent⁷⁹.

Abel et al⁸⁰ determined nonyl phenoxy carboxylic acids in sewage effluent by high resolution gas chromatography-mass spectrometry and high performance liquid chromatography. The predominant compounds were nonyl (phenoxy)

TABLE 38

Volatile acids concentrations in raw sewage and in lime treated raw sewage determined by the direct injection procedure and by that of standard methods

Gas-liquid chromatography

Propionic acid	Butyric acid	Isovaleric acid	Valeric acid	Total volatile acids (mg l ⁻¹) as HA ₂	Standard methods analysis and total organic acids (mg l ⁻¹) as HA _C	Comparison of g.I.c. and standard method difference (mg l ⁻¹) as HA _C	% of volatile acids			
(mg l ⁻¹)	(mg l ⁻¹) HA _C	(mg l ⁻¹) as HA _C	(mg l ⁻¹) as HA _C	(mg l ⁻¹) as HA _C	(mg l ⁻¹) as HA _C	(mg l ⁻¹) as HA _C	(mg l ⁻¹) as HA _C			
9.09	7.36	0	0	0	0	0	38.41	45.2	6.79	85
4.28	3.48	0.82	0.56	0.44	0.26	0	33.70	48	14.3	70
7.21	5.78	11.9	0.81	0.95	0.56	0	46.06	50.4	4.34	91.4
5.72	4.58	1.19	0.81	0.50	0.29	0	41.08	48.3	7.21	85

acetic acid. Nonyl(phenoxy) (ethoxy) acetic acid concentrations down to 1 µg l⁻¹ could be determined.

The analysis of carboxylic acids is also discussed in [section 3.5.30](#) (multiorganic analysis).

High performance liquid chromatography

See [section 3.5.30](#) (multiorganic analysis).

Preconcentration

See [section 3.5.30](#) (multiorganic analysis).

3.5.7

Formaldehyde

Spectrophotometric method

Musselwhite and Petts⁸¹ have described an automated procedure for the determination of formaldehyde in sewage and sewage effluents. The method is based on the reaction of formaldehyde with acetylacetone in the presence of excess of an ammonium salt to form a yellow compound, diacetyl dihydrolutidine which is determined colorimetrically.

3.5.8

*Methanol**Gas chromatography*

Fox⁸² has described a rapid gas chromatographic method for the determination of residual methanol in sewage. In this method the filtered sample is adjusted to pH2 and injected directly into a U-shaped stainless steel column packed with Tenax GC (60–80 mesh) and pretreated with 85 per cent phosphoric acid for 4 hours. For gas chromatography the column was operated at 70°C with nitrogen as carrier gas (25 ml min⁻¹) and nitrogen flame ionization detection. The detector response was rectilinear in the range 0.5–199 mg l⁻¹ of methanol, and for a sample containing 50 mg l⁻¹ of methanol, the coefficient of variation was 2.4 per cent.

Spectrophotometric method

An automated method has been described to determine methanol in dinitrified effluents⁸³. The method is based on oxidation of methanol to formaldehyde which is determined colorimetrically after reaction with acetylacetone.

3.5.9

*Carbohydrates**Preconcentration*

See [section 3.5.30](#), (multiorganic analysis).

Halogen containing compounds

3.5.10

*Chlorinated hydrocarbons**Gas chromatography*

Von Duzzeln et al⁸⁴ and Henderson and Glaze⁸⁵ have discussed the gas chromatographic determination of chlorinated hydrocarbons in sewage. Henderson and Glaze⁸⁵ used a gas chromatography-mass spectrometry computer program to manipulate the data to produce a limited cluster search, the resulting chromatogram indicates the peaks on the total ion chromatogram which possess a specific number of chlorine or bromine atoms.

HM Stationery Office (UK)⁸⁶ have described methods for the determination of chlorinated hydrocarbons, organochlorine pesticides, and polychlorinated biphenyls in sewage sludge.

Rudolph and Koppke⁸⁷ described apparatus for the determination of trace organo halogen compounds (AOX) in municipal sewage.

3.5.11

Chlorophenols

Gas chromatography-mass spectrometry has been used to measure the occurrence of pentachlorophenol and hexachlorophene in water and sewage⁸⁸.

3.5.12

Chlorophenoxyisobutyric acid

Miscellaneous

Chlorophenoxyisobutyric acid has been determined⁸⁹ in primary treated sewage works effluent and river waters.

3.5.13

Halofoms

Gas chromatography

De Leer⁹⁰ has described a procedure for the determination of trihalofoms (chloroform, bromodichloromethane, dibromochloromethane, bromoform) in secondary and tertiary treated sewages and in chlorinated sewage. The halofoms are extracted into pentane followed by gas chromatographic separation and quantification by electron capture detection. The sensitivity of this procedure was more than adequate (less than $2 \mu\text{g l}^{-1}$) for these types of sample.

3.5.14

Chlorinated insecticides

Miscellaneous

Andrade and Wheeler⁹¹ have studied the biodegradation of Mirex (dechlorane C10 H12) by sewage sludge or organisms utilizing ^{14}C labelled mirex. They did not succeed in identifying the metabolites.

Laseter et al⁹² and Kaiser⁹³ have both utilized gas chromatography and mass spectrometry for the determination of mirex. Kaiser⁹³ has pointed out that under standard gas chromatographic conditions, the mirex peak is superimposed on that of the polychlorinated biphenyls and, as a result, the presence of mirex may have been interpreted by several workers as a PCB isomer. He used a computer controlled gas chromatographic mass spectrometric system to positively identify mirex and distinguish it from other highly chlorinated insecticides that could have been present in the samples including aldrin, chlordane, dieldrin, endrin, endosulfan, heptachlor, Kepone (chlordecone), pentac, and toxaphene.

The determination of chlorinated insecticides is also discussed in [section 3.5.30](#) (multiorganic analysis).

3.5.15

*Polychlorinated biphenyls**Gas chromatography*

Gaffney⁹⁴ showed that PCBs were present in certain municipal sewages. He showed that various chlorobiphenyl isomers are produced during chlorination of sewage and sewage effluents.

Workers at the US Environmental Protection Agency⁹⁵ have evaluated protocols for chlorinated insecticides and PCBs in raw waste water and sewage effluents. They concluded that the gas chromatographic method performed satisfactorily at the parts per billion level.

Kaiser and Wong⁹⁶ studied the bacterial degradation of Aroclor 1242 in water and identified aliphatic and aromatic hydrocarbon metabolites using gas chromatography and mass spectrometry. No evidence was found for chlorine containing metabolites. ¹⁴C labelled PCBs have been used^{97,98} to ascertain the fate of PCBs in activated sludge in a sewage works. It was found that tri- and pentachlorobiphenyl were practically unaffected by bacterial attack and were partitioned, in unchanged form, between the water and the sludge, a major portion being retained by the sludge.

The analysis of polychlorinated biphenyls is also discussed in [section 3.5.30](#) (multiorganic analysis).

Ion-exchange chromatography

See [section 3.5.30](#) (multiorganic analysis).

Nitrogen containing organics

3.5.16

Amines

See [section 3.5.30](#) (multiorganic analysis).

3.5.17

*Acrylamide**High performance liquid chromatography*

The high performance liquid chromatography of acrylamide is discussed in [section 3.5.30](#).

3.5.18

*Amino acids**Preconcentration*

See [section 3.5.30](#) (multiorganic mixtures).

3.5.19

*Dodecylguanides**Thin layer chromatography*

These substances have been determined in sewage effluents by thin layer chromatography⁹⁹. Thin layer chromatography was carried out on 2.5 mm layers of Adsorbasil-1 that had been activated at 100°C for 1 hour. The best results were obtained with butanol-acetic acid-water (8:1:1) as solvent (R_f 0.6); iodine vapour was used as locating reagent. The sensitivity was equivalent to 0.5 mg l⁻¹ of dodecylguanidine.

3.5.20

Miscellaneous nitrogen compounds

Including uracil, substituted uracils, chlorocaffeines, 1-methyl inosine, 4 1-methyl xanthine, *n*-methyl 1-2-pyridine-5-carboxamide, see [section 3.5.30](#) (multiorganic analysis).

3.5.21

*Phosphorus containing organic compounds**Miscellaneous*

McIntyre et al¹⁰⁰ investigated methods for determining organophosphorus compounds in sewage sludge and made a survey of sewage sludges from 12 different UK sewage treatment works. Highest recoveries were achieved using the disperser method, together with an alumina column cleanup step, and analysis by flame photometric gas liquid chromatography. The survey results indicate that organophosphorus compounds are not common micropollutants of sewage sludges.

Organophosphorus insecticides

Thin layer chromatography has also been applied to the determination of Abate residues in water¹⁰¹. The sample of surface water or sewage, acidified with sulphuric acid, was extracted with chloroform. The extract was evaporated under nitrogen at 60–70°C and the residue was dissolved in acetone. This solution was applied to a layer of activated silica gel G for 1 hour at 90°C together with Abate standards. The plate was developed for 1 hour in hexane-acetone (10:1) air dried for 1 min exposed to bromine vapour for 1 min, exposed to air for 3 min, and sprayed with 1 per cent *N,N*-dimethyl-*p*-(phenylazo)aniline (Cl solvent yellow 2) solution in 95 per cent isopropyl alcohol. Abate gave distinct red spots (R_f 0.11±0.01) on a bright yellow background. Spot areas were related to concentration by a calibration graph. Down to 9 µg of Abate could readily be determined.

Sulphur containing organics

3.5.22

Mercaptans

Gas chromatography

Various workers have studied the occurrence of volatile odorous sulphur containing compounds in sewage water^{102–105}.

The method described by Jenkins et al¹⁰² involves gas chromatography coupled with the sulphur-specific flame photometric detector which can detect 0.25 ng hydrogen sulphide and 0.5 ng of methyl mercaptan. The method has been used to trace sources of odour due to mercaptans in the air surrounding a sewage works and in waste waters, sewer gases. They used these techniques to study the fate of various organosulphur compounds in raw sewage and activated sludge.

Jenkins et al¹⁰² used a gas chromatograph equipped with a Melpar flame photometric detector and a Perkin-Elmer 3920B gas chromatograph equipped with a linearized Perkin-Elmer, flame photometric detector were used for chromatographic analyses. Each instrument also had a flame ionization detector. A FEP Teflon column (18 in×0.625 in i.d.) containing acetone-treated Porapak QS, was used for all analyses. The PE 3920B used a glass lined flash vaporizer injector and the interface lines were in stainless steel. For the Tracor 550, the Porapak QS column was connected to glass capillary tubing which was inserted into the injector and outlet barrels. Teflon-backed septa were used in the injectors of both instruments.

Bailey and Viney¹⁰³ have also applied gas chromatography to the investigation of odours produced at sewage treatment plants. Samples of ambient air at a sewage treatment works were taken using Tedlar bags and also by using traps containing Tenax GC on site. Analyses were performed using gas chromatography. Their studies showed that methyl mercaptan found in the head space of these samples was produced by aerobic decomposition of hexyl mercaptan.

Roe¹⁰⁴ also determined volatile organosulphur compounds (methanoldiol, dimethyl sulphide) also hydrogen sulphide and sulphur dioxide in sewage samples. König et al¹⁰⁵ using gas chromatography-mass spectrometry have identified dimethyl di-, tri- and tetrasulphides in sewage works samples. These substances can be used by microorganisms as precursors of sulphuric acid which would explain unexpectedly high corrosion rates of concrete pipes.

3.5.23

Herbicides

Gas chromatography-mass fragmentography

The gas chromatography-mass fragmentography procedure has been used by Karlhuber et al¹⁰⁶ to identify apparent atrazine residues in sewage water. The samples were cleaned up by the procedure of Ramsteiner et al¹⁰⁷. An aliquot of sewage water was neutralized and extracted with dichloromethane. The extract was further cleaned up by passage through an alumina column. After concentration, atrazine was injected into the gas chromatograph equipped with a Coulson electrolytic conductivity detector.

Injection of a 12.5 µg sewage water aliquot into a gas chromatograph equipped with the nitrogen specific Coulson electrolytic conductivity detector showed a peak with the same retention time as atrazine. From a

standard injection an apparent atrazine concentration of 5.5 mg l^{-1} in the sewage sample was calculated. The value found seemed extremely high and the sample was reinjected on the gas chromatograph with mass fragmentographic detection. No peak showed up in the chromatogram at the retention time of atrazine, indicating that there was less than $0.01 \text{ } \mu\text{g l}^{-1}$ of atrazine in the sewage water. The peak in the nitrogen specific chromatogram, therefore, was a nitrogen containing interference with the same retention time as atrazine. Using a 41 water sample containing 2 mg atrazine 82–98 per cent recovery was obtained using this procedure.

Thin layer chromatography

Zawadzka et al¹⁰⁸ and Abbott¹⁰⁹ used thin layer chromatography to determine simazine, atrazine, and prometryne herbicides in sewage. After extraction of a sample of sewage, with dichloromethane or ethyl ether at pH 9, the organic extract was condensed and applied to a column of basic aluminium oxide (activity 111) and the herbicides were eluted with ether containing 0.5 per cent of water. The eluate was condensed and applied to a layer of silica gel G impregnated with fluorescein. The chromatograms were developed with chloroform-acetone (9:1). The plates were dried, and the spots were located by spraying with 0.5 per cent Brilliant Green (C.I. Basic Green 1) in acetone and exposing to bromine vapour. For samples containing 5–100 $\mu\text{g l}^{-1}$ of herbicide the recoveries were between 83 and 97 per cent.

High performance liquid chromatography

This procedure has been used to determine Aminocarb¹¹⁰.

Mullins and Kirkbright¹¹¹ determined sodium *N*-methylthiocarbamate (Metham Sodium) and methyl isothiocyanate fungicides in untreated sewage by high performance liquid chromatography using a micellar mobile phase and UV detection.

Miscellaneous organic compounds

3.5.24

Nitriloacetic acid

Gas chromatography

Warren and Malec¹¹² determined nitriloacetic acid and related aminopolycarboxylic acids (iminodiacetic acid, glycine, and sarcosine) in sewage effluents by converting to the butyl or the *N*-trifluoroacetyl esters followed by chromatography on dual glass U shaped columns (1.9 mm×2 mm) packed with a 0.65 per cent of ethanediol adipate on acid washed Chromosorb W (80–100 mesh), temperature programmed from 80 to 220°C and operated in the differential mode with flame ionization detectors. The signal was fed to a digital integrator and then to both channels of a dual-pen recorder operated at high and low sensitivities.

Aue et al¹¹³ determined $\mu\text{g l}^{-1}$ of nitriloacetic acid and citric acid in sewage effluents. Following a preliminary clean-up and concentration procedure the acids are converted to their butyl esters and chromatographed on a Carbowax on Celite 545 column at 183°C.

Rudling¹¹⁴ determined nitriloacetic acid gas chromatographically at the $0.1 \text{ } \mu\text{g l}^{-1}$ level in sewage. Following separation of the nitriloacetic acid on an anion-exchange column, it is derivatized with boron

trifluoride in 2-chloroethanol to produce 2-chloroethylnitrilotriacetate and gas chromatographed on a column packed with 2 per cent QF-1 on Varaport 30. Detection is achieved by electron capture. Chloride, sulphate, calcium and magnesium did not interfere in this procedure.

Rudling¹¹⁵ simultaneously determined 0.0–10.02 μg of nitriloacetic acid, EDTA, and diethylenetriaminepenta-acetic acid in sewage samples as their methyl esters by gas chromatography. The sample, adjusted to pH 7, is extracted with chloroform, 1,2-diaminocyclohexanetetra-acetic acid, an internal standard added and the mixture treated with methanolic boron trifluoride. Chloroform extracts are injected into a column packed with 5 per cent V-17 on Aeropak, temperature programmed from 150 to 285°C at 10° C min⁻¹ using helium as carrier gas. Cadmium, copper, zinc and nickel, and iron did not interfere.

Polarography

Afghan et al¹¹⁶ developed an automated method for the determination of nitriloacetic acid in natural water and sewage samples. The method is based on the formation of the bismuth nitrilotriacetic acid complex at pH 2 followed by determination by twin cell oscillographic d.c. polarography. As little as 10 $\mu\text{g l}^{-1}$ of nitrilotriacetic acid can be determined, with no preconcentration of the sample being required. The coefficient of variation for 100 mg l⁻¹ was 1.3 per cent.

Miscellaneous

Longman et al¹¹⁷ compared five procedures for removing interferences in the determination of nitriloacetic acid in sewage and sewage effluents. None of these methods completely overcame interference by metals. These workers then developed an alternative procedure based on passing the filtered sample through a column of Chelex 100 chelating resin (Na⁺ form). To the eluate was added zircon reagent and the extinction was measured at 620 nm. The method was applicable in the range 0–10 $\mu\text{g l}^{-1}$ nitriloacetic acid in sewage. Ferric iron did not interfere.

Sekerka et al¹¹⁸ described a thallium nitrate potentiometric titration procedure for the determination of down to 0.1 $\mu\text{g l}^{-1}$ of nitriloacetic acid in waste water and sewage. To the sample (100 ml) was added 0.01 M thallium nitrate (0.1 ml) and 10 M sodium hydroxide, the mixture was filtered, the filtrate adjusted to pH 7 by addition of 10 M nitric acid and hexamine (2 g) and 0.01 M ammonium pyrrolidine-1-carbodithioate added (this preliminary treatment removes interfering cations and reducing substances). The solution was titrated with 0.1 M thallium nitrate (Tl³⁺ forms a 1:2 complex with nitriloacetate and 1:1 complexes with EDTA) with the use of a combination platinum redox electrode (Orion 96-78). A second 100 ml sample is treated similarly, but in the first step 0.1 ml of 0.01 M cupric nitrate is added in place of the thallium nitrate and titrated with 0.1 mM cupric nitrate (Cu²⁺ forms 1:1 complexes with all the complexing agents tested). The titration curves exhibit two end points corresponding to:

- (1) Tl³⁺ or (Cu²⁺) consumed by ammonium pyrrolidine-1-carbodithioate and
- (2) nitriloacetic acid (or other ligands) present in the sample.

The content of nitriloacetic acid is calculated from the differences in titres. The recovery of nitriloacetic acid in admixture with EDTA in synthetic sewage samples range from 90 to 102 per cent.

3.5.25

*Ethylene diaminetetraacetic acid**Gas chromatography*

Rudling¹¹⁹ and Chau and Fox¹²⁰ have described a method in which the methyl ester was determined by gas-liquid chromatography using 1,2-cyclohexanediaminetetraacetic acid as internal standard. This presented problems as the retention times of the methyl esters of EDTA and those of certain C-18 fatty acids (stearic and oleic) which were also usually present in the samples being investigated, were very similar and the peaks were not resolved under the conditions employed. It was considered unlikely that any stationary phase would completely resolve EDTA from the range of C-18 fatty acids that might be found in samples of sewage and sewage effluent. It was also found that humic acid in the sample, most of which failed to react with the esterifying agent, produced a greater than theoretical recovery of EDTA, apparently because of interaction between EDTA and non-reactive fraction of humic acid.

3.5.26

Cholesterol

See [section 3.5.30](#) (multiorganic analysis).

3.5.27

Coprostanol

See [section 3.5.30](#).

3.5.28

*Nucleic acid**Miscellaneous*

Seibert and Zahn¹²¹ used precipitation titration with the cationic detergent *N*-cetyl-*N,N,N*-trimethylammonium bromide to quantify the nucleic acid content in activated sludge. With the introduction of toxins into the influent of a sewage treatment plant the ribonucleic acid content of the activated sludge fell sharply, and it was possible to correlate the deterioration in effective purification with a reduction in the ribonucleic acid fraction precipitate by *N*-cetyl-*N,N,N*-trimethylammonium bromide. Advantages of the method are simplicity and speed. DNA and RNA can be determined in one operation and the process is not affected by the presence of dyes or compounds absorbing ultraviolet light.

3.5.29

*Humic and fulvic acids**Miscellaneous*

Sposito et al¹²² used C_{13} and proton n.m.r. spectroscopy to investigate fulvic acid extracted from sewage sludge. C_{13} n.m.r. spectroscopy was found to be useful for studying the organic structures found in fulvic acids.

Rebhun and Mouka¹²³ have reported that about 40–50 per cent of the organics in secondary sewage effluents constitute humic substances, the remainder being anionic detergents, carbohydrates, proteins, tannins, lignins, and ether extractables. They extended this work¹²⁴ to a more detailed examination of the humic substances in secondary effluents obtained from high-rate trickling filters, the effluents from a stabilization pond and from an extended aeration activated sludge plant.

The investigation of humic substances included examination of their infrared spectrum, determination of carboxylic and phenolhydroxylic functional acidic groups, and estimation of their molecular weight distribution. The humic substances isolated from secondary effluents were further divided into humic, hymathomelanic, and fulvic acids. The humic and hymathomelanic fractions were then dissolved in 0.5 M sodium hydroxide, reprecipitated with 0.5 M hydrochloric acid, washed thoroughly with distilled water and dried in a vacuum desiccator. Each of the isolated fractions (including fulvic acid) was weighed and an aliquot was dissolved in ethylene diamine for carboxyl and phenolic hydroxyl determination. Another aliquot dissolved in 0.25 M sodium hydroxide was used for molecular sieving.

The acidic functional groups were determined by potentiometric titration in non-aqueous medium, using platinum-saturated calomel electrode combination¹²³. A 0.1 M solution of sodium aminoethoxide in ethylene diamine, calibrated against benzoic acid, was used as titrant. To avoid interferences of carbon dioxide from the air, the titrations were carried out in a current of nitrogen.

The molecular weight distribution was examined by fractionation on Sephadex gels G-25, G-50 and G-75 having exclusion limits 100–5000, 500–10 000 and 1000–50000 (by dextrans), respectively. For evaluating the molecular weight distribution, the elution patterns from the three gels were considered. The areas corresponding to the respective ranges of molecular weight were measured and expressed as a percentage of the total area included under the elution pattern from G-25.

The infrared spectra of humic and fulvic acids isolated from secondary effluents are fairly similar. The main adsorption bands (cm^{-1}) are in the regions of: 3400—hydrogen-bonded OH; 2980, 2940, 2860, 1460—methylene and methyl stretching; 1730—C=O of carboxyl and ketonic carbonyl; 1630—amine carbonyl or aromatic C=C; 1270, 1130, 1080—carbon-oxygen C—O stretching, which is in agreement with the results of other investigations^{125–128}.

Gel filtration chromatography

See [section 3.5.30](#) (multiorganic mixtures).

3.5.30

*Multiorganic analysis of sewage samples**Gas chromatography*

This is the technique used in the earlier work on the elucidation of the composition of mixtures of organic substances in sewage. Early on, the necessity was recognized of preconcentrating the organics in the sample, for example, by solvent extraction or freeze drying by a very large factor (10^4 – 10^5) in order to achieve the required analytical sensitivity. However, all earlier work suffered from the disadvantage that due to the complexity of the gas chromatograms obtained and the inherent risks of relying on retention data for component identification, many difficulties were encountered. Only when capillary gas chromatography coupled with mass spectrometric identification were introduced were the resolution and positive compound identification problems made less formidable.

An early gas chromatographic method¹²⁹ used direct gas chromatography of the sewage and achieved detection limits of only 0.2 g l^{-1} . Baird et al¹³⁰ tabulated gas chromatography data on the occurrence of selected trace organics in sewage. These included volatile halogenated organics, polynuclear hydrocarbons, chlorinated pesticides and polychlorinated biphenyls. Preconcentration techniques included the use of XAD-2 resins and ether-hexane extraction.

Roeraade¹³¹ used continuous flow extraction of the sewage sample together with on-line capillary gas chromatography to identify and determine organics. Continuous extraction was performed in a fused silica capillary tube with *n*-pentane as extractant, and phase separation using a semi-permeable PTFE membrane. The extract flowed through a fused silica sample loop connected to a fused silica capillary column or pre-column. Analysis was by gas chromatography with flame ionization detection and the system was controlled by a programmable timer.

The system was evaluated using water samples containing aromatic and aliphatic hydrocarbons, or trace amounts of a naphtha fraction, and samples from a municipal sewage works. Results were comparable with those using a batch extraction procedure although better reproducibility was obtained with the flow extraction procedure. Owing to absorption effects prior to extraction, a short length of capillary tubing was recommended for connecting the sample and segmenting device.

The Water Research Centre (UK)¹³² freeze dried 60 batches of sewage effluent to produce a powder containing about 5 per cent organic matter. This material was extracted with various polar organic solvents and the extracts concentrated by evaporation. The residues of organic matter extracted by each solvent were then treated with a suitable reagent in order to form the more volatile silyl derivatives (bis-(trimethylsilyl) acetamine) of the reactive compounds present before injection into the gas chromatograph. Various fatty acids, cholesterol and coprostanol were determined by this procedure.

Ellison and Wallbank¹³³ extended the technique slightly by applying infrared and ultraviolet spectroscopy to solvent extracts of the sewage. However, this finger-print approach to the problem frequently did not yield successful identifications and lacked sensitivity.

Gas chromatography-mass spectrometry

Several workers have discussed the application of this technique to the analysis of sewage samples^{134–137}. Warner et al¹³⁵ have described a systematic procedure for the determination of 54 semi-volatile organic constituents, designated as priority pollutants in US federal regulations. The procedure involves extraction of the sludge sample with methylene chloride or chloroform followed by column clean-up and detection of

specific compounds by gas chromatography mass spectrometry procedures involving high-resolution glass capillary columns and selective ion searches. The final analysis involves three separate fractions comprising benzidines, phenols, and neutrals. Detection limits of around 0.02 per 20 $\mu\text{g l}^{-1}$ were generally achieved with the aid of appropriate internal standards; recoveries of specific compounds were 50 per cent or greater, from a 100 ml sample of wet sludge.

Harris et al¹³⁷ injected filtered sewage samples directly into a gas chromatograph coupled to a mass spectrometer and achieved detection limits of 1–50 mg l^{-1} . This is intended as a supplemental method to solvent extraction for the identification of more volatile organic constituents in the sample. Garcia-Gutierrez et al¹³⁶ compared capillary column gas chromatography with packed-column techniques for the determination of polychlorinated biphenyls and organochlorine insecticides in sewage and sludge. Factors affecting the capillary column procedure have been evaluated, and its potential use in both gas chromatography and gas chromatography combined with mass spectrometry, for analysis of environmental samples are discussed.

Michael et al¹³⁸ demonstrate that equipment used to isolate volatile organics from sewage effluents and waste water could be interfaced directly with a gas chromatograph-mass spectrometer-computer.

High performance liquid chromatography

This technique has been applied to some specific organics in sewage effluents¹³⁴ (Table 39).

Because the greater proportion of the organic material in water samples is non-volatile and therefore not amenable to gas liquid chromatographic analysis, the Water Research Centre (UK) has an interest in developing a routine high performance liquid chromatographic system that is capable of separating unknown and complex extracts with the best possible resolution of individual non-volatile components. During the past few years a system has been developed employing liquid-solid adsorption chromatography with gradient elution by the application of a series of solvents of rising polarity. A series of solvent reservoirs is connected via a programmable multiple port rotary valve to a solvent mixing chamber containing primary solvent. A high pressure reciprocating pump draws solvent from this system at the same time, causing a solvent gradient to be generated by pulling a secondary solvent from one of the reservoirs into the mixing chamber. Solvent combinations are changed at appropriate intervals by switching the rotary valve position. Sample introduction is effected by loop or septum injection. The column is a high efficiency 250×4.2 mm prepacked column containing microparticulate silica. The detectors incorporated into the system are a combined, variable wavelength ultraviolet and fluorescence photometer and a transport ionization detector.

There remains some doubt concerning the optimum number of solvents to be employed in the multiple solvent, gradient elution programme. Scott and Kucera¹³⁹ recommend a twelve solvent series while Snyder¹⁴⁰ proposed a six solvent series to cover the entire polarity range adequately.

TABLE 39
HPLC analysis of sewage effluents

Substance	Concentration ($\mu\text{g/l}$)	Detection	Ref.
5-Acetylamino-6-amino-3-methyluracil	30	UV	130
8-Chlorocaffeine	1.7	UV	130
2-Chlorophenol	1.7	UV	130
5-Chlorouracil	4.3	UV	130

Substance	Concentration ($\mu\text{g/l}$)	Detection	Ref.
Coprostanol	10	UV and differential refractory	131
<i>p</i> -Cresol	90	UV, MS	130
Hippuric acid	2	Colorimetric reagent detector	130,132,133
1-Methylinosine	80	UV and cerate oxidation monitor	130
<i>N</i> -Methyl-2-pyridone-5-carboxamide	10	UV	130
1-Methylxanthine	6-17	UV	130
Perylene	0-1	Fluorescence	—
Uracil	13	UV	130

Ion-exchange chromatography

Among the limited applications of ion-exchange chromatography to the separation of organics in water are the separation of organics in sewage effluents¹⁴¹⁻¹⁴³ and the determination of chlorinated biphenyls¹⁴⁴. Pill et al¹⁴³ using high resolution ion-exchange chromatography identified and quantified 56 and 13 organics, respectively, in primary and secondary sewage effluents. Many more unidentified compounds were present.

Gel filtration chromatography

Gel filtration chromatography using Sephadex G100 as column packing, and ultraviolet detectors, have been used in studies carried out on the elution of humic acid¹⁴⁵ and in characterization studies on secondary sewage effluents¹⁴⁶ and in organic substances in river waters¹⁴⁷.

Preconcentration

A limited amount of work has been carried out on freeze concentration methods for organics in non-saline and saline waters. The method has been applied to the preconcentration of amino acids, carbohydrates, citric acid and phenylalanine¹⁴⁸ giving virtually complete recovery of these substances at concentrations up to 0-2 mg l⁻¹. The technique has been used in conjunction with Sephadex gel chromatography to characterize organic components in the molecular weight range 200-5000¹⁴⁹ in secondary sewage effluents. The filtered samples were concentrated using a freeze drying unit with methyl alcohol as the bath fluid. The organic carbon recovery in the freeze dried samples was between 92 and 96 per cent.

3.6

Organometallic compounds

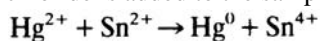
3.6.1

Mercury

Atomic absorption spectrometry

The Department of the Environment (UK)¹⁵⁰ has described a method for determining total organic plus inorganic mercury in non-saline sewage and effluents. All forms of mercury are converted to inorganic

mercury using prolonged oxidation with potassium permanganate¹⁵¹. Solid samples require a more prolonged and vigorous oxidation to bring the mercury completely into solution in the organic form. A modification of the Uthe digestion procedure is used for such samples¹⁵². The inorganic mercury is determined by the flameless atomic absorption spectrophotometric technique using a method similar to that described by Osland¹⁵³. Acid stannous chloride is added to the sample to produce elemental mercury:



The mercury vapour is carried by a stream of air or oxygen into a gas curvette placed in the path of the radiation from a mercury hollow cathode lamp and the absorption of this radiation at 253.7 nm by the mercury vapour is measured. Many of the potential interferences in the atomic absorption procedure are removed by the preliminary digestion/oxidation procedure. The most significant group of interfering substances is volatile organic compounds which absorb radiation in the ultraviolet. Most of these are removed by the pretreatment procedure used and the effects of any that remain are overcome by pre-aeration. Bromide and iodide ions may cause interference. Substances which are reduced to the elemental state by stannous chloride and then form a stable compound with mercury may cause interference, e.g. selenium, gold, palladium and platinum. The effects of various anions, including bromide and iodide, were studied. These are not likely to be important interferers.

Miscellaneous

Van Ettehoven¹⁵⁴ have described a direct semi-automatic scheme based on ultraviolet light absorption for the determination of total mercury in water and sewage sludge. The full determination time is about 10 min. The lower limit of detection of mercury in water is 0.03 $\mu\text{g l}^{-1}$ and 0.2 mg l^{-1} (mg kg^{-1} dry matter) in sewage sludge.

Takeshita et al¹⁵⁵ has used thin-layer chromatography to detect alkylmercury compounds and inorganic mercury in sewage. The dithizonates were prepared by mixing a benzene solution of the alkylmercury compounds and a 0.4 per cent solution of dithizone. When a green coloration was obtained the solution was shaken with N sulphuric acid followed by aqueous ammonia and washed with water. The benzene solution was evaporated under reduced pressure, and the dithizonates, dissolved in benzene, were separated by reversed phase chromatography on layers of corn starch and Avicel SF containing various proportions of liquid paraffin. Solutions of ethanol and of 2-methoxyethanol were used as developing solvents. The spots were observed in daylight. The detection limit was from 5 to 57 ng (calculated as organomercury chloride) per spot.

3.6.2

Tin

Preconcentration

Muller¹⁵⁶ preconcentrated organotin compounds from sewage sludge and lake sediments on Tropolin-C18 silica cartridges or by extraction with a solution of tropalone in diethyl ether. The extracted compounds were then ethylated by a Grignard reagent and analysed by high resolution gas chromatography with flame photometric detection.

3.7

Oxygen demand parameters

3.7.1

Total oxygen demand

Titration method

Stones¹⁵⁷ discusses the use of silver-catalysed dichromate to determine the strength of sewage and to assess the performance of treatment plants. By using an appropriate modification it is possible to eliminate interference by chlorides and thus measure the total carbonaceous oxygen demand of sewage. The relation between this and the BOD and total oxygen demand is discussed.

Electrochemical method

Cummings¹⁵⁸ has described an automated procedure for determining total oxygen demand in which two cells are set up separated by an anion-exchange resin. Each cell contains a nickel electrode. Sample is put in the cathode cell and sample adjusted to pH 10 in the anode cell. Upon passage of current an amount of oxygen is liberated the partial pressure of which is related to the total oxygen demand of the sample.

Miscellaneous

Musselwhite¹⁵⁹ has given results of tests on the performance of a commercially available total oxygen demand meter and on factors affecting performance. The tests showed that the figure given by the meter is a measure of the oxygen equivalent of oxidizable matter minus the oxygen liberated under the conditions of the test. It is concluded that this would be useful for sewages and non-nitrified and denitrified effluents but useless for nitrified effluents and waters containing appreciable amounts of oxidized nitrogen.

3.7.2

Chemical oxygen demand

Titration methods

Numerous workers have studied various aspects of the measurement of the chemical oxygen demand of sewage samples¹⁶⁰⁻¹⁶⁷ (Table 40). The use of conventional reflux methods versus sealed tube digestion versus micro and semi micro open tube methods in the acid dichromate method for determining the chemical oxygen demand of sewage has been the subject of debate^{168,169}. Best and de Casseres¹⁶⁹ evaluated the micro sealed tube method using synthetic standards and a variety of sewages. Comparison of the results with the conventional reflux method indicate that the sealed tube method using a reagent consisting of potassium dichromate (10.126 g), concentrated sulphuric acid (167 ml) and mercuric sulphate (33.3 g) is reliable and accurate and suitable for the analysis of large numbers of samples. It is however, subject to the changes inherent in any sealed tube method.

It was observed that the sealed tube method oxidized organic compounds

TABLE 40
Acid dichromate methods for measurement of chemical oxygen demand of sewage

Method	Comments	Ref.
Acid dichromate oxidation (automated)	Sample and acid dichromate in presence of silver catalyst heated to 160°C in flow through system in fluidized sand bath, then through a colorimeter	176
Acid dichromate oxidation	Effect of grade of silver sulphate	160
Acid dichromate oxidation	Correlation of COD, BOD and soluble organic carbon	161
Acid dichromate oxidation	Effect of oxidation temperature and dichromate concentration	162
Acid dichromate oxidation	Potentiometric titration of excess dichromate	163
Acid dichromate oxidation	Spectrophotometric measurement at 615 nm	164
Acid dichromate oxidation	Comparison of field method (spectrophotometric) and laboratory method (titration)	165
Acid dichromate oxidation	Elimination of sulphur dioxide interference by addition of manganese	166
Acid dichromate oxidation	Mercury free semi-micro open tube digestion with acid dichromate and silver sulphate catalyst. Comparison of results with sealed tube digestion	167 168
Acid dichromate oxidation	Correction of COD for losses of dichromate due to overheating of the reaction mixture	170

more efficiently than the reflux method. Thus ethanol was digested to the extent of 94 per cent in sealed tubes and only 54 per cent on the reflux method.

A dilution of at least 1–5 was necessary to obtain satisfactory precision at either 590 nm or at 440 nm which is λ_{\max} for the chromium VI species. The absorbance at 440 nm decreased with increasing COD, but the sensitivity was about 5 times greater at 440 nm than at 590 nm especially after the necessary 1–5 dilution of the digested sample. In these circumstances similar results were obtained by the manual titration and the spectrophotometric methods.

In further work De Casseres¹⁶⁸ compared chemical oxygen demand determination obtained by a sealed tube method and a semi micro open tube method and concluded that the semi micro open tube method is as precise and accurate as the sealed tube method whilst possible operational hazards are reduced.

Limits of detection were similar for both methods (13 mg l⁻¹ open tube versus 10 mg l⁻¹ sealed tube). It is concluded that the open tube method has all the advantages of the sealed tube method such as savings in space and cost of chemicals and increased sample throughput. In addition it has the advantage that possible operational hazards are greatly reduced. The precision data and recovery tests indicate that the method is as precise and accurate as the sealed tube method even for volatile compounds.

Goodwin et al¹⁷¹ report on studies of the kinetics of the dichromate oxidation of dissolved organic matter of the type that occurs in crude sewage and sewage effluents. A system of characterization of oxidizable material was derived comprising a set of four separate parameters calculated from second order reaction kinetics. Application of this process to chemical oxygen demand determinations allows solutions with the same chemical oxygen demand but different composition to be differentiated, owing to the changes in parameter values associated with changes in the relative proportions of different reacting species.

An automated method for the measurement of chemical oxygen demand which has been applied to the analysis of sewages is the Wosthoff Hydromat COD manufactured by Bochum, West Germany¹⁷². In this instrument sample and reagents are fed continuously into the instrument by means of a peristaltic pump. The sample is mixed in the ratio 1:1 with concentrated sulphuric acid and fed to a series of separators where

chloride is removed as hydrochloric acid by a vigorous air stream from the membrane pump. The stripped liquid is mixed with potassium dichromate and silver sulphate in concentrated sulphuric acid, segmented with air and passed through a glass coil in the oxidation reactor at 160°C. The digested fluid is then mixed with ferrous-ferric solution and the change in potential and hence the relative COD measured in a Radox cell.

Using this method a standard deviation of 7.5 mg l⁻¹ was obtained for a sample of settled sewage with a chemical oxygen demand of 626 mg l⁻¹ (i.e. RSD 1.2 per cent).

3.7.3

Biochemical oxygen demand

Extensive work has been carried out on various aspects of the measurements of the biochemical oxygen demand of sewage effluents. This is reviewed in Table 41. Topics covered include inhibition of nitrification during measurements on sewage^{173-175,177}, effect on biochemical oxygen demand of toxic substances^{178,179}, sample preservation¹⁸⁶, and reaction kinetics¹⁸¹⁻¹⁸³. The relationship between biochemical oxygen demand and other oxygen demand parameters of sewage has also been discussed¹⁸⁴⁻¹⁸⁸.

More recent work has been concerned with the semi or full automation of the biochemical oxygen demand procedure.

Crowther et al¹⁸⁹ have described a semi-automated procedure which has been applied to sewage and other types of samples. This method was capable of handling 1000 samples per week.

Galovaty and Smirnov¹⁹⁰ described an instrumental method of measuring the rate of consumption of oxygen for monitoring the biochemical demand of unpurified sewage effluents. The method is based on measuring the rate of oxygen consumption by a mixture of activated sludge and effluent and a reference liquid in a flow through respirometer. The latter comprises preparation vessels, metering pumps, a pulse generator, recorder, current stabilizer,

TABLE 41
Measurement of biochemical oxygen demand of sewage

Subject area	Comments	Ref.
Nitrification	Effect of inhibiting nitrification on BOD results. Allythiourea and 2-chloro-6-(trichloromethyl)pyridine studied	190
Nitrification	Difficulty of assessing efficiency of sewage treatment when nitrification is occurring	191
Nitrification	Analysis of data from sewage works shows that many violations of BOD effluent standards are due to nitrification occurring during BOD test, not to inadequate sewage treatment	175
Nitrification	Evaluation of various methods of determining ultimate BOD. Need to use nitrification inhibitor in samples of partially nitrified effluents because of problem of immediate or early onset of nitrification	177
Sample preservation	Effect of deep freezing sample on BOD	180
Effect of metals	Mercury, chromium, copper, zinc and aluminium in sample inhibit BOD	178
Sample dilution	Method of calculating sample dilution required when determining BOD	192

Subject area	Comments	Ref.
Effect of nutrients and toxic sub-stances	Study of effects of carbohydrates and protein on reported BOD of sewage. Inhibition of BOD by copper, zinc, cyanide and phenol	174
Relationships	BOD/COD correlation	184–186
	BOD/COD/PV correlation	185
	BOD/TOC correlation	187
	BOD/ODI (oxygen demand index)	188
Kinetics	Method of calculating constants for first order BOD equation	181
	Determination of rate of reaction in BOD reaction	182
	Determination of velocity coefficient of BOD reaction	183

electrolyser, pressure sensor, overflow device and a fermenter. The method has an accuracy of 20 per cent and is suitable for routine biochemical oxygen demand monitoring of unpurified effluents and for use in municipal sewage works.

Reigler¹⁹¹ has described a continuous biochemical oxygen demand measuring device. The equipment continuously samples a sewage or effluent flowing through a coarse cylindrical screen inserted into a pipeline, measures the oxygen consumed by the suspended biomass and prints out a continuous biochemical oxygen demand curve. Owing to the short measurement interval of 3 min, a continuous record of fluctuations in the strength of incoming or outgoing sewage is possible and a measurement range from 5 to 500 mg l⁻¹ can be accommodated. The screen retains particles greater than 0.5 mm in diameter, its surface being self-flushing. The liquid passing through is diluted with tap water and the oxygen uptake measured by oxygen-selective electrodes at the inlet and outlet from a culture flask in which the biomass is supported on a number of light plastic rings. The dilution ratio is selected to maintain the rate of oxygen uptake in the suspended growth medium constant at 5 mg oxygen l⁻¹.

3.8

Dissolved gases

3.8.1

Dissolved oxygen

Oxygen probe measurements

The determination of dissolved oxygen in sewage has been discussed by several workers^{193–197}.

Wilkes¹⁹⁴ has reviewed the use of dissolved oxygen probes for controlling aeration in the activated sludge process. He gives a brief description of the type of probe developed by pHox Systems. The problem of siting such probes in the aeration tank, the advantages of zone control over general control, the use of anoxic zones for denitrification and computerized control are discussed.

Johnston and Buhr¹⁹⁵ describe a simple electronic controller which has been successfully employed in conjunction with a standard dissolved oxygen meter, to regulate dissolved oxygen concentration in a completely mixed aeration tank. By adding a chart recorder, the system will permit the determination of the oxygen utilization rate in the aerator on a routine basis.

A dissolved oxygen transmitter which incorporates a self cleaning flotation system has been described¹⁹⁷. The problem of fouling and ragging up has been overcome by mounting the cell housing on a floating ball on the end of an adjustable arm, pivoted at its upper end in a bracket clamped to the tank. The cell is consequently subjected to a washing action which prevents the build-up of bacteriological growth. The cell operates on a modified Clark's principle, using a gold cathode and silver anode immersed in a potassium chloride electrolyte and covered with a gas permeable diaphragm.

The types of commercially available instruments for the measurement of dissolved oxygen in sewage have been reviewed¹⁹⁶.

3.8.2

Free chlorine and bromine

Spectrophotometric method

Van Dalen¹⁹⁸ has investigated the automated determination of total available chlorine in chlorinated sewage effluents. These methods are based on the spectrophotometric determination using o-tolidine and automated amperometric titration with phenyl arsenic oxide. Lin et al¹⁹⁹ compared various titrimetric and spectrophotometric methods for the determination of residual chlorine in sewage effluents.

Midgley²⁰⁰ has given details of a silver bromide single crystal membrane selective electrode-redox electrode cell for the potentiometric determination of bromine and free residual chlorine in chlorinated sewage effluents. Combined residual chlorine (chloramines NH_2Cl , NHCl_2 and NCl_3 and organic chloramines) do not interfere in this method, unless the sample contains both free and combined residual chlorine.

3.8.3

Chlorine dioxide

Spectrophotometric method

A method has been described for the determination of chlorine dioxide in disinfected sewage works effluents²⁰¹. This spectrophotometric method depends on the selective decolorization of acid chrome violet K (ACVK) and the decrease in absorbance of a buffered solution of ACVK at 550 nm allows the direct determination of chlorine dioxide. Other chlorine species and nitrites did not interfere at pH 8.1–8.4.

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Chapter 4

TRADE EFFLUENTS

4.1 Anions

4.1.1 *Borate*

Spectrophotometric method

The standard curcumin method^{1,2} has been found to be suitable for the determination of borate in industrial effluents.

Ion chromatography

Hill and Lash³ have described an ion chromatographic method for the determination of down to 0.05 mg l⁻¹ of borate in environmental waters, nuclear fuel dissolvent solutions and effluents.

Borate is selectively concentrated on Amberlite XE-243 ion-exchange resin and converted to tetrafluoroborate using 10 per cent hydrofluoric acid. Tetrafluoroborate is strongly retained by the resin, thus allowing excess fluoride to be eluted without loss of boron. The tetrafluoroborate is eluted with 1 M sodium hydroxide and is determined in the eluant by ion chromatography. Boron is quantified to a lower limit of 0.05 mg l⁻¹.

None of these common ions interferes at a 100 to 1 mole ratio to boron. In addition, at least a 280 to 1 mole ratio of fluoride to boron, as well as a 100 to 1 mole ratio of chloride to boron, can be tolerated. [Fig. 37](#) shows an ion chromatogram of a sample which initially contained sulphate, chloride, nitrate, fluoride and chromate at a 100 to 1 mole ratio and which was prepared according to the standard procedure. As shown, tetrafluoroborate peaks are well resolved from all the residual amounts of these anions not completely removed by the XE-243 column treatment.

The ion chromatography of borate is also discussed in [section 4.1.16](#) (multianion analysis).

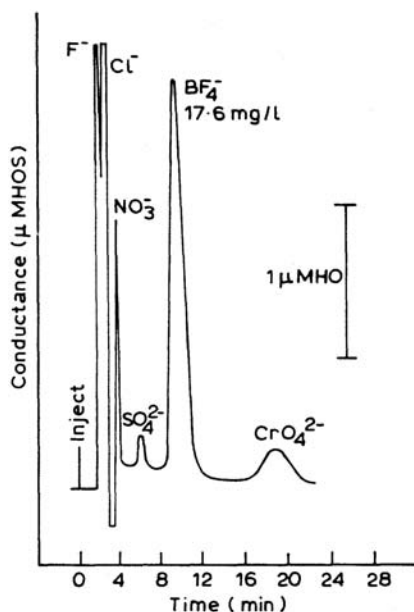


Fig. 37. Effects of diverse ions on IC determination of tetrafluoroborate ion.

4.1.2

Chloride

Filtration

Ilyukhina et al⁴ have described a volumetric method for the determination of chloride in aqueous effluents produced in the manufacture of the fungicides captan and phaltan (tolpet). This effluent contained tetrahydrophthalic acid, tetrahydrophthalimide, phthalic acid and phthalimide. The sample was treated with hydrogen peroxide, acidified with nitric acid and then titrated with 0.1 N mercurous nitrate in the presence of diphenylcarbozide indicator.

Interstitial chloride in very low volumes of pore waters from oil shale rocks has been determined by coulometric titration⁵.

High performance liquid chromatography

See section 4.1.16 (multianion analysis).

Ion chromatography

See section 4.1.16 (multianion analysis).

4.1.3 *Fluoride*

Hannah⁶ has described a high performance liquid chromatographic anionexclusion method for the determination of fluorides in complex trade effluents. Pharmaceutical industrial effluents were examined for fluoride using an Ion-100 anion-exchange column coupled with a GA-100 guard column. Organics were removed from the samples at pH 8.2–8.3 by passing through disposable G18 extraction columns. Conductivity detection allowed determination of fluoride at low mg l⁻¹ levels in the presence of high concentrations of chloride and sulphate through an ion-exclusion mechanism in the polymeric liquid chromatographic column. The limit of detection was 0.2 mg l⁻¹ fluoride l⁻¹ with a working linear dynamic range of 0.2–100 mg l⁻¹.

Ion-exclusion chromatography

See [section 4.1.16](#) (multianion analysis).

4.1.4 *Nitrite*

Miscellaneous

Paper chromatography has been used to identify nitrites in industrial effluents⁷. Maly and Kosikova⁸ have described two spectrophotometric methods for the determination of nitrites in industrial effluents. These workers compared their methods with the standard method using sulphanilic acid and *N*-(1-naphthyl) ethylene-diamine and a new modification of the process with sulphanilic acid and 1-naphthol. The advantage of the latter is the possibility of diluting coloured solutions where owing to high nitrite concentrations, the absorbance exceeds the range of the calibration curve. Urea and glycine (up to 100 mg l⁻¹) do not interfere with these methods. Iron at levels about 5 mg l⁻¹ can be eliminated by clarifying the sample with an aluminium salt.

Ion chromatography

See [section 4.1.16](#) (multianion analysis).

4.1.5 *Nitrate*

Spectrophotometric method

Dodin et al⁹ observed when a solution of nitrate at pH 2.0 is irradiated with ultraviolet light nitrate will oxidize methyl orange. They used this as the basis of a spectrophotometric method for determining nitrate in industrial effluents.

Ion chromatography

See [section 4.1.16](#) (multianion analysis).

4.1.6

*Phosphate**Ion chromatography*

See [section 4.1.16](#) (multianion analysis).

4.1.7

*Free cyanide**Titration method*

Kogan et al¹⁰ titrated down to 1 mg l⁻¹ cyanide in coke works effluents, amperometrically in a basal electrolyte of 0.1 N sodium hydroxide using silver nitrate as titrant. Titration was carried out at -0.2 V (versus SCE) using a vibrating platinum electrode. Up to 500 mg l⁻¹ thiocyanate, phenol and ammonia and 100 mg l⁻¹ of chloride or sulphate do not interfere. Lead carbonate is added to avoid interference by sulphide.

Cadmium carbonate-magnesium chloride mixtures have also been used to prevent interference by sulphide¹¹ and more theoretical yields are claimed for this procedure.

Spectrophotometric methods

Dimethylaminobenzylidenerhodamine¹² and pyrazolone¹³ have been used as chromogenic reagents in the determination of cyanide in industrial effluents. In the latter method¹³ free cyanide is separated from complex cyanides by distillation under reduced pressure in the presence of zinc and lead acetates. The hydrogen cyanide evolved is absorbed in sodium hydroxide solution, and Chloramine T is added, after slight acidification with acetic acid to produce cyanogen chloride. A pyridine/pyrazolone reagent is added, and an optical absorbance measurement of the resultant blue dye is made at 620 nm wavelength. Volatile aldehydes and ketones interfere in the final colour development. The detection limit is about 10 µg l⁻¹.

Fluorimetric method

McKinney et al¹⁴ have described a rapid fluorimetric method for the determination of cyanide in mine waters. The method is based on the liberation of naphtho (2,3-C) (1,2,5) selenadiazole from the reagent Pd₂I₂Cl₄ by cyanide at 25°C and pH 8. The naphthol (2,3-C) (1,2,5) selenadiazole is then extracted into hexane and its fluorescence is measured at 520 nm with excitation at 377 nm. The calibration graph is approximately rectilinear for up to 100 µg of cyanide per 3 ml of hexane. Mercuric and sulphide interfered.

Polarography

Cyanide has been determined in industrial effluents by methods based on measurement of the potential at -0.45 V (versus SCE) in 0.01 M sodium hydroxide medium¹⁵. There is no interference from phenol, acrylonitrile, urea or cyanide but sulphide and thiocyanate interfere.

Continuous flow analysis

Pihlar et al¹⁶ developed the amperometric method of determining cyanides in water to permit reliable and reproducible continuous flow measurements and flow injection analysis of discrete samples of galvanizing plant effluents at the $\mu\text{g l}^{-1}$ level. The method is based on the measurement of the diffusion current arising from the oxidation of silver to dicyanoargentate I. By use of the flow injection principle and a manifold arrangement, absolute amounts of less than 1 ng of cyanide can be determined precisely in volumes as small as $10 \mu\text{l}$ and at a rate exceeding 100 samples per hour.

Free cyanide was separated by microdiffusion in Conway cells. The volume of 0.1 M sodium hydroxide used as absorbing solution was between 0.1 and 1.0 ml according to the amount of free cyanide present in the sample. The free cyanide released upon acidifying the samples (up to 5 ml) with 0.5 ml of 3 M sulphuric acid was quantitatively recovered after 3 hours of distillation at room temperature (20 – 25°C). The absorption solution was subsequently injected directly into the analyser. A 0.1 M solution of sodium hydroxide was used as the carrier stream.

Of the numerous substances tested only sulphide, iodide and thiocyanate interfere seriously in this method and they can be eliminated by distillation or precipitation. Oxidants such as hypochlorite or hydrogen peroxide, which are common agents for detoxification of cyanide effluents, must be fixed by addition of arsenite or sulphite since they are reduced at the silver electrode and this results in a cathodic current. This is a disadvantage of the method compared with potentiometric techniques in which oxidants and reductants usually do not interfere; however, such compounds can be eliminated by simple chemical treatment ordinarily performed at the sampling stage.

Microdiffusion

Rubio et al¹⁷ give details of a simple rapid procedure for the determination of cyanide involving separation by microdiffusion followed by potentiometric determination in the inner chamber of the microdiffusion cell. The limit of detection was $0.02 \mu\text{g l}^{-1}$ cyanide.

Ion selective electrodes

The application of cyanide selective electrodes has been discussed^{18,19}. Cuthbert¹⁸ used the technique to analyse steel works effluents. For cyanide concentrations above 1 mg l^{-1} the electrode method and the standard argentimetric method gave similar results; for lower cyanide concentrations, the colorimetric pyridine-pyrazolone method gave higher results than either the potentiometric method or the colorimetric pyridine-barbituric acid method. Cuthbert discusses problems associated with the determination of cyanide in waste waters containing complex iron cyanides and sulphides.

Hafton²⁰ used a silver ion selective electrode for the continuous determination of free cyanide in effluents in concentrations of 0.01 – $1.0 \mu\text{g l}^{-1}$.

Gas chromatography

Nota and Improta²¹ determined cyanide in coke oven waste water by gas chromatography. The method is based on treatment of the sample with bromine and direct selective determination of the cyanogen bromide by gas-solid chromatography using a BrCN selective detection as an electron capture detector. No preliminary treatment of the sample to remove interferences is necessary in this method, and in this sense, it has distinct advantages over many of the earlier procedures. Bromine also oxidizes thiocyanate to cyanogen bromide. Previous treatment of the sample with aqueous formaldehyde destroys thiocyanate and prevents its interference in the method.

Nota et al²² have made the cyanogen bromide technique for determining cyanides and thiocyanate more sensitive and reproducible by adopting the head space technique. This technique lends itself to automation.

Nota et al²³ have also described a gas chromatographic head space method based on different principles for the determination of 0.01–100 mg l⁻¹ of cyanide and thiocyanate in coke oven waters and waste effluents. This method involves firstly transforming the cyanides, or the thiocyanates, into hydrogen cyanide by acidification, then removing hydrogen cyanide from the aqueous sample by the head space technique and finally separation of hydrogen cyanide by gas solid chromatography and selective detection with a nitrogen phosphorus detector. This procedure for the determination of cyanide is based on three stages: first, transformation into hydrogen cyanide by acidification; second, removal of hydrogen cyanide by the head space technique, and third, gas chromatographic separation of hydrogen cyanide and selective detection with a nitrogen phosphorus detector. A similar procedure is adopted for the determination of thiocyanate the only difference being the quantitative transformation of thiocyanate into hydrogen cyanide according to the reactions:



(where Red and Ox). If cyanide is present prior to the oxidation step, it must be transformed into unreactive cyanohydrin by an excess of formaldehyde or removed by boiling the solution previously acidified to pH 2.

The presence of iron II, iron III and copper II in the sample decreases the response for hydrogen cyanide. The greatest effect is caused by copper II. Reducing agents do not interfere in the analysis of cyanide but oxidizing substances have to be reduced prior to heating of the sample. Oxidants and reducing agents do not interfere in the determination of thiocyanate.

4.1.8

Total cyanide

Spectrophotometric methods

In a method described by Drikas and Rontley²⁴ a stoichiometric amount of lead acetate is added to the sample to remove sulphide interferences. Addition of excess lead caused a low recovery of cyanide. The stoichiometric amount of lead to be added was determined by titration with lead acetate using a redox electrode for endpoint detection; cyanide recoveries averaged 91 per cent.

In a continuous Technican Autoanalyser method²⁵ for determining total cyanide ion cyanide was reacted with pyridine-barbituric acid and the colour produced was evaluated spectrophotometrically. Percentage recoveries from industrial waste samples spiked with potassium ferricyanide and cyanide, respectively, were 98.9 per cent and 100 per cent.

4.1.9 *Complex cyanides*

Spectrophotometric method

Ferrocyanides in coke plant effluents have been determined spectrophotometrically using 2,2'-bipyridyl or 1,10-phenanthroline²⁶. The ferrocyanide is first broken down by digestion with formaldehyde prior to the determination of uncomplexed iron.

Ion pair chromatography

Grigorova et al²⁷ separated and determined stable metallo-cyanide complexes of copper II, silver I, iron II, cobalt III, nickel II, iron III and gold I in metallurgical plant solutions by reversed phase ion-pair partition chromatography and UV detection. The mobile phase contained 2.5 mm tetrabutyl ammonium hydrogen sulphate and methanol and the stationary phase consisted of carbon-18 Novapak cartridges with 4 μm packing. Precision was good with relative standard deviation ranging from 1.1 to 2.8 per cent.

4.1.10 *Thiocyanate*

Titration

Atkinson et al²⁸ have described a technique for titrating thiocyanate/cyanide mixtures in hydrometallurgical effluents. The mixtures are titrated with silver nitrate solution using an automatic potentiometric titration with a silver/glass electrode pair. When thiocyanate is to be determined, cyanide is masked with formaldehyde.

4.1.11 *Sulphate*

Spectrophotometric method

Pilipenko et al²⁹ compared various methods for the determination of sulphate in mine waters. These include a direct photometric method using octamine-u-amino-ol-dicobaltisol, which gave reproducible results in the concentration range 0.05–40 g l^{-1} .¹ Chelatometric methods using barium rhodizonate or acidic chrome blue indicators were both rapid and convenient though chloride concentrations of greater than 1 g l^{-1} interfered with barium rhodizonate determinations. For desalinated water turbidimetric methods proved satisfactory.

Atomic absorption spectroscopy

Stock³⁰ applied atomic absorption spectrometry to an indirect method for determining sulphate in pulp mill effluents. Sulphate was precipitated in barium sulphate and barium subsequently determined by atomic absorption spectrometry in amounts down to 0.12 $\mu\text{g l}^{-1}$. Potassium chloride was added for optimal suppression of barium ionization.

Solid state membrane electrode

Srivastava and Jain³¹ estimated sulphate in paper and tannery industry effluents using a solid state membrane electrode. The solid membrane electrode was prepared from hydrous thorium oxide gel with polystyrene as binder. Although the electrode is non-Nernstian in nature it can be utilized to estimate sulphate ions in the concentration range 10^{-1} – 10^{-4} M. The useful pH range for this assembly is 6–10. The membrane electrode shows good selectivity to sulphate ions and there is practically no interference of a large number of anions and cations.

Ion chromatography

See [section 4.1.16](#) (multianion analysis).

4.1.12

*Sulphide, polysulphide, sulphite**Ion selective electrodes*

A sulphide ion-selective electrode has been used³² as an indicator electrode in the potentiometric titration of sulphide in paper mill effluents with standard mercuric chloride. In 0.1 N sodium hydroxide medium, sulphide and polysulphides are titrated. As the electrode responds to mercuric ions thiosulphate and sulphite can also be titrated at pH 7.0–7.5. The polysulphide plus sulphite can be converted to thiosulphate and can be titrated. Sulphite can be decomposed with formaldehyde and, consequently, thiosulphate can be titrated alone.

Van Staden³³ determined sulphide in effluents using flow injection analysis with a coated tubular solid-state sulphide ion-selective electrode constructed from Tygon tubing and silver foil treated with a sodium sulphide solution.

Jovanovic and Jovanovic³⁴ determined low sulphide and cyanide levels using a deposited on wire silver-silver sulphide electrode.

Gas chromatography

Borchardt and Easty³⁵ developed a gas chromatographic method for determine elemental sulphur in buffer solution. The elemental sulphur is derivatized with ing polysulphide in kraft pulping liquors. The polysulphide is decomposed to triphenyl phosphine. The resulting triphenylphosphine sulphur is determined by flame ionization-gas chromatography.

Gas chromatography

Hawke et al³⁶ described a method for the determination of sulphides in effluents using gas chromatography with a flame photometric detector. Samples were acidified and the hydrogen sulphide brought to solution-vapour equilibrium. Following analysis by gas chromatography the concentration of hydrogen sulphide was determined by interpolation on a calibration graph. The precision, accuracy, bias and effect of potentially interfering substances were determined. The samples could be processed in 1 hour by this method.

4.1.13

*Thiosulphate and polythionates**Titration*

Makhija and Hitchen³⁷ determined these anions in mining effluents and mill effluents by an acidimetric method. It involves sodium hydroxide titration of the acid liberated on addition of mercuric chloride (which oxidizes thiosulphate and polythionates to sulphuric acid), after adjustment of the initial pH value to either 4.3 (using methyl orange) or 8.2 (using phenolphthalein).

In this method a suitable portion of the solution containing a polythionate having 3, 4 or 5 sulphur atoms is acidified to either pH 4.3 or pH 8.2 with 0.005 N sulphuric acid and sodium hydroxide and mercuric chloride is added to release acid quantitatively. The stoichiometric equation is:



A similar equation applies for the thiosulphate:



In both cases the acid generated is titrated with standard sodium hydroxide solution to determine the sum of the concentration of the four sulphur anions: .

High performance liquid chromatography

Takano et al³⁸ used high performance liquid chromatography on an anionexchange column with differential pulse polarographic detection to the determination of thiosulphate and tri-, tetra-, penta- and hexa-thionates in trade effluents. The method is accurate to within 10 per cent at the 0.001–1 mM concentration range.

Preconcentration

Chakraborty and Das³⁹ have described an indirect atomic absorption spectrometric method for determining thiosulphate in photographic processing effluents based on the formation of a stable ion-association complex between lead, thiourea and thiosulphate in alkaline medium. The complex is extracted into *n*-butylacetate:*n*-butanol 2:1 and analysed directly by flame atomic absorption spectrometry. Down to 0.2 µg l⁻¹ thiosulphate were determined.

4.1.14

*Selenate/selenite**Fluorimetry*

A fluorimetric procedure based on the use of 2,3-diaminonaphthalene has been used to determine microgram amounts of total selenate and selenite in industrial effluents⁴⁰. The fluorescent intensity of the complex is measured at 522 nm (excitation at 366 nm).

Differential pulse polarography

Batley⁴¹ has given details of a procedure for determination of tetravalent selenium in effluents, in the concentration range 2–100 $\mu\text{g l}^{-1}$ by using the sensitive adsorption controlled peak obtained by differential pulse polarography in dilute acid solution. Heavy metals which could interfere were removed on Chelex 100 resin. Hexavalent selenium could be determined by the same method after photolytic reduction in the absence of oxygen. For selenium concentrations below 2 $\mu\text{g l}^{-1}$ preconcentration by anion exchange was necessary.

4.1.15

*Silicate**Spectrophotometric method*

A modification of the standard molybdenum blue spectrophotometric method has been used to determine silicate in industrial effluents⁴².

Flameless atomic absorption spectrometry

This technique has been shown to be capable of determining down to 25 $\mu\text{g l}^{-1}$ silica in industrial process waters⁴³.

4.1.16

*Multianion analysis**Ion chromatography*

The work of Mosko⁴⁴ is important in that he is one of the few workers who have given serious consideration to the determination of chloride, sulphate, nitrate, nitrite, orthophosphate, fluoride and bromide in industrial effluents, waste water and cooling water. Two types of analytical columns were evaluated (standard anion and fast run series). Chromatographic conditions, sample pretreatment and the results of interference, sensitivity, linearity, precision, comparative and recovery studies are described. The standard column provided separation capabilities which permitted the determination of all seven anions. The fast run column could not be used for samples containing nitrite or bromide owing to resolution problems.

Table 42 contains some examples of comparative data. Most results agreed within experimental limits for the specific concentration range and test method used. Traditional methods of analysis used for comparison purposes were as follows: fluoride, ion selective electrode method, chloride, automated mercuric thiocyanate colorimetric method, nitrite, permanganate titration method, orthophosphate, automated ascorbic acid reduction colorimetric method, nitrate, automated copper-cadmium reduction colorimetric method. Sulphate was measured with a barium methylthymol blue colorimetric automated method.

4.2 Cations

4.2.1 Ammonium

Miscellaneous

Daughton et al⁴⁵ have reviewed four methods for the determination of ammonium in oil shale retort waters. The methods were automated distillation and acidimetric titration, phenate colorimetry, glutamate dehydrogenase enzymatic analysis and reverse-phase fractionation with combustion and chemiluminescence detection. Samples were prepared by centrifugation and pressure filtration of the supernatant fluid to remove particulate and suspended

TABLE 42
Comparison of results (mg l⁻¹) obtained with automated IC vs. results obtained with traditional methods

Water type	Fluoride (F)		Chloride (Cl)		Nitrite (NO ₂)		Orthophosphate (PO ₄)		Bromide (Br)		Nitrate (NO ₃)		Sulfate (SO ₄)	
	Electrode	IC	Wet chem	IC	Wet chem	IC	Wet chem	IC	Wet chem	IC	Wet chem	IC	Wet chem	
Boiler feed	0.1		16	16	<0.5		<0.2	<0.05	0.5		2.0	1.9	42	40
Boiler	0.2		1.2	1.5	<0.5		11	9.9	<0.5		<0.2		47	55
Boiler	1.2		140	125	<5		14	14.4	<0.5		1.0	1.0	70	60
Cooling	4.0		20	24	<0.5		2.0	2.5	1.4		14	15	68	75
Cooling	0.4		23	28	<0.5		4.2	4.2	<0.5		6.0		46	45
Zeolite softened	0.1		18	18	<0.5		<0.2	<0.05	<0.5		2.2	2.0	37	35
Softened	0.2	0.2	40	38	<0.5		0.4	0.2	<0.5		<0.2		32	25
Nitrite treated	<0.5		15	16	<2.5	<100	<10		<25		1000	990	88	80
Nitrite treated	5.0		13	16	<2.5	<100	0.6	0.55	<2.5		140	155	38	40
City make-up	1.0	1.0	16	16	<0.5		<0.2	<0.05	<0.5		9.0	8.3	23	25
Well water	0.6	0.6	2.2	3.0	<0.5		<0.2	<0.05	<0.5		<0.2	<0.2	10	5
Waste effluent	<1	0.1	260	280	<5		16	16.1	150		22	19	240	260

materials. Statistical comparisons showed that precisions were best for the titrimetric and colorimetric methods. Paired comparison analyses of intermethod ammonia data showed that each pair of methods gave significantly different results for the majority of samples. The method based on reverse phase fractionation with combustion and chemiluminescent detection gave the most rapid estimates of ammonia and is recommended for rapid monitoring or range finding situations.

Boyd⁴⁶ has discussed the determination of ammonia in effluents from intensive rearing fish farms.

Merz and Oldeweme⁴⁷ have described a continuous flow technique for determining ammonia in effluents in which the sample is mixed with an alkaline carrier stream and passed over a semipermeable membrane through which free ammonia diffused into a solution of boric acid. The change in conductivity of the boric acid provided the concentration of ammonia. Merz and Oldewene⁴⁷ also described a selective ion chromatographic procedure coupled with fluorescence detection for the determination of ammonia in which ammonia is separated from amines and alkaline metals and reacted with *o*-phthalic acid dialdehyde on a separate column.

4.2.2

Aluminium

Fluorescence method

Simeonov et al⁴⁸ have described a method for continuous successive determination of aluminium (and fluoride) in the same sample, which is based on the mathematical correction of a complex analytical signal obtained by a fluorescence technique. A mathematical model describing the analytical signal in terms of the ratio of aluminium and fluoride concentrations is used for the correction. After masking interference from other ions, fluoride is determined potentiometrically. The method is of interest for continuous monitoring of industrial effluents, containing both fluoride and aluminium.

The determination of aluminium is also discussed in [section 4.2.43](#) (multication analysis).

4.2.3

Antimony

Spectrophotometric method

In a method for the determination of antimony in industrial effluents, Agrawal and Patki⁴⁹ form a greenish yellow coloured antimony complex with *N*-phenylbenzohydroxamic acid at 4 M hydrochloric acid which is extracted from chloroform.

The complex is back extracted in 0.01 M ammonia and then antimony is estimated with rhodamine B in 6 M hydrochloric acid media. This bluish violet coloured complex is extractable in benzene. The maximum absorbance of the antimony rhodamine B complex is observed at 565 nm.

The determination of antimony is discussed further in [section 4.2.43](#) (multication analysis).

Preconcentration

See [section 4.2.44](#) (preconcentration).

4.2.4 *Arsenic*

Miscellaneous

Howe⁵⁰ has compared differential pulse polarography, atomic absorption spectrometry and spectrophotometry as methods for the determination of arsenic in water samples from ash ponds at steam generating plants. As a result of this investigation a differential pulse polarographic method was developed for determining total arsenic concentrations. After digestion of the sample and isolation of arsenic by solvent extraction, the peak current for arsenic is measured and compared to a standard curve. The effective range of concentrations for this method is from 2 to 50 $\mu\text{g l}^{-1}$ of arsenic.

The precision and accuracy of this polarographic method for determining concentrations of arsenic in water samples were compared with results obtained by two standard methods, atomic absorption and colorimetry. The three methods compared favourably for the split samples; however, results of the colorimetric method for the replicate analyses were slightly negatively biased.

Leung et al⁵¹ investigated factors affecting the determination of arsenic by differential pulse anodic stripping voltammetry. This method was compared with linear scan anodic stripping voltammetry and atomic absorption spectroscopy and was shown to give satisfactory results.

The determination of arsenic is discussed further in [section 4.2.43](#).

4.2.5 *Barium*

See [section 4.2.43](#) (multication analysis).

4.2.6 *Beryllium*

Emission spectrography

Beryllium and heavy metals in neutral mine waters have been preconcentrated using 8-hydroxyquinoline, sodium diethyldithiocarbamate and acetylacetone at pH 5⁵². In acidic mine waters the beryllium was separated with other metals, from the matrix by extraction with dithizone or complexone III, sodium diethyldithiocarbamate and acetylacetone at pH 8. The analysis was completed on a quartz spectrograph under arc conditions. The method was valid for a concentration range of 0.05–100 $\mu\text{g l}^{-1}$ beryllium. The relative standard deviation did not exceed 0.2.

The determination of beryllium is discussed further in [section 4.2.43](#).

4.2.7 *Bismuth*

See [section 4.2.43](#) (multication analysis).

Preconcentration

See [section 4.2.44](#) (preconcentration).

4.2.8

Boron

See [section 4.2.43](#) (multication analysis).

4.2.9

*Cadmium**Atomic absorption spectrometry*

This technique has been used⁵³ to determine down to $0.1 \mu\text{g l}^{-1}$ cadmium (and copper) in plating works effluents. The sample, buffered at pH 10, is extracted with a butyl acetate solution of 2-mercaptobenzothiazole and this solution aspirated directly into an air acetylene flame. The cadmium absorption at 229.9 nm is evaluated.

X-ray fluorescence spectrometry

Cadmium is transferred from an industrial effluent sample onto an ionexchange membrane contained in the sample flask. X-ray fluorescence of the resin enables $5 \mu\text{g l}^{-1}$ of cadmium to be determined⁵⁴. The determination of cadmium is discussed further in [section 4.2.43](#) (multication analysis).

Preconcentration

See [section 4.2.44](#) (preconcentration).

4.2.10

Calcium

The determination of calcium is discussed in [section 4.2.43](#) (multication analysis).

4.2.11

*Cerium**Preconcentration*

See [section 4.2.44](#) (preconcentration).

4.2.12 Chromium

Atomic absorption spectrometry

Morrow and McElhane⁵⁵ determined chromium in industrial waters using a modified flameless atomic absorption spectroscopic technique. The heated graphite atomizer consists of a commercial carbon rod atomizer modified to accept graphite tubes. This technique is rapid, accurate and sensitive.

Liquid chromatography

The determination of chromium is also discussed in [section 4.2.43](#) (multication analysis).

High performance liquid chromatography

A post-chromatographic technique for the determination and speciation of chromium ions has been described⁵⁶. Chromium species at a lower oxidation state than the hexavalent forms were oxidized to chromate in a lead dioxide solid phase reactor. Detection was performed by complexation of chromate with 1,5-diphenylcarbazide which formed a red violet complex detectable at 540 nm. This allowed the speciation of chromium by a simple column switching technique. Conditions necessary for the fast oxidation of chromium inside the solid phase reactor are discussed. The method has been applied to the detection and speciation of chromium in steelworks effluents.

4.2.13 Cobalt

The determination of cobalt is discussed in [section 4.2.43](#) (multication analysis).

Preconcentration

See [section 4.2.44](#) (preconcentration).

4.2.14 Copper

Spectrophotometric method

Copper has been determined in milk processing effluents⁵⁷ by a method involving extraction of the acidified sample with a carbon tetrachloride solution of zinc dibenzylthiocarbamate. The extraction of the copper complex formed is then evaluated at 435 nm. In the absence of free chlorine in the samples, recoveries were in the range 93–107 per cent. Free chlorine interfered in the determination of copper.

The determination of copper is also discussed in [section 4.2.43](#) (multication analysis).

Preconcentration

See [section 4.2.44](#) (preconcentration).

4.2.15

Gadolinium

Preconcentration

See [section 4.2.44](#) (preconcentration).

4.2.16

Gallium

The determination of gallium is discussed in [section 4.2.43](#) (multication analysis).

4.2.17

Indium

The determination of indium is discussed in [section 4.2.43](#) (multication analysis).

4.2.18

Iron

The determination of iron is discussed in [section 4.2.43](#) (multication analysis).

4.2.19

Lead

Spectrophotometric method

Thind and Singh⁵⁸ have described a method for the recovery and selective separation of lead ions from lead acid battery manufacturing effluents.

The determination of lead is also discussed in [section 4.2.43](#) (multication analysis).

4.2.20

Lithium

The determination of lithium is discussed in [section 4.2.43](#) (multication analysis).

4.2.21

Magnesium

The determination of magnesium is discussed in [section 4.2.43](#) (multication analysis).

4.2.22 *Manganese*

Spectrophotometric method

Manganese has been determined in industrial effluents by a method based on the formulation of the red manganese M complex of 4-(2-pyridylazo) resorcinol which has an absorption maximum at pH 9.7–10.7, at 500 nm⁵⁹.

On addition of EDTA after colour development only the manganese complex is decomposed and the manganese concentration can be calculated from the decrease in extinction.

The determination of manganese is also discussed in [section 4.2.43](#) (multication analysis).

4.2.23 *Mercury*

Flameless atomic absorption method

Carpenter⁶⁰ has described a flameless method for the determination of mercury in paper mill effluents and showed that the practical limit of detection was $1 \mu\text{g l}^{-1}$.

H.M. Stationery Office (UK)⁶¹ have published cold-vapour atomic absorption spectrometric methods for determining mercury in amounts down to $1 \mu\text{g l}^{-1}$.

Churchill et al⁶² have discussed cold-vapour atomic absorption spectrometric methods published by the Environmental Protection Agency (USA) for the determination of mercury in effluents.

Emission spectrography

In a method⁶³ for determining down to $1 \mu\text{g l}^{-1}$ mercury in effluents, the sample is extracted with a 0.004 per cent solution of dithizone in carbon tetrachloride. The extract is adsorbed on to carbon powder which is then placed in an electrode at 500°C. The intensity of the mercury 2536 nm line in the arc spectrum is evaluated.

The determination of mercury is also discussed in [section 4.3.43](#) (multication analysis).

4.2.24 *Molybdenum*

Preconcentration

See [section 4.2.44](#) (preconcentration).

4.2.25 *Nickel*

The determination of nickel is discussed in [section 4.2.43](#) (multication analysis).

4.2.26
Niobium

Preconcentration

See [section 4.2.44](#) (preconcentration).

4.2.27
Potassium

The determination of potassium is discussed in [section 4.2.43](#) (multication analysis).

4.2.28
Rubidium

The determination of rubidium is discussed in [section 4.2.43](#) (multication analysis).

4.2.29
Ruthenium

Preconcentration

See [section 4.2.44](#) (preconcentration).

4.2.30
Selenium

The determination of selenium is discussed in [section 4.2.43](#) (multication analysis).

4.2.31
Silver

Atomic absorption spectrometry

This technique has been applied⁶⁴ to the determination of down to 1.5 mg l⁻¹ silver in industrial effluents. A hollow cathode lamp is used as source and an air-propane flame for excitation; measurements are made at 328 nm. The sensitivity is 1.5 mg l⁻¹ silver.

The determination of silver is also discussed in [section 4.2.43](#) (multication analysis).

4.2.32
Strontium

The determination of strontium is discussed in [section 4.2.43](#) (multication analysis).

4.2.33

Sodium

The determination of sodium is discussed in [section 4.2.43](#) (multication analysis).

4.2.34

Thallium

The determination of thallium is discussed in [section 4.2.43](#) (multication analysis).

4.2.35

Tantalum

Rossokha and Rehkola⁶⁵ used X-ray spectrochemical analysis to determine down to 0.4 mg l⁻¹ tantalum in effluents from tantalum manufacture. Prior to spectrochemical analysis tantalum is converted to its fluoride and then extracted with cyclohexanone.

The determination of tantalum is also discussed in [section 4.2.43](#) (multication analysis).

4.2.36

Tellurium

The determination of tellurium is discussed in [section 4.2.43](#) (multication analysis).

4.2.37

Tin

The determination of tin is discussed in [section 4.2.43](#) (multication analysis).

Preconcentration

See [section 4.2.44](#) (preconcentration).

4.2.38

Tungsten and lead

Neutron activation analysis

These elements have been determined in dried evaporates of mine water⁶⁶. After irradiation, tungsten and gold carriers are added and after a detailed workup procedure the gold is extracted into diethyl ether and metallic gold precipitated with hydrazine and the tungsten is precipitated as tungstic acid. After weighing these solids to determine chemical yield the activities of tungsten 187 and gold 198 are measured by γ -ray scintillation spectrometry.

Preconcentration

The preconcentration of tungsten is discussed in [section 4.2.44](#) (preconcentration).

4.2.39

*Uranium**Spectrophotometric method*

Uranium in mine waters is reacted with brilliant green and the coloured complex extracted into toluene prior to spectrophotometric evaluation⁶⁷.

Ion chromatography

Uranium has been determined in process liquids by ion chromatography using an ammonium sulphate sulphuric acid element. Uranium was determined in the eluant. Uranium was determined in the eluate spectrophotometrically at 520 nm as the 4-(2-pyridylazo) resorcinol complex⁶⁸.

4.2.40

Vanadium

The determination of vanadium is discussed in [section 4.2.43](#) (multication analysis).

Preconcentration

See [section 4.2.44](#) (preconcentration).

4.2.41

*Zirconium**Preconcentration*

See [section 4.2.44](#) (preconcentration).

4.2.42

Zinc

The determination of zinc is discussed in [section 4.2.43](#) (multication analysis).

Preconcentration

See [section 4.2.44](#) (preconcentration).

4.2.43

Multication analysis of trade effluents

Various techniques used for multimetal analysis of trade effluents are reviewed in Table 43. Whilst atomic absorption spectrometry is a very popular technique for this type of analysis there is no doubt that inductively coupled plasma atomic emission spectrometry and anodic or cathodic stripping voltammetry are featuring strongly in the more recently published work.

The Environmental Protection Agency (US) has published details of graphite furnace atomic absorption spectrometric methods for a range of metals in industrial and power station effluents⁷¹.

In this method samples are introduced into a graphite furnace of the mini-Massman design. Separate drying, charring and atomizing program steps are incorporated in a controller that establishes appropriate resistance heating of the graphite tube. This unit is used with a double beam Perkin-Elmer atomic absorption spectrophotometer equipped with a deuterium background corrector. The decrease in energy of the hollow cathode or electrodeless discharge lamp is detected on a strip chart recorder as a transient peak and this peak height is proportional to concentration.

Recoveries obtained in this procedure when various effluent samples were spiked with $10 \mu\text{g l}^{-1}$ of the eight elements were in the range 100 ± 5 per cent.

4.2.44

*Preconcentration**Solvent extraction methods*

Petrov et al⁸⁹ assessed the suitability of 0.05 M solution of diantipyryl methane in chloroform or dichloromethane as an extractant for preconcentrating traces of 20 metals in mine waters to which ammonium thiocyanate has been added. This reagent does not complex with nickel, aluminium, iron or manganese but can be used for the preconcentration of copper, zinc, vanadium, tin, molybdenum, niobium, bismuth, tungsten, gadolinium, cobalt, cadmium and antimony in the presence of 0.2–5.0 mg l⁻¹ of iron.

TABLE 43
Multimetal analysis of trade effluents

Elements	Type of sample	Technique	Detection limit ($\mu\text{g l}^{-1}$)	Ref.
Cadmium	Nuclear power plant cooling water	Flameless atomic absorption spectrometry graphite tube with automatic sampling unit	0.0025	69,70
Vanadium	5			
Cobalt	—			
Chromium		—		
Copper			—	
Iron			—	
Manganese			—	
Nickel			—	
Lead	Metals	Flameless atomic absorption spectrometry	1	71

Elements	Type of sample	Technique	Detection limit ($\mu\text{g l}^{-1}$)	Ref.
Selenium	Industry effluents	1		
Silver	Trade effluents	Graphite furnace miniMassman design (see text)	0.5	
Tellurium	Power plant effluents	1		
Antimony		0.5		
Arsenic			1	
Beryllium			1	
Cadmium			1	
				1
Calcium	Acid mine water	Inductively coupled plasma atomic emission spectrometry	0.2	72
Magnesium		1.4		
Sodium		2.0		
Cadmium			1.8	
Copper			6.2	
Iron			15.8	
Potassium			3.5	
Lithium			0.3	
Zinc			1.2	
Arsenic	Waste metal leachates	Barium, cadmium, chromium, lead and silver: inductively coupled plasma emission spectrometry	0.5–50	73
Selenium				
Mercury				
Barium				
Cadmium				
Chromium		Arsenic, selenium and mercury: above with mercury/hydride accessory		
Lead				
Silver				
19 elements	Nuclear industry waste	Inductively coupled plasma atomic emission spectrometry on solvent extracts of sample	0.004– 4000	74
Misc. elements	Industrial effluents	Direct reading emission spectrometry	—	75
36 elements	Industrial effluents	Direct reading emission spectrometry	5	76

Elements	Type of sample	Technique	Detection limit ($\mu\text{g l}^{-1}$)	Ref.
15 elements including 20	Pickling plant effluents	Direct reading emission spectrometry	20	77

Elements	Type of sample	Technique	Detection limit ($\mu\text{g l}^{-1}$)	Ref.
Sodium			870	
Magnesium			870	
Boron			1100	
Barium				
Zinc				
Iron	Electroplating effluents	Polarography in 0.8 M acetate buffer (pH 5.5) containing EDTA	—	78
Copper				
Chromium				
Copper	Industrial effluents	Inversion chromopotentiometry electrical reduction of metal at a mercury electrode with formation of amalgam and its anodic oxidation by the current	—	79
Zinc				
Cadmium				
Gallium				
Indium				
Thallium				
Tin				
Lead				
Bismuth				
Manganese				
Nickel	Pressurized water reactor coolant	Differential pulse anodic scanning voltammetry of dimethylglyoxinate complexes at a hanging mercury drop electrode	2	80
Cobalt	8			
Lead	Galvanizing plant effluents	Continuous flow reverse phase anodic scanning voltammetry	—	81
Cadmium				
Zinc	Industrial and sewage effluents	Differential pulse anodic stripping voltammetry, 50 samples can be analysed per day. Results in good agreement with atomic absorption spectrometry	sub	82
Cadmium	$\mu\text{g l}^{-1}$			
Lead		to		

Elements	Type of sample	Technique	Detection limit ($\mu\text{g l}^{-1}$)	Ref.
Bismuth		$\mu\text{g l}^{-1}$		
Copper				
Thallium				
Indium				
Antimony				
Tin				
Nickel				
Aluminium	Paper works effluents	Neutron activation analysis followed by X-ray spectrometry	—	83
Calcium				
Potassium				
Magnesium				
Phosphorus				
Silicon				
Chlorine				
Silicon	Power station fly ash leachates	X-ray fluorescence spectrometry	—	84
Sulphur				
Potassium				
Calcium				

Elements	Type of sample	Technique	Detection limit ($\mu\text{g l}^{-1}$)	Ref.
Manganese				
Iron				
Nickel				
Zinc				
Rubidium				
Strontium				
Barium				
Copper	Galvanizing plant effluents	Paper chromatography	—	85
Cadmium	Nickel, copper, zinc, chromium, cadmium, with 1,4-dioxan nitric acid-water (200:2:5) as solvent and ethanolic alizarin as spray reagent			
Mercury				
Zinc				
Chromium				
Nickel		Copper, cadmium, mercury, butanol saturated with 3 N hydrochloric acid and		

Elements	Type of sample	Technique	Detection limit ($\mu\text{g l}^{-1}$)	Ref.
		chloroformic dithizone as spray reagent		
Miscellaneous	Industrial effluents	Review of methods	—	86
Vanadium	Gas and coke works effluents	Review of methods	—	87
Zinc				
Miscellaneous	Paper mill effluents	Review of methods	—	88

Adsorption on chitosan

Chitosan has been used for the preconcentration of molybdenum and of zirconium, niobium, cerium and ruthenium⁹⁰⁻⁹⁴ in nuclear fuel solutions.

4.3

Elemental analysis

4.3.1

Total nitrogen

Titration

To determine total nitrogen, including nitrate, nitrite and organic nitrogen in industrial effluents, Moore and McNulty⁹⁵ pyrolysed 20 μl of the sample over a granular nickel catalyst at 800°C in a stream of humidified hydrogen converting nitrogen compounds to ammonia which is absorbed in sodium sulphate solution and titrated by the electrogeneration of hydrogen ions in the presence of a pH electrode until the original pH of the solution is restored. The method is suitable for determining total nitrogen in concentrations between 0.2 and 1000 mg l^{-1} .

Starck and Haapala⁹⁶ used a modified Kjeldahl procedure to measure total nitrogen in industrial and municipal effluents. Nitrate and nitrite were reduced with Devarda's alloy and organic material was reacted with sulphuric acid in the presence of copper. Resultant ammonia liberated by addition of sodium hydroxide was distilled into boric acid and then titrated with sulphuric acid. The extent to which organic nitrogen was converted to ammonia depended on the carbon-nitrogen bonding. The method accounted for at least 80 per cent of the total nitrogen in the effluent and the standard deviation between 16 laboratories involved in the study was 8 per cent for municipal effluents and 13 per cent for industrial effluents.

Daughton et al⁹⁷ addressed themselves to the problem of determining organic nitrogen in samples which also contain relatively high concentrations of ammonia, a situation which occurs in the case of oil shale retort waters. Oil shale process waste waters usually contain concentrations of ammonia, an order of magnitude greater than organic nitrogen compounds. The removal of ammonia from such samples using reverse phase chromatography to separate polar from non-polar nitrogenous compounds is described. A second method used non-osmotic dissolved gas dialysis to separate volatile from non-volatile nitrogenous solutes. Organic nitrogen is determined by a combustion/ chemiluminescence method. Comparison with the Kjeldahl method yielded correlation coefficients of 0.920 and 0.996 for the first and second method

respectively. Combining both methods yielded correlation coefficients of 0.989 against the Kjeldahl method and higher estimates of organic nitrogen.

4.3.2

Total phosphorus

Flow injection analysis

Aoyagi et al⁹⁸ have described a rapid spectrophotometric determination of total phosphorus in industrial effluents by flow injection analysis including a capillary digester. The method is based on peroxydisulphate oxidation in a heated capillary tube (160°C) containing a platinum wire. Subsequent spectrophotometric determination of phosphate in an acidified ammonium molybdate solution containing malachite green completed the technique. A detection limit of 2 $\mu\text{g l}^{-1}$ phosphorus was achieved.

4.3.3

Total organic carbon

Combustion to carbon dioxide

Earlier methods involved either combustion of the sample in the presence of cupric oxide⁹⁹ or digestion with a mixture of concentrated sulphuric and phosphoric acids containing potassium dichromate and potassium iodate¹⁰⁰. In all cases complete conversion occurs of organic carbon to carbon dioxide. After drying with magnesium perchlorate the carbon dioxide is determined by a katharometer⁹⁹ or by weighing¹⁰⁰. More recently automated methods based on exposure of the acidified sample to ultraviolet light have come to the fore, for the determination of total organic carbon in effluents¹⁰¹. In the Technicon Industrial Systems Monitor 650 continuous flow analyser, the sample in a silica coil is exposed to ultraviolet light for approximately 2 min which completely breaks down any organic carbon. Any carbon dioxide thus generated is diffused across a gas permeable membrane to separate it from the reaction matrix, and analysed colorimetrically.

Methods based on reduction to methane

An alternative method that has been used for the determination of total organic carbon in trade wastes involves injection of the sample into a stream of pure nitrogen which passes over cupric oxide at 850–900°C to convert carbon to carbon dioxide¹⁰². Hydrogen is then introduced and the mixed gas passes over nickel on fire-brick at 350°C to reduce carbon dioxide to methane which is detected by means of a flame ionization detector after chromatography on silica gel. Down to 1 mg l^{-1} carbon can be determined.

Croll¹⁰³ has investigated this procedure in detail and in conjunction with Phase Separations Ltd (UK) has developed a commercial instrument.

The sample is first acidified with nitric acid and then purged with carbon dioxide free air in order to remove inorganic carbonates. It is then pumped to the oxidation stage where the sample is vaporized and the organic materials present are oxidized to carbon dioxide. After the addition of nitrogen, the steam is condensed and the nitrogen plus carbon dioxide separated from the water, which is pumped to waste.

Hydrogen is added to the gas stream and passage over a nickel catalyst at 450°C reduces the carbon dioxide to methane which is then measured using a flame ionization detector.

4.3.4

Dissolved organic carbon

Persulphate oxidation

Oxidation with potassium persulphate is commonly used to determine dissolved organic carbon in effluents¹⁰⁴. Oxidation is carried out in the presence of silver ions for 30 min at 50–80°C. The carbon dioxide formed is carried by an inert gas over heated cupric oxide and absorbed in potassium hydroxide solution. Inorganic carbon dioxide is determined first by acidification of the sample and collection of the carbon dioxide. In both instances after precipitation of the carbonate with barium chloride the unconsumed potassium hydroxide is titrated.

4.4

Miscellaneous determinands

4.4.1

Suspended solids

Kendall¹⁰⁵ investigated the problem of determining total suspended solids in pulp and paper effluents. He compared five methods and evaluated factors such as precision and care of filtration. Centrifuging followed by filtration through a 2.4 cm fibre glass filter in a porous bottom crucible proved a satisfactory technique suitable for routine monitoring.

Granatstein et al¹⁰⁶ investigated the effect of pollutant concentrations in turbid water on the polarization of scattered light and suggested that polarimetry might be used to investigate suspensions in polluted water.

4.4.2

Colour

Carpenter and Berger¹⁰⁷ have presented the results of an inter-laboratory comparison of colour measurement procedures and of studies on factors affecting the measurements of low concentrations of colour in pulp mill waste waters and receiving waters. They suggest a tentative procedure for spectrophotometric determination of colour in such samples.

Wagner and Ruck¹⁰⁸ have described a method for the determination of the colour value, of industrial effluents, involving the entire visible spectrum, from 380 to 780 nm. By determining the form of the absorption spectrum over this range, a mean value for the absorption intensity can be calculated, as well as the magnitude of peaks in the absorption curve corresponding to specific wavelengths. A colour standard is proposed based on the mean spectral absorption coefficient which is an additive parameter. The nature of this parameter is similar to the ADMI colour value adopted by the American Dye Manufacturers Institute, but can be much more easily determined.

4.4.3

Odour

The US Environmental Protection Agency¹⁰⁹ has discussed the aqueous odour thresholds of organic pollutants in industrial effluents.

4.4.4

Cyanogen chloride and cyanogen bromide

Bailey and Bishop¹¹⁰ have described a spectrophotometric procedure using *p*-phenylenediamine chromogenic reagent for the determination of cyanogen chloride and cyanogen bromide in industrial effluents.

4.5

Organic substances

4.5.1

Hydrocarbons

Infrared spectroscopy

Bogatie¹¹¹ applied infrared spectroscopy to the rapid identification of oil and grease spills from pulp and paper mills. In the case of oils and greases classical infrared methods are most useful in differentiating between broad groups or families of oils and greases. For example, [fig. 38](#) shows infrared spectra for three major groups: (a) tall oil, (b) petroleum fuel oil and (c) a non-petroleum product. Tall oil shows a strong band at 1700 cm^{-1} representing carboxylic acid. The petroleum product has no 1700 cm^{-1} band because it does not contain carboxylic acid groups. The non-petroleum hydraulic fluid has a spectrum much different from either tall oil or petroleum, especially in the carbon-hydrogen bonding region (2950 cm^{-1}) which shows

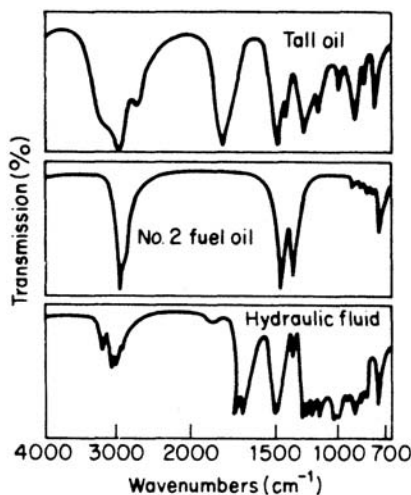


Fig. 38. Infrared spectra for three groups of oils.

only a fraction of the carbon-hydrogen content found in the other two oils. Thus, the classical method is most useful in distinguishing between broad groups or families of oil and grease.

Spectrophotometric method

Lee and Walden¹¹² have described a photometric method for determining traces of kerosene in effluents. The method, which is based on the miscibility of kerosene with acetone and its relative insolubility in water, can be applied to samples containing up to 10 mg l⁻¹ of kerosene. To the sample (11) is added activated carbon (0.2 g). The sample is stirred for 5 min then filtered through a glass wool plug in the stem of a funnel. Excess of water is removed from the stem by suction with a water pump for 5 min. The carbon column is washed with acetone (5×3 ml). The combined washings are evaporated to 2 ml and diluted to 10 ml with acid lauryl sulphate solution (1 ml of concentrated sulphuric acid and 1 g of sodium lauryl sulphate per litre cooled to 10°C before use) to produce a stable turbidity. The extinction is measured at 550 nm and the kerosene concentration obtained from a calibration graph.

Gas chromatography-mass spectrometry

See [section 4.5.22](#) (multiorganic analysis).

Column chromatography

Bundt et al¹¹³ separated low boiling petroleum hydrocarbons from the aliphatic, mono-, di- and polyaromatics by column chromatography. This separation was simplified by removal of non-volatile polar components using a silica gel-aluminium oxide column.

Preconcentration

Concawe¹¹⁴ have applied the gas stripping analysis technique developed by the Environmental Protection Agency^{115–117} for the preconcentration of organics in oil refinery wastes prior to their identification and determination by gas chromatography-mass spectrometry. The method has been used to determine down to $1 \mu\text{g l}^{-1}$ of benzene, toluene, ethylbenzene and mono- and di-chloro benzenes in aqueous refinery wastes¹¹⁶ and up to 29 purgeable chlorine and bromine containing organics in aqueous industrial wastes. For the determination of purgeable trace aromatic and aliphatic hydrocarbons a flame ionization detector should be used. For the determination of purgeable halogenated organics a halide selective detector should be used (the Hall 700 A electrolytic conductivity detector is recommended, but the alkali flame ionization or electron capture devices could be used).

4.5.2

Polyaromatic hydrocarbons

Gas chromatography

Owing to their very low solubility in water, polyaromatic hydrocarbons occurring in industrial waste water are largely adsorbed on suspended solids. For example, Kadar et al¹¹⁸ showed that waste water from the aluminium industry has a polyaromatic hydrocarbon content of $10\text{--}150 \mu\text{g l}^{-1}$ after filtering through a Micropore filter. Adsorption on a solid phase, such as Amberlite XAD, porous polyurethane resin and Tenax (a porous polymer based on 2,6-diphenylphenylene oxide) was used to prepare an extract for gas chromatography.

Gas chromatography-mass spectrometry

Lao et al¹¹⁹ described a computerized gas chromatographic—mass spectrometric analysis of polyaromatic hydrocarbons in environmental samples such as coke oven emissions, coal tar. This method involves a three-step method: preliminary separation of polycyclic aromatic hydrocarbons by solvent and/or column chromatography, identification by gas chromatogram combined with a quadruple mass spectrometer and data processor, and measurement by computerized gas chromatography using internal standards. The efficiencies of different Dexsil gas chromatographic columns were also evaluated during the study.

The gas chromatography-mass spectrometry of polyaromatic hydrocarbons is also discussed in [section 4.5.22](#) (multiorganic mixtures).

High performance liquid chromatography

Kasiske et al¹²⁰ have described a high performance liquid chromatographic method for six polynuclear aromatic hydrocarbons whose concentration in potable water is regulated by European Economic Community standards, viz. fluoranthrene, benz(e)acetphenanthracene benzo(k)fluoranthrene, benzo(d,e,f)chrysene, indeno(1,2,3,c,d)pyrene and benzo(g,h,i)perylene.

In this method a 1 l sample of water is extracted three times with 30 ml of cyclohexane. The combined organic phase is concentrated in a vacuum rotary evaporator to a volume of about 0.5 ml and filtered through alumina, activity II. The polycyclic aromatic hydrocarbons adsorbed to the alumina are eluted with 3 ml of cyclohexane-benzene (1:1 v/v) and evaporated to dryness.

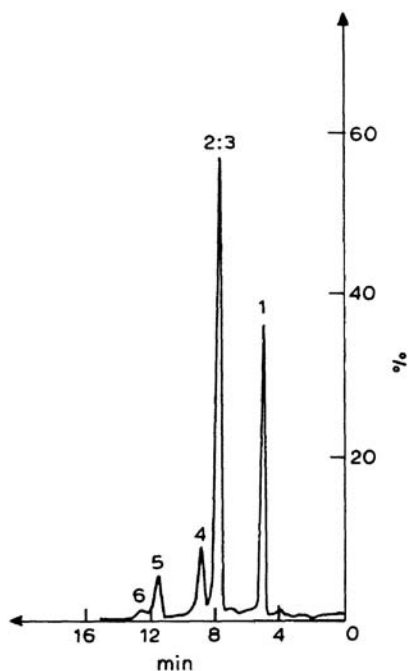


Fig. 39. Chromatogram of PAH standard. Sample 1.0 μl . Total concentration 20 ng l^{-1} . Peaks, 1, fluoranthrene; 2, benz(e)acephenanthrene; 3, benzo(k)fluoranthrene; 4, benzo(def)chryzene; 5, indeno[1,2,3-c,d]pyrene; 6 benzo(g, h²)perylene. Full scale attenuation 0.5 \times (Ex 254 nm Em 408 nm filter).

The residue is taken up in 200 μl of methanol and 20 μl of the latter are injected into the chromatograph. Separation is achieved by elution through a 250 \times 4 mm i.d. column packed with Nucleosil reversed phase C18 (particle size 5 μm).

Using the conditions the chromatograms shown in [fig. 39](#) were obtained for a standard sample and a trade effluent sample.

Concawe¹²¹ recommend methods described by the Environmental Protection Agency for the determination of polyaromatic hydrocarbons in oil refinery effluents. The method involves extraction of the effluent with methylene dichloride followed by clean-up procedures followed by gas chromatography or liquid chromatography.

For the gas chromatographic method no detector is specified; flame ionization seems to be the best choice. Lack of selectivity in the method can lead to interference by compounds that are not completely removed by the clean-up. Higher selectivity can be achieved by use of a photoionization detector. In addition some pairs of the polyaromatic hydrocarbon isomers are incompletely separated by the 6 in column used in this method while the heavier polyaromatic hydrocarbons often show tailing peaks.

Almost all polyaromatic hydrocarbon isomers can be separated using a longer column (30 in) with the same packing material, or by using a glass capillary column; only benzo(b)fluoranthrene-benzo(k)fluoranthrene are not resolvable even by the long packed or capillary column approach, both of which are recommended as a final step in preference to a conventional column.

The liquid chromatographic procedure¹²² uses reversed phase liquid chromatography with fluorescence detection to separate all 16 polyaromatic hydrocarbons completely. The method is sensitive and so selective

as often to allow the method to be applied without clean up procedure. For gas chromatographic methods detection limits are about $1 \mu\text{g l}^{-1}$ whereas for the liquid chromatographic methods limits are between 1 and $100 \mu\text{g l}^{-1}$ for 2- and 3-ring aromatics and below $1 \mu\text{g l}^{-1}$ for the 4-, 5- and 6-ring compounds.

For polyaromatic hydrocarbon analysis the extraction with methylene chloride may successfully be substituted by cyclohexane allowing high recoveries by one single extraction. Isolation of polyaromatic hydrocarbons from the water matrix may also conveniently be performed via adsorption using prepacked small high performance liquid chromatography columns circumventing the problems of emulsification often arising during liquid liquid extraction. Recently, this technique has been used in a study of polynuclear aromatic hydrocarbons in aqueous effluents from refineries as it was shown to differentiate between certain compounds which were not resolved by gas chromatography-mass spectrometry.

Separations on C18 columns have also been used to analyse polyaromatic hydrocarbons in trade effluents^{123,124}.

Preconcentration

TENAX RESINS: Kadar et al¹²⁵ studied the efficiencies of Tenax for the removal of polyaromatic hydrocarbons from standard water solutions. The method was applied to waste water samples from an aluminium plant. In this method the water samples were passed through the Tenax column at the rate of about 5 ml min^{-1} . Residual water was removed from the Tenax by passing nitrogen gas through the column. The Tenax material was then transferred to a Soxhlet apparatus. Polyaromatic hydrocarbons and other organic compounds were extracted by reflux for 4 hours with 35 ml of acetone. The Tenax can then be dried and reused.

Total polyaromatic hydrocarbons were then separated from parafins, naphthenes, acids and phenols on a thin-layer plate prior to determination of the individual polyaromatic hydrocarbons by gas chromatography.

Excellent agreement is obtained at the 100 ng ml^{-1} level between the method and a much more time consuming liquid-liquid extraction technique. The overall recovery of polyaromatic hydrocarbons from water at the 100 and the 10 ng ml^{-1} levels were 90–95 per cent and 70–90 per cent respectively.

The preconcentration of polyaromatic hydrocarbons is also discussed in [section 4.5.22](#) (multiorganic mixtures).

4.5.3

Non-ionic detergents

Flow injection analysis

Bos et al¹²⁶ give details of equipment and a procedure for the determination of both ionic and non-ionic surfactants by flow injection analysis with tensammetric detection. A mercury coated gold electrode is used. Both surfactant types can be determined in the concentration range $10\text{--}100 \mu\text{M}$ with an accuracy of plus or minus 4 per cent. Sample rate is roughly 60 per hour.

High performance liquid chromatography

Cassidy and Niro¹²⁷ have applied high speed liquid chromatography combined with infrared spectroscopy to the analysis of polyoxyethylene surfactants and their decomposition products in industrial process waters. Molecular sieve chromatography combined with infrared spectroscopy gives a selective method for the

analysis of trace concentrations of these surfactants. These workers found that liquid solid chromatography and reversed phase chromatography are useful for the characterization and analysis of free fatty acids.

Organic compounds containing oxygen

4.5.4

Phenols

Spectrophotometric methods

Various workers have investigated 4-aminoantipyrine (4-aminophenazone) spectrophotometric methods for the determination of phenols in effluents^{128,129}.

Vinzon¹³⁰ used adsorption of phenols on a column followed by desorption prior to spectrophotometric estimation with 4-amino-antipyrine to improve the sensitivity of the determination of phenols.

Automation of the 4-aminoantipyrine method using an autoanalyser has been investigated¹³¹. Gales and Booth¹³² used this method to estimate phenols in waste waters, sewage and industrial wastes.

Ultraviolet spectroscopy

Jones and Woodcock¹³³ determined 1–10 mg l⁻¹ 2-naphthol and 1-nitroso-2-naphthol in electrolytic plant effluents by a combination of solvent extraction and ultraviolet spectroscopy.

Miscellaneous

Thielemann^{134,135} has discussed the German standard bromination method for the determination of steam volatile phenols in water samples and industrial waste waters.

Hangesheimer et al¹³⁶ evaluated an aqueous acetylation method for the identification and quantification of simple phenolic compounds in oils and extraction plant effluents. Samples were acetylated by the addition of acetic anhydride and sodium bicarbonate and extracted into methylene chloride. The concentrations were determined by gas chromatography.

The determination of phenols is also discussed in [section 4.5.22](#) (multiorganic analysis).

High performance liquid chromatography

This technique has been used to determine phenols in coal gasifier condensate. Separation is achieved by elution with methanol on an octadecyl bonded silica gel column¹³⁷.

4.5.5

Fatty acids

Spectrophotometric methods

Abietic type resin acids have been determined in hexane extracts of kraft mill effluents¹³⁸. The effluent was adjusted to pH 2.4–2.7 prior to spectro-photometric evaluation at 490 nm of the levoprimary acid –1,

amino-2-naphthol-4-sulphonic acid-potassium ferricyanide reaction product. Down to 1 mg l^{-1} of abietic type resin acids could be determined in the water sample.

Rapid methods of determining formic acid and formaldehyde have been described¹³⁹ in which the acid is reduced with nascent hydrogen to the formaldehyde. The formaldehyde is determined by the chromotropic acid method in 6–7.5 M sulphuric acid. A detection limit of $0.05 \text{ } \mu\text{g l}^{-1}$ can be achieved without preconcentration. Preconcentration by extraction with diethyl ether decreases the lower detection limit to 0.05 ng l^{-1} . The method has been used successfully for a number of effluent water samples.

Gas chromatography

Gas chromatography has been used for the determination of acetic acid in industrial waste waters¹⁴⁰, short chain C_1 – C_4 fatty acids in anaerobic digester samples¹⁴¹ and dilute aqueous solutions. Van Huyssteen¹⁴¹ completely separated normal and iso acids on glass columns (2.13 m \times 3 mm i.d.) packed with 3 per cent FFAP on Chromosorb 101 (80–100 mesh) at 180°C in an instrument equipped with a dual flame ionization detector; nitrogen was used as carrier gas (77 ml min^{-1}).

C_1 – C_4 fatty acids have been determined in wood and paper processing effluents as *p*-bromophenacyl esters using glass capillary gas chromatography and electron capture detection¹⁴². A comparison was made of three techniques to treat the samples. Although there was a high response of the electron capture detector to the *p*-bromophenacyl esters of the C_1 – C_4 carboxylic acids, this technique could not be used to its full potential. Electron capture was however preferred to flame ionization detection. In terms of application, in pulp bleaching, to characterize degradation products from wood carbohydrates, formic acid and acetic acid have to be determined; extractive alkylation of tetrahexylammonium ion pairs at pH 7, when used for analysis of a paper kraft sample, showed levels of 54 and 11 mg l^{-1} respectively.

Voss and Rapsomatotis¹⁴³ determined resin and fatty acids in paper pulp mill effluents by a solvent extraction-gas chromatographic method.

Resin and fatty acids were isolated from the effluent sample by solvent extraction with methyl tert-butyl ether at pH 9 and derivatized with diazomethane. The methylated extract was analysed by split capillary chromatography with flame ionization detection. The detection limit was $5 \text{ } \mu\text{g l}^{-1}$. The method was applied to the fatty and resin acid determination in combined pulp mill effluent entering and leaving the aerated lagoon treatment system of a softwood bleached kraft pulp mill.

The analysis of fatty acids is also discussed in [section 4.5.22](#) (multiorganic analysis).

High performance liquid chromatography

Fatty acids have been resolved on Zorhex ADS prior to the determination¹⁴⁴.

Preconcentration

See [section 4.5.22](#) (multiorganic mixtures).

4.5.6

Phthalic acid esters

Gas chromatography

Rhoades et al¹⁴⁵ examined several alternative steps in the procedures for the determination of six phthalate esters in order to develop a satisfactory protocol for determining these pollutants in water and effluents. Two gas chromatographic columns and two detection systems (electron capture and flame ionization) were compared, while extractions were performed with two solvents (dichloromethane and a 15/85 mixture of dichloromethane and hexane) at three pH values. Other factors such as storage of samples prior to analysis in the presence or absence of chlorine and the use of alumina and florisil as absorbents for extract clean up were also investigated. Based on these studies a method was devised which gives good recoveries and reproducibility for phthalate esters in clean water and sewage, provided the level of background interference is low.

Gas chromatography-mass spectrometry

See [section 4.5.22](#) (multiorganic analysis).

4.5.7

Aldehydes and ketones

Spectrophotometric method

Vajta et al^{146, 147} investigated the determination of down to $5 \mu\text{g l}^{-1}$ acetone in aqueous petroleum refinery effluents. The effluent (1 ml) containing acetone (or ethylmethyl ketone) is mixed with 1 ml of saturated methanolic 2,4-dinitrophenylhydrazine and 1 drop of concentrated hydrochloric acid. The mixture is maintained at 50°C for 30 min and after being set aside for 1 hour is made alkaline with 5 ml of a 10 per cent solution of potassium hydroxide in aqueous methanol (1:4). After 10 min the extinction is measured at 490 and 540 nm. The concentration of acetone is determined by reference to a calibration graph.

Gas chromatography

Syringaldehyde has been determined gas chromatographically in oxidizing neutral sulphite pulping effluents¹⁴⁸. A copper column (2 m×2 mm i.d.) containing Apiezon N on graduated Teflon was used. It was operated at 220°C using nitrogen as carrier gas and hydrogen flame ionization detection. Preconditioning of the column by repeated injection of vanillin and syringaldehyde is necessary.

Gas chromatography-mass spectrometry

See [section 4.5.22](#) (multiorganic analysis).

4.5.8

*Quinones**Thin layer chromatography*

Thielemann¹⁴⁹ used 4-aminopyrine as a spray reagent for the thin-layer chromatographic identification of p-benzoquinone and anthraquinone in extracts of coal processing plant effluents. The separation is achieved on Kieselgel G with benzene-acetone (9:1) as solvent and the spots are revealed by spraying with an aqueous solution of the reagent. Red-brown and violet colours are obtained with benzoquinone and anthraquinone respectively. The intensity of the colour may be increased by spraying the plates with 0.1 M hydrochloric acid before development of the chromatogram.

Thielemann¹⁵⁰ has discussed the determination of hydroquinone and its oxidation product 1,4-benzoquinone, both of which are toxic constituents of coal industry waste water. He reviews methods for the qualitative detection of benzoquinone and describes a semi-quantitative method for its determination by thin layer chromatography on Kieselgel G using a 2 per cent ethanolic solution of 4-aminoantipyrine (1-phenyl, 2,3-dimethyl-4-aminopyrazol-6-one) as spray reagent.

Polarography

Suslov and Stom¹⁵¹ have described a polarographic method for determining quinones formed during the oxidation of phenols in effluents. These workers showed that a change of half-wave potentials with quinone concentration can be used for determining quinones in the presence of excess phenols in waste water.

High performance liquid chromatography

Anthraquinone has been determined in pulping legions on a Sep-pak C18 column using methanol as eluant¹⁵².

4.5.9

*Miscellaneous oxygen compounds**Carbohydrates*

SPECTROPHOTOMETRIC METHOD: The applicability of the phenol sulphuric acid reagent to carbohydrate analysis in waste water and biological sludges has been examined by Benefield and Randall¹⁵³. The test is based on the formation of a yellow colour when concentrated sulphuric acid is added to the sample mixed with phenol solution. This method includes sugars such as heptoses, pentoses, uronic acids and the sugar components of nucleic acids.

GAS CHROMATOGRAPHY: Bark et al¹⁵⁴ determined mono- and disaccharides in aqueous effluents by gas chromatography of the polytrimethylsilyl derivatives. Difficulties due to the low solubility of sucrose (and other disaccharides) in the silylation reagent were overcome by hydrolysing the sucrose to glucose and fructose under reflux in 0.01 M hydrochloric acid medium for 10 min, then immediately neutralizing the solution before the evaporation stage. The increase in fructose concentration effected by the hydrolysis was used as a measure of the original sucrose concentration.

Collins and Webb¹⁵⁵ used gel chromatography to detect and determine carbohydrates in pulp mill effluents. The phenol-sulphuric acid method was used to monitor column effluents.

Dihydroxyabiatic acid

MISCELLANEOUS: Brownlee and Strachan¹⁵⁶ determined dihydroxyabiatic acid in the receiving waters of a kraft pulp and paper mill.

Halogen containing compounds

4.5.10

Chlorohydrocarbons

Chlorinated alkyl naphthalenes

MISCELLANEOUS: Bjorseth et al¹⁵⁷ have determined these substances in bleach works effluents by a combination of glass capillary gas chromatography, gas-liquid chromatography-mass spectrometry and neutron activation analysis.

Vinyl chloride

GAS CHROMATOGRAPHY: Direct aqueous injection gas chromatography using flame ionization, microcoulometry, electrolytic conductivity, and mass spectrometry for detection has been used for the identification and measurement of vinyl chloride in industrial effluents¹⁵⁸. The reported lower limits of detection vary but $100 \mu\text{g l}^{-1}$ appears to be conservative for vinyl chloride using a flame ionization detector. Halogen-specific detectors, for example, the microcoulometric and electrolytic conductivity, are less sensitive (approximately $1000 \mu\text{g l}^{-1}$). However, they do improve the qualitative accuracy of the determination.

4.5.11

Halofoms

Gas chromatography

Eklund et al^{159,160} have developed a method for the determination of down to $1 \mu\text{g l}^{-1}$ volatile organohalides in waters which combines the resolving power of the glass capillary column with the sensitivity of the electron capture detector. The eluate from the column is mixed with purge gas of the detector to minimize band broadening due to dead volumes. This and low column bleeding give enhanced sensitivity. Ten different organohalides were quantified in industrial effluent from a pulp mill.

4.5.12

Chlorophenols

Gas chromatography-mass spectrometry has been applied to the identification and determination of chlorophenols in spent bleach liquor trade effluents from sulphate plants^{161,162}.

4.5.13

*Chlorinated carboxylic acids**Isotachophoresis*

Onodera et al¹⁶³ examined the applicability of isotachophoresis to the identification and determination of chlorinated mono- and dicarboxylic acids in chlorinated effluents. Four electrolyte systems for the separation of the acids were evaluated. The potential unit values in each system were determined for the chlorinated acids. A mechanism for the reaction of phenol with hypochlorite in dilute aqueous solutions is suggested, based on results from the isotachophoretic analysis of diethyl ether extracts taken from phenol treated with hypochlorite.

4.5.14

*Polychlorinated biphenyls**Gas chromatography*

Various workers have described methods (gas chromatographic) for determining PCBs in paper mill effluents. The method described by Delfino and Easty¹⁶⁴ is capable of detecting down to $2 \mu\text{g l}^{-1}$ PCB. Easty and Wabers^{165,166} have studied the effect of suspended solids on the determination of Aroclor 1242 in paper mill effluents.

Lopez-Avila et al¹⁶⁷ evaluated Environmental Protection Agency column chromatographic method no. 8080 for the determination of chlorinated insecticides and polychlorinated biphenyls in hazardous waters. They found that the Florasil column procedure recommended by the EPA did not separate organochlorine insecticides from polychlorinated biphenyls and developed an alternative procedure using a silica gel column and a sulphur clean-up for achieving this separation. The revised procedure had detection limits of 0.02–0.09 and 0.5–0.9 $\mu\text{g l}^{-1}$, respectively, for organochlorine insecticides and polychlorinated biphenyls.

Nitrogen containing organics

4.5.15

*Amines**Miscellaneous*

HEXANE 1,6-DIAMINE: This substance has been determined in amounts down to $5 \mu\text{g}$ in water and industrial effluents by thin layer chromatography and paper chromatography¹⁶⁸.

HEXAMINE: Fishman and Pevzner¹⁶⁹ determined down to 0.15 g l^{-1} of this substance in effluents from polyformaldehyde manufacture by potentiometric titration with 0.2 M hydrochloric acid.

AROMATIC AMINES: Diphenylamine and other aromatic bases have been determined respectively in industrial effluents¹⁷⁰ and coal carbonization¹⁷¹ products utilizing gas chromatography. Aniline derivatives at the microgram level have been determined in natural waters by a spectrophotometric procedure involving diazotization with sulphuric acid and naphthol¹⁷².

BENZIDINE: Jenkins¹⁷³ determined benzidine at the $\mu\text{g l}^{-1}$ concentration range in effluents by spectrophotometric, gas chromatographic and thin-layer chromatographic procedures. The American Public and Health Association¹⁷⁴ has also described a method for the determination of benzidine and its salts at the $0.3 \mu\text{g l}^{-1}$ level in water and waste water. In this method the water sample is made basic and the benzidine is extracted with ethyl acetate. Clean-up is accomplished by extracting the benzidine from the ethyl acetate with hydrochloric acid. Chloramine-T is added to the acid solution to oxidize the benzidine. The yellow oxidation product is extracted with ethyl acetate and measured with a scanning spectrophotometer. The spectrum from 510 nm to 370 nm is used for qualitative identification.

Gas chromatography-mass spectrometry

See [section 4.5.22](#) (multiorganic mixtures).

4.5.16

Nitrocompounds

Spectrophotometric methods

Trinitrotoluene has been determined in effluents from munitions plants by spectrophotometric^{175,176} and fluorimetric procedures¹⁷⁷. The fluorimetric procedure by Heller et al¹⁷⁷ is capable of determining down to $0.07 \mu\text{g l}^{-1}$ trinitrotoluene in munition plant wastes. The basis of the method is the absorption of trinitrotoluene on a quaternary ammonium ion-exchange resin which darkens on contact with trinitrotoluene. The resin is irradiated with ultraviolet radiation and the fluorescent output is monitored by a photomultiplier.

Total aliphatic and aromatic nitro compounds have been determined in industrial effluents in amounts down to 1.5 mg l^{-1} by a method¹⁷⁸ based on the chemical reduction of all the nitro compounds in the sample to amino compounds using titanium chloride in hydrochloric acid as reducing agent. For the final spectrophotometric determination the amines are reacted with sodium naphthoquinone sulphonate. The method is sensitive, reliable and precise.

Gas chromatography

Spangord et al¹⁷⁹ used gas chromatography mass spectrometry to identify over 30 nitroaromatic compounds present in effluents produced during the manufacture of trinitrotoluene. Three major components were consistently identified and represented about 75 per cent of the total component distribution, 2,4- and 2,6-dinitrotoluene and 1,3-dinitrobenzene.

Richard and Junk¹⁸⁰ used solid phase extraction using XAD-4 resin elution with ethyl acetate and separation by gas chromatography to determine $\mu\text{g l}^{-1}$ quantities of nitrocompounds in munitions works effluents.

A method for the quantitative analysis of explosive compounds in effluents has been described¹⁸¹ which includes 2,4,6-TNT, tetryl, 2,4-DNT and 2,6-DNT at the $\mu\text{g l}^{-1}$ level. The compounds were extracted from water with toluene and analysed by capillary gas chromatography with electron capture detection. Recoveries of 96–103 per cent were obtained in samples spiked at 1, 10 and 100 $\mu\text{g l}^{-1}$. The stabilities of these compounds in water at pH values ranging from 0.5 to 10 were studied over 33 days. The compounds were stable at pH 1–4 and significant losses occurred at pH values greater than 6.

High performance liquid chromatography

This technique has been used to determine nitro compounds in munition plant wastes¹⁸².

Preconcentration

POROPAK RESIN: A method has been described¹⁸³ for the preconcentration of nitro compounds in munitions works effluents by adsorption on Poropak resins. Following desorption with acetone the nitro compounds (nitramines, nitrotoluenes and nitroaliphatics) were measured by high performance liquid chromatography at a gold/mercury/electrode. The results of analysis of munitions in test samples showed that Poropak resins were superior in performance to RDX resins. Analysis time was approximately 2 hours per sample for isolation and quantification. Detection limits of 1 $\mu\text{g l}^{-1}$ were approached.

4.5.17

Miscellaneous nitrogen compounds

Heterocyclic nitrogen compounds

Gas chromatography has been used to determine down to 40 $\mu\text{g l}^{-1}$ of pyridine and its homologues in waste water¹⁸⁴. 2-Picoline and 2,5-lutidine have been determined spectrophotometrically in the ultraviolet region of the spectrum¹⁸⁵.

N-methyl pyrrolidone

This substance which occurs as a biodegradation product in industrial waste water can be determined at the 1–10 mg l^{-1} level by a method which involves concentration from an aqueous solution of sodium chloride by adsorption on XAD-2 resin, elution with methanol and examination of the eluate by flame ionization gas liquid chromatography¹⁸⁶.

e-Caprolactam (polarography)

Eremin and Kopylova¹⁸⁷ have described a polarographic method for the determination of e-caprolactam in synthetic fibre production effluent.

Zectran (4-dimethylamine-3,5-xylol) methylcarbamate

HIGH PERFORMANCE LIQUID CHROMATOGRAPHY: Hasler¹⁸⁸ has studied the rate of degradation of this substance in alkaline water effluents. High performance liquid chromatography was used to identify xylenol as a degradation product of this herbicide.

Nitriloacetic acid

Dai and Helz¹⁸⁹ described a liquid chromatographic method for determining nitriloacetic acid, ethylene diamine tetraacetic acid and related aminopolycarboxylic acids. An amperometric detector was used.

Nitriles

GAS CHROMATOGRAPHY–MASS SPECTROMETRY: See [Section 4.5.22](#) (multiorganic mixtures).

Acrylonitrile

TITRATION METHOD: Ghersin et al¹⁹⁰ compared colorimetric and titrimetric procedures for the determination of acrylonitrile in effluent waters. A titration method based on addition of sodium sulphide to the acrylonitrile followed by titration of liberated sodium hydroxide gave a sensitivity of 20 mg l⁻¹ acrylonitrile.

Provided that the sample is not yellow or brown in colour, a titrimetric method involving the use of mercaptoacetic acid has a sensitivity of 2 mg acrylonitrile per litre, or down to 0.4 mg l⁻¹ if the acrylonitrile is separated by a preliminary distillation from methanol sulphuric acid medium; such a distillation also separates acrylonitrile from interfering substances.

Acrylamide

MISCELLANEOUS: Bezazyan et al¹⁹¹ have described a phototurbidimetric method for the determination of polyacrylamide flocculants in effluents.

Jungreis¹⁹² has described a simple technique for the micro-determination of polymer flocculants in processed mine water which involves measuring the laminar flow rate of the mine water through a membrane filter under vacuum.

SIZE EXCLUSION CHROMATOGRAPHY: Leung et al¹⁹³ determined polyacrylamides in coal washery effluents by ultrafiltration size exclusion chromatography with ultraviolet detection. A column of TSK 5000 PW hydrophilic and semi rigid porous polymer gel was used with 0.05 M sodium sulphate as mobile phase.

HIGH PERFORMANCE LIQUID CHROMATOGRAPHY: This technique has been applied to the determination of acrylamide in trade effluents¹⁹⁴.

Dimethylformamide

FLOW INJECTION ANALYSIS: Ludi et al¹⁹⁵ carried out an enzymic determination of dimethylformamide in process effluents using flow injection analysis.

Details concerning the determination of further nitrogenic containing compounds are given in [Table 44](#).

Sulphur containing organics

4.5.18

Mercaptans and disulphides

Gas chromatography

Vitenberg et al^{201,202} have described a gas chromatographic method for the determination of traces (down to $\mu\text{g l}^{-1}$) sulphur compounds, such as hydrogen sulphide, mercaptans, sulphides and disulphides in industrial waste waters

TABLE 44
Determination of organic nitrogen compounds in waste waters

Substance	Method	Detection limit	Ref.
Guanazole and aminotriazoles	Spectrophotometric		196
1-methyl-2- pyrrolidene in raffinate waters	Sample extracted with heptane or xylene, then back extracted with dilute hydrochloric acid. Analysed by gas chromatography using N-P specific detector	mg l ⁻¹	197
5,5-dialkyl and 5-alkyl hydrantoinis in condensate water from lignin gasification	Gas chromatography on fused silica capillary column. Identity confirmed by mass spectrometry	—	198
Chloroanilines and chloronitroanilines in water works sludges	Simultaneous gas chromatography using Hall and NP specific detectors	trace levels	199
6-chloro-2-trichloromethane in fertilizer works effluents	Thin layer chromatography on hexane extract. Ethanolic rhodamine C and sodium bicarbonate spray reagents	<0.02 mg l ⁻¹	200

(kraft paper mill effluents) by a combination of head space analysis, with microcoulometric detector and flame ionization detectors. The head space sampling technique increases the analytical sensitivity by 10^2 – 10^3 .

Devonald et al²⁰³ have described a gas chromatographic method utilizing a flame photometric detector for the determination of hydrogen sulphide, sulphur dioxide, methane diol, dimethyl sulphide and dimethyl disulphide in industrial effluents in amounts down to 0.1 mg l^{-1} . Sulphur free organic compounds often present in these effluents, such as lactones, alcohols and terpenes do not interfere.

Gas chromatography-mass spectrometry

See [section 4.5.22](#) (multiorganic analysis).

4.5.19

*Benzthiazole and 2-mercaptobenzothiazole**Gas chromatography*

Jungclaus et al²⁰⁴ used gas chromatography mass spectrometry to identify benzthiazole and 2-mercaptobenzothiazole in tyre manufacturing plant effluents. The gas chromatograph was equipped with a flame ionization detector. Separations were achieved on a 180 cm×0.32 cm of stainless steel column packed with 3 per cent SP 2100 (methyl silicone fluid) of 80–100 mesh supelcoport and was temperature programmed for 70–300°C at 16°C min⁻¹. Approximately 44 compounds were identified in the waste water samples including benzthiazole and 2-mercaptobenzothiazole at concentrations, respectively, of 0.06 and 0.03 µg l⁻¹.

Cox²⁰⁵ determined mercaptobenzothiazole in trade effluent samples by a high performance liquid chromatographic procedure. An ultraviolet detector operating at 325 nm was used to monitor the column effluent. The column was constructed from stainless steel tubing (15 cm×4–6 mm 11) and was packed with Microkosorb Sil60 (5 µm) silica gel at 3,500 p.s.i. pressure from a slurry in 2,2,4-trimethylpentane. The packing material was retained in the column by stainless steel wire mesh of nominal pore size 8 µm (Sankey Wire Weaving, Warrington, Great Britain) inserted into a drilled-out Swagelok coupling. A similar disc of wire mesh was pressed on the top of the column packing and was retained by a plug of silanized glass wool. Ethanol: 2,2,4-trimethylpentane (1:9) was used as the mobile phase with a flow rate of 1 ml min⁻¹. All solvents used were of spectroscopic quality (Fisons, Loughborough, Great Britain).

The aqueous sample (2 ml) was acidified with two drops of concentrated hydrochloric acid. This mixture was shaken with chloroform (2 ml) for 1 min using a flask shaker. Aliquots (2 µl) of the chloroform layer were used for the chromatographic analysis.

4.5.20

*Miscellaneous sulphur compounds**Hydroxymethanesulphinite salts*

POLAROGRAPHY: These substances and their decomposition products (formaldehyde, zinc and sulphites) have been determined by polarographic procedure in waste waters²⁰⁶, originating from textile industries. In an alkaline medium it is possible to have well defined and separated waves relative to the oxidation of hydroxymethane sulphinite ion and to the reduction of formaldehyde and zincate ion. The sulphite is determined in 0.1 M perchloric acid and in the same sample it is possible to determine hydromethane sulphite salts, formaldehyde, and zinc after addition of sodium hydroxide up to 0.1 M. An indirect method for the determination of hydroxymethanesulphinite salts is described. This method is based on the determination of formaldehyde released by means of a weak oxidation of these salts which is stoichiometrically proportional to total hydroxylmethylsulphinite content.

Calcium lignosulphonate

ULTRAVIOLET SPECTROSCOPY: This substance has been determined by ultraviolet spectroscopy in sulphite containing effluents²⁰⁷.

GEL PERMEATION CHROMATOGRAPHY: Sagfors and Starck²⁰⁸ used gel permeation chromatography to study substances of high molecular mass in acid and alkaline kraft pulp bleaching effluents.

Phosphorus containing organics

4.5.21

A denosine triphosphate

Bioluminescence technique

Hysert et al²⁰⁹⁻²¹¹ have applied a bioluminescence adenosine triphosphate assay method to brewery waste water studies. They described an assay using partially purified luciferase and synthetic firefly luciferin for the bioluminescence reaction, a liquid scintillation counter in the out of coincidence phase and a sludge adenosine triphosphate extraction technique involving dimethyl sulphoxide at room temperature. Experiments with several pure bacteria cultures showed good linear correlation between adenosine triphosphate and mixed liquor suspended solids, return sludge suspended solids and effluent suspended solids.

When adenosine-5'-diphosphate and adenosine-5'-monophosphate as well as adenosine triphosphate assays were to be done, the extractions were done with boiling acetone²¹¹⁻²¹³. Typically 0.1 ml sample was added to 1 ml boiling acetone in a 7 ml vial immersed in a 90°C water bath and the acetone was removed by blowing a stream of air over the liquid, 10 µl of extracts were added to 1.0 ml, pH 7.0, 10 mM tris (hydroxymethyl)aminomethane (TRIS)-3.5 mM magnesium sulphate buffer and 10 µl of a purified luciferase synthetic D-luciferin premix were added to initiate the bioluminescent reaction. The light output of the reaction was measured with a scintillation counter.

4.5.22

Multiorganic mixtures in trade effluents

Gas chromatography

Some examples of the application of gas chromatography to the analysis of mixtures of organics in trade effluents are quoted in [Table 45](#).

Gas chromatography-mass spectrometry

Examples of the application of this technique are given in [Table 45A](#). A particularly noteworthy example of the application of this technique to the examination of industrial and municipal waste waters is that of Burlingame²¹⁴. This worker reports the findings of experiments to determine the potential of high resolution gas chromatography/high resolution mass spectrometry for assessing trace levels of organic compounds in waste waters. The technique was applied to effluent from a Southern California waste water treatment plant and to primary effluent from a petroleum refinery, and it is concluded that it can provide useful data on the organic constituents of waste water samples, even when they are present in extremely complex mixtures.

Complete high resolution mass spectra were recorded during elution of components from a glass capillary gas chromatographic column connected to a flame ionization detector; data were subsequently examined with an on line real-time software system for fast cyclic scanning high resolution mass

TABLE 45

Applications of gas chromatography and gas chromatography mass spectrometry to multiorganic analysis of trade effluents

Substance	Type of effluent	Method	Ref.
A Gas chromatography			
Solvent residues	Chemical and fermentation wastes	Gas chromatography on various porous polymer packed columns	215
Acids, nitriles, aldehydes, ketones	Shale process waters	Steam distillation, solvent extraction, ion-exchange chromatography, gas chromatography	216
Miscellaneous	Industrial effluents	Capillary gas chromatography with simultaneous head space injection on two columns of different polarity	217
Chlorinated diones, enol lactones	Spent pulp bleaching liquors	Gas chromatography	218
36 compounds	Industrial effluents	Microextraction capillary gas chromatography	219
B Gas chromatography-mass spectrometry			
Hydrocarbons; mercaptans, phenols	Petroleum refinery effluents	Isolation-gas chromatography mass spectrometry	220
Miscellaneous	Petrochemical waste waters	Isolation by freeze concentration or isolation on carbon, gas chromatography with flame ionization detection, mass spectrometry	221
Aliphatic acids, phenol, pyridine, methyl pyridines, aniline, isoquinoline, <i>n</i> -alkyl-amines, <i>n</i> -acrylo-nitriles, benzonitrile, formaldehyde, acetaldehyde, propanone and butanone	Shale process waters	Isolation by solvent extraction ion exchange chromatography and steam distillation; determination by gas chromatography mass spectrometry	222
Miscellaneous, stabilizers etc.	Tyre manufacturing plant waste waters	Isolation, gas chromatography mass spectrometry	223
570 organic compounds	Industrial effluents	Isolation by helium gas stripping methylene dichloride extraction. Analysed by computerized capillary column gas chromatography mass spectrometry	224
C2–C8 aliphatic aromatics, polaromatic hydrocarbons, glycols, polyglycols, indenes, naphthalenes, styrene derivs, phenols, ketones, phthalic acid esters	Chemical works effluents; insecticides; coal gasification plant effluents; synthetic rubber	Combination of gas-chromatography mass spectrometry with computerized matching of mass spectra	214

spectrometry. Searches for specific compounds were accomplished through the generation of accurate mass chromatograms specific to particular elemental compositions, i.e. elemental composition chromatography. The Southern California secondary effluent contained an extremely complex mixture of organic constituents; di-, tri-, tetra- and pentachlorobenzenes, tri-, tetra- and pentachloroanisoles and a variety of alkylbenzenes were among the components identified. Pentachloroanisole and alkylbenzenes were present in the tertiary effluent, indicating incomplete removal of these constituents. In the case of a refinery waste water the neutral phenolic and acidic organic constituents—present in the waste water at three different stages of treatment—were studied by elemental composition, which provides the capability for detection and identification of specific components in waste waters containing extremely complex mixtures of organic constituents. This technique holds promise for surveying the qualitative and semi-quantitative nature of organics in water and how they are altered in complex treatment trains.

Fig. 40(a) shows the capillary gas chromatogram obtained for a fraction. Fig. 40(b) shows the total ionization chromatograms for the fraction obtained from the high resolution mass spectral data set. In general, the correlation between the total ionization chromatogram profile and the flame ionization detector profile is low due to both the differing relative detector responses and the consideration of scan cycle time (9.6 s) with respect to chromatographic peak elution time (~20 s).

The availability of accurate mass measurements on all the peaks in each mass spectrum provides a very accurate and highly specific method of locating compounds of interest in such mixtures. This simply involves searching the data set for particular accurate masses (specific elemental compositions) vs scan number (chromatographic retention time) i.e. elemental composition chromatograms.

Three elemental composition chromatograms for this fraction are shown in fig. 41, where the accurate masses (m/e 179.9300, 181.9271 and 183.9241) correspond to the three major peaks in the isotope cluster for $C_6H_3Cl_3$, i.e. $C_6H_3^{35}Cl_3$, $C_6H_3^{35}Cl_2^{37}Cl$, and $C_6H_3^{35}Cl^{37}Cl_2$. In all three elemental composition chromatograms the relative intensities of these ions maximize at scans 26 and 32 indicating the presence of two components whose mass spectra contain ions having these elemental compositions.

Infrared spectrometry

Ying et al²²⁵ developed a computer program to identify the principal components of a complex organic mixture by interpreting the infrared spectra and applied this procedure to the identification of organic compounds in hazardous industrial wastes.

Miscellaneous

Jones et al²²⁶ review the procedures involved in the sample preparation and analysis of industrial waste waters with the object of providing a rational, systematic approach to pollution monitoring and control programmes. A simple sequence of analytical procedures is described as a basic approach to the detection of pollutants, followed by a more complex and detailed scheme for samples selected for further examination on the basis of the initial survey. Details of the separations achieved and operating conditions for high performance liquid chromatography and spectroscopic techniques are given followed by the use of gas liquid chromatographic separation in conjunction with other techniques for identification and quantitation of individual compounds.

A thin layer chromatographic method has been developed²²⁷ for the determination of organic compounds capable of cis-trans isomerization, using dibutyl ethylenedicarboxylate, stilbene, azobenzene and azoxybenzene as examples. The cis-isomers were formed from the trans by irradiating solutions with UV

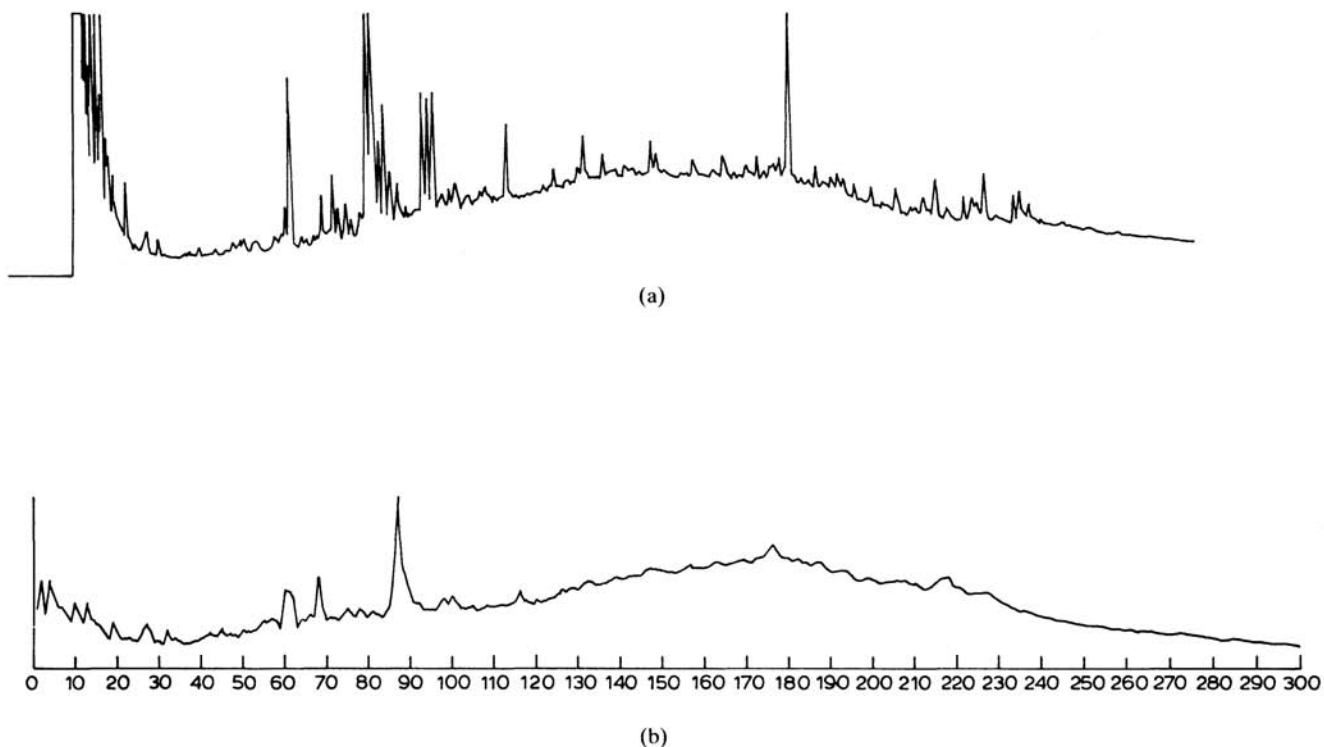


Fig. 40. (a) Flame ionization detector (FID) capillary gas chromatogram of secondary effluents, 6 per cent fraction, (b) total ionization chromatogram.

light. For chromatography, plates with a layer of silica gel fixed with gypsum and plates with a similar layer fixed with starch were used. The presence of isomerizing compounds was indicated by a characteristic arrangement of spots at the corners of a square on the prolongation of one of the diagonals passing through the deposition point and the point of intersection of the solvent fronts, or the 'magic square' technique. This method can be used without a standard, and may be suitable for analysis of complex samples containing compounds with close R_f values and identical coloration.

High performance liquid chromatography

The application of this technique to the determination of miscellaneous organics in trade effluents has been discussed²²⁸.

Preconcentration

XAD resins have been used to preconcentrate various organics from trade effluent^{229,230}.

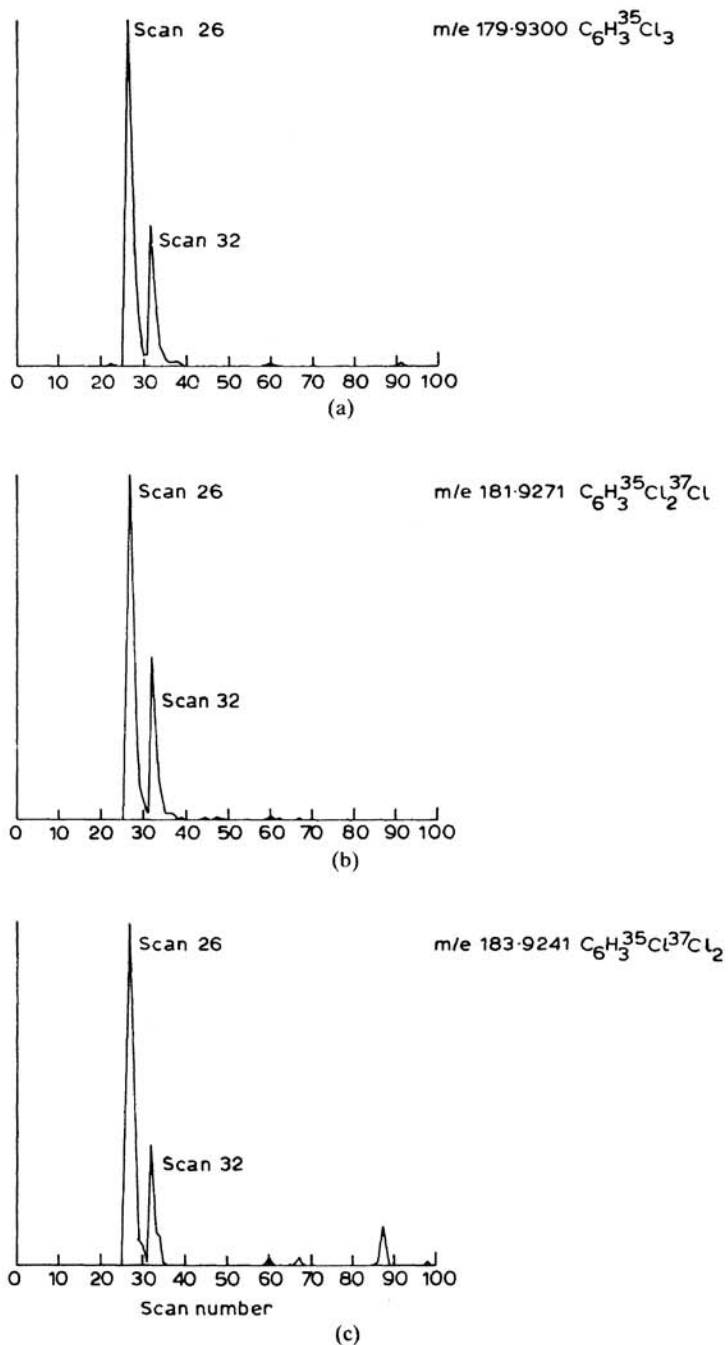


Fig. 41. Elemental composition chromatograms for secondary effluent, 6 per cent fraction, showing accurate masses 179.9300, 181.9271 and 183.9241 corresponding to three major peaks in the isotope cluster for $C_6H_3Cl_3$.

Cation ion-exchange resins

In determinations of organic impurities in waste water, e.g. in industrial effluents, treatment with a cation-

exchange resin in the free acid form is often used to remove metal cations and cationic organic solutes such as amino acids. Possible losses of compounds such as fatty acids and aromatic compounds have been discussed²³¹⁻²³⁵.

The preconcentration of phenols and amino phenols on Dowex 1-X8 resin has been discussed²³⁶.

4.6 Organometallic compounds

4.6.1

Lead

Spectrophotometric methods

Imura et al²³⁷ have described a spectrophotometric procedure employing 1-hydroxy-4-(4-nitrophenylazo)-2-naphthoate as chromogenic reagent for the determination of triethyllead ions in industrial effluents. The coloured adduct is extracted with chloroform. The absorption maximum is at 440 nm and the optimum pH for the extraction from 1 per cent aqueous sodium chloride is 8.1-8.3. In the determination of about 60 μg of triethyllead ions, dimethyl and diethyllead ions (100 μg) and Pb^{2+} (1-8 mg) are masked with 0.01 M ethylenediamine NN'-bis (2-hydroxyphenylacetic acid) (disodium salt) and copper and ferrous iron are masked with 0.01 M 1,2-diaminocyclohexane-NNN'N'-tetraacetate. Several other ions do not interfere. The limit of determination is 0.2 mg l^{-1} of triethyllead.

4.6.2

Mercury

Spectrophotometric method

Murakami and Yoshinaga²³⁸ determined organomercury compounds in industrial effluents by a spectrophotometric procedure using dithizone.

Atomic absorption spectrometry

Carpenter²³⁹ has reviewed the application of flameless atomic absorption spectroscopy to the determination of mercury in paper mill effluents. Thiosulphate oxidation is recommended as a means of converting organomercury compounds to inorganic mercury. Carpenter concludes that the practical limit of detection of mercury in effluents using this technique is 1 μg l^{-1} .

Thin layer chromatography

Thin layer chromatography has been used to evaluate²⁴⁰ organomercury compounds in industrial effluents. C_1 - C_6 *n*-alkylmercury chlorides were separated on layers prepared with silica gel (27.75g) plus sodium chloride using as development solvent cyclohexane-acetone-28 per cent aqueous ammonia (60:40:1). The R_F values decrease with increasing carbon chain length and phenylmercury acetate migrated between the C_1 and C_2 compounds. The spots are detected by spraying with dithizone solution in chloroform.

4.7 Oxygen demand parameters

4.7.1 *Total oxygen demand*

Voorn and Frampton²⁴¹ have given a description of the Phillips TOD meter and have discussed its application to industrial effluents. They confirm its usefulness for continuous monitoring of effluents.

Arin²⁴² discusses total oxygen demand meters and their effectiveness for monitoring industrial effluents, although he emphasizes that its limitations must be appreciated before it can be applied successfully.

TABLE 46
Determination of chemical oxygen demand of trade effluents

Method	Type of sample	Comments	Ref.
Open tube digestion with dichromate titration	Trade effluents	Discussion of standard dichromate oxidation procedure	245 248,249 250
	Trade effluents	Digestion with dichromate sulphuric acid-phosphoric acid with silver catalyst, back titration with iron II at 165°C	246
	Trade effluents	COD measurement in presence of volatile organic compounds	247
	Trade effluents	Rapid versions of standard dichromate method	250–253
	Municipal and industrial effluents	Comparison of methods of pretreatment to remove or homogenize solids prior to applications of standard digestion procedure. Homogenization of sample in presence of coarse settleable solids increased COD	253
	Laboratory wastes	Effect of concentration of silver on COD. Attempts to reduce analysis cost	254
	Trade effluents	Digestion of sample with dichromate in sealed vials or ampoules for 2 hours at 150°C	255 256
Automation of dichromate digestion procedure	Trade effluents	Dichromate oxidation at 110–170°C using autoanalyser system with spectrophotometric finish.	257
	Dichromate oxidation at 160°C in a fluidized sand bath, with a spectrophotometric finish	258 Dichromate oxidation back titration with iron II using	259

Method	Type of sample	Comments	Ref.
Electrical conductivity finish	Trade effluents	automatic titrator, sample changer, control unit and closing pumps Oxidation by boiling under reflux with potassium dichromatesulphuric acid liberated carbon dioxide swept into cadmium hydroxide solution and measurement made conductometrically	260
Spectrophotometric finish	Trade effluents	Standard dichromate oxidation then titration of excess chromium with iron II at 480 and 600 nm	261
Flow injection analysis	Food industries effluents	Oxidation with potassium permanganate, determination of excess chromium by spectroscopy based on flow injection analysis	262
Method	Type of sample	Comments	Ref.
Infrared spectroscopy	Municipal and trade effluents	Carbon in sample reacted with carbon dioxide over platinum at 875°C to produce equivalent amount of carbon monoxide. Carbon monoxide content of gas stream determined by non-dispersive infrared spectroscopy	263
Miscellaneous	Domestic and trade effluents	Use of potassium ferrate in COD measurement. Evaluation of pollution loading of effluents from COD	264 265
Comparison of closed tube and open tube methods	Municipal effluents	Good agreement	266
Mercury-free COD method	Tannery effluents	Chloride suppressed by adding extra silver and chromium III ions. No bias found between this method and standard method	267

4.7.2

Chemical oxygen demand

Work on the determination of the chemical oxygen demand of trade effluents is summarized in [Table 46](#).

4.7.3

Biochemical oxygen demand

The definitive UK method for determining 5-day biochemical oxygen demand has been published²⁴³. Various workers have discussed particular aspects of this method in relation to measurements made on trade effluents (Table 47).

A departure from the classical method for determining biochemical oxygen demand is the electrolysis method described by Young and Baumann²⁴⁴. In this procedure the oxygen content of the space above the sample is enriched with electrolytically generated oxygen. As the oxygen is used up by the sample the concentration in the head space is made up and consequently the amount of oxygen reacted is obtained. Young and Baumann²⁴⁴ conducted biochemical oxygen demand measurements under air containing 21 per cent oxygen and under an atmosphere of above 80 per cent oxygen and obtained good agreement between the results. Chemical methods of controlling nitrification were used in both methods. The electrolysis biochemical oxygen demand method provides a direct and continuous measure of oxygen uptake in an effluent sample. The principal advantages of this method are that (1) little or no dilution of the sample is required, (2) larger and more representative

TABLE 47
Determination of biochemical oxygen demand of trade effluents

Type of sample	Comments	Ref.
Sterile effluents	Effect of nitrogen compounds, ammonia nitrate on BOD. Nitrate reduces BOD	268
Trade effluents	Intermittent sample stirring increased BOD	269
Trade effluents	Effect of cadmium on BOD at various temperatures	270
Stabilization lagoons	Presence of algae increases BOD. COD recommended as alternative test for samples containing algae	271
Starch and molasses effluents	Yeast sensors for amperometric estimation of BOD. Good agreement with conventional BOD measurements	272
Trade effluents	Measurement of BOD of heavily contaminated effluents	273
Kraft mill effluents	200 day BOD measurements on effluents at temperatures between 2 and 20°C	274
Board mill effluents	Relationship between 5 day BOD, COD and TOC, claimed that BOD and COD can be calculated from TOC	275
Kraft mill effluents	Prediction of BOD on effluents based on incubation with sodium hypiodite followed by titration with sodium thiosulphate. Reaction period 1 hour at 20°C	276

samples can be analysed, (3) tests can be run for days or weeks without interruption, (4) the equipment is simple to operate, (5) no titrations are required and oxygen uptake can be obtained by simply reading a dial and (6) biochemical oxygen demand can be measured with significantly greater precision than by the classical method.

Biochemical oxygen demands obtained by electrolysis measured at any time after 2 days of incubation can be correlated reasonably well with those obtained by standard dilution. The most promising use of the method however, was not for a single point measurement but for evaluating the oxygen uptake characteristics of effluents and for determining the effect of dilution and the presence of toxic materials on effluent treatability.

Relationship between oxygen demand parameters

Voorn²⁷⁷ has reported that he obtained an excellent correlation between chemical oxygen demand and total oxygen demand on settled samples of industrial effluents.

Arin²⁷⁸ on the other hand found that in the case of effluents containing suspended matter the total oxygen demand measurement was consistently greater than the chemical oxygen demand but both followed the same trend. The discrepancy between the two measurements was attributed to the more efficient oxidation of the particulates in the total oxygen demand measurement.

4.8

Dissolved gases

4.8.1

Dissolved oxygen

Titration method

In a method²⁷⁹ to determine dissolved oxygen in iron-rich mine waters, Evsina and Nagibina adjusted the pH of the sample to 2 and added potassium fluoride to complex iron. Addition of potassium permanganate produces a red violet colour. After destruction of excess permanganate with oxalic acid the sample is treated with saturated manganous sulphate and potassium hydroxide. The supernatant layer is separated from the precipitate, acidified and titrated with 0.05 N quinol solution to the diphenylamine end-point.

TABLE 48
Determination of radioactive substances in trade effluents

Element	Method	Detection limit	Ref.
Strontium-90	Strontium-90 converted to 2-theonyl trifluoroacetate and extracted into carbon tetrachloride, back extracted into aqueous ammonia at pH 5-8 then into a benzene solution of 2-theonyl trifluoroacetone. Residue submitted to β -counting to estimate strontium-90	—	283
Polonium-210	Sample digested with nitric acid hydrogen peroxide then residue sublimed with potassium bromide. Polonium collected on cold finger is removed with acid and reduced to metal with hydrazinium chloride on to a silver plate for counting	—	284
Polonium-210	Polonium-210 reduced with hydroxylamine in presence of bismuth carrier at 85–90°C and spontaneously deposited on to silver foil suspended in sample. Polonium-210 on silver foil counted	—	285
Plutonium-241	Determination of plutonium and activity	—	286
Plutonium-241	Sample digested with potassium sulphate, sulphuric acid, nitric acid and perchloric acid. Solution reduced with sulphur dioxide and plutonium collected by coprecipitation on barium sulphate. Precipitate dissolved in nitric acid and plutonium extracted with bis(2-ethylhexyl) phosphate in scintillator solution for β -counting in a liquid scintillation spectrometry	—	287
Zinc-65	Zinc selectively extracted from effluent concentrate with xylene solution of Aliquot-336. Zinc determined by β -ray spectrometry	—	288

4.8.2 *Chlorine*

Voltammetry

Chlorine in amounts down to 1 mmole l⁻¹ has been determined in industrial effluents²⁸⁰, by evaluation of the voltammetric curve, +0.8 and -0.1V (versus SCE) using a graphite electrode. The peak current is proportional to chlorine content except at very low concentrations.

4.8.3 *Hydrogen sulphide*

Ion selective electrode

An Orion silver sulphide membrane electrode has been used²⁸¹ to determine hydrogen sulphide in trade effluents.

Gas chromatography

Butaeva et al²⁸² determined hydrogen sulphide in the gas phase that is in equilibrium with industrial effluents using gas chromatography on a column packed with Poropak P. After equilibration is complete the head space gas above the sample is swept into the gas chromatographic column with a stream of helium.

4.9 **Radioactive substances**

4.9.1 *Strontium-90, polonium-210, polonium-241 and zinc-65*

These elements have been determined in trade effluents (Table 48).

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Chapter 5

MISCELLANEOUS WATERS

MINERAL WATERS

5.1 Anions

5.1.1 *Chloride and fluoride*

Miscellaneous

Midgley¹ has described a method for determining traces of chloride and fluoride in boronated water.

5.1.2 *Arsenate*

Polarography

An indirect polarographic method has been used to determine traces of arsenate in mineral waters². In this method arsenate is converted to uranyl arsenate which is filtered off and excess uranyl ion is determined by polarography at -3.60 V. Phosphates interfere in this procedure.

5.1.3 *Nitrate*

Spectrophotometric method

A spectrophotometric method using 3,3'-dimethylnaphthidine as the chromogenic agent has been used to determine down to $5.0 \mu\text{g l}^{-1}$ nitrite in mineral waters³.

5.1.4 *Sulphide and cyanide*

Ion selective electrodes

Jovanovic and Jovanovic⁴ have described a method for the determination of sulphide and cyanide in spa water using a deposited on wire silver-silver sulphide ion selective electrode.

5.2 Cations

5.2.1 *Miscellaneous*

Methods for the determination of individual metals and mixtures of metals in mineral and spring waters are reviewed in [Table 49](#).

TABLE 49
Determination of waters in mineral, spa and spring waters

Type of water	Elements	Technique	Detection limit ($\mu\text{g l}^{-1}$)	Interferences	Ref.
Individual metals					
Mineral	Arsenic	Amperometric titration with standard potassium bromate	50	—	5
Mineral	Calcium	Ring colorimetry	—	Cerium phosphate	6
Hot spring water	Lithium Sodium Potassium Rubidium Caesium	Ion-exchange chromatography with hydrogen flame ionization detection	—	—	7
Mineral	Sodium	Autoanalyser system with sodium selective electrode	1000	Excess potassium i.e. >5 fold excess	8
Mineral	Nickel	Ion-exchange chromatography on Dowex A-1 then Dowex 1-X10	0.05 μg	Removed	9
Hot spring water	Copper	Cation-exchange separation in ammoniacal pyrophosphate medium	—	Iron interference overcome	10
Mineral	Molybdenum	Graphite furnace aas	Detection limit 0.19 $\mu\text{g l}^{-1}$		11
Mineral	Molybdenum	Electro-thermal aas	Preconcentration on Amberlite IRA-400		12

Type of water	Elements	Technique	Detection limit ($\mu\text{g l}^{-1}$)	Interferences	Ref.
Mixtures of metals					
Hot spa water	32 elements	Mass spectrometric analysis	<2 mg l ⁻¹	—	13
Hot mineral waters	Arsenic Antimony Germanium Selenium Cadmium	Atomic absorption spectrometry with L'vov platform	1	—	14
Mineral	Silver Beryllium Copper Germanium Manganese Molybdenum Nickel	Emission spectrography	—	—	15
Type of water	Elements	Technique	Detection limit ($\mu\text{g l}^{-1}$)	Interferences	Ref.
Mineral	Lead Titanium	Neutron activation analysis	—	—	16
	Iron Zinc				
	Selenium				
Mineral and spring Manganese Iron	Chromium exchange column containing	Separation on ion- exchange column 1.6	0.4	—	17
	Cobalt Nickel Copper Zinc Tantalum Lead Uranium	hyphan cellulose, elution with hydrochloric acid then X-ray fluorescence spectroscopy	1.0 0.7 0.7 0.6 0.6 0.5 0.7		

5.3 Elemental Analysis

5.3.1 *Boron*

Ion-exchange chromatography

Boron has been determined in mineral waters¹⁸ by ion-exchange chromatography on Dowex 50 WX-8 cation-exchange resin and Dowex 3 weakly basic anion-exchange resin to remove interfering strong electrolytes. Boron is estimated in the column percolate by mass spectrometry.

5.4 Organic substances

Preconcentration

Korenman et al¹⁹ preconcentrated organics from mineral waters by passage through a bed of Polysorb-1 presaturated with 1.5–2.0 parts of *n*-amyl acetate per weight of sorbent. The extracted organics were eluted with diazotized sulphanic acid and photometric determination. Infrared and ultraviolet spectroscopy, gas chromatography and luminescence analysis were all used to detect and identify extracted organics.

5.5 Radioactive elements

5.5.1 *Radon-220 and Radon-222*

Liquid scintillation counting has been used to determine radon-220 and radon-222 in hot spring waters from volcanic areas^{20,21}.

TABLE MINERAL WATERS

5.6
Cations*5.6.1*
*Miscellaneous**Atomic absorption spectrometry*

Potassium, lithium, magnesium, strontium, chromium, manganese, nickel, copper and zinc have been determined in Portuguese medicinal mineral waters by atomic absorption spectrometry²². Sodium and calcium were determined by flame photometry, boron was determined spectrophotometrically. The concentration of mercury, lead, cadmium and chromium in bottled Austrian medicinal and table waters has been determined by atomic absorption spectrometry²³.

HIGH PURITY AND BOILER FEED WATER

5.7
Anions*5.7.1*
Chloride

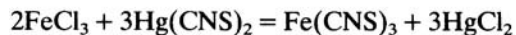
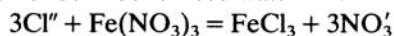
It is generally accepted that the presence of chloride in the steam-water circuit of power stations can be associated with corrosive conditions within the boiler, consequently chloride levels have to be controlled. The concentration of chloride treated in boiler waters varies with the design of the boiler and the chemical treatment accorded to the boiler water, but in every instance it is essential that any ingress of chloride is detected so that remedial action can be taken. In order to identify the source of the chloride, it is necessary to monitor plant streams, e.g. feed water or the effluent from a water treatment plant, where chloride levels may be as low as a few micrograms per litre.

Titration method

A titrimetric method for the determination of milligram per litre quantities of chloride (plus bromide) in boiler feed water involves titration of the sample at pH 1–4 with 0.1 N mercuric nitrate to the tetra(ethyl-di-(1-sodiotetrazol-5-ylazo)) acetate yellow to red end point²⁴. 300 fold excesses of sulphate, nitrate, carbonate or acetate can be tolerated but cobalt, fluoride, iodide or nickel interfere.

Spectrophotometric method

Two spectrophotometric procedures involving the formation of the red coloured ferric thiocyanate complex formed between chloride ion and ethanolic mercuric thiocyanate in the presence of ferric ions have been described for the determination of chloride in boiler feed water^{25,26}.



In these methods the sample is acidified with perchloric acid or nitric acid and ferric nitrate solution is added followed by ethanolic²⁵ or methanolic²⁶ thiocyanate. The extinction of the mercuric thiocyanate complex is measured at 460 nm²¹ or 463 nm²⁶. Down to 1 $\mu\text{g l}^{-1}$ chloride can be determined by these procedures. Hydrogen peroxide, hydrazine used as boiler water treatment chemicals did not interfere. Interference arises from the presence of comparatively large amounts of cupric sulphate, potassium dichromate, lithium hydroxide or ammonium fluoride. The coefficient of variation at the 50 $\mu\text{g l}^{-1}$ level was 12 per cent.

Fluorescence spectroscopy

This technique has been used to determine down to 1 $\mu\text{g l}^{-1}$ chloride in high purity water. The method is based on the quenching effect of silver chloride on the fluorescence of sodium fluorescein. The coefficient of variation is within 15 per cent at the 10 $\mu\text{g l}^{-1}$ chloride level²⁷.

Ion selective electrodes

Silver-silver chloride electrodes²⁸⁻³¹ and solid state mercurous chloride electrodes³²⁻³⁴ have been used to determine traces of chloride in high purity power station waters. Detection limits claimed from 6 $\mu\text{g l}^{-1}$ ³¹ to 100 $\mu\text{g l}^{-1}$ ³⁰ (silver-silver chloride electrodes) to 10 $\mu\text{g l}^{-1}$ (solid-state mercurous chloride electrodes).

(a) SILVER-SILVER CHLORIDE ELECTRODES: Measurements have been made in two ways. In one method³¹ two solid-state Orion 94-17A silver chloride membrane electrodes are used. The reference electrode is contained in a compartment connected to the sample compartment by a ground glass sleeve. The reference compartment contains a 100 $\mu\text{g l}^{-1}$ solution of chloride in 0.1 M nitric acid. A graph is constructed from cell potential readings after adding increments of standard chloride solution to the sample solution (made 0.1 M in nitric acid) in the sample compartment. A similar graph is obtained by adding increments of the chloride solution to a blank solution containing 0.1 M nitric acid. The chloride content of the sample is given by the distance along the concentration axis between the two lines.

Concentrations of copper II, iron II, nickel II and aluminium interfere when present at concentrations exceeding 10 mg l^{-1} and ammonia and hydrazine interfere. It is claimed that better precision is obtained using these electrodes than is obtained using the conventional silver-silver chloride electrodes discussed below.

In the alternative method measurements are made using silver-silver chloride electrodes versus a mercurous sulphate reference electrode^{28,30}.

A manual version of this procedure has been described having a detection limit of 100 $\mu\text{g l}^{-1}$, also, the continuous analyser version (discussed below) has been described with a detection limit nearer to 1 $\mu\text{g l}^{-1}$ ²⁸. In most instances there was no significant interference in this procedure by substances likely to occur in boiler feed water. The small effects noted for sodium hydroxide, trisodium orthophosphate and sodium carbonate could be explained by a change in the pH of the system. The unexpected interference from sodium

sulphate and sodium sulphite could arise from trace amounts of chloride in the reagent chemicals. However, the effects were so small, even at the excess levels of these substances added, that for most practical purposes they could be ignored.

(b) SOLID-STATE MERCUROUS CHLORIDE ELECTRODES: This is the more recent development in the determination of chloride in high purity water^{32,33}. Marshall and Midgley^{32,33} have described a procedure for the determination of 0–20 $\mu\text{g l}^{-1}$ chloride in high purity water, using two types of ion selective membrane electrode incorporating mercurous chloride. At these low concentrations, more chloride will dissolve from the mercury I chloride in the electrode than is present in the sample itself. The extent of the dissolution is controlled however, by the chloride in the sample. In these circumstances the electrode potential is linearly related to the concentration of chloride in the sample. With the electrode housed in a flow cell with a thermostatically controlled water jacket, the correlation coefficient between e.m.f. and concentration was always greater than 0.99. The sensitivity (0.18 mV per $\mu\text{g l}^{-1}$ of chloride at 25°C and 0.4–0.5 mV per $\mu\text{g l}^{-1}$ of chloride at 4°C) was about ten times greater than that of the silver-silver chloride electrode. Total standard deviations at 10, 5 and 2 $\mu\text{g l}^{-1}$ of chloride were 0.4, 0.5 and 0.3 $\mu\text{g l}^{-1}$ of chloride respectively.

Potentials were measured with a digital pH meter reading to 0–1 mV and displayed on a chart recorder. Two types of ion selective electrodes were used, those made from Radiometer F3012 Universal Selectrodes and the Ionel Model SL-01 (Ionel electrodes, Mount Hope, Ontario, Canada). Both have membranes made of a mixture of mercury II sulphide and mercury II chloride. In the electrode developed at CERL the mixture is used to impregnate a graphite PTFE electrode while in the Ionel electrode the mixture is hot pressed into a disc. The reference electrode was a mercury I sulphate electrode with a 0.5 mol l^{-1} sodium sulphate filling solution (instead of the usual 1 mol l^{-1} solution, which would have precipitated at the lowest operating temperature of 4°C).

The use of mercury I chloride electrodes for determining chloride concentrations can be extended from the levels attainable by manual analysis to very low levels (less than 20 $\mu\text{g l}^{-1}$) by housing the electrode in a flow cell at a controlled temperature. At a given temperature, the electrode is about ten times more sensitive than the silver chloride electrode. One advantage of this greater sensitivity is that the mercury I chloride electrode does not need to be operated at sub-ambient temperatures in order to obtain adequate precision in the concentration range 1–20 $\mu\text{g l}^{-1}$.

5.7.2

Sulphate

Sulphate has been determined in high purity water by molecular emission cavity analysis³⁴.

5.7.3

Silicate

Spectrophotometric methods

Spectrophotometric methods have been described for the determination of traces of silicate in high pressure boiler feed water^{35,36}, and deionized water³⁷. Silicomolybdate procedures employing 4-amino-3-hydroxynaphthalene-1-sulphonic acid have been employed^{24,25}. Spectrophotometric evaluation of the reduced complex is carried out at 805–810 nm in these methods.

It is essential in order to avoid silica contamination, to use precleaned polyethylene sample bottles and apparatus. Ramachandran and Gupta³⁷ performed studies on the effects of different reducing agents on silicate determination by the molybdenum blue method. Best results were obtained using ascorbic acid and antimony. The antimony did not participate in the complex but enhanced its absorbance. The recommended procedure is described. It was relatively rapid and sensitive. Beer's Law was obeyed for silicate concentrations of 20–1000 $\mu\text{g l}^{-1}$.

Pilipenko et al³⁸ compared spectrophotometric and chemiluminescent methods of determining silicate in deionized water. They studied different reducing agents in the molybdenum blue spectrophotometric method, viz. tungstosilicic acid, stannous chloride, 1-amino-2-naphthol-sulphonic acid and mixtures of metol and sodium sulphite. They also studied the extraction of the blue tungstosilicic acid with crystal violet and methylene blue. The chemiluminescent method was based on the oxidation of luminol by molybdosilicic acid in alkaline medium. These workers concluded that the best method, from the points of view of detection limit, reproducibility, simplicity and rapidity, was one based on the reduction of molybdosilicic acid by 1-amino-2-naphthol-4-sulphonic acid.

5.7.4

Carbonate

Ion chromatography

Carbonate has been determined in high priority water in amounts down to 0.02 $\mu\text{g l}^{-1}$ by ion chromatography on Zipox SAX phthalic acid or muconic acid at pH 6.5 and 7.2 as eluting agent and an indirect ultraviolet detector set at 321 μm .³⁹

5.7.5

Multianion analyses

Ion chromatography

Roberts et al⁴⁰ have described a single column ion chromatographic method for the determination of chloride and sulphate in steam condensate and boiler feed water. This was shown to be a valuable technique for analysing $\mu\text{g l}^{-1}$ levels of chloride and sulphate in very pure waters. The anions are concentrated on a short precolumn, separated on a low capacity ion-exchange column and detected by an electrical conductivity detector. The apparatus is simple and no 'suppressor' column is needed. Adaptation to on-line analysis would be inexpensive and automation would require control of only the load/inject valve.

The preliminary work by Roberts et al⁴⁰ was carried out using a resin of very low exchange capacity (0.003 mequiv g^{-1}) and a 7.5×10^{-4} M solution of benzoic acid as the eluant. Unusually good sensitivity can be obtained in single column anion chromatography using this eluant. To increase the sensitivity further, the size of the sample loop was increased to 500 μl from the usual 100 μl . This method adequately separated chloride and sulphate with detection limits of 10 mg l^{-1} chloride and 100 mg l^{-1} sulphate. However, a prolonged dip in the base line occurred sometime after the sulphate peak and made this procedure inefficient for repetitive analyses. Chloride must be separated from the water dip before it can be analysed reliably in the same run with a sulphate. This was accomplished by carefully constructing a concentrator column and by careful choice of the column dimensions, resin capacity and eluant strength. The effect of

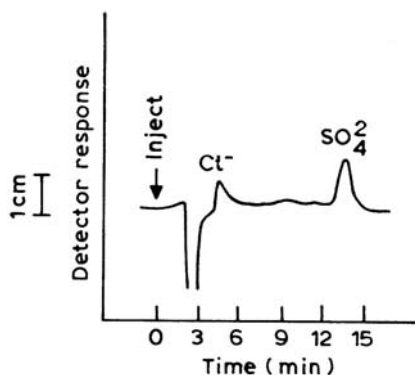


Fig. 42. Standard containing $19 \mu\text{g l}^{-1}$ chloride and $22 \mu\text{g l}^{-1}$ sulphate concentrated from 20.0 ml; eluant, 2.0×10^{-4} potassium phthalate, pH 6.2; concentrator column resin, XAD-4 0.5 mequiv g^{-1} ; separator column resin, XAD-1 0.013 mequiv g^{-1} , 44–57 μm .

column and eluant parameters on anion retention times has been discussed previously by Gjerde et al^{41,42}. If eluant flow rate and anion selectivity coefficients are taken to be constant then the effects of column resin weight w , resin capacity c , and eluant concentration $[E]$ on the adjusted retention time of anions, t' , are shown by the following equation where y is the sample anion charge and x is the eluant anion charge.

$$\log t' = \log w + y/x \log c - y/x \log [E] - \text{constant}$$

It can be seen that the log of column resin weight can be directly proportional to log adjusted retention time regardless of the anionic charges. Increasing the weight of resin in a column will shift both chloride and sulphate to later retention times. However, lowering the resin capacity and/or increasing the eluant concentration will shift the sulphate faster relative to chloride to shorter retention times. These parameters were adjusted until chloride eluted away from the water dip and sulphate still eluted in a reasonable amount of time. The determination of chloride and sulphate in one run greatly reduced the time needed to do the analysis. Sample concentrations for which peaks were at least three times the background signal were 3–5 $\mu\text{g l}^{-1}$ chloride and 1–2 $\mu\text{g l}^{-1}$ sulphate with this procedure.

A chromatogram of the determination of chloride and sulphate in a single run is shown in [fig. 42](#). Data from 20 ml injections of 5–100 $\mu\text{g l}^{-1}$ chloride and sulphate in 'pure' water were used to plot standard addition calibration graphs. A straight line of the form $y=0.401x+1.56$ and a correlation coefficient of 0.997 were obtained for chloride and $y=0.516x+3.70$ and a correlation coefficient of 0.995 were obtained for sulphate. Extrapolation of these plots showed a 4.0 $\mu\text{g l}^{-1}$ chloride concentration and 6.5 $\mu\text{g l}^{-1}$ sulphate concentration for this sample of 'pure' water. Detection limits under these conditions were 3–5 $\mu\text{g l}^{-1}$.

Ion chromatography has been employed to analyse mixtures of chloride, nitrite and sulphate in amounts down to 1 $\mu\text{g l}^{-1}$ in high priority water⁴³ and mixtures of sulphite and orthophosphate in amounts down to 1 $\mu\text{g l}^{-1}$ in boiler blow down water⁴⁴.

5.8 Cations

5.8.1 *Ammonium*

Ion selective electrode

The application of the ammonia selective glass electrode to the determination of ammonium in boiler feed water has been discussed by several workers⁴⁵⁻⁴⁹. Manual^{45,47-49} and autoanalyser⁴⁶ versions of the method have been described. Detection limits claimed range between $3 \mu\text{g l}^{-1}$ and $100 \mu\text{g l}^{-1}$ ⁴⁶⁻⁴⁸. Generally, the sample is buffered to pH 8 to 8.4 with triethanolamine^{45,46}. Potassium and sodium interfere especially at low ammonium concentrations. Midgley et al⁴⁷⁻⁴⁹ have described a system which is essentially an electrochemical cell in which a membrane of a hydrophobic polymer permits passage of free ammonia but not ammonium from the sample solution to a glass silver-silver chloride-electrode measuring system. It is very similar in precision to the ammonium selective electrode and is not subject to interference by ionic species. Cyclohexylamine and octadecylamine in boiler feed water do however, interfere and the temperature must be controlled to within 1°C .

Hara et al⁵⁰ have described a continuous flow determination of low concentrations of ammonium ions using a gas dialysis concentration and a gas electrode detector system. The detection limit of the system was $3 \mu\text{g l}^{-1}$ ammonium.

5.8.2 *Copper*

Spectrophotometric method

Spectrophotometric methods have been described based on the formation of the 4-(2-pyridylazo) resorcinol copper complex⁵¹ and on the catalytic effect of copper on the oxidation of hydroquinone with hydrogen peroxide in the presence of ammonium salts⁵². In the 4-(2-pyridylazo) resorcinol method the sample, adjusted to 7.1, is treated with hydrogen peroxide, citrate (to complex iron) and the chromogenic reagent to produce a colour with a maximum extinction at 510 nm. Iron and zinc do not interfere.

5.8.3 *Cobalt*

Spectrophotometric method

Down to $0.05 \mu\text{g l}^{-1}$ cobalt in nuclear reactor cooling water circuits has been determined by a method based on the catalysis of the reaction of hydrogen peroxide with alizarin at pH 11⁵³. Interfering metals are removed by ion exchange chromatography.

5.8.4 *Sodium*

Atomic absorption spectrometry

A flameless atomic absorption technique has been developed for the determination of down to $0.01 \mu\text{g l}^{-1}$ sodium in power plant boiler feed water⁵⁴. No interference has been found for the anions chloride, sulphate and hydroxide. A comparison of the atomic absorption results with those obtained by using a sodium selective glass electrode indicated a positive bias in the electrode results. This bias was however, found to be reduced when the glass electrode was presented with a low sodium water over a period of days. Thus the sluggish response of the electrode system may have contributed to the observed bias in the laboratory tests. The method is unaltered by the presence of ammonia at concentrations of up to 8 mg l^{-1} . Chloride, sulphate and hydroxide ions did not interfere.

Precision ranged between a standard deviation of $0.006 \mu\text{g l}^{-1}$ at the $0.13 \mu\text{g l}^{-1}$ sodium level to $0.021 \mu\text{g l}^{-1}$ at the $0.92 \mu\text{g l}^{-1}$ sodium level.

Flame photometry

Down to $2 \mu\text{g l}^{-1}$ sodium has been determined in high purity water by flame photometry involving scanning the emission spectrum of an air propane flame into which the sample is aspirated from 610 to 580 nm⁵⁵.

Ion selective electrodes

Webber and Wilson⁵⁶ have investigated the accuracy of the sodium responsive glass electrode for determining sodium in high purity boiler feed water. If the potential of the electrode is affected only by the activity of sodium ions in the water the potential should follow the usual Nernst equation and it is shown that the pH of the solution should be adjusted to 10 to 11 by addition of aqueous ammonia. To obtain significant results at sodium concentrations of $1 \mu\text{g l}^{-1}$ it is necessary to minimize contamination with other ions and measurements were therefore made on the flowing water with the reference electrode downstream from the measuring electrode.

5.8.5 *Molybdenum*

Amperometry

Amperometry has been investigated as a method for the determination of molybdenum in high purity water⁵⁷. The method involves conversion of the molybdenum into the yellow 12-molybdophosphate complex, extraction of this into butyl acetate, decomposition of the heteropoly-compound with aqueous ammonia and back-extraction of the liberated molybdenum into aqueous solution for biamperometric determination.

5.8.6

*Zinc**Atomic fluorescence spectroscopy*

Marshall and Smith⁵⁸ tested a high intensity hollow cathode lamp, a vapour discharge tube and a microwave excited discharge tube as sources to excite the zinc fluorescence at 213.9 nm in an air hydrogen flame. Detection limits were 30, 2.4 and 0.4 $\mu\text{g l}^{-1}$ respectively and coefficient of variation ranged from 1.2 to 6 per cent. The last named source is preferred. Interference from elements likely to be present in feed waters caused errors of less than 4 per cent. Results obtained by this method are in agreement with those obtained by atomic absorption spectrometry.

5.8.7

*Multication analysis of high purity waters**Miscellaneous*

Various techniques used for the multimetal analysis of high purity boiler feed waters are summarized in Table 50. Despite the large variety of methods that have been investigated over the past twenty years for the examination of trace metals in high purity waters, it is true to say that the methods of choice

TABLE 50
Techniques used in multimetal analysis of boiler feed and high purity waters

Technique	Element	Comments	Detection limit ($\mu\text{g l}^{-1}$)	Ref.
Atomic absorption spectrometry	Cadmium, manganese, vanadium, nickel, cobalt, chromium, copper, iron	Automatic injection of sample into graphite cup of Massman furnace (boiler feed water)	0.0025 (Cd) to 5 (V)	59
Atomic absorption spectrometry	Miscellaneous	Analysis of distilled deionized water		60
Non-dispersive atomic fluorescence spectrometry	Miscellaneous	—	—	61
Zeeman atomic absorption spectrometry	Cadmium, chromium, cobalt, copper, lead, manganese, nickel, zinc	Comparison of Zeeman background correction and deuterium background correction techniques (low ionic strength waters)	—	62
Spark source mass spectrometry	25 elements	High purity waters	Down to 5	63
Continuous potentiometric analysis	Miscellaneous	High purity waters	—	64
Anodic stripping voltametry	Cadmium, lead, copper	ASV with water collection at a glassy carbon ring disc electrode (high purity water)	6(Cd) 8 (Pb) 5(Cu)	65

Technique	Element	Comments	Detection limit ($\mu\text{g l}^{-1}$)	Ref.
Spectrophotometry	Iron, silver, copper	10–100 l sample taken. After ignition and fusion elements determined using 1:10 phenanthroline and neocuproine	—	66
Spectrophotometric; ion selective electrodes, atomic absorption spectrometry; gas chromatography	Iron, copper, nickel, zinc, sodium, calcium, magnesium, ammonium, silicon	Reviews of various methods (steam water circuits in power stations)	—	67

now emerging are those based on the variants of atomic absorption spectrometry and scanning voltammetry.

Jones et al⁶⁸ have described chromatographic separation systems using either a low capacity silica based cation-exchange material with a lactate eluant, or a high capacity resin based cation exchanger with a tartrate eluant. Photometric detectors made use of post column reactors for incorporating a reagent, the most successful of which was eriochrome black-T, which produced changes in absorption or fluorescence when mixed with metal species as they eluted from the column. These methods were applied to on-line monitoring of trace metals, notably manganese, iron, cobalt and nickel, in the primary coolant of a pressurized water reactor.

5.9

Miscellaneous determinands

5.9.1

pH

Various workers have discussed the problems associated with the accurate measurement of the pH of low concentrations (less than $10 \mu\text{S cm}^{-1}$) in high purity water including boiler feed water^{69–72}. Temperature compensation during the measurement of pH of boiler feed water has been discussed⁷².

Kent Instruments (EIL Ltd.) have described a pH monitor (Model 7680) for use on feed water to high pressure boiler plants used in electricity production.

5.9.2

Electrical conductivity

Measurement of electrical conductivity of high purity water has been discussed by Maurer⁷³ and Light⁷⁴. Maurer⁷³ discussed ac and dc measurements. Light⁷⁴ studied temperature dependence and measurement of resistivity of pure water. He gives details for theoretical and maximum resistivity, conductivity, temperature coefficient, and neutral pH values of pure water for 0–300°C. Calibration techniques for detection of ionic impurities are discussed.

5.9.3

Hydroxylamine, hydrazine and ammonia

Hydrazine is commonly added to steam boiler water to act as a reducing agent for dissolved oxygen and metal oxides. Because its reaction products are nitrogen and water, hydrazine is the reagent of choice for inhibiting corrosion or scale build-up in boilers used by electric utility companies.

Hydrazine

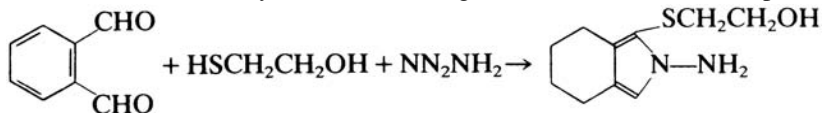
SPECTROPHOTOMETRIC METHOD. An official UK method published by the Department of the Environment⁷⁵ for the determination of hydrazine in waters is based on its reaction with *p*-dimethylaminobenzaldehyde with the formation of a yellow azine, the concentration of which is determined spectrophotometrically at 455 nm. The limit of detection is 0.4–1.0 $\mu\text{g l}^{-1}$ hydrazine and the method is applicable up to 100 $\mu\text{g l}^{-1}$.

Basson and Van Staden⁷⁶ determined low levels of hydrazine in water by reaction with 4-dimethylaminobenzaldehyde followed by spectrophotometric measurement of the absorbance at 460 nm.

Marty and Ganguly⁷⁷ used a silver gelatin complex to determine micro amounts of hydrazine in water.

Hydrazine and ammonia

FLUORIMETRIC METHOD: *o*-phthalaldehyde and mercaptoethanol have been found⁷⁸ to form derivatives with hydrazine and ammonia which can be determined by fluorimetry. Because the optimum pH values for formation of the hydrazine and ammonia derivatives were different, analysis of mixtures of the two components without prior separation is possible. Boiler water samples containing 5–200 mg l^{-1} levels of hydrazine and ammonia have been analysed with an average relative error of about 10 per cent.

*Hydrazine and hydroxylamine*

VOLTAMMETRY: Dias and Jaselskis⁷⁹ have described a voltammetric method using a rotating platinum electrode for the determination of hydrazine and hydroxylamine, separately or together. The reduction is carried out in a pH 5 buffer and measurements are made at 0.85 V (versus SCE). Hydrazine or hydroxylamine when present at concentrations of 0.32–5.7 mg l^{-1} are readily determined in an acetate buffer at pH 5.0 by voltammetry using a rotating platinum electrode and measuring the current plateau. In mixtures, hydrazine and hydroxylamine are determined by measuring the plateau current before and 5 min after the addition of acetone. Amounts of hydrazine and hydroxylamine are obtained graphically. In this manner, the amounts can be determined with a relative standard deviation of better than 2 per cent when present alone. In mixtures the relative standard deviation varies from 2 to 5 per cent depending on the amount present.

Cyanide, urea, nickel and cobalt when present at concentrations as high as 50 times that of hydrazine or hydroxylamine do not interfere. However, the presence of copper not only changes the voltammogram but also lowers the peak current, indicating that some of the copper II is reduced to copper I at the expense of hydrazine or hydroxylamine. Nitrite enhances the peaks of the hydroxylamine and hydrazine and should not

be present at concentrations of greater than 5×10^{-6} M. Iodide interferes and the concentration of iodide must be below 1×10^{-6} M.

5.10 Organic substances

5.10.1 *Nitrosamines*

Gas chromatography

Nitrosamines have been reported in deionized water by Fiddler et al⁸⁰, Cohen and Backman⁸¹ and Gough et al⁸². *N*-Nitrosodimethylamine and *N*-nitrosodiethylamine have been confirmed in water exposed to deionizing resins by Fiddler et al⁸⁰. Levels of *N*-nitrosodiethylamine detected were 0.03–0.34 $\mu\text{g l}^{-1}$ and *N*-nitrosodiethylamine 0.33 and 0.83 $\mu\text{g l}^{-1}$. The highest levels of nitrosamines were found after resin regeneration. *N*-Nitrosodimethylamine levels of 0.25 $\mu\text{g l}^{-1}$ and lower concentrations were also detected in deionized water by Cohen and Backman⁸¹. The origin of the nitrosamines in these reports was not identified. However Gough et al⁸² suggested that *N*-nitrosodimethylamine present in the ion-exchange resins (up to 125 $\mu\text{g kg}^{-1}$) as manufacturing contaminants not the reaction of the components in the water with the resins, was responsible for the occurrence of trace levels of *N*-nitrosodimethylamine (0.01 $\mu\text{g l}^{-1}$) detected in deionized water. *N*-Nitrosodimethylamine was detected in the effluent when a 1 M sodium nitrite solution was passed through a mixed strong anion and cation resin column by Angeles et al⁸³. Formation of *N*-nitrosodimethylamine was postulated by the cation acid catalysed nitrosation of the amine/ammonium functional group on the strong anion resin during the deionization process.

Kimoto et al⁸⁴ attempted to ascertain whether one of the explanations offered by these earlier workers^{82,83} for the occurrence of nitrosamines in water deionized with strong cation and anion resins is correct or whether other factors are involved. They showed that *N*-nitrosodimethylamine was formed when tap water was passed through a column containing only the anionexchange resin, thereby indicating that nitrosamine formation by the conventional acid-catalysed nitrosation reaction, as would be expected in the case of a mixed strong anion and cation resin system, was not the primary mechanism. The quaternary ammonium ion of the strong anion resin may be the amine precursor for nitrosamine formation. Strong anion and strong cation resins (Amberlite and Dowex brands) were ineffective in concentrating low levels of *N*-nitrosodimethylamine that were added to the influent. Accumulation of extremely low levels of nitrosamine already present in the water, therefore, also did not contribute importantly to the concentration of nitrosamine found in deionized water. In addition, the normal levels of cations and anions in water, and heavy metal ions were also not primarily responsible for this occurrence. There was however, an unknown substance(s) in the tap water that promoted nitrosamine formation. This unknown soluble substance(s) can be removed by activated carbon treatment or degassing techniques.

Kimoto et al⁸⁴ extracted nitrosamines from 11 water samples with 3×150 ml portions of dichloromethane with shaking for 5 min per extraction. The extracts were combined, dried over anhydrous sodium sulphate and concentrated in a Kuderna Danish evaporator to 1.0 ml. These workers determined nitrosamines in dichloromethane extracts by a gas chromatographic procedure.

5.10.2

Octadecylamine and cyclohexylamine

Thin layer chromatography

Octadecylamine a corrosion-inhibiting boiler water additive, has been isolated from water by solvent extraction with ethylene dichloride or by trapping on a micro Chromosorb column⁸⁵. The levels of octadecylamine were determined using high performance thin layer chromatography and reflectance densitometry. Recovery at 3 mg l⁻¹ averaged 81.3 per cent using solvent extraction and 94.0 per cent with the column. Recovery at 0.3 mg l⁻¹ was 94.2 per cent using the column procedure. Other permitted boiler water additives did not interfere with the analysis.

Sherma and Pallasta⁸⁶ determined cyclohexylamine in water by solid-phase extraction and high performance thin-layer chromatography.

5.11

Dissolved gases

5.11.1

Dissolved oxygen

Spectrophotometric method

Goodfellow and Webber⁸⁷ have described a simple, fast manual technique for the routine determination of low concentrations of oxygen in power-station waters. The method is based on the reaction of dissolved oxygen with the leuco-base of methylene blue to produce a soluble blue oxidation product with an absorbance which is a function of the oxygen concentration. A specially designed glass cell is used as a sample collection vessel, a reaction vessel and also as a spectrophotometric cuvette.

These workers also describe modifications to the manual absorptiometric technique for determining low oxygen concentrations in power station waters, which enable it to be used on a continuous basis with a Technicon AutoAnalyser⁸⁸.

Amperometric method

Hissel⁸⁹ has described a modification of the Winckler method for the determination of dissolved oxygen in boiler waters in which iodine was generated in the solution by electrolysis using a steady current for a measured period of time. The excess iodine was then back titrated amperometrically using 0.05 N sodium thiosulphate solution.

Gas chromatography

In a gas chromatographic procedure, Ropars⁹⁰ degasses the water and collects the gases. The oxygen in this gas is separated from other gases on a column of molecular 5A at 20–40°C with helium as carrier gas and a thermal conductivity detector. After corrections are made for changes in detector current, helium pressure and temperature, the graph of peak height vs concentration of oxygen is rectilinear for up to 1 per cent of

oxygen in the desorbed gas. Calibration is obtained by injection of known volume of air into degassed water. Hydrazine interferes in the determination, an error of ± 4 per cent at the $1 \mu\text{g}$ level is obtained.

5.11.2 *Chlorine*

Spectrophotometric method

Le Cloirec et al⁹¹ in their investigation of the relationship between organic nitrogen content and chlorine demand of cooling waters found that chlorine demand generally corresponded to twice the amount of ammonia and organic nitrogen. They found that chlorine demands obtained by spectrophotometric DPD amperometric titration and amperometric membrane methods were subject to interference.

Amperometry

Manabe⁹² has given details of an amperometric method for determining residual chlorine in cooling tower blowdown. Sodium pyrophosphate is added as a complexing agent to reduce interference by ferric and cupric ions. The method is applicable to other water systems containing metals in concentrations similar to those found in blowdown.

5.12 Radioactive elements

5.12.1 *Radium-226*

Pomansk et al⁹³ determined ultra micro amounts of radium-226 in ultra high purity water. The sample liquid or in solution was treated with a stream of purified helium xenon in a bubbler to collect accumulated radium-222 and the resulting gas stream is passed through traps at -60°C to -70°C to remove entrained liquid and then through a trap containing active carbon at -78°C on which the radium and xenon were adsorbed. After completion of the bubbling process (with use of 100 vol of gas per vol of liquid) the carbon trap was evacuated, then heated in boiling water. The liberated gases were passed into a furnace containing titanium metal at 950°C to remove all gases other than the inert gases. After 20 min, the temperature was reduced to 400°C and the radium and xenon were fed by a Toepler pump to a proportional counter to determine the concentration of radium 226, which was converted into the content of radium 226 in the sample. The accuracy of the method was within ± 20 per cent.

SWIMMING POOL WATERS

5.13
Cations*5.13.1*
*Ammonium**Ion selective electrode*

Pacik and Roerig⁹⁴ have described a method for the determination of ammonium and urea in swimming pool waters. It is based on the use of an ion selective electrode and the preliminary hydrolysis of urea to ammonium carbonate with the enzyme urease, ammonia being liberated by the addition of alkali. Details are given concerning the application of the method, and preparation of calibration curves, while the effects of impurities in the urease preparation and its storage life are also considered. The method is claimed to have given reproducible results.

5.14
Organic substances*5.14.1*
*Chlorinated isocyanurates**Spectrophotometric method*

These substances have been determined in amounts down to 10 mg l^{-1} in swimming pool water by a spectrophotometric procedure⁹⁵. The method is based on the production of isocyanuric acid and reaction with cobalt acetate, in the presence of isopropylamine. The water sample is evaporated and the residue dissolved in methanol; 5 ml is mixed with 5 ml chloroform. Cobalt acetate solution is added followed by 0.5 ml isopropylamine. After 30 min, the extinction is read at 565 nm against a blank of methanol-chloroform-isopropylamine (10:10:1).

5.14.2
*Cyanuric acid**Differential pulse polarography*

This technique has been described using the peak at 60 mV, and a static mercury drop electrode and a silver-silver chloride reference electrode⁹⁶. Down to $1 \mu\text{g l}^{-1}$ cyanuric acid were determined in swimming pool waters.

High performance liquid chromatography

This technique has been used to determine cyanuric acid in swimming pool waters⁹⁷.

5.14.3

Haloforns

Gas chromatography

A gas chromatographic procedure for determination of volatile organochlorine compounds in swimming pool water has been described⁹⁸. A column packed with Carboxen 101 with 0.8 per cent SE.30 as the mobile phase is used, the sample being extracted by *n*-pentane in the sampling container. Retention times are given for a range of chlorinated and bromo-chloro derivatives. The method was applied to samples from enclosed public swimming baths, originally filled with water from the mains, and to medicinal baths, filled with thermal spring water containing detectable amounts of bromine in solution. While chloroform was the major chlorinated product in the enclosed baths, dibromochloromethane was the principal product in the baths containing thermal spring water, while chloroform was present only in very small quantities.

5.14.4

Miscellaneous

Maierski et al⁹⁹ have studied the differential determination of volatile and non-volatile organochlorine compounds in swimming pool waters. They describe methods for fractionating organochlorine compounds into groups of differing polar properties during the analysis of swimming pool waters. The volatile chlorine compounds are vaporized, mineralized at 1100°C and determined by a microcoulometer, for non-volatile compounds an enrichment technique is used based on the principle of reverse phase liquid chromatography. Retained organochlorine derivatives of medium polarity are eluted with methanol and the polar compounds are separated using ion pair chromatography. Details of the separation and quantification of each class of compounds are given, together with results of their application to swimming baths waters subjected to various types of disinfection treatment, including filtration, ozonation and carbon adsorption. The tests showed that ozonation contributed to a marked increase in the polar fraction, from 500 to 700 $\mu\text{g l}^{-1}$ which was only slightly lowered by subsequent active carbon filtration.

5.15

Dissolved gases

5.15.1

Chlorine

Chronoamperometry

A rapid and sensitive electroanalytical method has been described for measuring free chlorine in water, using a wax impregnated carbon electrode with linear potential sweeps¹⁰⁰. The method can be used to measure free chlorine at sub-ng l^{-1} levels in the presence of chlorinated isocyanurates and cyanuric acid.

The equilibrium between free and combined chlorine is not disturbed and the sum of hypochlorous acid and hypochlorite ion in the solution is measured, so that the measurement is not affected by pH variation.

5.15.2 *Bromine*

Spectrophotometric method

Kelus¹⁰¹ has reviewed methods for the determination of bromine in swimming pool waters. A method based on the spectrophotometric determination of free bromine, liberated by the addition of potassium iodide, is recommended. Free chlorine does not interfere in this procedure.

NUCLEAR REACTOR COOLING WATERS

5.16 Radioactive elements

5.16.1 *Miscellaneous*

James¹⁰² determined trace metal impurities in reactor cooling waters using ion-exchange membranes. The membranes (Acropore SA and SB) consisted of finely divided ion-exchange resin in acrylonitrile poly(vinyl chloride) copolymer reinforced with nylon. Experiments are described in which stacks consisting of a pre-filter (pore size 0.45 μm) and three membranes were used to recover μg amounts of cobalt, iron, chromium, zinc, copper and nickel from large volumes of sample. For a sample size of 250 l containing cobalt at a concentration of 0.01 or 0.1 $\mu\text{g l}^{-1}$ the recovery was 85 or 99 per cent respectively. Acid digestion was used to separate the elements from the stack and atomic absorption spectrophotometry was used for their determination.

Neeb et al¹⁰³ carried out a radiochemical analysis of the primary cooling medium of water cooled nuclear reactors by use of the lithium drifted germanium detector.

A gamma-spectrum is recorded (100 s measuring time) with use of a Ge(Li) detector (40–50 cm^3) and a multi channel analyser, of a 50 ml portion of the water 10 min after taking the sample. Krypton 85 m, krypton 87, xenon 133, xenon 135, iodine 131, iodine 132, iodine 135, caesium 138 and sodium 24 are readily observed. A second gamma-spectrum of the sample after it has been degassed for 10 min with nitrogen or argon gives undisturbed peaks for technetium 101 and iodine 133, comparison of the peak intensities in the two spectra gives the activity of xenon 138. Alternatively, gaseous fission nuclides can be isolated by adsorption on activated carbon at low temperature. Overlapping of the peaks of iodine and caesium isotopes can be resolved by extractive removal of iodine from the degassed sample with carbon tetrachloride. The gamma-spectrum of the organic phase gives peaks due to iodine 131, iodine 132, iodine 133, iodine 134 and iodine 135 and that of the aqueous phase peaks due to caesium 134, caesium 135 and caesium 137. Other nuclides, e.g. chromium 51, iron 59, cobalt 58, cobalt 60, manganese 54 and manganese 56 can be detected from gamma-spectra obtained when a sample of the water to which carriers have been added, is filtered, and to the filtrate a mixture of aqueous ammonia and ammonium sulphide is added, the precipitate being collected on a second filter and the activity of the two residues being measured.

Moskvin et al¹⁰⁴ determined fission products in primary circuit water by chromatographic group separation. The fission products can be separated by passing the sample (100 ml) made 0.1 M in formic acid and in ammonium chloride through a column containing pellets of porous PTFE (each 3 cm high, and 1 cm in diam), impregnated, respectively, with trioctylamine (to retain iodine and molybdenum); AV-17 anion-exchange resin (formate form) (to retain anionic forms of molybdenum); bis-(2-ethylhexyl) hydrogen phosphate (for rare earth metals); ammonium molybdophosphate (for heavy alkali metals); and KU-2 cation exchange resin (H⁺ or NH⁴⁺ form) for alkaline earth metals. The column is washed with a solution 0.1 M in formic acid and in ammonium chloride then blown with air until dry. The pellets are then removed and the radioactivity of each is analysed on a gamma-spectrometer with a Ge(Li) detector. The gamma-ray spectra of pellets obtained from primary circuit water of a water moderated nuclear reactor are discussed. The errors for individual elements are less than ± 20 per cent.

Niese and Niese¹⁰⁵ determined actinide elements in water samples from the primary circuit of a nuclear reactor. Neptunium-239 was determined using isotope dilution analysis with neptunium-238 as a tracer. Neptunium-237 and uranium-238 determinations were carried out by isotope dilution neutron activation analysis with neptunium-239 or neptunium-238 as tracer. Alpha spectroscopic isotope dilution analysis was used for the determination of plutonium-239 and plutonium-240 with plutonium-238 as tracer. Activity ratios for the various actinide nuclides which related to the activity of uranium-238 or plutonium-238 are given.

From the onset of the Three-Mile Island reactor incident (March 28, 1979), the distinct possibility existed that actinide and fission product pollutants could escape into the surrounding environment. Experienced analytical chemists in command of techniques which achieve the highest sensitivity were called upon for assistance in performing analysis. The results of this work was reviewed by Carter et al¹⁰⁶. Cooling water was analysed for uranium and plutonium, certain fission products, additives and possible corrosion products by isotope dilution mass spectrometry. In particular, the thermal emission isotope dilution technique, in which an anion-exchange resin bead was used to concentrate the uranium and plutonium, provided technical information on samples orders of magnitude smaller than those necessary for conventional counting techniques.

The resin bead loaded sample acts as a point source in a pulse counting two stage high abundance sensitivity mass spectrometer, enhancing the sensitivity so that levels as low as 10^{-3} M plutonium and 10^{-11} M uranium concentrations were detected in 1 ml of water. The methodology employed for this exercise also provided isotopic information which was informative with respect to material source, location, and condition.

The technique uses Dowex 1, 2 per cent cross-lined anion resin beads in the nitrate form. An aliquot of the sample is adjusted at 8 M in nitric acid. Under these conditions, only plutonium and uranium absorb appreciably and essentially complete separation from fission products and other actinides is achieved. Optimal adsorption of plutonium and uranium from solutions containing both elements is achieved when the uranium concentration is adjusted to about 1 μg uranium per bead. The samples were too dilute to allow this desideratum to be met, but satisfactory adsorption was still obtained. After standing in contact with the solution for 16–24 hours, the beads are extracted and washed, they will have adsorbed a maximum of 3 ng of plutonium and uranium per bead, the exact amount being a function of the concentration of the solution and the exposure time. Exposure times can be reduced to 30 min or less by agitating the beads with the solution.

Each bead serves as a sample for mass spectrometric analysis, and plutonium and uranium are analysed sequentially from it. Plutonium ionizes from the single uranium filament at about 1450°C and uranium at about 1700°C. The bead serves as a good approximation to a point source for the ion optics of the

instrument, and the carbon matrix left from the bead acts as a reservoir for the sample from which it is slowly fed to the ionizing region. Both of these factors serve to improve the ion collection efficiency. A substantial carbon matrix of the bead remains that contains virtually all of the uranium sample which does not migrate along the rhenium filament.

The mass spectrometers used in this work were multi-staged, pulse counting instruments with high abundance sensitivity and possessed the ability to analyse very small samples.

Table 51 lists concentrations and isotopic compositions for plutonium and uranium for samples taken from storage tanks at Long Mile Island. Plutonium concentrations below 10^{-11} molar gave insufficient ion signals for reliable measurement of isotopic composition.

Boron was added to the primary cooling water by engineers at the scene. The large cross-section of boron-10 for neutron capture makes this element a good means of controlling and measuring nuclear reactivity. It is therefore important to be able to monitor and verify the concentration of boron-10 in solution. Isotope-dilution spark source mass spectrometry¹⁰⁷ was used to determine the levels of boron and other elements such as caesium-135 and caesium-137 in the primary cooling water. These results are presented in Table 52. Secondary ion mass spectrometry was used to determine the isotopic composition of both boron and lithium in these solutions. A compound containing enriched lithium-7 had been added to the solution at the site for pH

TABLE 51
Uranium and plutonium concentration by isotope dilution thermal emission mass spectrometry

Sample	Concentration $\times 10^{-10}$ Molar							
U	Pu							
A-1	25							
A-2	655							
A-3	71							
U and Pu isotopic measurement in atom percent								
Sample	234	235	236	238	239	240	241	242
A-1	<0.01	0.6	<0.01	99.4	a			
A-2	0.0075	0.84	0.026	99.126	84.42	12.10	4.67	0.81
A-3	<0.01	0.6	<0.01	99.4	a			

^a Ultra low Pu concentration; insufficient sample for isotopic analysis.

TABLE 52
Elemental composition measurements on TMI primary cooling water

Element	Concentration ($\mu\text{g ml}^{-1}$)	Method ^a
B	3440	SSMS
¹⁰ B=20%		SIMS
¹¹ B=80%		
Ag	0	SSMS
Al	10	SSMS
Cs	8	SSMS
¹³³ Cs=45%		
¹³⁵ Cs=13%		

Element	Concentration ($\mu\text{g ml}^{-1}$)	Method ^a
¹³⁷ Cs=42%		
Cd	0.3	SSMS
Li	4.6	SIMS
⁶ Li=0.02%		
⁷ Li=99–98%		
Fe	1	SSMS
13II	0.9	SSMS
In	0.5	SSMS
K	0.4	SSMS
Na	960	FES
P	0.1	SSMS
S	20	SSMS
Si	5	SSMS
⁸⁹ Sr, Y	1	SSMS

^a Spark-Source Mass Spectrometry (SSMS); Flame Emission Spectrometry (FES); and Secondary Ion Mass Spectrometry (SIMS).

Note: Approximately 20 other elements also measured by SSMS.

control. The need for accurate knowledge of the isotopic composition of boron and lithium was partially responsible for the development of a secondary ion mass spectrometric method for performing such measurements.

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Appendix

STANDARD UK AND US METHODS OF TREATED WATER ANALYSIS

UK methods for the Examination of Waters and Associated Materials. HMSO (London) Blue Book Series.

A

Potable waters

Arsenic-waters, AAS	Arsenic in potable waters by AAS (semi automatic method) 1982.
Arsenic-waters, spectrophotometry	Arsenic in potable and sea water by spectrophotometry. 1978.
Cadmium	Cadmium in potable waters. 1976.
Cobalt	Cobalt in potable waters. 1981.
Copper	Copper in potable waters by atomic absorption spectrophotometry. 1980.
Iron and manganese	Iron and manganese in potable water by AAS. 1983.
Lead	Lead in potable waters. 1976.
Nickel	Nickel in potable waters. 1981.
Zinc	Zinc in potable waters by atomic absorption spectrophotometry. 1980.

B

Waste waters

Chemical oxygen demand	Chemical oxygen demand of polluted and waste waters. 1977.
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C

Sewage

Acids, volatile organic	Determination of volatile fatty acids in sewage sludge. 1979.
Metals-rivers, sewages extractable material	Carbon tetrachloride The determination of material extractable by carbon tetrachloride and of certain hydrocarbon oil and grease components in sewage sludge. 1978.
Cation-exchange capacity	Cation-exchange capacity and exchangeable cation (including water soluble ions) in soils, related materials and sewage sludge.

For US methods see American Public Health Authority Standard Methods for Examination of Water and Wastewater (1955). Also US Environmental Protection Agency Method Series.

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