ANNEX 3
EPA Test Methods for Evaluating Solid Wastes

SW-846 On-Line

Test Methods for Evaluating Solid Wastes Physical/Chemical Methods

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CHAPTER FOUR
ORGANIC ANALYTES

Prior to employing the methods in this chapter, analysts are advised to consult the disclaimer statement at the front of this manual and the information in Chapter Two for guidance on the allowed flexibility in the choice of apparatus, reagents, and supplies. In addition, unless specified in a regulation, the use of SW-846 methods is not mandatory in response to Federal testing requirements. The information contained in this chapter is provided by EPA as guidance to be used by the analyst and the regulated community in making judgements necessary to meet the data quality objectives or needs for the intended use of the data.

4.1 SAMPLING CONSIDERATIONS

4.1.1 Introduction

Following the initial and critical step of designing a sampling plan (Chapter Nine) is the implementation of that plan such that a representative sample of the solid waste is collected. Once the sample has been collected it must be stored and preserved to maintain the chemical and physical properties that it possessed at the time of collection. The sample type, type of containers and their preparation, possible forms of contamination, and preservation methods are all items which must be thoroughly examined in order to maintain the integrity of the samples. This section highlights considerations which must be addressed in order to maintain a sample's integrity and representativeness. This section is, however, applicable only to trace analyses.

Quality Control (QC) requirements need not be met for all compounds presented in the Table of Analytes for the method in use, rather, they must be met for all compounds reported. A report of non-detect is considered a quantitative report, and must meet all applicable QC requirements for that compound and the method used.

4.1.2 Sample Handling and Preservation

This section deals separately with volatile and semivolatile organics. Refer to Chapter Two and Table 4-1 of this section for sample containers, sample preservation, and sample holding time information.

Volatile Organics

Standard 40 mL glass screw-cap VOA vials with Teflon lined silicone septa may be used for liquid matrices. Special 40 mL VOA vials for purge-and-trap of solid samples are described in Method 5035. VOA vials for headspace analysis of solid samples are described in Method 5021. Standard 125 mL widemouth glass containers may be used for Methods 5031 and 5032. However, the sampling procedures described in Method 5035 may minimize sample preparation analyte loss better than the procedures described in Methods 5031 and 5032. The vials and septa should be washed with soap and water and rinsed with distilled deionized water. After thoroughly cleaning the vials and septa, they should be placed in an oven and dried at 100°C for approximately one hour.

NOTE: Do not heat the septa for extended periods of time (i.e., more than one hour, because the silicone begins to slowly degrade at 105°C).

When collecting the samples, liquids and solids should be introduced into the vials gently to reduce agitation which might drive off volatile compounds.

In general, liquid samples should be poured into the vial without introducing any air bubbles within the vial as it is being filled. Should bubbling occur as a result of violent pouring, the sample must be poured out and the vial refilled. The vials should be completely filled at the time of sampling, so that when the septum cap is fitted and sealed, and the vial inverted, no headspace is visible. The sample should be hermetically sealed in the vial at the time of sampling, and must not be opened prior to analysis to preserve their integrity.

- Due to differing solubility and diffusion properties of gases in LIQUID matrices at different temperatures, it is possible for the sample to generate some headspace during storage. This headspace will appear in the form of micro bubbles, and should not invalidate a sample for volatiles analysis.
- The presence of a macro bubble in a sample vial generally indicates either improper sampling technique or a source of gas evolution within the sample. The latter case is usually accompanied by a buildup of pressure within the vial, (e.g. carbonate-containing samples preserved with acid). Studies conducted by the USEPA (EMSL-Ci, unpublished data) indicate that "pea-sized" bubbles (i.e., bubbles not exceeding 1/4 inch or 6 mm in diameter) did not adversely affect volatiles data. These bubbles were generally encountered in wastewater samples, which are more susceptible to variations in gas solubility than are groundwater samples.

Immediately prior to analysis of liquid samples, the aliquot to be analyzed should be taken from the vial using the instructions from the appropriate sample introduction technique:

- For smaller analysis volumes, a gas-tight syringe may be inserted directly through the septum of the vial to withdraw the sample.
- For larger analysis volumes, (e.g. purge-and-trap analyses) the sample may be carefully poured into the syringe barrel. Opening a volatile sample to pour a sample into a syringe destroys the validity of the sample for future analysis. Therefore, if there is only one VOA vial, it is strongly recommended that the analyst fill a second syringe at this time to protect against possible loss of sample integrity. This second sample is maintained only until such time as the analyst has determined that the first sample has been analyzed properly.

If these guidelines are not followed, the validity of the data generated from the samples may be suspect.

VOA vials for samples with solid or semi-solid matrices (e.g., sludges) should be filled according to the guidance given in the appropriate 5000 series sample introduction method (see Table 4-1) to be used. When 125-mL widemouth glass containers are used, the containers should be filled as completely as possible. The 125-mL vials should be tapped slightly as they are filled to try and eliminate as much free air space as possible. A minimum of two vials should also be filled per sample location.

At least two VOA vials should be filled and labeled immediately at the point at which the sample is collected. They should <u>NOT</u> be filled near a running motor or any type of exhaust system because discharged fumes and vapors may contaminate the samples. The two vials from each sampling location should then be sealed in separate plastic bags to prevent cross-contamination between samples, particularly if the sampled waste is suspected of containing high levels of volatile organics. (Activated carbon may also be included in the bags to prevent cross-contamination from highly contaminated samples). VOA samples may also be contaminated by diffusion of volatile organics through the septum during shipment and storage. To monitor possible contamination, a trip blank prepared from organic-free reagent water (as defined in Chapter One) should be carried throughout the sampling, storage, and shipping process.

Semivolatile Organics (including Pesticides, PCBs and Herbicides.)

Containers used to collect samples for the determination of semivolatile organic compounds should be soap and water washed followed by methanol (or isopropanol) rinsing (see Sec. 4.1.4 for specific instructions on glassware cleaning). The sample containers should be of glass or Teflon, and have screw-caps with Teflon lined septa. In situations where Teflon is not available, solvent-rinsed aluminum foil may be used as a liner. However, acidic or basic samples may react with the aluminum foil, causing eventual contamination of the sample. Plastic containers or lids may NOT be used for the storage of samples due to the possibility of sample contamination from the phthalate esters and other hydrocarbons within the plastic. Sample containers should be filled with care so as to prevent any portion of the collected sample coming in contact with the sampler's gloves, thus causing contamination. Samples should not be collected or stored in the presence of exhaust fumes. If the sample comes in contact with the sampler (e.g. if an automatic sampler is used), run organic-free reagent water through the sampler and use as a field blank.

4.1.3 Safety

Safety should always be the primary consideration in the collection of samples. A thorough understanding of the waste production process, as well as all of the potential hazards making up the waste, should be investigated whenever possible. The site should be visually evaluated just prior to sampling to determine additional safety measures. Minimum protection of gloves and safety glasses should be worn to prevent sample contact with the skin and eyes. A respirator should be worn even when working outdoors if organic vapors are present. More hazardous sampling missions may require the use of supplied air and special clothing.

4.1.4 Cleaning of Glassware

In the analysis of samples containing components in the parts per billion range, the preparation of scrupulously clean glassware is necessary. Failure to do so can lead to a myriad of problems in the interpretation of the final chromatograms due to the presence of extraneous peaks resulting from contamination. Particular care must be taken with glassware such as Soxhlet extractors, Kuderna-Danish evaporative concentrators, sampling-train components, or any other glassware coming in contact with an extract that will be evaporated to a smaller volume. The process of concentrating the compounds of interest in this operation may similarly concentrate the contaminating substance(s), which may seriously distort the results.

The basic cleaning steps are:

1. Removal of surface residuals immediately after use;
2. Hot soak to loosen and float most particulate material;
3. Hot water rinse to flush away floated particulates;
4. Soak with an oxidizing agent to destroy traces of organic compounds;
5. Hot water rinse to flush away materials loosened by the deep penetrant soak;

6. Distilled water rinse to remove metallic deposits from the tap water;

7. Alcohol, e.g., isopropanol or methanol, rinse to flush off any final traces of organic materials and remove the water; and

8. Flushing the item immediately before use with some of the same solvent that will be used in the analysis.

Each of these eight fundamental steps are discussed here in the order in which they appeared on the preceding page.

1. As soon possible after glassware (i.e., beakers, pipets, flasks, or bottles) has come in contact with sample or standards, the glassware should be flushed with alcohol before it is placed in the hot detergent soak. If this is not done, the soak bath may serve to contaminate all other glassware placed therein.

2. The hot soak consists of a bath of a suitable detergent in water of 50°C or higher. The detergent, powder or liquid, should be entirely synthetic and not a fatty acid base. There are very few areas of the country where the water hardness is sufficiently low to avoid the formation of some hard-water scum resulting from the reaction between calcium and magnesium salts with a fatty acid soap. This hard-water scum or curd would have an affinity particularly for many chlorinated compounds and, being almost wholly water-insoluble, would deposit on all glassware in the bath in a thin film.

   There are many suitable detergents on the wholesale and retail market. Most of the common liquid dishwashing detergents sold at retail are satisfactory but are more expensive than other comparable products sold industrially. Alconox, in powder or tablet form, is manufactured by Alconox, Inc., New York, and is marketed by a number of laboratory supply firms. Sparkleen, another powdered product, is distributed by Fisher Scientific Company.

3. No comments required.

4. The most common and highly effective oxidizing agent for removal of traces of organic compounds is the traditional chromic acid solution made up of concentrated sulfuric acid and potassium or sodium dichromate. For maximum efficiency, the soak solution should be hot (40-50°C). Safety precautions must be rigidly observed in the handling of this solution. Prescribed safety gear should include safety goggles, rubber gloves, and apron. The bench area where this operation is conducted should be covered with fluorocarbon sheeting because spattering will disintegrate any unprotected surfaces.

   The potential hazards of using chromic-sulfuric acid mixture are great and have been well publicized. There are now commercially available substitutes that possess the advantage of safety in handling. These are biodegradable concentrates with a claimed cleaning strength equal to the chromic acid solution. They are alkaline, equivalent to ca. 0.1 N NaOH upon dilution, and are claimed to remove dried blood, silicone greases, distillation residues, insoluble organic residues, etc. They are further claimed to remove radioactive traces and will not attack glass or exert a corrosive effect on skin or clothing. One such product is "Chem Solv 2157," manufactured by Mallinckrodt and available through laboratory supply firms. Another comparable product is "Detex," a product of Borer-Chemie, Solothurn, Switzerland.

5, 6, and 7. No comments required.

8. There is always a possibility that between the time of washing and the next use, the glassware could pick up some contamination from either the air or direct contact. To ensure against this, it is good practice to flush the item immediately before use with some of the same solvent that will be used in the analysis.

The drying and storage of the cleaned glassware is of critical importance to prevent the beneficial effects of the scrupulous cleaning from being nullified. Pegboard drying is not recommended. It is recommended that laboratory glassware and equipment be dried at 100°C. Under no circumstances should such small items be left in the open without protective covering. The dust cloud raised by the daily sweeping of the laboratory floor can most effectively recontaminate the clean glassware.

As an alternate to solvent rinsing, the glassware can be heated to a minimum of 300°C to vaporize any organics. Do not use this high temperature treatment on volumetric glassware, glassware with ground glass joints, or sintered glassware.

4.1.5 High Concentration Samples

Cross contamination of trace concentration samples may occur when prepared in the same laboratory with high concentration samples. Ideally, if both type samples are being handled, a laboratory and glassware dedicated solely to the preparation of high concentration samples would be available for this purpose. If this is not feasible, as a minimum when preparing high concentration samples, disposable glassware should be used or, at least, glassware dedicated entirely to the high concentration samples. Avoid cleaning glassware used for both trace and high concentration samples in the same area.

TABLE 4-1.
SAMPLE CONTAINERS, PRESERVATION, TECHNIQUES, AND HOLDING TIMES

VOLATILE ORGANICS			
Sample Matrix	Container	Preservative	Holding Time
Concentrated Waste Samples	Method 5035: 40-mL vials with stirring bar. Method 5021: See method. Methods 5031 & 5032: 125-mL widemouth glass container. Use Teflon-lined lids for all procedures.	Cool to 4°C.	14 days
Aqueous Samples With No Residual Chlorine Present	Methods 5030, 5031, & 5032: 2 X 40-mL vials with Teflon-lined septum caps	Cool to 4°C and adjust pH to less than 2 with H_2SO_4, HCl, or solid $NaHSO_4$.	14 days
Aqueous Samples WITH Residual Chlorine Present	Methods 5030, 5031, & 5032: 2 X 40-mL vials with Teflon-lined septum caps	Collect sample in a 125-mL container which has been pre-preserved with 4 drops of 10% sodium thiosulfate solution. Gently swirl to mix sample and transfer to a 40-mL VOA vial. Cool to 4°C and adjust pH to less than 2 with H_2SO_4, HCl, or solid $NaHSO_4$.	14 days
Acrolein and Acrylonitrile in Aqueous Sample	Methods 5030, 5031, & 5032: 2 X 40-mL vials with Teflon-lined septum caps	Adjust to pH 4-5. Cool to 4°C.	14 days
Solid Samples (e.g. soils, sediments, sludges, ash)	Method 5035: 40-mL vials with septum and stirring bar. Method 5021: See method. Methods 5031 & 5032: 125-mL widemouth glass container with Teflon-lined lids.	See the individual methods.	14 days

SEMIVOLATILE ORGANICS/ORGANOCHLORINE PESTICIDES/PCBs AND HERBICIDES			
Sample Matrix	Container	Preservative	Holding Time
Concentrated Waste Samples	125-mL widemouth glass with Teflon-lined lid	None	Samples extracted within 14 days and extracts analyzed within 40 days following extraction.
Aqueous Samples With No Residual Chlorine Present	1-gal., 2 x 0.5-gal., or 4 x 1-L amber glass container with Teflon-lined lid	Cool to 4°C	Samples extracted within 7 days and extracts analyzed within 40 days following extraction.
Aqueous Samples WITH Residual Chlorine Present	1-gal., 2 x 0.5-gal., or 4 x 1-L, amber glass container with Teflon-lined lid.	Add 3-mL 10% sodium thiosulfate solution per gallon (or 0.008%). Addition of sodium thiosulfate solution to sample container may be performed in the laboratory prior to field use. Cool to 4°C.	Samples extracted within 7 days and extracts analyzed within 40 days following extraction.
Solid Samples (e.g. soils, sediments, sludges, ash)	250-mL widemouth glass container with Teflon-lined lid	Cool to 4°C	Samples extracted within 14 days and extracts analyzed within 40 days following extraction.

4.2 SAMPLE PREPARATION METHODS

Prior to employing the methods in this chapter, analysts are advised to consult the disclaimer statement at the front of this manual and the information in Chapter Two for guidance on the allowed flexibility in the choice of apparatus, reagents, and supplies. In addition, unless specified in a regulation, the use of SW-846 methods is not mandatory in response to Federal testing requirements. The information contained in each procedure is provided by EPA as guidance to be used by the analyst and the regulated community in making judgements necessary to meet the data quality objectives or needs for the intended use of the data.

4.2.1 EXTRACTIONS AND PREPARATIONS

The following methods are included in this section:

Method 3500B:	Organic Extraction and Sample Preparation
Method 3510C:	Separatory Funnel Liquid-Liquid Extraction
Method 3520C:	Continuous Liquid-Liquid Extraction
Method 3535:	Solid-Phase Extraction (SPE)
Method 3540C:	Soxhlet Extraction
Method 3541:	Automated Soxhlet Extraction
Method 3542:	Extraction of Semivolatile Analytes Collected Using Method 0010 (Modified Method 5 Sampling Train)
Method 3545:	Pressurized Fluid Extraction (PFE)
Method 3550B:	Ultrasonic Extraction
Method 3560:	Supercritical Fluid Extraction of Total Recoverable Petroleum Hydrocarbons
Method 3561:	Supercritical Fluid Extraction of Polynuclear Aromatic Hydrocarbons
Method 3580A:	Waste Dilution
Method 3585:	Waste Dilution for Volatile Organics
Method 5000:	Sample Preparation for Volatile Organic Compounds
Method 5021:	Volatile Organic Compounds in Soils and Other Solid Matrices Using Equilibrium Headspace Analysis
Method 5030B:	Purge-and-Trap for Aqueous Samples
Method 5031:	Volatile, Nonpurgeable, Water-Soluble Compounds by Azeotropic Distillation
Method 5032:	Volatile Organic Compounds by Vacuum Distillation
Method 5035:	Closed-System Purge-and-Trap and Extraction for Volatile Organics in Soil and Waste Samples
Method 5041A:	Analysis for Desorption of Sorbent Cartridges from Volatile Organic Sampling Train (VOST)

4.2 SAMPLE PREPARATION METHODS

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4.2.2 CLEANUP

The following methods are included in this section:

Method 3600C:	Cleanup
Method 3610B:	Alumina Cleanup
Method 3611B:	Alumina Column Cleanup and Separation of Petroleum Wastes
Method 3620B:	Florisil Cleanup
Method 3630C:	Silica Gel Cleanup
Method 3640A:	Gel-Permeation Cleanup
Method 3650B:	Acid-Base Partition Cleanup
Method 3660B:	Sulfur Cleanup
Method 3665A:	Sulfuric Acid/Permanganate Cleanup

4.3 DETERMINATION OF ORGANIC ANALYTES

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4.3.1 GAS CHROMATOGRAPHIC METHODS

The following methods are included in this section:

Method 8000B:	Determinative Chromatographic Separations
Method 8011:	1,2-Dibromoethane and 1,2-Dibromo-3-chloropropane by Microextraction and Gas Chromatography
Method 8015B:	Nonhalogenated Organics Using GC/FID
Method 8021B:	Aromatic and Halogenated Volatiles by Gas Chromatography Using Photoionization and/or Electrolytic Conductivity Detectors
Method 8031:	Acrylonitrile by Gas Chromatography
Method 8032A:	Acrylamide by Gas Chromatography
Method 8033:	Acetonitrile by Gas Chromatography with Nitrogen-Phosphorus Detection
Method 8041:	Phenols by Gas Chromatography
Method 8061A:	Phthalate Esters by Gas Chromatography with Electron Capture Detection (GC/ECD)
Method 8070A:	Nitrosamines by Gas Chromatography
Method 8081A:	Organochlorine Pesticides by Gas Chromatography
Method 8082:	Polychlorinated Biphenyls (PCBs) by Gas Chromatography
Method 8091:	Nitroaromatics and Cyclic Ketones by Gas Chromatography
Method 8100:	Polynuclear Aromatic Hydrocarbons
Method 8111:	Haloethers by Gas Chromatography
Method 8121:	Chlorinated Hydrocarbons by Gas Chromatography: Capillary Column Technique
Method 8131:	Aniline and Selected Derivatives by Gas Chromatography
Method 8141A:	Organophosphorus Compounds by Gas Chromatography: Capillary Column Technique
Method 8151A:	Chlorinated Herbicides by GC Using Methylation or Pentafluorobenzylation Derivatization

4.3 DETERMINATION OF ORGANIC ANALYTES

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4.3.2 GAS CHROMATOGRAPHIC/MASS SPECTROMETRIC METHODS

The following methods are included in this section:

Method 8260B:	Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS)
Method 8270C:	Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS)
Method 8275A:	Semivolatile Organic Compounds (PAHs and PCBs) in Soils/Sludges and Solid Wastes Using Thermal Extraction/Gas Chromatography/Mass Spectrometry (TE/GC/MS)
Method 8280A:	The Analysis of Polychlorinated Dibenzo-*p*-Dioxins and Polychlorinated Dibenzofurans by High Resolution Gas Chromatography/Low Resolution Mass Spectrometry (HRGC/LRMS)
Method 8290:	Polychlorinated Dibenzodioxins (PCDDs) and Polychlorinated Dibenzofurans (PCDFs) by High-Resolution Gas Chromatography/High-Resolution Mass Spectrometry (HRGC/HRMS)
Attachment A:	Procedures for the Collection, Handling, Analysis, and Reporting of Wipe Tests Performed within the Laboratory

4.3 DETERMINATION OF ORGANIC ANALYTES

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4.3.3 HIGH PERFORMANCE LIQUID CHROMATOGRAPHIC METHODS

The following methods are included in this section:

Method 8310:	Polynuclear Aromatic Hydrocarbons
Method 8315A:	Determination of Carbonyl Compounds by High Performance Liquid Chromatography (HPLC)
Appendix A:	Recrystallization of 2,4-Dinitrophenylhydrazine (DNPH)
Method 8316:	Acrylamide, Acrylonitrile and Acrolein by High Performance Liquid Chromatography (HPLC)
Method 8318:	N-Methylcarbamates by High Performance Liquid Chromatography (HPLC)
Method 8321A:	Solvent Extractable Nonvolatile Compounds by High Performance Liquid Chromatography/Thermospray/Mass Spectrometry (HPLC/TS/MS) or Ultraviolet (UV) Detection
Method 8325:	Solvent Extractable Nonvolatile Compounds by High Performance Liquid Chromatography/Particle Beam/Mass Spectrometry (HPLC/PB/MS)
Method 8330:	Nitroaromatics and Nitramines by High Performance Liquid Chromatography (HPLC)
Method 8331:	Tetrazene by Reverse Phase High Performance Liquid Chromatography (HPLC)
Method 8332:	Nitroglycerine by High Performance Liquid Chromatography

4.3 DETERMINATION OF ORGANIC ANALYTES

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4.3.4 INFRARED METHODS

The following methods are included in this section:

Method 8410:	Gas Chromatography/Fourier Transform Infrared (GC/FT-IR) Spectrometry for Semivolatile Organics: Capillary Column
Method 8430:	Analysis of Bis(2-chloroethyl) Ether and Hydrolysis Products by Direct Aqueous Injection GC/FT-IR
Method 8440:	Total Recoverable Petroleum Hydrocarbons by Infrared Spectrophotometry

4.3 DETERMINATION OF ORGANIC ANALYTES

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4.3.5 MISCELLANEOUS SPECTROMETRIC METHODS

The following method is included in this section:

Method 8520: Continuous Measurement of Formaldehyde in Ambient Air

4.4 IMMUNOASSAY METHODS

Prior to employing the methods in this chapter, analysts are advised to consult the disclaimer statement at the front of this manual and the information in Chapter Two for guidance on the allowed flexibility in the choice of apparatus, reagents, and supplies. In addition, unless specified in a regulation, the use of SW-846 methods is not mandatory in response to Federal testing requirements. The information contained in each procedure is provided by EPA as guidance to be used by the analyst and the regulated community in making judgements necessary to meet the data quality objectives or needs for the intended use of the data.

The following methods are included in this section:

Method 4000:	Immunoassay
Method 4010A:	Screening for Pentachlorophenol by Immunoassay
Method 4015:	Screening for 2,4-Dichlorophenoxyacetic Acid by Immunoassay
Method 4020:	Screening for Polychlorinated Biphenyls by Immunoassay
Method 4030:	Soil Screening for Petroleum Hydrocarbons by Immunoassay
Method 4035:	Soil Screening for Polynuclear Aromatic Hydrocarbons by Immunoassay
Method 4040:	Soil Screening for Toxaphene by Immunoassay
Method 4041:	Soil Screening for Chlordane by Immunoassay
Method 4042:	Soil Screening for DDT by Immunoassay
Method 4050:	TNT Explosives in Soil by Immunoassay
Method 4051:	Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) in Soil by Immunoassay

4.5 MISCELLANEOUS SCREENING METHODS

Prior to employing the methods in this chapter, analysts are advised to consult the disclaimer statement at the front of this manual and the information in Chapter Two for guidance on the allowed flexibility in the choice of apparatus, reagents, and supplies. In addition, unless specified in a regulation, the use of SW-846 methods is not mandatory in response to Federal testing requirements. The information contained in each procedure is provided by EPA as guidance to be used by the analyst and the regulated community in making judgements necessary to meet the data quality objectives or needs for the intended use of the data.

The following methods are included in this section:

Method 3810:	Headspace
Method 3820:	Hexadecane Extraction and Screening of Purgeable Organics
Method 8515:	Colorimetric Screening Method for Trinitrotoluene (TNT) in Soil
Method 9078:	Screening Test Method for Polychlorinated Biphenyls in Soil
Method 9079:	Screening Test Method for Polychlorinated Biphenyls in Transformer Oil

CHAPTER THREE

INORGANIC ANALYTES

Prior to employing the methods in this chapter, analysts are advised to consult the disclaimer statement at the front of this manual and the information in Chapter Two for guidance on the allowed flexibility in the choice of apparatus, reagents, and supplies. In addition, unless specified in a regulation, the use of SW-846 methods is not mandatory in response to Federal testing requirements. The information contained in each procedure is provided by EPA as guidance to be used by the analyst and the regulated community in making judgements necessary to meet the data quality objectives or needs for the intended use of the data.

3.1 SAMPLING CONSIDERATIONS

3.1.1 Introduction

This manual contains procedures for the analysis of inorganic analytes in a variety of matrices. These methods are written as specific steps in the overall analysis scheme -- sample handling and preservation, sample digestion or preparation, and sample analysis for specific inorganic components. From these methods, the analyst must assemble a total analytical protocol which is appropriate for the sample to be analyzed and for the information required. This introduction discusses the options available in general terms, provides background information on the analytical techniques, and highlights some of the considerations to be made when selecting a total analysis protocol.

3.1.2 Definition of Terms

Optimum concentration range: A range, defined by limits expressed in concentration, below which scale expansion must be used and above which curve correction should be considered. This range will vary with the sensitivity of the instrument and the operating conditions employed.

Sensitivity: (a) Atomic Absorption: The concentration in milligrams of metal per liter that produces an absorption of 1%; (b) Inductively Coupled Plasma (ICP): The slope of the analytical curve, i.e., the functional relationship between emission intensity and concentration.

Method detection limit (MDL): The minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero. The MDL is determined from analysis of a sample in a given matrix containing the analyte which has been processed through the preparative procedure.

Total recoverable metals: The concentration of metals in an unfiltered sample following treatment with hot dilute mineral acid (Method 3005).

Dissolved metals: The concentration of metals determined in a sample after the sample is filtered through a 0.45-µm filter (Method 3005).

Suspended metals: The concentration of metals determined in the portion of a sample that is retained by a 0.45-µm filter (Method 3005).

Total metals: The concentration of metals determined in a sample following digestion by Methods 3010, 3015, 3020, 3050, 3051, or 3052.

Instrument detection limit (IDL): The concentration equivalent to a signal due to the analyte which is equal to three times the standard deviation of a series of 7 replicate measurements of a reagent blank's signal at the same wavelength.

Interference check sample (ICS): A solution containing both interfering and analyte elements of known concentration that can be used to verify background and inter-element correction factors.

Initial calibration verification (ICV) standard: A certified or independently prepared solution used to verify the accuracy of the initial calibration. For ICP analysis, it must be run at each wavelength used in the analysis.

Continuing calibration verification (CCV): Used to assure calibration accuracy during each analysis run. It must be run for each analyte as described in the particular analytical method. At a minimum, it should be analyzed at the beginning of the run and after the last analytical sample. Its concentration should be at or near the mid-range levels of the calibration curve.

Calibration standards: A series of known standard solutions used by the analyst for calibration of the instrument (i.e., preparation of the analytical curve).

Linear dynamic range: The concentration range over which the analytical curve remains linear.

Method blank: A volume of reagent water processed through each sample preparation procedure.

Calibration blank: A volume of reagent water acidified with the same amounts of acids as were the standards and samples.

Laboratory control standard: A volume of reagent water spiked with known concentrations of analytes and carried through the preparation and analysis procedure as a sample. It is used to monitor loss/recovery values.

Method of standard addition (MSA): The standard-addition technique involves the use of the unknown and the unknown plus one or more known amounts of standard. See Method 7000, for detailed instructions.

Sample holding time: The storage time allowed between sample collection and sample analysis when the designated preservation and storage techniques are employed.

Check Standard: A solution containing a known concentration of analyte derived from externally prepared test materials. The check standard is obtained from a source external to the laboratory and is used to check laboratory performance.

3.1.3 Sample Handling and Preservation

Sample holding times, digestion volumes and suggested collection volumes are listed in Table 3-1. The sample volumes required depend upon the number of different digestion procedures necessary for analysis. This may be determined by the application of graphite-furnace atomic absorption spectrometry (GFAA), flame atomic absorption spectrometry (FLAA), inductively coupled argon plasma emission spectrometry (ICP), hydride-generation atomic absorption spectrometry (HGAA), inductively coupled plasma mass spectrometry (ICP-MS) or cold-vapor atomic absorption spectrometry (CVAA) techniques, each of which may require different digestion procedures. The indicated volumes in Table 3-1 refer to that recommended for the individual digestion procedures and to that recommended for sample collection volumes. In all cases for waste testing, representative sampling must be maintained.

In the determination of trace metals, containers can introduce either positive or negative errors in the measurement of trace metals by (a) contributing contaminants through leaching or surface desorption, and (b) depleting concentrations through adsorption. Thus the collection and treatment of the sample prior to analysis require particular attention. The following cleaning treatment sequence has been determined to be adequate to minimize contamination in the sample bottle, whether borosilicate glass, linear polyethylene, polypropylene, or Teflon: detergent, tap water, 1:1 nitric acid, tap water, 1:1 hydrochloric acid, tap water, and reagent water.

NOTE: **Chromic acid should not be used to clean glassware**, especially if chromium is to be included in the analytical scheme. Commercial, non-chromate products (e.g., Nochromix) may be used in place of chromic acid if adequate cleaning is documented by an analytical quality control program. (Chromic acid should also not be used with plastic bottles.)

3.1.4 Safety

The toxicity or carcinogenicity of each reagent used in these methods has not been precisely defined. However, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in these methods. A reference file of material data-handling sheets should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available. They are:

1. "Carcinogens - Working with Carcinogens," Department of Health, Education, and Welfare, Public Health Service, Center for Disease Control, National Institute for Occupational Safety and Health, Publication No. 77-206, August 1977.

2. "OSHA Safety and Health Standards, General Industry," 29 CFR 1910.

3. "Proposed OSHA Safety and Health Standards, Laboratories," Occupational Safety and Health Administration, 51 FR 26660, July 24, 1986.

4. "Safety in Academic Chemistry Laboratories," American Chemical Society Publication, Committee on Chemical Safety.

TABLE 3-1.

SAMPLE HOLDING TIMES, RECOMMENDED DIGESTION VOLUMES AND RECOMMENDED COLLECTION VOLUMES FOR INORGANIC DETERMINATIONS IN AQUEOUS AND SOLID SAMPLES

Measurement	Digestion Volume. (mL)[a, c]	Collection Volume (mL)[a,c]	Treatment/ Preservative Holding Time[b]
Inorganic Analytes (except hexavalent chromium and mercury):			
Aqueous			
Total	100	600	HNO_3 to pH <2 6 months
Dissolved	100	600	Filter on site; HNO_3 to pH <2 6 months
Suspended	100	600	Filter on site 6 months
Solid			
Total	2 g	200 g	6 months
Hexavalent Chromium:			
Aqueous	100	400	24 hours Store at 4°± 2°C until analyzed
Solid	2.5 g	100 g	One month to extraction, 4 days after extraction Store at 4°± 2°C until analyzed
Mercury:			
Aqueous			
Total	100	400	HNO_3 to pH <2 28 days
Dissolved	100	400	Filter; HNO_3 to pH <2 28 days
Solid			
Total	0.2 g	200 g	28 days Store at 4°± 2°C until analyzed

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[a] Unless stated otherwise.

[b] Either glass or plastic containers may be used.

[c] Any sample volume reduction from the reference method's instructions must be made in the exact proportion as described in the method and representative sampling must be maintained.

3.2 SAMPLE PREPARATION METHODS

The methods in SW-846 for sample digestion or preparation are as follows[1]:

Method 3005 prepares ground water and surface water samples for total recoverable and dissolved metal determinations by FLAA, ICP-AES, or ICP-MS. The unfiltered or filtered sample is heated with dilute HCl and HNO_3 prior to metal determination.

Method 3010 prepares waste samples for total recoverable metal determinations by FLAA, ICP-AES, or ICP-MS. The samples are vigorously digested with nitric acid followed by dilution with hydrochloric acid. The method is applicable to aqueous samples, EP and mobility-procedure extracts.

Method 3015 prepares aqueous samples, mobility-procedure extracts, and wastes that contain suspended solids for total recoverable metal determinations by FLAA, GFAA, ICP-AES, or ICP-MS. Nitric acid is added to the sample in a Teflon digestion vessel and heated in a microwave unit prior to metals determination.

Method 3020 prepares waste samples for total recoverable metals determinations by furnace GFAA or ICP-MS. The samples are vigorously digested with nitric acid followed by dilution with nitric acid. The method is applicable to aqueous samples, EP and mobility-procedure extracts.

Method 3031 prepares waste oils, oil sludges, tars, waxes, paints, paint sludges and other viscous petroleum products for analysis by FLAA, GFAA, and ICP-AES. The samples are vigorously digested with nitric acid, sulfuric acid, hydrochloric acid, and potassium permanganate prior to analysis.

Method 3040 prepares oily waste samples for determination of soluble metals by FLAA, GFAA, and ICP-AES methods. The samples are dissolved and diluted in organic solvent prior to analysis. The method is applicable to the organic extract in the oily waste EP procedure and other samples high in oil, grease, or wax content.

Method 3050 prepares waste samples for total recoverable metals determinations by FLAA and ICP-AES, or GFAA and ICP-MS depending on the options chosen. The samples are vigorously digested in nitric acid and hydrogen peroxide followed by dilution with either nitric or hydrochloric acid. The method is applicable to soils, sludges, and solid waste samples.

Method 3051 prepares sludges, sediments, soils and oils for total recoverable metal determinations by FLAA, GFAA, ICP-AES or ICP-MS. Nitric acid is added to the representative sample in a fluorocarbon digestion vessel and heated in a microwave unit prior to metals determination.

Method 3052 prepares siliceous and organically based matrices including ash, biological tissue, oil, oil contaminated soil, sediment, sludge, and soil for total analysis by FLAA, CVAA, GFAA, ICP-AES, and ICP-MS. Nitric acid and hydrofluoric acid are added to a representative sample in a fluorocarbon digestion vessel and heated in a microwave unit prior to analysis.

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[1] Please note that chlorine is an interferant in ICP-MS analyses and its use should be discouraged except when absolutely necessary.

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3.3 METHODS FOR DETERMINATION OF INORGANIC ANALYTES

This section of the manual contains seven analytical techniques for trace inorganic analyte determinations: inductively coupled argon plasma atomic emission spectrometry (ICP-AES), inductively coupled plasma mass spectrometry (ICP-MS), direct-aspiration or flame atomic absorption spectrometry (FLAA), graphite-furnace atomic absorption spectrometry (GFAA), hydride-generation atomic absorption spectrometry (HGAA), cold-vapor atomic absorption spectrometry (CVAA), and several procedures for hexavalent chromium analysis. Each of these is briefly discussed below in terms of advantages, disadvantages, and cautions for analysis of wastes.

ICP's primary advantage is that it allows simultaneous or rapid sequential determination of many elements in a short time. The primary disadvantage of ICP is background radiation from other elements and the plasma gases. Although all ICP instruments utilize high-resolution optics and back-ground correction to minimize these interferences, analysis for traces of inorganic analytes in the presence of a large excess of a single analyte is difficult. Examples would be traces of inorganic analytes in an alloy or traces of metals in a limed (high calcium) waste. ICP and Flame AA have comparable detection limits (within a factor of 4) except that ICP exhibits greater sensitivity for refractories (Al, Ba, etc.). Furnace AA, in general, will exhibit lower detection limits than either ICP or FLAA. Detection limits are drastically improved when ICP-MS is used. In general ICP-MS exhibits greater sensitivity than either GFAA or FLAA for most elements. The greatest disadvantage of ICP-MS is isobaric elemental interferences. These are caused by different elements forming atomic ions with the same nominal mass-to-charge ratio. Mathematical correction for interfering ions can minimize these interferences.

Flame AAS (FLAA) direct aspiration determinations, as opposed to ICP, are normally completed as single element analyses and are relatively free of interelement spectral interferences. Either a nitrous-oxide/acetylene or air/acetylene flame is used as an energy source for dissociating the aspirated sample into the free atomic state, making analyte atoms available for absorption of light. In the analysis of some elements, the temperature or type of flame used is critical. If the proper flame and analytical conditions are not used, chemical and ionization interferences can occur.

Graphite Furnace AAS (GFAA) replaces the flame with an electrically heated graphite furnace. The furnace allows for gradual heating of the sample aliquot in several stages. Thus, the processes of dissolution, drying, decomposition of organic and inorganic molecules and salts, and formation of atoms which must occur in a flame or ICP in a few milliseconds may be allowed to occur over a much longer time period and at controlled temperatures in the furnace. This allows an experienced analyst to remove unwanted matrix components by using temperature programming and/or matrix modifiers. The major advantage of this technique is that it affords extremely low detection limits. It is the easiest to perform on relatively clean samples. Because this technique is so sensitive, interferences can be a real problem; finding the optimum combination of digestion, heating times and temperatures, and matrix modifiers can be a challenge for complex matrices.

Hydride AA utilizes a chemical reduction to reduce and separate arsenic or selenium selectively from a sample digestate. The technique therefore has the advantage of being able to isolate these two elements from complex samples which may cause interferences for other analytical procedures. Significant interferences have been reported when any of the following is present: 1) easily reduced metals (Cu, Ag, Hg); 2) high concentrations of transition metals (>200 mg/L); 3) oxidizing agents (oxides of nitrogen) remaining following sample digestion.

Cold-Vapor AA uses a chemical reduction to reduce mercury selectively. The procedure is extremely sensitive but is subject to interferences from some volatile organics, chlorine, and sulfur compounds.

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