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25 FUNDAMENTALS OF ANALYTICAL CHEMISTRY

25.1 NATURE AND IMPORTANCE OF CHEMICAL ANALYSIS

Analytical chemistry is that branch of the chemical sciences employed to determine the composition of a sample of material. A **qualitative analysis** is performed to determine *what* is in a sample. The amount, concentration, composition, or percent of a substance present is determined by **quantitative analysis**. Sometimes both qualitative and quantitative analyses are performed as part of the same process.

Analytical chemistry is important in practically all areas of human endeavor and in all spheres of the environment. Industrial raw materials and products processed in the anthrosphere are assayed by chemical analysis, and analytical monitoring is employed to monitor and control industrial processes. Hardness, alkalinity, and trace-level pollutants (see Chapters 11 and 12) are measured in water by chemical analyses. Nitrogen oxides, sulfur oxides, oxidants, and organic pollutants (see Chapters 15 and 16) are determined in air by chemical analysis. In the geosphere (see Chapters 17 and 18), fertilizer constituents in soil and commercially valuable minerals in ores are measured by chemical analysis. In the biosphere, xenobiotic materials and their metabolites (see Chapter 23) are monitored by chemical analysis.

Analytical chemistry is a dynamic discipline. New chemicals and increasingly sophisticated instruments and computational capabilities are constantly coming into use to improve the ways in which chemical analyses are done. Some of these improvements involve the determination of ever smaller quantities of substances; others greatly shorten the time required for analysis; and some enable analysts to tell with much grater specificity the identities of a large number of compounds in a complex sample.

Understanding some of the material in Chapter 1 is essential to understanding and practicing analytical chemistry. A good understanding of numbers, their meanings, their uncertainties, and calculations involving numbers are essential for the practice of analytical chemistry. These concepts are discussed in Sections 1.6 and

1.7. Analytical chemistry is a science of measurement. Therefore, basic concepts of chemical measurement discussed in Sections 1.8–1.13 must be mastered before studying analytical chemistry. Calculating and expressing the results of a chemical analysis must be done accurately and with a thorough knowledge of units, unit conversion factors, and their use in computations, as discussed in Section 1.14. Chemical analysis requires the proper use of laboratory apparatus. Crucial laboratory apparatus used in analytical chemistry include the laboratory balance for accurate mass measurement and volumetric glassware, specifically the pipet, buret, and volumetric flask shown in Figure 1.10.

Many of the calculations of analytical chemistry involve quantities of materials that take part in chemical reactions. Therefore, stoichiometric calculations may be very important in analytical chemistry. The reader should refer back to stoichiometry in Chapter 5.

This chapter is written to provide an overview of analytical chemistry. Chapter 26, "Environmental and Xenobiotics Analysis," covers some specific aspects of the analysis of environmental samples of various kinds. For those users who may become directly involved in doing chemical analyses, more-detailed coverage of the topic and specific analytical procedures are discussed in reference works listed at the end of the chapter.

25.2 THE CHEMICAL ANALYSIS PROCESS

It is important to regard chemical analysis within the framework of an overall *chemical analysis process*, rather than an isolated "laboratory experiment." Each step in the analysis process is crucial to getting accurate and meaningful results. Figure 25.1 outlines the process.

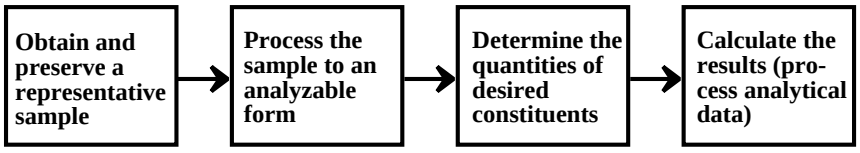


Figure 25.1 Schematic representation of the major steps involved in the chemical analysis process.

The first step in the analytical process is to obtain a representative **sample** or samples, that portion of matter upon which the analysis is performed. The sample should be a **representative sample**, the composition of which is as close as possible to the whole mass of whatever is being analyzed. Obtaining a good sample is a crucial step in the chemical analysis process. Failure to obtain and properly preserve a good sample means that the whole analysis may be incorrect, rendering all the other steps involved worthless.

Sample processing is performed to get the sample into a form that can be analyzed. For a few kinds of analysis, the sample is analyzed without further processing or after minimal steps, such as grinding and mixing. Often, sample processing requires putting the sample into solution. Sample dissolution can be as simple as stirring a soil sample with hydrochloric acid to dissolve potassium required

for soil fertility. Or it can be complicated and severe, such as oxidizing and dissolving fish tissue for metals analysis with a hot concentrated mixture of HNO_3 and $HClO_4$.

The discussion of sample processing above leads to the definition of two kinds of analyses, depending upon what is done with the sample. When a sample is oxidized, dissolved in acid, or otherwise greatly altered as part of the analytical process, the chemical analysis is termed *destructive.* In some cases, such as those where evidence of a crime is involved, it is important to preserve the sample in an unaltered form. This requires *nondestructive* methods of analysis, such as can be performed by making the sample radioactive by irradiation with neutrons in a nuclear reactor and measuring the energies and intensities of gamma radiation given off by the activated elements (neutron activation analysis).

After sample processing, it is often necessary to eliminate **interferences** from substances in the sample that can cause erroneous results. This can be done by removing interfering substances or by treating the sample with substances that react with interferences to render them non-interfering.

After all the steps outlined above have been performed, the actual measurement of whatever is being determined is performed. The substance that is measured, such as calcium in a water sample or *trans*,*trans*-muconic acid measured in blood as evidence of occupational exposure to toxic benzene, is called the **analyte**. The specific measurement of the analyte is referred to as a **determination**, whereas the total process to which the sample is subjected is called an **analysis**.

The final step in a chemical analysis is **calculation** of results. This step may consist of a few simple calculations, or it may involve a complicated data processing operation that calculates analyte levels and compensates for interferences in the method. In addition to providing a number for the quantity or percentage of analyte in a sample, the calculation of results usually involves an evaluation of the reliability of the data (precision and accuracy) of the analytical values. In modern analytical laboratories, results are calculated and stored by computer, frequently as part of the process by which analyte levels are measured with an appropriate instrument.

25.3 MAJOR CATEGORIES OF CHEMICAL ANALYSIS

Both qualitative and quantitative analysis are divided between **classical** methods involving primarily chemical reactions and simple measurements of mass and volume, and **instrumental methods** that use instruments of varying degress of complexity and sophistication to measure quantities of analyte. Classical methods are often **wet chemical** procedures using reagents in solution and reactions of dissolved analyte. Instrumental methods use various devices to measure physical manifestations of chemical species and chemical reactions, such as absorption of light, electrical potentials, or small changes in temperature.

Analytical chemistry can also be divided between **chemical** and **physical** methods of analysis. Chemical methods almost always involve the measurement of a mass of a chemical species or volume of a reagent solution produced or consumed by a chemical reaction. For example, the acid in an acid mine water sample can be determined by adding exactly enough of a solution of base of accurately known concentration to exactly neutralize the strong acid in the sample,

$$H^+ + Na^+ + OH^- \rightarrow H_2O + Na^+ \quad (25.3.1)$$

exactly measuring the amount of NaOH required, and calculating the quantity of acid neutralized; such a procedure is an acid-base **titrimetric** procedure.

Physical methods of analysis normally involve a measurement of a physical parameter other than mass or volume. For example, a water sample suspected of being polluted with hexavalent chromium can be injected into an inductively coupled plasma atomic emission spectrometer and the intensity of light given off by very hot chromium atoms emitted by the sample measured to give the chromium concentration. Or fluoride in a water sample can be determined by measuring the potential versus a reference electrode of a fluoride ion-selective electrode immersed in the sample and comparing that value with the potential measured in a standard F^- solution to give the value of $[F^-]$.

25.4 ERROR AND TREATMENT OF DATA

A chemical analysis is only as good as the numbers that go into calculating and expressing the result. Therefore, data analysis is a crucial aspect of chemical analysis. All analytical measurements are subject to greater or lesser degrees of error. So every reasonable effort is made to reduce the amount of error in an analytical measurement. Since some error is inevitable, it is important to know the degree of error and express it correctly in the final result.

One of the major objectives of analytical measurements is to obtain *reproducible results*. For example, if three determinations of the percentage of iron in the same iron ore sample gave values of 18.76, 18.71, and 18.73 percent, the analyst would have a relatively high degree of confidence in the validity of the results because the three values are so close together. The degree to which numbers in a group of analytical results are in agreement with each other is the **precision** of the group of numbers. A lack of precision may indicate the presence of **indeterminate**, or **random**, **errors**. Such errors vary randomly in direction and magnitude and are from sources that cannot be determined.

However, just because the results of a set of analyses are in close agreement does not necessarily mean that the values are correct. This is because of the possibility of **determinate errors**. Such errors have a definite cause (although it may be unknown to the analyst), and each type of determinate error is always in the same direction. For example, if an analytical chemist were using a pipet rated to deliver 25.00 mL of solution that through a manufacturing mistake actually delivered 25.35 mL, a determinate error would be introduced into the analysis; in this case, it could readily be detected by calibrating the pipet.

The extent to which the data or the average value of a set of data agree with the true value being determined is the **accuracy** of the data. The relationship between accuracy and precision is shown graphically in Figure 25.2. Although the average of a set of randomly scattered, imprecise results may be close to the true value, normally the average of a set of imprecise results is inaccurate as well.

In doing analytical calculations and expressing analytical results, it is important to know and correctly handle and express the **uncertainties** of the numbers used, a

concept discussed in Chapter 1, Section 1.7. For example, a skilled analyst can read the volume delivered by a laboratory buret to the nearest 0.01 mL. Therefore, a volume expressed as 36.27 mL implies that the volume is within ± 0.01 mL of 36.27 mL and has an uncertainty of 0.01 mL. It would be incorrect to express the volume 36.270 mL because it is not known to the nearest 0.001 mL as that number would imply. It would also be incorrect to express the volume as 36.3 mL because the value is known more accurately than ± 0.1 mL. In calculations involving measured laboratory quantities the rules for handling significant figures as discussed in Section 1.7 must be followed.

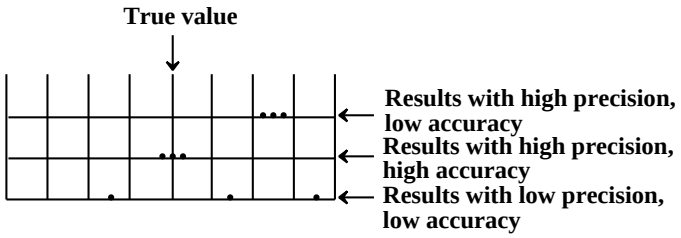


Figure 25.2 Representation of precision and accuracy. Each solid circle, •, stands for an experimentally determined value.

The uncertainty of a number from an analytical measurement, such as the ± 0.01 mL discussed above, is the **absolute uncertainty** of the measurement. The **relative uncertainty** of a measured value is given by the equation

$$\text{Relative uncertainty} = \frac{\text{Absolute uncertainty}}{\text{Measured value}} \qquad (25.4.1)$$

Commonly, relative uncertainty is expressed in parts per thousand (ppt) a value given by multiplying the result of the above equation by 1000. In the example of the volume of 36.27 mL delivered by a buret as discussed above, the relative uncertainty in parts per thousand is

$$\text{Relative uncertainty} = \frac{0.01\ \text{mL}}{36.27\ \text{mL}} \times 1000 = 0.3\ \text{ppt} \qquad (25.4.1)$$

If the buret had been used to deliver only 1.52 mL, the absolute uncertainty would still be 0.01 mL, but the relative uncertainty would be the following:

$$\text{Relative uncertainty} = \frac{0.01\ \text{mL}}{1.52\ \text{mL}} \times 1000 = 6\ \text{ppt} \qquad (25.4.1)$$

The relative uncertainty in measuring the smaller volume is much greater. That is why in such measurements it is generally more accurate to measure a larger quantity, when it is possible to do so.

Error and the uncertainty that it adds to analytical calculations are very important aspects of analytical chemistry. It is beyond the scope of this book to discuss those concepts in detail. However, any reader required to do chemical analysis and the calculations resulting therefrom should consult more-extensive works dealing with the topic.

25.5 GRAVIMETRIC ANALYSIS

Conceptually the most straightforward kind of quantitative analysis, **gravimetric analysis** consists of isolating in a pure form a species produced stoichiometrically by the analyte, weighing it, and calculating the percentage of analyte in the sample. Obtaining a pure, weighable product is often a complicated process. A number of ways of doing that have been developed. The most common of these is formation of a precipitate by a reaction of the analyte in solution. As an example, the chloride content of a weighed, water-soluble sample can be determined by precipitating the chloride in the dissolved sample with excess silver nitrate solution:

$$\underbrace{Ag^+(aq) + NO_3^-(aq)}_{\text{Silver nitrate reagent}} + \underbrace{Cl^-(aq)}_{\text{Chloride analyte}} \rightarrow \underbrace{AgCl(s)}_{\text{Silver chloride precipitate}} + NO_3^-(aq) \qquad (25.5.1)$$

The silver chloride precipitate, which can be produced in a very pure form, is collected on a weighed filter crucible (Figure 25.3) and washed to remove extraneous residual salts. After drying to remove excess water, the crucible and precipitate are weighed to get the mass of precipitate and the percentage of chloride is calculated by stoichiometric calculation. Where the atomic mass of chloride is 35.45 g/mol and the molar mass of AgCl is 143.32 g/mol, the calculation is

$$\text{Mass chloride} = \text{mass AgCl} \times \frac{1 \text{ mol AgCl}}{143.32 \text{ g AgCl}} \times \frac{1 \text{ mol } Cl^-}{1 \text{ mol AgCl}} \times \frac{35.45 \text{ g } Cl^-}{1 \text{ mol Cl}} \qquad (25.5.2)$$

$$\text{Percent chloride} = \frac{\text{mass chloride}}{\text{mass sample}} \times 100 \qquad (25.5.3)$$

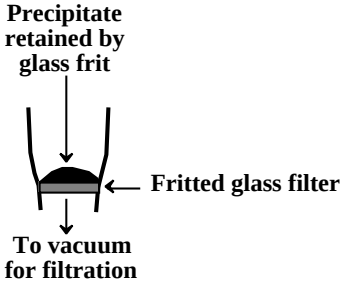


Figure 25.3 Filter crucible used to collect and weigh precipitates for gravimetric analysis.

Suppose, for example, that a 1.2643 g sample containing chloride yielded 0.9285 g of AgCl precipitate. The percentage of chloride in the sample is

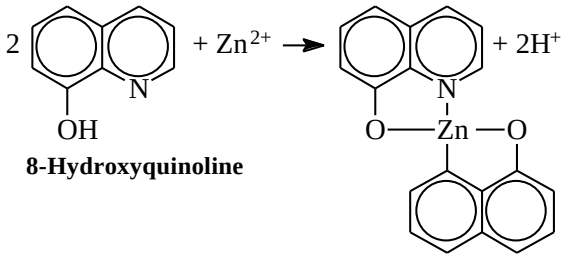
$$\text{Mass chloride} = 0.9285 \text{ g AgCl} \times \frac{1 \text{ mol AgCl}}{143.32 \text{ g AgCl}} \times \frac{1 \text{ mol } Cl^-}{1 \text{ mol AgCl}} \times \frac{35.45 \text{ g } Cl^-}{1 \text{ mol Cl}}$$

$$\text{Mass chloride} = 0.2297 \text{ g}$$

$$\text{Percent chloride} = \frac{0.2997 \text{ g}}{1.2643 \text{ g}} \times 100 = 18.17\%$$

Over the decades before more-modern instrumental methods of analysis were developed, gravimetric techniques were developed for a wide range of analytes. Examples include sulfate determined by precipitating $BaSO_4$ with $BaCl_2$ reagent; calcium precipitated as the oxalate CaC_2O_4, which, in turn, could be heated to produce weighable $CaCO_3$ or CaO; and magnesium precipitated as an ammonium phosphate salt, then heated to produce $Mg_2P_2O_7$.

The versatile nature of organic chemistry led to a number of organic reagents used to form precipitates with analytes, especially metals. One widely used reagent was 8-hydroxyquinoline shown forming a precipitate with zinc ion in the reaction below:



8-Hydroxyquinoline

Precipitate of the 8-hydroxyquinolate chelate of zinc(II)

(25.5.4)

Two 8-hydroxyquinoline anions (formed by loss of H^+) bind with Zn^{2+} ion as shown above to produce a chelate species (see Chapter 11, Section 11.9) that can be weighed to calculate the amount of zinc in the sample. Organic precipitants with high molar masses, such as 8-hydroxyquinoline, offer an advantage for gravimetric analysis in that they produce a relatively high mass of precipitate from comparatively little analyte. Higher masses of precipitates translate to less relative error in weighing, thus increasing the accuracy of the determination.

One of the simplest gravimetric techniques in those limited cases where it is applicable is the precipitation of a metal from solution by electrodeposition onto a cathode. A good example is the determination of copper, which can be plated onto a weighed platinum electrode by the following electrochemical half-reaction:

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s) \qquad (25.5.5)$$

weighing the platinum electrode after electrodeposition is complete gives a mass of copper that can then be used to calculate the percentage of copper in the sample.

In some cases, gravimetric analysis can be performed by collecting a gas given off by a chemical reaction and weighing it. One of the classic methods for determining the percentage of carbon in an organic species is to oxidize the organic to convert the carbon to CO_2, collect the carbon dioxide given off quantitatively, and weigh it in the collection tube. Volatile matter contents of samples can be determined by weighing a sample before and after heating, with the difference being the mass of volatile matter in the sample. One such means of gravimetric analysis still widely applied is the gravimetric determination of water in a solid sample by this

method.

Although gravimetric analysis is now largely of historical interest, it remains a versatile analytical technique. In addition to being applicable to a wide range of analytes, gravimetric analysis is capable of giving highly accurate results.

25.6 VOLUMETRIC ANALYSIS: TITRATION

Other than gravimetric analysis, the other major type of classical "wet chemical" analysis technique consists of measuring the volume of a reagent required to react with an analyte. Such a procedure is called **titration**, which involves the following:

- A measured quantity of sample that may consist of a weighed quantity of a solid, or a measured volume of a solution and the unknown, is placed in solution.
- A **standard solution** of known concentration of a reagent that reacts quantitatively with the analyte is added to the unknown with a buret so that the volume of standard solution can be measured accurately.
- An **indicator** consisting of a dye that changes color, or some other means, is used to detect an **end point**, the experimental representation of the **equivalence point** at which exactly the stoichiometric amount of reagent required to react with analyte occurs. The volume at which the end point occurs is recorded from the buret.
- The quantity or concentration of analyte is calculated from the stoichiometry of the titration reaction.

The most common type of titration reaction consists of acid-base titration in which an unknown quantity or concentration of acid is titrated with standard base or vice versa. For example, a solution of hydrochloric acid of unknown concentration can be titrated with a standard solution of sodium hydroxide base using as an indicator phenolphthalein, which changes from colorless to pink at the end point. The physical steps involved in the titration are shown in Figure 25.4. The reaction between the HCl and NaOH is the following:

$$\underset{\text{Hydrochloric acid analyte}}{H^+ + Cl^-} + \underset{\text{sodium hydroxide titrant}}{Na^+ + OH^-} \rightarrow H_2O + Na^+ + Cl^- \qquad (25.6.1)$$

Before the end point, there is excess H^+, so the pH is less than 7 (see Section 6.6 for a discussion of pH and the pH values in acidic and basic solutions). Beyond the end point, there is excess base, and the pH is greater than 7. Since HCl is a strong (completely ionized) acid and NaOH is a strong (completely ionized) base, the pH at the end point is exactly 7. (See Section 6.4 for a discussion of strong and weak acids and bases.) Furthermore, the pH changes very markedly by several pH units with the addition of just a few drops of sodium hydroxide titrant at a volume that is in the immediate vicinity of the end point. This change is reflected by the abrupt change in color of the phenolphthalein indicator from colorless to pink at the end point, where the addition of titrant is stopped, and the end point volume recorded.

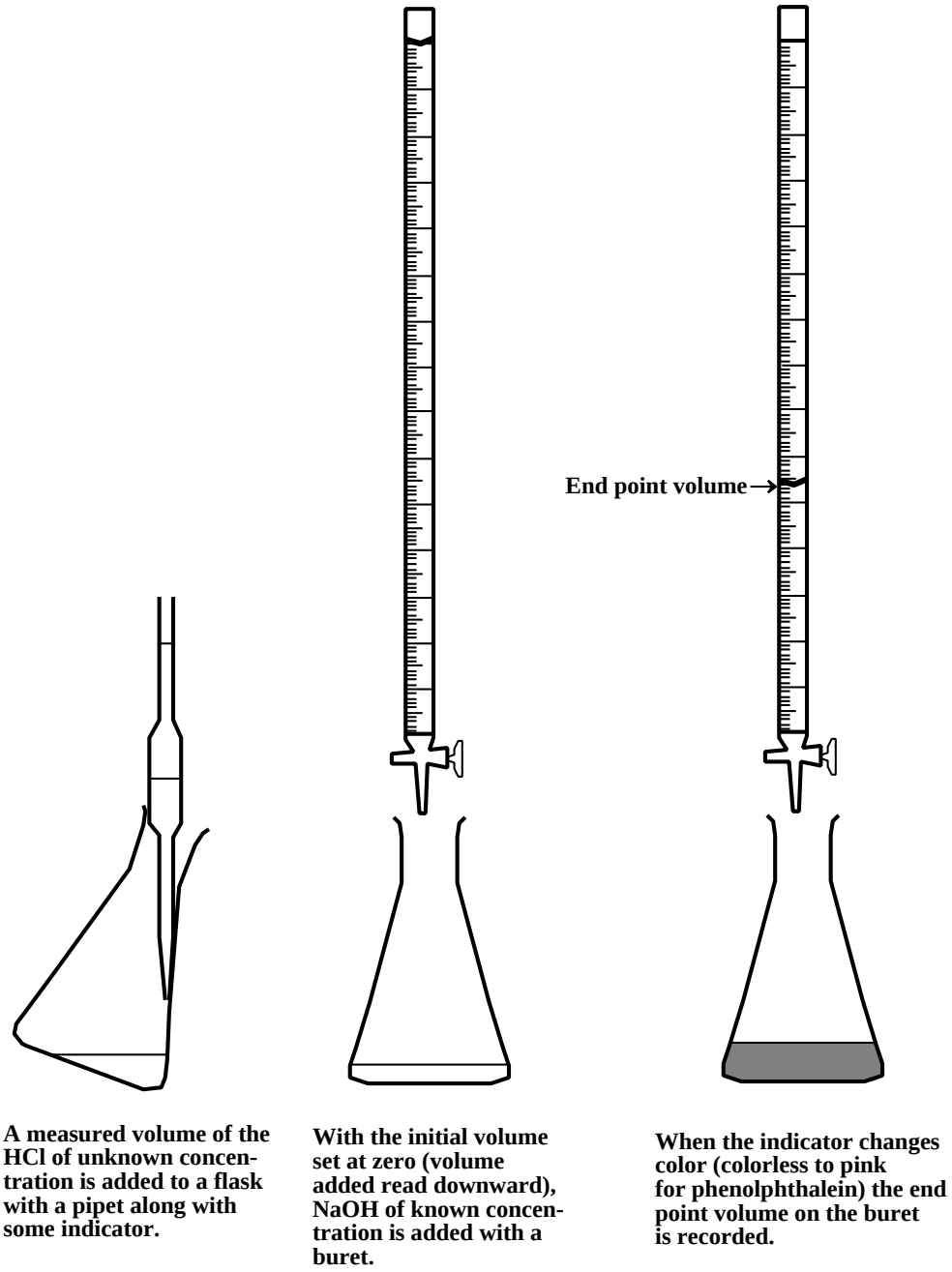


Figure 25.4 Steps in the titration of an unknown HCl solution with standard NaOH.

As noted in the preceding discussion, the course of acid-base titrations is reflected by the pH of the solution in the reaction flask as titrant is added. By using a device called a pH meter, the pH can be recorded and plotted as a function of added titrant. The result is a **titration curve** (Figure 25.5).

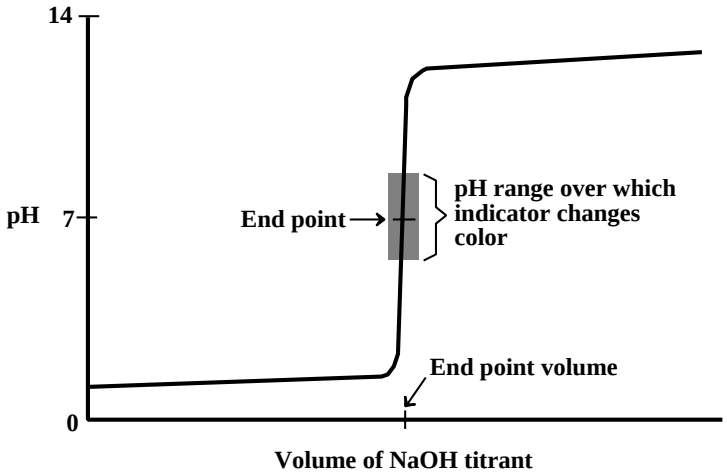


Figure 25.5 Titration curve as a plot of pH versus volume of titrant for the titration of HCl with NaOH titrant. A indicator changes color over a pH range, which indicates the end point.

Stoichiometry is the basis of calculations in titrimetric analysis. In the reaction,

$$H^+ + Cl^- + Na^+ + OH^- \rightarrow H_2O + Na^+ + Cl^- \qquad (25.6.1)$$

there is a 1/1 mole ratio of NaOH added to HCl in the sample at the end point, so the following relationship holds:

$$\text{Moles HCl} = \text{moles NaOH} \qquad (25.6.2)$$

From the definition of molarity, where M is the molar concentration and volume is in liters, the equations

$$M_{HCl} = \frac{\text{moles HCl}}{\text{Volume HCl}}, \text{ Moles HCl} = M_{HCl} \times (\text{Volume HCl}) \qquad (25.6.3)$$

and

$$M_{NaOH} = \frac{\text{moles NaOH}}{\text{Volume NaOH}}, \text{ Moles NaOH} = M_{NaOH} \times (\text{Volume NaOH}) \qquad (25.6.4)$$

relate the molar concentrations and volumes of HCl and NaOH. From the equations above, the concentration of a sample of HCl of carefully measured volume titrated with NaOH of known concentration and measured with a buret is given by the following:

$$M_{HCl} = \frac{(\text{Volume NaOH}) \times M_{NaOH}}{\text{Volume HCl}} \qquad (25.6.5)$$

Example: A 50.0 mL sample of HCl required 42.53 mL of 0.1005 M NaOH for titration. What was the concentration of HCl?

$$M_{HCl} = \frac{(\text{Volume NaOH}) \times M_{NaOH}}{\text{Volume HCl}} = \frac{0.04253\ \text{L} \times 0.1005\ \text{mol/L}}{0.05000\ \text{L}}$$

$$= 0.0855\ \text{mol/L}$$

Titration can also be used to determine percentage composition of samples. For example, consider that a 1.136 g sample containing solid NaOH and inert material was weighed out, dissolved and titrated with 0.1036 M standard HCl, of which 48.61 mL was required. What was the percentage of NaOH, molar mass 40.0, in the sample? At the end point, the number of moles of NaOH in the sample exactly equals the number of moles of HCl added. But, because the NaOH is in a solid and the mass of NaOH is needed to calculate the percentage of it in the sample, the following equation can be used:

$$\frac{\text{Mass NaOH}}{\text{molar mass NaOH}} = \text{mol NaOH} = \text{mol HCl} = (\text{Volume HCl}) \times M_{HCl} \qquad (25.6.6)$$

$$\text{Mass NaOH} = (\text{molar mass NaOH}) \times (\text{Volume HCl}) \times M_{HCl}$$

$$\text{Mass NaOH} = 40.0\ \text{g/mol} \times 0.04861\ \text{L} \times 0.1306\ \text{mol/L}$$

$$= 0.254\ \text{g NaOH}$$

$$\text{Percent NaOH} = \frac{0.254\ \text{g}}{1.136\ \text{g}} \times 100 = 22.4\%\ \text{NaOH}$$

Hydrochloric acid and sodium hydroxide react in a 1/1 mole ratio. But titrations can also be considered when the reaction is in a different mole ratio. For example, if a standard solution of NaOH is used to neutralize sulfuric acid, H_2SO_4, the reaction is

$$\underbrace{2H^+ + SO_4^{2-}}_{\textbf{Sulfuric acid}} + \underbrace{2(Na^+ + OH^-)}_{\textbf{Sodium hydroxide}} \rightarrow 2H_2O + 2Na^+ + SO_4^{2-} \qquad (25.6.7)$$

From this reaction it is seen that there are 2 moles NaOH reacting for each mole H_2SO_4 so

$$\text{moles NaOH} = 2 \times (\text{moles } H_2SO_4) \qquad (25.6.8)$$

Therefore, the relationship between the molar concentration of a sulfuric acid solution, its volume, the molar concentration of an NaOH solution used to neutralize the H_2SO_4 and its volume is

$$M_{NaOH} \times \text{volume NaOH} = 2 \times (M_{H_2SO_4} \times \text{volume } H_2SO_4) \qquad (25.6.9)$$

Several different kinds of reactions other than acid-base reactions can be used for titrations. The oldest titration is a precipitation titration of chloride with silver nitrate, the Mohr method dating from 1856:

$$Ag^{+}(aq) + NO_3^{-}(aq) + Cl^{-}(aq) \rightarrow AgCl(s) + NO_3^{-} \quad (25.6.10)$$

Chromate ion, CrO_4^{2-}, is added to the mixture to indicate the end point. When excess Ag^{+} is added beyond the end point, red solid Ag_2CrO_4—which is more soluble than the white AgCl precipitate—begins to form, indicating that the end point has been reached.

Salts of the strong chelating agent ethylenediaminetetraacetic acid can be used to chelate metal ions in a 1/1 reaction. The chelating EDTA anion, represented Y^{4-}, reacts with metal ions being titrated, such as Ca^{2+},

$$Ca^{2+} + Y^{4-} \rightarrow CaY^{2-} \quad (25.6.11)$$

to produce the stable metal chelate, in this case CaY^{2-}. An indicator can be used that forms a colored chelate with the metal being titrated. This species is less stable than the EDTA chelate and when the last of the excess metal ion is chelated by EDTA, the metal-indicator chelate disappears and the color of the solution changes showing that the end point has been reached. The titration of calcium with EDTA has been used for decades to measure water hardness.

Another type of titration reaction that can be used for volumetric analysis is oxidation-reduction. For example, Fe^{2+} ion can be determined by its oxidation to Fe^{3+} ion by a solution of potassium permanganate, $KMnO_4$. The reaction is

$$5Fe^{2+} + 8H^{+} + MnO_4^{-} \rightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O \quad (25.6.12)$$

and it is self-indicating because in solution MnO_4^{-} has an intense purple color and the solution turns color when the end point is reached and a slight excess of MnO_4^{-} appears.

25.7 SPECTROPHOTOMETRIC METHODS

Up to this point, this chapter has covered classical methods of analysis based upon simple weighing and volume measurement. At an accelerating pace over recent decades, analytical chemistry has benefited from a wide array of analysis techniques that use instruments to observe a variety of phenomena that reflect kinds and concentrations of analytes. There are many such instrumental techniques. The main ones, based upon absorption or emission of electromagnetic radiation, production of electrical voltages or currents, separation and detection of small quantities of analytes (chromatography), and separation and detection of ions produced by analytes (mass spectrometry), are introduced in the remainder of this chapter. These are all **instrumental methods** of analysis. Several other techniques of analysis are introduced in Chapter 26.

Superimposed on instrumental methods of analysis since about 1980 have been an array of computerized control and data analysis techniques. Essentially all modern instruments for chemical analysis of any size are now computerized. A related development has been the miniaturization of instruments and the placing of instrument components and even whole instruments on microchips fabricated from silica, glass, or plastic.

Absorption Spectrophotometry

Absorption spectrophotometry of light-absorbing species in solution, historically called colorimetry when visible light is absorbed, is still used for the analysis of many water, and some air, pollutants. Basically, absorption spectrophotometry consists of measuring the percent transmittance (%T) of monochromatic light passing through a light-absorbing solution as compared with the amount passing through a blank solution containing everything in the medium but the sought-for constituent (100%). The absorbance (A) is defined as the following:

$$A = \log \frac{100}{\%T} \tag{25.7.1}$$

The relationship between A and the concentration (C) of the absorbing substance is given by Beer's law:

$$A = abC \tag{25.7.2}$$

where a is the absorptivity, a wavelength-dependent parameter characteristic of the absorbing substance; b is the path length of the light through the absorbing solution; and C is the concentration of the absorbing substance. A linear relationship between A and C at constant path length indicates adherence to Beer's law. In many cases, analyses can be performed even when Beer's law is not obeyed, if a suitable calibration curve is prepared. A color-developing step usually is required in which the sought-for substance reacts to form a colored species, and in some cases a colored species is extracted into a nonaqueous solvent to provide a more intense color and a more concentrated solution.

Atomic Absorption and Emission Analyses

Atomic absorption analysis is commonly used for the determination of metals in environmental samples. This technique is based upon the absorption of monochromatic light by a cloud of atoms of the analyte metal. The monochromatic light can be produced by a source composed of the same atoms as those being analyzed. The source produces intense electromagnetic radiation with a wavelength exactly the same as that absorbed by the atoms, resulting in extremely high selectivity. The basic components of an atomic absorption instrument are shown in Figure 25.6. The key element is the hollow cathode lamp in which atoms of the analyte metal are energized such that they become electronically excited and emit radiation with a very narrow wavelength band characteristic of the metal. This radiation is guided by the appropriate optics through a flame into which the sample is aspirated. In the flame, most metallic compounds are decomposed, and the metal is reduced to the elemental state, forming a cloud of atoms. These atoms absorb a fraction of radiation in the flame. The fraction of radiation absorbed increases with the concentration of the sought-for element in the sample according to the Beer's law relationship (Eq. 25.7.2). The attenuated light beam next goes to a monochromator to eliminate extraneous light resulting from the flame, and then to a detector.

Atomizers other than a flame can be used. The most common of these is the graphite furnace, an electrothermal atomization device that consists of a hollow graphite cylinder placed so that the light beam passes through it. A small sample of up to 100 µL is inserted in the tube through a hole in the top. An electric current is passed through the tube to heat it—gently at first to dry the sample, then rapidly to vaporize and excite the metal analyte. The absorption of metal atoms in the hollow portion of the tube is measured and recorded as a spike-shaped signal. A diagram of a graphite furnace with a typical output signal is shown in Figure 25.7. The major advantage of the graphite furnace is that it gives detection limits up to 1000 times lower than those of conventional flame devices.

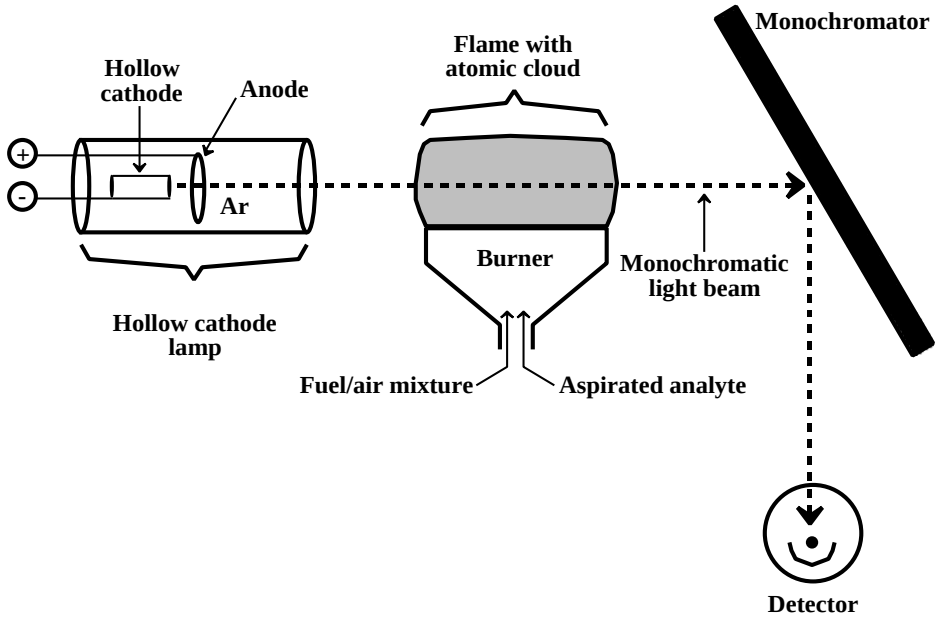


Figure 25.6 The basic components of a flame atomic absorption spectrophotometer.

A special technique for the flameless atomic absorption analysis of mercury involves room-temperature reduction of mercury to the elemental state by tin(II) chloride in solution, followed by sweeping the mercury into an absorption cell with air. Nanogram (10^{-9}g) quantities of mercury can be determined by measuring mercury absorption at 253.7 nm.

Atomic Emission Techniques

Metals can be determined in water, atmospheric particulate matter, and biological samples very well by observing the spectral lines emitted when they are heated to a very high temperature. An especially useful atomic emission technique is inductively coupled plasma atomic emission spectroscopy (ICP/AES). The "f1ame" in which analyte atoms are excited in plasma emission consists of an incandescent plasma (ionized gas) of argon heated inductively by radiofrequency energy at 4–50 MHz and 2–5 kW (Figure 25.8). A stream of ionized argon absorbs the energy from

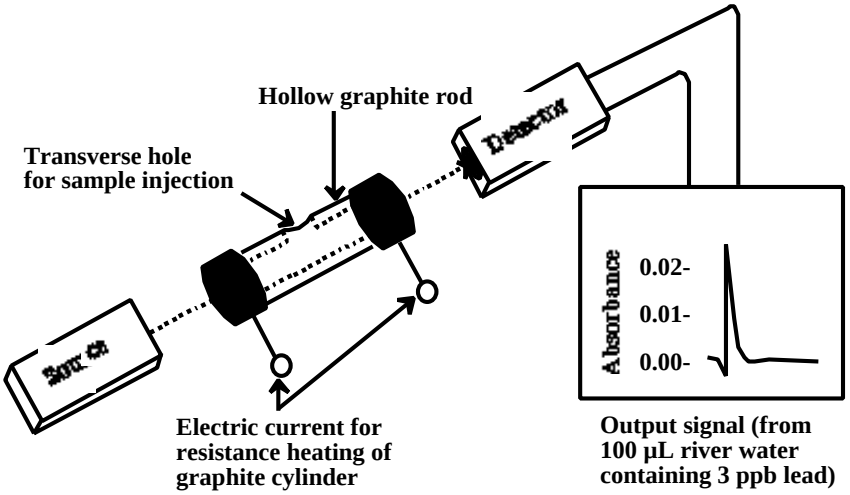


Figure 25.7 Graphite furnace for atomic absorption analysis and typical output signal.

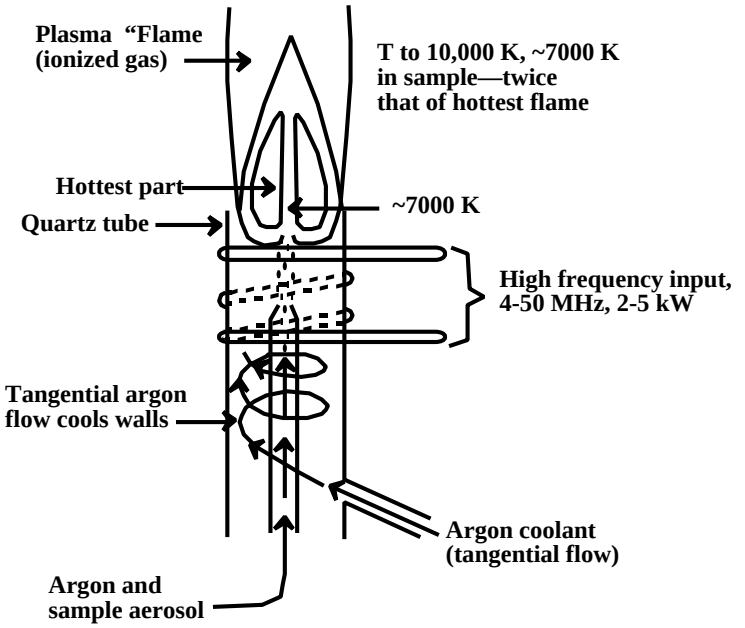


Figure 25.8 Schematic diagram showing inductively coupled plasma used for optical emission spectroscopy.

an induction coil, producing temperatures up to 10,000 K. The sample atoms are subjected to temperatures around 7000 K, twice those of the hottest conventional flames (for example, nitrous oxide-acetylene operates at 3200 K). Since emission of light increases exponentially with temperature, lower detection limits are obtained. Furthermore, the technique enables emission analysis of some of the environmentally important metalloids such as arsenic, boron, and selenium. Interfering chemical

reactions and interactions in the plasma are minimized as compared with flames. Of greatest significance, however, is the capability of analyzing as many as 30 elements simultaneously, enabling a true multielement analysis technique. Plasma atomization combined with mass spectrometric measurement of analyte elements is a relatively new technique that is an especially powerful means for multielement analysis.

25.8 ELECTROCHEMICAL METHODS OF ANALYSIS

Several useful techniques for water analysis utilize electrochemical sensors. These techniques can be potentiometric, voltammetric, or amperometric. Potentiometry is based upon the general principle that the relationship between the potential of a measuring electrode and that of a reference electrode is a function of the log of the activity of an ion in solution. For a measuring electrode responding selectively to a particular ion, this relationship is given by the Nernst equation,

$$E = E^o + \frac{2.303RT}{zF} \log(a_z) \qquad (25.8.1)$$

where E is the measured potential; E^o is the standard electrode potential; R is the gas constant; T is the absolute temperature; z is the signed charge (+ for cations, - for anions); *F* is the Faraday constant; and a is the activity of the ion being measured. At a given temperature, the quantity 2.303RT/*F* has a constant value; at 25°C it is 0.0592 volt (59.2 mv). At constant ionic strength, the activity, a, is directly proportional to concentration, and the Nernst equation can be written as the following for electrodes responding to Cd^{2+} and F^-, respectively:

$$E \text{ (in mv)} = E^o + \frac{59.2}{2} \log [Cd^{2+}] \qquad (25.8.2)$$

$$E = E^o - 59.2 \log [F^-] \qquad (25.8.3)$$

Electrodes that respond more or less selectively to various ions are called **ion-selective electrodes**. Generally, the potential-developing component is a membrane of some kind that allows for selective exchange of the sought-for ion. The glass electrode used for the measurement of hydrogen-ion activity and pH is the oldest and most widely used ion-selective electrode. The potential is developed at a glass membrane that selectively exchanges hydrogen ion in preference to other cations, giving a Nernstian response to hydrogen ion activity, a_{H^+}:

$$E = E^o + 59.2 \log(a_{H^+}) \qquad (25.8.4)$$

Of the ion-selective electrodes other than glass electrodes, the fluoride electrode is the most successful. It is well-behaved, relatively free of interferences, and has an adequately low detection limit and a long range of linear response. Like all ion-selective electrodes, its electrical output is in the form of a potential signal that is proportional to log of concentration. A small error in E leads to a variation in log of concentration, which leads to relatively high concentration errors.

Voltammetric techniques, the measurement of current resulting from potential applied to a microelectrode, have found some applications in water analysis. One

such technique is differential-pulse polarography, in which the potential is applied to the microelectrode in the form of small pulses superimposed on a linearly increasing potential. The current is read near the end of the voltage pulse and compared with the current just before the pulse was applied. It has the advantage of minimizing the capacitive current from charging the microelectrode surface, which sometimes obscures the current due to the reduction or oxidation of the species being analyzed. Anodic-stripping voltammetry involves deposition of metals on an electrode surface over a period of several minutes followed by stripping them off very rapidly using a linear anodic sweep. The electrodeposition concentrates the metals on the electrode surface, and increased sensitivity results. An even better technique is to strip the metals off using a differential pulse signal. A differential-pulse anodic-stripping voltammogram of copper, lead, cadmium, and zinc in tap water is shown in Figure 25.9.

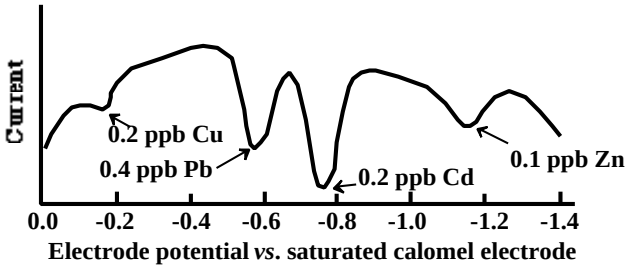


Figure 25.9 Differential-pulse anodic-stripping voltammogram of tap water at a mercury-plated, wax-impregnated graphite electrode.

25.9 CHROMATOGRAPHY

First described in the literature in the early 1950s, gas chromatography has played an essential role in the analysis of organic materials. Gas chromatography is both a qualitative and quantitative technique; for some analytical applications of environmental importance, it is remarkably sensitive and selective. Gas chromatography is based upon the principle that when a mixture of volatile materials transported by a carrier gas is passed through a column containing an adsorbent solid phase or, more commonly, an absorbing liquid phase coated on a solid material, each volatile component will be partitioned between the carrier gas and the solid or liquid. The length of time required for the volatile component to traverse the column is proportional to the degree to which it is retained by the nongaseous phase. Since different components may be retained to different degrees, they will emerge from the end of the column at different times. If a suitable detector is available, the time at which the component emerges from the column and the quantity of the component are both measured. A recorder trace of the detector response appears as peaks of different sizes, depending upon the quantity of material producing the detector response. Both quantitative and (within limits) qualitative analyses of the sought-for substances are obtained.

The essential features of a gas chromatograph are shown schematically in Figure 25.10. The carrier gas generally is argon, helium, hydrogen, or nitrogen. The sample

is injected as a single compact plug into the carrier gas stream immediately ahead of the column entrance. If the sample is liquid, the injection chamber is heated to vaporize the liquid rapidly. The separation column may consist of a metal or glass tube packed with an inert solid of high surface area covered with a liquid phase, or it may consist of an active solid, which enables the separation to occur. More commonly, capillary columns are now employed that consist of very small-diameter, very long tubes in which the liquid phase is coated on the inside of the column.

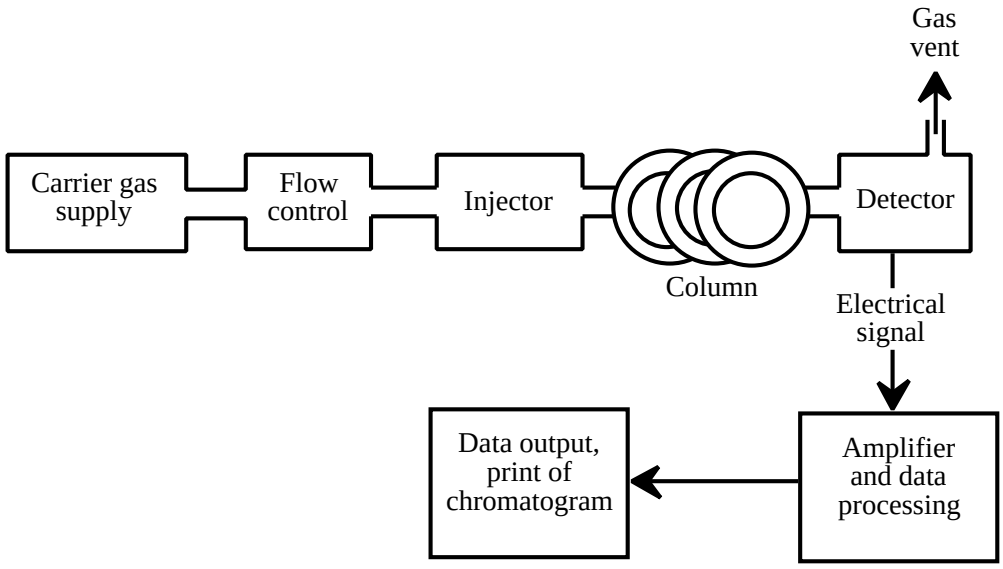


Figure 25.10 Schematic diagram of the essential features of a gas chromatograph.

The component that primarily determines the sensitivity of gas chromatographic analysis and, for some classes of compounds, the selectivity as well, is the detector. One such device is the thermal conductivity detector, which responds to changes in the thermal conductivity of gases passing over it. The electron-capture detector, which is especially useful for halogenated hydrocarbons and phosphorus compounds, operates through the capture of electrons emitted by a beta-particle source. The flame-ionization gas chromatographic detector is very sensitive for the detection of organic compounds. It is based upon the phenomenon by which organic compounds form highly conducting fragments, such as C^+, in a flame. Application of a potential gradient across the flame results in a small current that can be readily measured. The mass spectrometer, described in Section 25.10, can be used as a detector for a gas chromatograph. A combined gas chromatograph/mass spectrometer (GC/MS) instrument is an especially powerful analytical tool for organic compounds.

Gas chromatographic analysis requires that a compound exhibit at least a few mm of vapor pressure at the highest temperature at which it is stable. In many cases, organic compounds that cannot be passed through a chromatographic column directly can be converted to derivatives that are amenable to gas chromatographic analysis. It is seldom possible to analyze organic compounds in water by direct

injection of the water into the gas chromatograph; higher concentration is usually required. Two techniques commonly employed to remove volatile compounds from water and concentrate them are (1) extraction with solvents and (2) purging volatile compounds with a gas, such as helium; concentrating the purged gases on a short column; and driving them off by heat into the chromatograph.

High-Performance Liquid Chromatography

A liquid mobile phase used with very small column-packing particles enables high-resolution chromatographic separation of materials in the liquid phase. Very high pressures up to several thousand psi are required to get a reasonable flow rate in such systems. Analysis using such devices is called **high-performance liquid chromatography** (HPLC) and offers an enormous advantage in that the materials analyzed need not be changed to the vapor phase, a step that often requires preparation of a volatile derivative or results in decomposition of the sample. The basic features of a high-performance liquid chromatograph are the same as those of a gas chromatograph, shown in Figure 25.10, except that a solvent reservoir and high-pressure pump are substituted for the carrier gas source and regulator. A hypothetical HPLC chromatogram is shown in Figure 25.11. Refractive index and ultraviolet detectors are both used for the detection of peaks coming from the liquid chromatograph column. Fluorescence detection can be especially sensitive for some classes of compounds. Mass spectrometric detection of HPLC effluents has led to the development of LC/MS analysis. Somewhat difficult in practice, this technique can be a powerful tool for the determination of analytes that cannot be subjected to gas chromatography. High-performance liquid chromatography has emerged as a very useful technique for the analysis of a number of water pollutants.

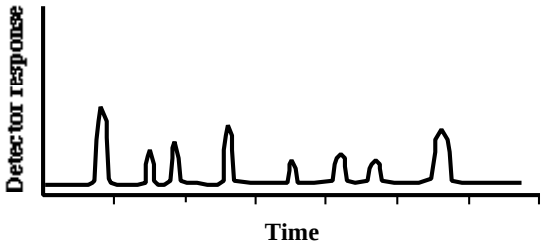


Figure 25.11 Hypothetical HPLC chromatogram.

25.10 MASS SPECTROMETRY

Mass spectrometry is particularly useful for the identification of specific organic pollutants. It depends upon the production of ions by an electrical discharge or chemical process, followed by separation based on the charge-to-mass ratio and measurement of the ions produced. The output of a mass spectrometer is a mass spectrum, such as the one shown in Figure 25.12. A mass spectrum is characteristic of a compound and serves to identify it. Computerized data banks for mass spectra have been established and are stored in computers interfaced with mass spectrometers. Identification of a mass spectrum depends upon the purity of the compound from which the spectrum is taken. Prior separation by gas

chromatography with continual sampling of the column effluent by a mass spectrometer, commonly called gas chromatography-mass spectrometry (GC/MS), is particularly effective in the analysis of organic pollutants.

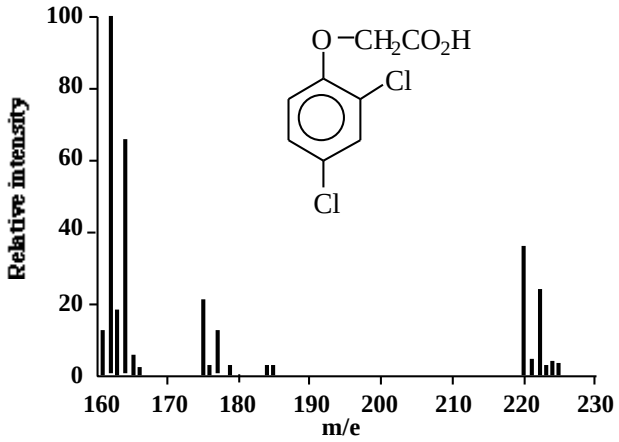


Figure 25.12 Partial mass spectrum of the herbicide 2,4-dichlorophenoxyacetic acid (2,4-D), a common water pollutant.

25.11 AUTOMATED ANALYSES

Huge numbers of analyses must often be performed to get meaningful results and for reasons of economics. This has resulted in the development of a number of automated procedures in which traditional "wet chemical" methods of analysis have been adopted to automated procedures. With such procedures, the samples are introduced through a sampler and the analyses performed and results posted without manual manipulation of reagents and apparatus. Such procedures have been developed and instruments marketed for the determination of a number of analytes. In water, automated analyses have been developed from wet chemical procedures for alkalinity, sulfate, ammonia, nitrate/nitrite, and metals. The somewhat cumbersome West-Gaeke determination of sulfur dioxide in air has been adapted to automated analyzers. Colorimetric procedures are popular for such automated analytical instruments, using simple, rugged colorimeters for absorbance measurements.

Figure 25.13 shows an automated analytical system for the determination of water alkalinity. The reagents and sample liquids are transported through the analyzer by a peristaltic pump. This relatively simple device consists basically of rollers moving over flexible tubing, which "squeezes" solutions through the tubing. By using different sizes of tubing and varying the speed of the rollers, the flow rates of the reagents are proportioned. Air bubbles are introduced into the liquid stream to aid mixing and to separate one sample from another. Mixing of the sample and various reagents is accomplished in mixing coils. Since many color-developing reactions are not rapid, a delay coil is provided that allows the color to develop before reaching the colorimeter. Bubbles are removed from the liquid stream by a debubbler pror to introduction into the flowcell for colorimetric analysis.

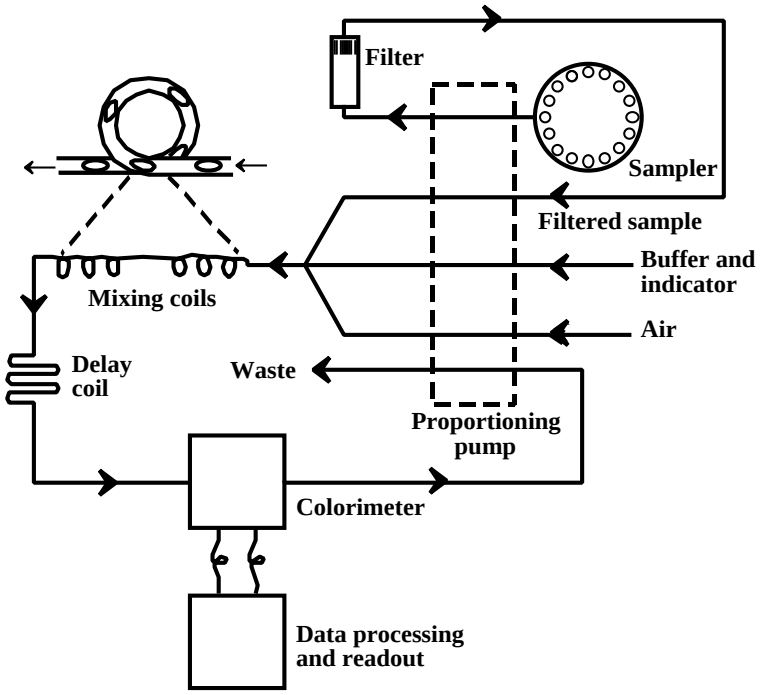


Figure 25.13 Automated analyzer system for the determination of total alkalinity in water. Addition of a water sample to a methyl orange solution buffered to pH 3.1 causes a loss of color in proportion to the alkalinity in the sample.

25.12 IMMUNOASSAY SCREENING

Immunoassay has emerged as a useful technique for screening samples, such as hazardous-waste residues, for specific kinds of pollutants. Commercial immunoassay techniques have been developed that permit very rapid analyses of large numbers of samples. A variety of immunoassay techniques have been developed. These techniques all use biologically produced antibodies that bind specifically to analytes or classes of analytes. This binding is combined with chemical processes that enable detection through a signal-producing species (reporter reagent) such as enzymes, chromophores, fluorophores, and luminescent compounds. The reporter reagent binds with the antibody. When an analyte is added to the antibody to displace the reagent, the concentration of displaced reagent is proportional to the level of analyte displacing it from the antibody. Detection of the displaced reporter reagent enables quantification of the analyte.

Immunoassay techniques are divided into the two major categories of heterogeneous and homogeneous; the former requires a separation (washing) step, whereas the latter does not require such a step. Typically, when heterogeneous procedures are used, the antibody is immobilized on a solid support on the inner surface of a disposable test tube. The sample is contacted with the antibody displacing reporter reagent, which is removed by washing. The amount of reagent displaced, commonly

measured spectrophotometrically, is proportional to the amount of analyte added. Very widely used enzyme immunoassays make use of reporter reagent molecules bound with enzymes, and kits are available for enzyme-linked immunosorbent assays (ELISA) of a number of organic species likely to be found in hazardous wastes.

Immunoassay techniques have been approved for the determination of numerous analytes commonly found in hazardous wastes. Where the EPA method numbers are given in parentheses, these include pentachlorophenol (4010), 2,4-dichlorophenoxyacetic acid (4015), polychlorinated biphenyls (4020), petroleum hydrocarbons (4030), polycyclic aromatic hydrocarbons (4035), toxaphene (4040), chlordane (4041), DDT (4042), TNT explosives in soil (4050), and hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) in soil (4051). Enzyme-linked immunosorbent assays have been reported for monitoring pentachlorophenol, BTEX (benzene, toluene, ethylbenzene, and *o*-, *m*-, and *p*-xylene) in industrial effluents.

CHAPTER SUMMARY

The chapter summary below is presented in a programmed format to review the main points covered in this chapter. It is used most effectively by filling in the blanks, referring back to the chapter as necessary. The correct answers are given at the end of the summary.

In performing chemical analysis, a [1]_____ is performed to determine *what* is in a sample. The amount, concentration, composition, or percent of a substance present is determined by [2]_____. The major steps involved in the chemical analysis process are [3]_____ _____ _____. The first step in the analytical process is to obtain [4]_____. Sample processing is performed to [5]_____ _____. Based upon whether a sample is retained essentially in its original form, chemical analyses can be divided into the two categories of [6]_____. After sample processing, it is often necessary to eliminate [7]_____. The substance that is measured in a chemical analysis is the [8]_____, the specific measurement of this substance is referred to as a [9]_____, whereas the total process to which the sample is subjected is called [10]_____. Both qualitative and quantitative analysis are divided between [11]_____ methods involving primarily chemical reactions and simple measurements of mass and volume and [12]_____ that use instruments of varying degress of complexity and sophistication to measure quantities of analyte. Classical methods are often [13]_____ procedures using reagents in solution and reactions of dissolved analyte. The actual measurements involved in a chemical analysis can be divided into the two major categories of [14]_____ _____. The degree to which numbers in a group of analytical results are in agreement with each other is the [15]_____ of the group of numbers, a lack of which may indicate the presence of [16]_____ _____. [17]_____ errors vary randomly in direction

and magnitude and are from sources that [18]_____. [19]_____ errors always have a definite cause and are in the same direction. The extent to which the data or the average value of a set of data agree with the true value being determined is the [20]_____ of the data. Since a buret can be read to 0.01 mL, a volume of 36.27 mL read from a buret implies that the volume is between [21]____ and [22]____ mL. Dividing the absolute uncertainty of a number by the value being expressed gives the [23]_____. A conceptually simple means of quantitative analysis that consists of weighing samples, analytes and products of analytes is [24]_____. A precipitate is often collected for weighing in a [25]_____. The organic compound 8-hydroxyquinoline is useful as [26]_____ in the gravimetric analysis of metals. Other than gravimetric analysis, the other major type of classical "wet chemical" analysis technique is [27]_____ which consists of [28]_____ _____. The major aspects of this analytical procedure are [29]_____ _____ _____ _____ _____.

For the titration of an acid with a standard base, a plot of pH versus volume of added base titrant is a [30]_____. When a particular volume of a solution of an acid with one ionizable H per formula unit reacts with a base with one hydroxide per formula unit contained in a specified volume of base solution, the basic stoichiometric equation used that applies is [31]_____ _____. Other than acid-base reactions, titration reactions include [32]_____ _____ reactions. When titration with standard HCl is used to determine the mass of NaOH in a solid sample containing inert material along with the HCl, the equation used for the calculation is [33]_____.

In terms of percent transmittance in absorption spectrometry, absorbance, A, is given by the equation [34]_____. The relationship between the absorbance and the concentration of absorbing substance is called [35]_____ expressed mathematically as [36]_____. The principle of atomic absorption analysis is the [37]_____ by a [38]_____.

Often much lower detection limits can be determined by atomic absorption by using a device known as a [39]_____. A special technique of flameless atomic absorption analysis uses a cloud of "cold" atoms for the determination of the metal [40]_____. An atomic emission technique for elemental analysis that uses a particularly hot "flame" is [41]_____ _____.

Electrochemical methods of analysis may belong to the categories of [42]_____ _____. Ion-selective electrodes produce an electrical [43]_____ in response to various kinds of ions. Gas chromatography is based upon the principle that when a mixture of volatile materials transported by a carrier gas is passed through a [44]_____ that has the ability to retain analytes to varying degrees, different analytes come out at [45]_____ and appear as [46]_____ on a recorder trace. The

essential features of a gas chromatograph are [47]_____ _____ _____.
A chromatography system that uses a liquid mobile phase under very high pressure is called [48]_____.
A mass spectrum is [49]_____ of a compound and serves to [50]_____. The reagents and sample liquids are transported through an automated analyzer by a [51]_____ and [52]_____ are introduced into the liquid stream to aid mixing and to separate one sample from another. Immunoassay techniques of analysis use biologically produced [53]_____ _____ that act by [54]_____ _____.

Answers to Chapter Summary

1. qualitative analysis
2. quantitative analysis
3. (1) obtaining and preserving a representative sample, (2) sample processing, (3) measurement of analyte quantity, and (4) calculating results
4. a representative sample
5. get the sample into a form that can be analyzed
6. destructive and nondestructive
7. interferences
8. analyte
9. determination
10. an analysis
11. classical
12. instrumental methods
13. wet chemical
14. chemical and physical methods
15. precision
16. indeterminate, or random, errors
17. Indeterminate
18. cannot be determined
19. Determinate
20. accuracy
21. 36.26
21. 36.28
23. relative uncertainty
24. gravimetric analysis
25. filter crucible
26. an organic precipitant
27. titration
28. measuring the volume of a reagent required to react with an analyte
29. a measured quantity of sample is taken, a standard solution of standard solution is reacted with analyte, and indicator is used to show end point, and the quantity or concentration of analyte are calculated

30. titration curve
31. (volume acid) × M_{acid} = (volume base) × M_{base}
32. precipitation, chelation, and oxidation-reduction
33. $$\frac{\text{Mass NaOH}}{\text{molar mass NaOH}} = (\text{Volume HCl}) \times M_{HCl}$$
34. $$A = \log \frac{100}{\%T}$$
35. Beer's law
36. A = abc
37. absorption of light
38. cloud of atoms
39. graphite furnace atomizer
40. mercury
41. inductively coupled plasma atomic emission spectroscopy (ICP/AES)
42. potentiometric, voltammetric, or amperometric
43. potential
44. column
45. different times
46. peaks
47. carrier gas supply, flow control, injector, column, detector, and amplifier for the signal from the detector
48. high-performance liquid chromatography
49. characteristic
50. identify it
51. peristaltic pump
52. air bubbles
53. antibodies
54. binding specifically to analytes or classes of analytes

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QUESTIONS AND PROBLEMS

1. What is the general term applied to a constituent determined in a sample?
2. Mass and volume are the two parameters most generally measured in a chemical or wet chemical method of analysis. What two broad categories of analysis do these two measurements represent?
3. Match the following:

A. Representative sample	1.Must be removed or chemically sequestered to avoid affecting the determination
B. Sample processing	2.Actual process of finding out how much of an analyte is present
C. Interferences	3.Usually involves putting the sample into solution
D. Determination	4.Ideally should have a composition the same as that of the material whose composition is to be determined

4. Mass and volume are the two parameters most generally measured in a chemical or wet chemical method of analysis. What two broad categories of analysis do these two measurements represent?
5. The heat released per unit mass of coal was determined for the coal in a unit train containing 10,000 metric tons of coal. A representative sample was obtained by "grab sampling" 64 approximately 1-kg portions of coal from the train. These were reduced to three 1-g samples, for which the heat content was determined and the average taken. What percentage of the total coal in the train was taken for analysis?
6. What mass of $BaSO_4$, molar mass 233.4, can be precipitated from a solution containing 1.538 g of $Fe_2(SO_4)_3$, molar mass 399.9, by the addition of excess $BaCl_2$?
7. What mass of Fe_2O_3, molar mass 159.7, can be obtained by the reaction of 0.948 g of pure Fe, molar mass 55.8?

8. The chemical analysis of a sample of lake water for dissolved O_2 showed 0.668 mg of O_2 dissolved in a 75.0 mL sample of the water. What was the molar concentration of O_2 in the water?

9. A 25.00 mL sample of an industrial water stream containing Na_2CO_3 required 32.60 mL of a 0.1104 M solution of standard HCl to react with the Na_2CO_3 according to the reaction

   $$2HCl + Na_2CO_3 \rightarrow 2NaCl + H_2O + CO_2$$

   What was the concentration of Na_2CO_3 in the solution in units of mg/L?

10. Define titrant.

11. Describe the general characteristics of a titration curve for the titration of HCl with NaOH.

12. How is the end point found in the titration of HCl with NaOH using either a titration curve or an indicator?

13. A 3.471-g sample of a compound containing C, H, and O was ignited in a stream of O_2 and the CO_2 and H_2O were collected. Masses of 8.758 g of CO_2 and 1.537 g of H_2O were collected. Calculate the percentages of C and H in the compound.

14. A fertilizer sample weighing 0.6379 g was dissolved and treated with $NaClO_4$ solution, yielding 0.3816 g of $KClO_4$. What was the percentage of K in the fertilizer sample?

15. A corrosion product scraped from the surface of a lightweight metal alloy was analyzed to determine the percentage of $MgCO_3$ in the product by precipitation of magnesium ammonium phosphate and ignition to $Mg_2P_2O_7$. A 0.5626-g sample of the corrosion product yielded 0.3982 g of $Mg_2P_2O_7$. What was the percentage of $MgCO_3$ in the sample?

16. Calcium ion, Ca^{2+}, reacts with the chelating titrant EDTA, as shown in Reaction 25.6.11, whereas sodium ion, Na^+, does not react with EDTA. A 0.327-g portion of a caustic mixture of solid $Ca(OH)_2$, molar mass 74.1 g/mol, and Na_2CO_3 was dissolved and titrated with 0.0917 M EDTA, requiring 33.8 mL of the EDTA solution to reach the end point. What was the percentage of $Ca(OH)_2$ in the mixture?

17. How many mL of a 0.0500 M solution of $KMnO_4$ acting as an oxidizing titrant would be required to react with all the Fe^{2+} ion produced by dissolving 0.623 g of a sample that is 36.2 % FeO, molar mass 71.9 g/mol, mixed with inert material?

18. Based upon material covered elsewhere in the book regarding the nature of electrons in atoms, quantum chemistry, and photochemistry, attempt to explain the phenomena of atomic absorption and atomic emission discussed as analytical techniques in this chapter.

19. In reference to Equation 25.8.4, calculate the voltage change at a glass electrode used to measure pH for each unit change in pH.

20. Distinguish among the electron-capture detector, flame-ionization detector, and mass spectrometer as detectors for gas chromatographic separations.
21. What is required to get a reasonable flow rate in a high performance liquid chromatographic separation?
22. What is the basis of separations made in mass spectrometry? Why is mass spectrometry one of the most specific means of detecting organic compounds?
23. What are the main components of an automated analyzer system? What are the functions of each?
24. What is the basis of immunoassay analysis? What is meant by its being classified as a good screening technique?
25. A sample of a colored analyte at a concentration of 3.60×10^{-3} mol/L shows 34.2 percent transmittance in a 2.00 cm cell. What is the value of a in the Beer's law equation for this substance at the wavelength measured? If a sample of the colored analyte of unknown concentration gives an absorbance, A, of 0.520 in the same cell at the same wavelength, what is the concentration of the analyte in this solution?