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25 ANALYSIS OF WASTES AND SOLIDS

25.1. INTRODUCTION

The analysis of hazardous wastes of various kinds for a variety of potentially dangerous substances is one of the most important aspects of hazardous waste management.[1] These analyses are performed for a number of reasons including tracing the sources of wastes, assessing the hazards posed by the wastes to surroundings and to waste remediation personnel, and determining the best means of waste treatment. This chapter is a brief overview of several of the main considerations applied to the analysis of wastes. Here, wastes are broadly defined to include all kinds of solids, semisolids, sludges, liquids, contaminated soils, sediments, and other kinds of materials that are either wastes themselves or are contaminated by wastes.

For the most part, the substances determined as part of waste analysis, the *analytes*, are measured by techniques that are used for the determination of the same analytes in water (see methods described in Chapter 24) and, to a lesser extent, in air. However, the preparation techniques that must be employed for waste analysis are usually more complex than those used for the same analytes in water. That is because the matrices in which the waste analytes are contained are usually relatively complicated, which makes it difficult to recover all the analytes from the waste and which introduces interfering substances. As a result, the lower limits at which substances can be measured in wastes (the practical quantitation limit, see Section 24.1) are usually much higher than in water.

There are several distinct steps in the analysis of a waste. Compared to water, wastes are often highly heterogeneous, which makes the first step, collection of representative samples, difficult. Whereas water samples can often be introduced into an analytical instrument with minimal preparation, the processing of hazardous wastes to get a sample that can be introduced into an instrument is often relatively complicated. Such processing can consist of dilution of oily samples with an organic solvent, extraction of organic analytes into an organic solvent, evolution and collection of volatile organic carbon analytes, or digestion of solids with strong acids and oxidants to extract metals for atomic spectrometric analysis. The products of these

processes must often be subjected to relatively complicated sample cleanup procedures to remove contaminants that might interfere with the analysis or damage the analytical instrument.

Over a number of years, the U. S. Environmental Protection Agency has developed specialized methods for the characterization of wastes. These methods are given in the publication entitled *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods*, which is periodically updated to keep it current.[2] Because of the difficult and exacting nature of many of the procedures in this work and because of the hazards associated with the use of reagents such as strong acids and oxidants used for sample digestion and solvents used to extract organic analytes, anyone attempting analyses of hazardous waste materials should use this resource and follow procedures carefully with special attention to precautions. "SW-846," as it is commonly known, is available in a convenient CD/ROM form as part of a comprehensive summary of environmental analytical methods.[3]

25.2. SAMPLE DIGESTION

In order to analyze a solid waste sample by flame atomic absorption spectroscopy, graphite furnace absorption spectroscopy, inductively coupled argon plasma spectroscopy, or inductively coupled argon plasma mass spectrometry, the sample must first be digested to get the analyte metals in solution. Digestion dissolves only those fractions of metals that can be put into solution under relatively extreme conditions and therefore enables measurement of available metals. It should be noted that sample digestion procedures generally use highly corrosive, dangerous reagents which are strong acids and strong oxidants. Therefore, digestion should be carried out only by carefully trained personnel using the proper equipment, including fume hoods and adequate personnel protection.

EPA Method 3050 is a procedure for acid digestion of sediments, sludges, and soils. A sample of up to 2 g is treated with a mixture of nitric acid and hydrogen peroxide; the sample is then refluxed with either con. HNO_3 or con. HCl, then refluxed with dilute HCl, filtered, and the filtrate analyzed for metals.

Microwave heating can be used to assist the digestion of samples. The procedure for the digestion of aqueous liquids consists of mixing a 45 mL sample with 5 mL of concentrated nitric acid, placing it in a fluorocarbon (Teflon) digestion vessel, and heating for 20 minutes. After digestion is complete, the sample is cooled, solids are separated by filtration or centrifugation, and the liquid remaining is analyzed by the appropriate atomic spectrometric technique.

Method 3052 is a procedure for microwave assisted acid digestion of siliceous and organically based matrices. It can be used on a variety of kinds of samples including biological tissues, oils, oil-contaminated soils, sediments, sludges, and soil. This method is not appropriate for analyses of leachable metals, but is used for measurement of total metals. A sample of up to 0.5 g is digested with microwave heating for 15 minutes in an appropriate fluorocarbon polymer container in an appropriate acid mixture. Commonly, the reagents employed are a mixture of 9 mL of con. nitric acid and 3 mL hydrofluoric acid, although other acid mixtures employing reagents such as con. HCl and hydrogen peroxide may be used. The sample is heated in the microwave oven to 180˚C and held at that temperature for at

least 9.5 minutes. After heating, the residual solids are filtered off and the filtrate analyzed for metals.

Many kinds of hazardous waste samples contain metals dissolved or suspended in viscous petroleum products, including oils, oil sludges, tars, waxes, paints, paint sludges, and other hydrocarbon materials. Method 3031 can be used to dissolve these metals—including antimony, arsenic, barium, beryllium cadmium, chromium, cobalt, copper, lead molybdenum, nickel, selenium, silver, thallium, vanadium, and zinc—in a form suitable for atomic spectrometric analysis. The procedure involves mixing 0.5 g of sample with 0.5 g of finely ground $KMnO_4$ and 1.0 mL of con. H_2SO_4, which causes a strongly exothermic reaction to occur as the hydrocarbon matrix is oxidized. After the reaction has subsided, 2 mL of con. HNO_3 and 2 mL of con. HCl are added, the sample is filtered with filter paper, the filter paper is digested with con. HCl, and the sample is diluted and analyzed for metals.

25.3. ANALYTE ISOLATION FOR ORGANICS ANALYSIS

The determination of organic analytes requires that they be isolated from the sample matrix. Since organic analytes are generally soluble in organic solvents, they can usually be extracted from samples with a suitable solvent. Although extraction works well for nonvolatile and semivolatile analytes, it is not so suitable for volatile organic compounds, which are readily vaporized during sample processing. The volatile materials are commonly isolated by techniques that take advantage of their high vapor pressures.

SOLVENT EXTRACTION

Method 3500 is a procedure for extracting nonvolatile or semivolatile compounds from a liquid or solid sample. The sample is extracted with an appropriate solvent, dried, and concentrated in a Kuderna-Danish apparatus prior to further processing for analysis.

A number of methods more complicated than Method 3500 have been devised for extracting nonvolatile and semivolatile analytes from waste samples. Method 3540 uses extraction with a Soxhlet extractor. This device, illustrated in Chapter 21, Figure 21.7, for the extraction of lipids from biological tissue, provides for recirculation of continuously redistilled fresh solvent over a sample of soils, sludges, and wastes. The sample is first mixed with anhydrous Na_2SO_4 to dry it, then placed inside an extraction thimble in the Soxhlet apparatus, which redistills a relatively small volume of extraction solvent over the sample. After extraction, the sample may be dried, concentrated, and exchanged into another solvent prior to analysis.

Method 3545 uses pressurized fluid extraction at 100˚C and a pressure up to 2000 psi to remove organophilic analyte species from solid samples including soils, clays, sediments, sludges, and waste solids. Used for the extraction of semivolatile organic compounds, organophosphorus pesticides, organochlorine pesticides, chlorinated herbicides, and PCBs, it requires less solvent and takes less time than the Soxhlet extraction described above. Before extraction, the finely ground 10–30 g sample should be dried to prevent residual water from interfering with the extraction. It may be air-dried or dried with anhydrous Na_2SO_4 or pelletized diatomaceous earth. An extraction time of 5 minutes is typically used.

Method 3550 uses sonication with ultrasound to expedite the extraction of nonvolatile and semivolatile organic compounds from solids including soils, sludges, and wastes. The procedure calls for subjecting the finely divided dried sample mixed with solvent to ultrasound for a brief period of time. Low concentration samples may be subjected to multiple extractions with additional fresh solvent.

Although the requirement for specialized high pressure equipment has limited its application, extraction with supercritical carbon dioxide maintained at temperatures and pressures above the critical point where separate liquid and vapor phases do not exist is a very effective means of extracting some organic analytes. Method 3561 is used to extract polycyclic aromatic hydrocarbons such as acenaphthene, benzo(a)pyrene, fluorene, and pyrene from solid samples. The actual procedure is relatively complicated and is divided into three steps. The first step extracts the more volatile compounds with pure supercritical carbon dioxide at moderately low density and temperature. Less volatile PAHs are removed in the second step using supercritical carbon dioxide and methanol modifier. A third step using pure carbon dioxide is employed to purge the modifier from the system. The theory of supercritical fluid extraction of PCBs from sediments has been described.[4]

A comparison of several means of extracting PCBs from sewage treatment plant sludge (Soxhlet extraction, ultrasound, and shaking) has shown differences in the efficacy of extraction among these techniques depending upon the congeners extracted. The authors concluded that no single extraction method was optimum for all congeners.[5]

Sample Preparation for Volatile Organic Compounds

Many different volatile organic compounds are found at waste sites and in various kinds of waste solid and sludge samples. These include benzene, bromomethane, chloroform, 1,4-dichlorobenzene, dichloromethane, styrene, toluene, vinyl chloride, and the xylene isomers. Various methods are employed to isolate and concentrate volatile organic compounds from the solid, sludge, or liquid matrices in which they are contained.

Method 5021, “Volatile Organic Compounds in Soils and Other Solid Matrices Using Equilibrium Headspace Analysis” is used to isolate volatile organic compounds from soil, sediment, or solid waste samples for determination by gas chromatography or gas chromatography/mass spectrometry. This procedure makes use of a special glass headspace vial that contains at least 2 g of sample. A matrix modifying preservative solution, internal standards, and surrogate compounds may be added to the sample and mixed thoroughly by rotating the vial. The sample is heated to 85˚C for approximately one hour prior to injection into the gas chromatograph. For injection, helium is forced under pressure into the vial and a sample of the gas in the headspace above the solid sample is forced out of the vial and into the gas chromatograph system for quantitation.

Method 5030 is a purge-and-trap procedure that can be used to collect for gas chromatographic analysis poorly water soluble compounds that have boiling points below 200˚C, which includes a wide variety of compounds commonly occurring in hazardous wastes. For samples in water, helium is bubbled through the sample and the volatile analyte compounds are absorbed on a sorbent column. Solid samples can

be dispersed in methanol and the methanol added to water for the purging step. After purging is complete, the sorbent column is heated and flushed with carrier gas to sweep the sample compounds into the gas chromatograph for qualitative and quantitative analysis of the volatile organic compounds present.

Method 5035 is a closed-system, purge-and-trap and extraction method applicable to the determination of volatile organic compounds in soil, sediment, and waste samples. For the determination of very low levels of volatile organic compounds in soil, a sealed sample vial is used that remains sealed throughout the sample processing operations. An approximately 5-gram sample is weighed into a sample vial containing a stirring bar and sodium bisulfate preservative solution, and the vial is sealed and transported to the laboratory as soon as possible. For analysis, reagent water, surrogates, and internal standards are injected into the vial without opening it. The contents of the vial are purged with helium gas into an appropriate sampling trap, then flushed into the gas chromatograph for measurement.

Method 5031 is used to isolate volatile, nonpurgeable, water-soluble compounds by azeotropic distillation. The analyte compounds for which it is suitable include acetone, acetonitrile, acrylonitrile, allyl alcohol, 1-butanol, *t*-butyl alcohol, crotonaldehyde, 1,4-dioxane, ethanol, ethyl acetate, ethylene oxide, isobutyl alcohol, methanol, methylethyl ketone, methylisobutyl ketone, *n*-nitroso-di-*n*-butylamine, paraldehyde, 2-pentanone, 2-picoline, 1-propanol, 2-propanol, propionitrile, pyridine, and, *o*-toluidine. The technique takes advantage of the formation of an azeotrope liquid mixture of water and analytes which boil at a constant temperature and give off vapors of a constant composition. For separation of the analyte species, a 1-liter sample is adjusted to pH 7 with a buffer, and a small sample of condensate enriched in analyte species is collected. The organics are measured in the azeotrope solution distilled from the sample.

Method 5032 employs vacuum distillation to isolate volatile organic analytes from liquid, solid, and oily waste matrices, and even animal tissues. Examples of compounds isolated for analysis by this procedure include acetone, benzene, carbon disulfide, chloroform, ethanol, styrene, tetrachloroethene, vinyl chloride, and the *o*,*m*,*p*-xylene isomers. Such compounds should be no more than minimally soluble in water and should boil below 180˚C. The sample in water is distilled under a vacuum and the water condensed in a chilled condenser. Volatile analyte constituents not condensed with the water vapor are swept into a cryogenic trap maintained at liquid nitrogen temperature of -196˚C for collection. For analysis, the contents of the trap are evaporated at an elevated temperature and swept into the chromatograph.

Method 3585, Waste Dilution for Volatile Organics, is employed to place a non-aqueous waste sample of volatile organics into the appropriate form for injection into a gas chromatograph. It is applicable to samples containing analytes at levels of 1 mg/kg or higher. The procedure calls for placing a 1 g oil-phase sample into a vial marked for a volume of 10 mL, sealing the vial, diluting with *n*-hexadecane or other appropriate solvent, and mixing to dissolve the sample. Because the diluted sample usually contains residual materials from the sample with a tendency to foul the gas chromatograph, the sample is injected through a replaceable direct injection liner containing Pyrex glass wool.

25.4. SAMPLE CLEANUP

Most waste, soil, and sediment samples result in extraction of extraneous substances that can result in the observation of extraneous peaks, be detrimental to peak resolution and column efficiency, and be damaging to expensive columns and detectors. **Sample cleanup** refers to a number of measures that can be taken to remove these constituents from sample extracts by a number of procedures including distillation, partitioning with immiscible solvents, adsorption chromatography, gel permeation chromatography, or chemical destruction of interfering substances with acid, alkali, or oxidizing agents; two or more of these techniques may be used in combination. The most widely applicable cleanup technique is gel permeation chromatography, which can be used to separate substances with high molecular weights from the analytes of interest. Treatment by adsorption column chromatography with alumina, Florisil, or silica gel can be used to isolate a relatively narrow polarity range of analytes away from interfering substances. Acid-base partitioning can be used in the determination of materials such as chlorophenoxy herbicides and phenols to separate acidic, basic, and neutral organics. Table 25.1 shows the uses of the main sample cleanup techniques.

Table 25.1. Sample Cleanup Techniques and Their Applications

Number	Type	Applications
3610	Alumina column	Phthalate esters, nitrosamines
3611	Alumina column cleanup and separation of petroleum wastes	Polycyclic aromatic hydrocarbons, petroleum wastes
3620	Florisil column	Phthalate esters, nitrosamines, organochlorine pesticides, PCBs, chlorinated hydrocarbons, organophosphorus pesticides
3630	Silica gel	Polycyclic aromatic hydrocarbons
3630(b)	Silica gel	Phenols
3640	Gel permeation chromatography	Phenols, phthalate esters, nitrosamines, organochlorine pesticides, PCBs, nitroaromatics, cyclic ketones, polycyclic aromatic hydrocarbons, chlorinated hydrocarbons, organophosphorus pesticides, priority pollutant semivolatiles
3650	Acid-base liquid/liquid partition	Phenols, priority pollutant semivolatiles
3660	Sulfur cleanup	Organochlorine pesticides, PCBs, Priority pollutant semivolatiles

Alumina column cleanup makes use of highly porous granular aluminum oxide. Available in acidic, neutral, and basic pH ranges, this solid is packed into a column topped with a water-absorbing substance over which the sample is eluted with a suitable solvent, which leaves interferences on the column. After elution, the sample is concentrated, exchanged with another solvent if necessary, then analyzed. Florisil is an acidic magnesium silicate and a registered trade name of Floridin Co. It is used in a column cleanup procedure in a manner similar to alumina. Silica gel is a weakly acidic amorphous silicon oxide. It can be activated by heating for several hours at 150-160˚C and used for the separation of hydrocarbons. Deactivated silica gel containing 10-20% water acts as an adsorbent for compounds with ionic and nonionic functionalities such as dyes, alkali metal cations, terpenoids, and plasticizers. It is used in a column as described for alumina above. Gel-permeation chromatography separates solutes by size carried over a hydrophobic gel by organic solvents. A gel must be chosen that will separate the appropriate size range of analytes and interferences. The gel is preswelled before loading onto a column and flushed extensively with solvent before the sample is introduced for separation.

25.5 IMMUNOASSAY SCREENING OF WASTES

Immunoassay has emerged as a useful technique for screening wastes 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.[6]

25.6. DETERMINATION OF CHELATING AGENTS

Strong chelating agents in wastes have been found to play an important role in the mobility of heavy metals and metal radionuclides at waste disposal sites, with their potential to contaminate groundwater. Therefore, the determination of chelating agents, such as ethylenediaminetetraacetic acid (EDTA) and N-(2-hydroxyethyl)-ethylenediaminetriacetic acid (HEDTA), is an important analytical procedure for wastes. Most chelating agents of concern at waste sites are polar and nonvolatile, which prevents their determination by direct gas chromatographic methods. One of the more satisfactory methods for their determination makes use of derivatization to produce volatile species suitable for gas chromatographic analysis.

A method has been described for the determination of chelating agents in hazardous wastes from radioactive wastes using derivatization followed by gas chromatographic/mass spectrometric analysis (GC/MS).[7] The study involved wastes contained in a potentially leaking double-shell storage tank at the U. S. Department of Energy Hanford site. Treatment with BF_3 and methanol produced volatile derivatives that were measured by GC/MS. In addition to EDTA and HEDTA, the study showed the presence of nitrilotriacetate (NTA) and citrate chelating agents, and chelating nitrosoiminiodiacetate was produced as an artifact of the analytical procedure.

25.7. TOXICITY CHARACTERISTIC LEACHING PROCEDURE

The **Toxicity Characteristic Leaching Procedure** (**TCLP**) is specified to determine the potential toxicity hazard of various kinds of wastes.[8] The test was designed to estimate the availability to organisms of both inorganic and organic species in hazardous materials present as liquids, solids, or multiple phase mixtures by producing a leachate, the TCLP extract, which is analyzed for the specific toxicants listed in Table 25.2.

The procedure for conducting the TCLP is rather involved. The procedure need not be run at all if a total analysis of the sample reveals that none of the pollutants specified in the procedure could exceed regulatory levels. At the opposite end of the scale, analysis of any of the liquid fractions of the sample showing that any regulated species would exceed regulatory levels even after the dilutions involved in the TCLP measurement have been carried designate the sample as hazardous, and the TCLP measurement is not required.

In conducting the TCLP test, if the waste is a liquid containing less than 0.5% solids, it is filtered through a 0.6–0.8 µm glass fiber filter and the filtrate is designated as the TCLP extract. At solids levels exceeding 0.5%, any liquid present is filtered off for separate analysis and the solid is extracted to provide a TCLP extract (after size reduction, if the particles exceed certain size limitations). The choice of the extraction fluid is determined by the pH of the aqueous solution produced from shaking a mixture of 5 g of solids and 96.5 mL of water. If the pH is less than 5.0, a pH 4.93 acetic acid/sodium acetate buffer is used for extraction; otherwise, the

extraction fluid used is a pH of 2.88±0.05 solution of dilute acetic acid. Extractions

Table 25.2. Contaminants Determined in TCLP Procedure

EPA hazardous waste number	Contaminant	Regulatory level, mg/L	EPA hazardous waste number	Contaminant	Regulatory level, mg/L
Heavy metals (metalloids)					
D004	Arsenic	5.0	D033	Hexachlorobutadiene	0.5
D005	Barium	100.0			
D006	Cadmium	1.0	D034	Hexachloroethane	3.0
D007	Chromium	5.0			
D008	Lead	5.0	D035	Methylethyl ketone	200.0
D009	Mercury	0.2			
D010	Selenium	1.0	D036	Nitrobenzene	2.0[2]
D011	Silver	5.0	D037	Pentachlorophenol	100.0
Organics			D038	Pyridine	5.0[2]
			D039	Tetrachloroethylene	0.7
D018	Benzene	0.5			
D019	Carbon tetrachloride	0.5	D040	Trichloroethylene	0.5
			D041	2,4,5-Trichlorophenol	400.0
D021	Chlorobenzene	100.0			
			D042	2,4,6-Trichlorophenol	2.0
D022	Chloroform	6.0			
D023	*o*-Cresol	200.0[1]	D043	Vinyl chloride	0.2
D024	*m*-Cresol	200.0[1]			
D025	*p*-Cresol	200.0[1]	*Pesticides*		
D026	Cresol	200.0[1]			
D027	1,4-Dichlorobenzene	7.5	D012	Endrin	0.02
			D013	Lindane	0.4
D028	1,2-Dichloroethane	0.5	D014	Methoxychlor	10.0
			D015	Toxaphene	0.5
D029	1,1-Dichloroethylene	0.7	D016	2,4-D	10.0
			D017	2,4,5-TP (Silvex)	1.0
D030	2,4-Dinitrotoluene	0.13[2]	D020	Chlordane	0.03
			D031	Heptachlor (and its epoxide)	0.008
D032	Hexachlorobenzene	0.13[2]			

[1] If *o*-, *m*-, and *p*-Cresol concentrations cannot be differentiated, the total cresol (D026) concentration is used. The regulatory level of total cresol is 200 mg/L.

[2] Quantitation limit is greater than the calculated regulatory level. The quantitation limit therefore becomes the regulatory level.

are carried out in a sealed container rotated end-over-end for 18 hours. The liquid portion is then separated and analyzed for the specific substances given in Table 25.2. If values exceed the regulatory limits, the waste is designated as "toxic."

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QUESTIONS AND PROBLEMS

1. Explain the uses of microwave in hazardous waste analysis. How is ultrasound employed in hazardous waste analysis?
2. Does sample digestion necessarily give an analysis leading to total metals? Why might it not be advantageous to measure total metals in a sample?
3. What is the distinction between a Kuderna-Danish apparatus and a Soxhlet apparatus?
4. How is anhydrous Na_2SO_4 used in organics analysis?
5. How does the purge-and-trap procedure differ from azeotropic distillation? For what kinds of compounds would the two procedures be employed?
6. What is the purpose of sample cleanup? Why is cleanup more commonly applied to samples to be analyzed for organic contaminants than for metals?
7. For what purpose is a cryogenic trap used in organics analysis? What advantage might it have over the solid sorbent traps used in conventional purge-and-trap analysis?
8. What do benzene, bromomethane, chloroform, 1,4-dichlorobenzene, dichloromethane, styrene, toluene, vinyl chloride, and *o*-xylene have in common?
9. What is the principle of immunoassay? What makes it specific for compounds or narrow classes of compounds? Why might it be especially suitable as a survey technique for hazardous waste sites? What is ELISA?
10. In what sense is the TCLP a measure of available toxicants?
11. Under what circumstances is it unnecessary to run the TCLP in evaluating the toxicity hazard of a waste material?
12. Which is the most widely applicable sample cleanup technique? What are three other kinds of materials used in column cleanup of samples?