CHAPTER FOUR
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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 judgments necessary to meet the data quality objectives (DQOs) 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 (or other material) 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 matrix, type of containers and their preparation, analytes of interest, preservation techniques, and sample holding times must be thoroughly examined in order to maintain the integrity of the samples. This section highlights practices relevant to maintaining sample integrity and representativeness from the time of sampling until analysis is complete. This section is, however, applicable primarily to trace analyses. Some of these considerations may be less relevant for source level samples.

4.1.2 Sample Handling and Preservation: General Considerations

This following sections deal separately with volatile organic chemicals (VOCs) and semivolatile organic chemicals (SVOCs). Refer to Chapter Two and Table 4-1 of this section for recommended sample containers, sample preservation, and holding time information. The guidelines in Table 4-1 are intended to improve chemical stability in the sample matrix between the time of sample collection and laboratory preparation/analysis by minimizing loss of the analytes of interest from the sample container and limiting biological and/or chemical degradation (e.g., hydrolysis) (Sec. 4.6 Refs 1, 3-6). Sample preservation recommendations for analysis of organic chemicals almost always include refrigeration or freezing and may also include chemical preservation (e.g., addition of pH modifier). Improper handling, preservation, and storage of samples can negatively impact the representativeness of the field sample data.

The preservation and holding time information presented in Table 4-1 does not represent EPA requirements, but rather is intended solely as guidance. Selection of preservation techniques and applicable holding times should be based on all available information, including the properties of the analytes of interest for the project, their anticipated concentration levels, the composition of the sample matrix itself, and the stated project-specific DQOs. A shorter holding time may be appropriate if the analytes of interest are reactive (e.g., 2-chloroethyl vinyl ether, acrylamide) or the sample matrix is complex (e.g., wastewater). Conversely, a longer holding time may be appropriate if it can be demonstrated that the analytes of interest are not adversely affected from preservation, storage and analyses performed outside the recommended holding times. Prior to collecting samples for analysis, the project team may consider existing information and data regarding analyte stability or conduct field screening for the samples to be collected in

order to determine how best to preserve sample integrity for the analytes of interest. The use of site-specific performance evaluation material is a high confidence mechanism to ensure reliability of project data. The references in Sec. 4.6 provide examples of study designs that may be useful for this purpose.

4.1.3 Sample Handling and Preservation for Volatile Organics

4.1.3.1 VOC Sample Containers

The containers used for collecting VOC samples are frequently volatile organics analysis (VOA) vials that are directly compatible with the equipment used for sample preparation and analysis in the laboratory. Use of these containers for sampling helps minimize loss of VOCs resulting from opening sample containers and/or transferring materials from one container to another. Certified pre-cleaned VOA vials are commonly used as sample containers for VOCs and are commercially available from a number of vendors. The vials should be absent of burrs around the caps that might prevent the vial from sealing, and septa should be lined with a polytetrafluoroethylene (PTFE) layer of sufficient thickness to limit diffusion of VOCs out of the vials during storage. PTFE thicknesses of 0.13 to 0.25 mm have been shown to be effective. See reference # 18 in Sec. 4.6 below and Sec. A.8 in Method 5035A for more detail. If they are suspected of being a source of interferences, VOA vials and unpunctured septa should be washed with soap and water and rinsed with distilled de-ionized 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: Heating the septa for extended periods of time (i.e., more than one hour) or at higher temperatures should be avoided, because the silicone begins to slowly degrade at 105 °C). Also, punctured silicone-backed PTFE-lined septa should generally not be reused, because some VOCs have high affinity for the silicone material, and puncturing the PTFE septum face exposes the gas phase vial contents to the silicone backing material, causing loss of certain VOCs depending on length of exposure time and vial temperature.

Air-tight, sealable coring devices (e.g., En Core™, Core N' One™ or equivalent) may also be useful for collection and storage of cohesive soil samples for VOC analysis. These devices are designed to limit loss of VOCs from samples during cold storage and shipping over a limited time frame and for quantitative transfer of solids and associated VOCs into VOA vials for immediate analysis or further preservation. Their use during field sampling of solids helps reduce or eliminate the need to handle solvents or chemical preservatives in the field and eliminates some shipping restrictions on field samples that may otherwise contain flammable solvents (e.g., methanol). Additional information regarding stability studies of VOCs in solid materials stored in sealable coring devices is contained in the Sec. A.7 of the appendix of Method 5035A and is described in more detail in the sources referenced therein. An American Society for Testing and Materials (ASTM) standard practice for use of the En Core™ type samplers is also included in the references in Sec. 4.6 below.

4.1.3.2 VOC Sample Collection:

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

At least two replicate VOA vials should be collected and labeled immediately for each collected field sample. They should not be filled near a running motor or any type of exhaust system because discharged fumes and vapors may contaminate the samples. Replicate vials from a single sampling point may be sealed together in a single plastic bag, but different samples should be segregated into separate plastic bags to prevent contamination of samples with little to no VOCs from those with high concentrations. Sample containers may also become contaminated by diffusion of VOCs into the vials through the septa from the surrounding environment during shipment and storage. To monitor for this potential source of contamination, a trip blank prepared from organic-free reagent water (as defined in Chapter One) should be maintained with the samples throughout sampling, shipping, and storage. Including activated carbon in the bags containing the sample vials may help reduce concerns related to these potential sources of sample contamination.

Improper vial sealing (e.g., due to solids retained on the vial threads) and improper tightening of caps or closing of sealable coring devices are primary factors in the loss of volatiles due to sample collection activities. Sealing surfaces and any closure threads should be inspected to ensure they are free of debris prior to container closure.

Procedures should also be established for selection and appropriate use of sample collection devices (i.e., bailer, coring tool, etc.) including appropriate decontamination measures. If the sample comes in contact with the sampling device, organic free reagent water may be run through the device and tested as a field blank.

In general, liquid samples should be poured into vials without introducing any air bubbles into the samples as vials are filled. Should bubbling occur as a result of violent pouring, the sample should 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 is inverted, no headspace is visible. The sample should be hermetically sealed in the vial at the time of sampling, and not opened prior to analysis to preserve its integrity.

4.1.3.3 VOC Sample Preservation and Holding Times:

Samples containing analytes that can be subject to biological degradation need to be preserved as soon as possible (preferably in the field) to avoid the loss of target analytes. Refrigeration or freezing is a primary means of sample preservation, because rates of biotic and abiotic degradation decrease with decreasing temperature, and VOCs are also less volatile at lower temperature. Samples containing analytes that are most subject to biological degradation (e.g., aromatic hydrocarbons) also should be chemically preserved (e.g., by addition of acid), unless they are analyzed immediately. Chemical preservation may be inappropriate for highly reactive compounds (e.g., 2-chloroethyl vinyl ether, acrylamide, etc.), since it may accelerate loss by rapid chemical reaction. Aqueous samples containing free chlorine should also be preserved with a dechlorinating agent in order to minimize formation of trihalomethanes and other possible chemical reactions.

Although VOC samples may be held for up to 7 days unpreserved or 14 days or longer preserved, it is generally not recommended as good laboratory

practice to hold them that long. VOC samples should be run as soon as possible after receipt by the laboratory. Samples in which highly reactive compounds (e.g., 2-chloroethyl vinyl ether, acrylamide, etc.) are analytes of interest should be analyzed as soon as they are received in the laboratory.

4.1.4 Sample Handling and Preservation for Semivolatile Organics, Including Pesticides, PCBs and Herbicides

4.1.4.1 Sample Containers for Analysis of Semivolatile Organics

The containers specified for samples intended for analysis of SVOCs are typically constructed of glass with PTFE-lined threaded caps. In situations where PTFE liners are 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. Use of new, disposable pre-cleaned and certified containers reduces concerns about contamination from reusing sample containers. Plastic containers or plastic lids without PTFE liners should not be used for storage of samples due to potential contamination by phthalate esters and other hydrocarbons within the plastic or absorption of any chemicals of concern in the native sample into the container material. If sample containers are suspected of being a source of interferences, particularly for low-level analysis, they should be soap and water washed followed by rinsing with solvent(s) appropriate for the analytes of interest. (See Sec. 4.1.6 for specific instructions on glassware cleaning.). Caps may be cleaned by solvent rinsing or replaced with new ones. Monitoring for contamination introduced from sample containers should be accomplished through preparation and analysis of a method blank.

4.1.4.2 Sample Collection for SVOCs

Sample containers should be filled with care so as to prevent any portion of the collected samples from coming in contact with the sampler's gloves, potentially leading to sample contamination. Samples should not be collected or stored in the presence of exhaust fumes. If the sample comes in contact with the sampling device, run organic-free reagent water through the sampling device and test this water as a field blank.

4.1.4.3 Sample Preservation and Holding Times for SVOCs

Field samples to be analyzed for SVOCs are typically preserved by refrigeration or freezing. In order to minimize opportunities for the most labile SVOCs to degrade, these samples are typically recommended to be solvent extracted shortly after being taken, within 7-14 days for many classes of chemicals. However, some classes of SVOCs, like polychlorinated biphenyls and polychlorinated dibenzodioxins and dibenzofurans are very recalcitrant and do not readily degrade during refrigerated storage. Sample matrices to be analyzed for these SVOCs have no maximum recommended holding time. Depending on the composition of the sample matrix and the levels of concern for the target analytes, other classes of SVOCs (e.g., polycyclic aromatic hydrocarbons [PAHs]) may also be stable in refrigerated or frozen storage for longer than the maximum holding time recommended in Table 4-1 (see Reference #12 in Sec. 4.6 below). However, the composition of the sample matrix can be an important determinant of chemical stability, and minimizing the holding time between sampling and solvent extraction is generally a good practice to obtain representative data.

Solvent extracts of samples should be carefully maintained. Solvent extraction generally stabilizes SVOCs, because the chemicals are typically physically removed from the sample matrix, and some loss mechanisms are eliminated (i.e., biological degradation). Holding times of 40 days are recommended for solvent extracts for most classes of SVOCs. Many analytes of interest may be stable in solvent for a longer time period even in extracts of complex matrices, but problems maintaining small volumes of very volatile solvent extracts preclude storage of extracts indefinitely, and some SVOCs may still chemically degrade or may be slightly volatile in certain solvents.

Freezing solvent extracts particularly of complex sample matrices may cause precipitation of solids resulting from interaction of some co-extracted sample matrix components. Storing extracts at 0 to 6 ^{o}C may limit problems resulting from analyzing extracts containing precipitated solids, like contaminating or clogging the injector syringe or introducing insoluble components into the flow pathway of the mobile phase. One way to remove precipitated solids from a solvent extract is by filtration with a sub-micron particle size filter made of inert material (e.g., PTFE). As with other preparation steps, batch quality control (QC) samples should be subjected to the same filtration procedure as the field samples in order to assess the cumulative impact of all sample preparation steps on analyte recovery and evaluate the potential for contamination resulting from all reagents, and other materials that come into contact with the samples.

4.1.5 Safety

The methods listed in this chapter do not address all safety issues associated with their use. The laboratory is responsible for maintaining a safe work environment and a current awareness file of OSHA regulations regarding the safe handling of the chemicals used in these methods. A reference file of material safety data sheets (MSDSs) and/or safety data sheets (SDSs) should be available to all personnel involved in these analyses.

Safety should always be the primary consideration in the collection and analysis of samples. A thorough understanding of the waste production process, as well as all of the potential hazards of the waste itself, should be investigated whenever possible. The site should be evaluated just prior to sampling to determine whether any additional safety measures are necessary. 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.

4.1.6 Cleaning of Reusable Glassware

In order to successfully analyze samples containing components in the parts per billion or lower concentration range, the preparation of scrupulously clean glassware is necessary. Failure to do so can lead to a myriad of problems interpreting data due to the presence of interferences 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 that comes into contact with an extract, particularly if the extract 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 distort the results and complicate data interpretation.

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

Comments regarding each of the eight fundamental steps are discussed here in the order in which they appeared above:

Step 1: As soon as analysis is complete, the glassware (e.g., beakers, pipettes, flasks, or bottles) that came into contact with samples or standards should be flushed with water and then alcohol or other appropriate solvent before it is placed in the hot detergent soak. Otherwise, the soak bath may serve to contaminate all other glassware placed therein.

Step 2: The hot soak consists of a bath of a suitable detergent in water at 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 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.

Step 3: No comments

Step 4: **Chromic acid should not be used to clean glassware.** Commercial, non-chromate products (e.g., Nochromix) may be used in place of chromic acid, if adequate cleaning is documented by an analytical quality assurance (QA) program. Chromic acid should also not be used with plastic bottles.

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 roughly 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. Other similarly effective products are Nochromix (Godax Laboratories) and Contrad 70 (Decon Labs).

Steps 5, 6, and 7: No comments

Step 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 prevent 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 realize the benefit of scrupulous cleaning. 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. Otherwise, dust and soot in a laboratory environment can re-contaminate the clean glassware.

As an alternative to solvent rinsing, glassware may be heated to a minimum of 300 °C for sufficient time to vaporize any residual organic chemicals. Glassware should be allowed to cool fully before use. This high temperature treatment should not be used on volumetric glassware, glassware with ground glass joints, or sintered glassware.

4.1.7 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, at a minimum, disposable glassware or glassware dedicated solely to the preparation of high concentration samples should be used. Avoid cleaning glassware used for both trace and high concentration samples in the same area.

TABLE 4-1
RECOMMENDED SAMPLE CONTAINERS, PRESERVATION TECHNIQUES, AND HOLDING TIMES[a]
(Note: Footnotes are located on the last page of the table.)

VOLATILE ORGANICS

Sample Matrix	Container[1]	Preservative[2]	Holding Time[3]
Concentrated waste samples	Method 5035: See the method. Method 5021: See the method. Methods 5031 and 5032: See the methods. Use PTFE-lined lids for all procedures.	Cool to 0 - 6 °C.	14 days
Aqueous samples with no residual chlorine present	Methods 5021, 5030, 5031, and 5032: 3 x 40-mL vials with PTFE-lined septum caps	Cool to 0 - 6°C and adjust pH to less than 2 with H_2SO_4, HCl, or solid $NaHSO_4$	14 days
		If carbonaceous materials are present, or if MTBE and other fuel oxygenate ethers are present and a high temperature sample preparative method is to be used, do not acid preserve the samples.	*7 days*
		If compounds that readily degrade in acidified water (e.g., 2-chloroethyl vinyl ether[b]) are analytes of interest, collect a second set of samples without acid preservatives and analyze as soon as possible.	*7 days*

TABLE 4-1 (continued)
RECOMMENDED SAMPLE CONTAINERS, PRESERVATION TECHNIQUES, AND HOLDING TIMES[a]

VOLATILE ORGANICS (continued)

Sample Matrix	Container[1]	Preservative[2]	Holding Time[3]
Aqueous samples WITH residual chlorine present	Methods 5021, 5030, 5031, and 5032: 3 x 40-mL vials with PTFE-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 0 - 6 °C and adjust pH to less than 2 with H_2SO_4, HCl, or solid $NaHSO_4$.	14 days
		If carbonaceous materials are present, or if MTBE and other fuel oxygenate ethers are present and a high temperature sample preparative method is to be used, do not acid preserve the samples.	*7 days*
		If compounds that readily degrade in acidified water (e.g., 2-chloroethyl vinyl ether[b]) are analytes of interest, collect a second set of samples without acid preservatives and analyze as soon as possible.	*7 days*
Acrolein and Acrylonitrile Aqueous samples	Methods 5021, 5030, 5031, and 5032: 3 x 40-ml vials with PTFE-lined septum caps	Adjust to pH 4 - 5. Cool to 0 - 6 °C. These compounds are highly reactive and should be analyzed as soon as possible.	7 days
Solid samples (e.g., soils, sediments, sludges, ash)	Method 5035: See the method. Method 5021: See the method. Methods 5031 and 5032: See the methods.	See the individual methods.	14 days
		If compounds that may be reactive in acidified soils (e.g., vinyl chloride, styrene, 2-chloroethyl vinyl ether) are analytes of interest, collect a second set of samples without acid preservatives and analyze as soon as possible.	7 days

TABLE 4-1 (continued)
RECOMMENDED SAMPLE CONTAINERS, PRESERVATION TECHNIQUES, AND HOLDING TIMES[a]

SEMIVOLATILE ORGANICS/ORGANOCHLORINE PESTICIDES AND HERBICIDES

Sample Matrix	Container[1]	Preservative[2]	Holding Time[3]
Concentrated waste samples	125-mL wide-mouth glass with PTFE-lined lid	Cool to 0 - 6 °C.	Samples extracted within 14 days and extracts analyzed within 40 days following extraction.
Aqueous samples with no residual chlorine present	4 x 1-L amber glass container with PTFE-lined lid, or other size, as appropriate, to allow use of entire sample for analysis.	Cool to 0 - 6 °C.	Samples extracted within 7 days and extracts analyzed within 40 days following extraction.
Aqueous samples WITH residual chlorine present	4 x 1-L amber glass container with PTFE-lined lid, or other size, as appropriate, to allow use of entire sample for analysis.	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 0 - 6 °C.	Samples extracted within 7 days and extracts analyzed within 40 days following extraction.
Solid samples (e.g., soils, sediments, sludges, ash)	250-mL wide-mouth glass container with PTFE-lined lid	Cool to 0 - 6 °C.	Samples extracted within 14 days and extracts analyzed within 40 days following extraction.

TABLE 4-1 (continued)
RECOMMENDED SAMPLE CONTAINERS, PRESERVATION TECHNIQUES, AND HOLDING TIMES[a]

POLYCHLORINATED BIPHENYLS, POLYCHLORINATED DIBENZO-*p*-DIOXINS, AND POLYCHLORINATED DIBENZOFURANS

Sample Matrix	Container[1]	Preservative[2]	Holding Time[3]
Concentrated waste samples	125-mL wide-mouth glass with PTFE-lined lid	None	None
Aqueous samples with no residual chlorine present	4 x 1-L amber glass container with PTFE-lined lid, or other size, as appropriate, to allow use of entire sample for analysis.	Cool to 0 - 6 °C.	None
Aqueous samples WITH residual chlorine present	4 x 1-L amber glass container with PTFE-lined lid, or other size, as appropriate, to allow use of entire sample for analysis.	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 0 - 6 °C	None
Solid samples (e.g., soils, sediments, sludges, ash)	250-mL wide-mouth glass container with PTFE-lined lid.	Cool to 0 - 6 °C.	None

[a] The information presented in this table does not represent EPA requirements, but rather it is intended solely as guidance. Selection of containers, preservation techniques and applicable holding times should be based on the stated project-specific DQOs.
[b] See References 1-10 for the preservation and holding times studies for volatile organics. It is the intention of the Agency that separate unpreserved vials be collected when 2-chloroethylvinyl ether is an analyte of interest.
[1] PTFE-lined caps are acceptable for all recommended container types. Additional replicate sample containers should also be collected to perform all necessary laboratory QC (e.g., duplicate, matrix spike / matrix spike duplicate QC samples).
[2] The exact sample, extract, and standard storage temperature should be based on project-specific requirements and/or manufacturer's recommendations for commercially available standards. Furthermore, alternative storage temperatures may be appropriate based on demonstrated analyte stability in a given matrix, provided the stated DQOs for a project-specific application are still attainable.
[3] A longer holding time may be appropriate if it can be demonstrated that the reported analyte concentrations are not adversely affected from preservation, storage and analyses performed outside the recommended holding times.

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 judgments necessary to meet the DQOs or needs for the intended use of the data.

4.2.1 Extractions and preparations

The following methods are included in this section:

Method 3500C:	Organic Extraction and Sample Preparation
Method 3510C:	Separatory Funnel Liquid-Liquid Extraction
Method 3511:	Organic Compounds in Water by Microextraction
Method 3520C:	Continuous Liquid-Liquid Extraction
Method 3535A:	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 3545A:	Pressurized Fluid Extraction (PFE)
Method 3546:	Microwave Extraction
Method 3550C:	Ultrasonic Extraction
Method 3560:	Supercritical Fluid Extraction of Total Recoverable Petroleum Hydrocarbons
Method 3561:	Supercritical Fluid Extraction of Polynuclear Aromatic Hydrocarbons
Method 3562:	Supercritical Fluid Extraction of Polychlorinated Biphenyls (PCBs) and Organochlorine Pesticides
Method 3570:	Microscale Solvent Extraction (MSE)
Method 3571:	Extraction of Solid and Aqueous Samples for Chemical Agents
Method 3572:	Extraction of Wipe Samples for Chemical Agents
Method 3580A:	Waste Dilution
Method 3585:	Waste Dilution for Volatile Organics
Method 5000:	Sample Preparation for Volatile Organic Compounds
Method 5021A:	Volatile Organic Compounds in Soils and Other Solid Matrices Using Equilibrium Headspace Analysis
Method 5030B:	Purge-and-Trap for Aqueous Samples
Method 5031:	Volatile, Non-purgeable, 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)

4.2.2 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 3620C: 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

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 judgments necessary to meet the DQOs or needs for the intended use of the data.

4.3.1 Gas chromatographic methods

The following methods are included in this section:

Method 8000D: Determinative Chromatographic Separations
Method 8011: 1,2-Dibromoethane and 1,2-Dibromo-3-chloropropane by Microextraction and Gas Chromatography
Method 8015C: Non-halogenated Organics by Gas Chromatography
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 8041A: Phenols by Gas Chromatography
Method 8061A: Phthalate Esters by Gas Chromatography with Electron Capture Detection (GC/ECD)
Method 8070A: Nitrosamines by Gas Chromatography
Method 8081B: Organochlorine Pesticides by Gas Chromatography
Method 8082A: Polychlorinated Biphenyls (PCBs) by Gas Chromatography

Method 8085: Compound-independent Elemental Quantitation of Pesticides by Gas Chromatography with Atomic Emission Detection (GC/AED)
Method 8091: Nitroaromatics and Cyclic Ketones by Gas Chromatography
Method 8095: Explosives 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 8141B: Organophosphorus Compounds by Gas Chromatography
Method 8151A: Chlorinated Herbicides by GC Using Methylation or Pentafluorobenzylation Derivatization

4.3.2 Gas chromatographic/mass spectrometric 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 judgments necessary to meet the DQOs or needs for the intended use of the data.

The following methods are included in this section:

Method 8260B: Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS)
Method 8261: Volatile Organic Compounds by Vacuum Distillation in Combination with Gas Chromatography/Mass Spectrometry (VD/GC/MS)
Method 8270D: 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 8276: Toxaphene and Toxaphene Congeners by Gas Chromatography/Negative Ion Chemical Ionization Mass Spectrometery (GC-NICI/MS)
Method 8280B: Polychlorinated Dibenzo-*p*-Dioxins (PCDDs) and Polychlorinated Dibenzofurans (PCDFs) by High-Resolution Gas Chromatography/Low Resolution Mass Spectrometry (HRGC/LRMS)
Method 8290A: Polychlorinated Dibenzo-*p*-dioxins (PCDDs) and Polychlorinated Dibenzofurans (PCDFs) by High-Resolution Gas Chromatography/High-Resolution Mass Spectrometry (HRGC/HRMS)
Appendix A: Procedures for the Collection, Handling,

Analysis and Reporting of Wipe Tests Performed within the Laboratory

4.3.3 High performance liquid chromatographic 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 judgments necessary to meet the DQOs or needs for the intended use of the data.

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: Re-crystallization of 2,4-Dinitrophenylhydrazine (DNPH)
Method 8316: Acrylamide, Acrylonitrile and Acrolein by High Performance Liquid Chromatography (HPLC)
Method 8318A: *N*-Methylcarbamates by High Performance Liquid Chromatography (HPLC)
Method 8321B: 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 8330A: 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

4.3.4 Infrared 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 judgments necessary to meet the DQOs or needs for the intended use of the data.

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

4.3.5 Miscellaneous spectrometric 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 judgments necessary to meet the DQOs or needs for the intended use of the data.

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 judgments necessary to meet the DQOs 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 4025: Screening for Polychlorinated Dibenzodioxins and Polychlorinated Dibenzofurans (PCDD/Fs) 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
Method 4425:	Screening Extracts of Environmental Samples for Planar Organic Compounds (PAHs, PCBs, PCDDs/PCDFs) by a Reporter Gene on a Human Cell Line
Method 4430:	Screening For Polychlorinated Dibenzo-p-Dioxins And Furans (PCDD/Fs) By Aryl Hydrocarbon-Receptor PCR Assay
Method 4435:	Method For Toxic Equivalents (TEQS) Determinations For Dioxin-Like Chemical Activity with the CALUX® Bioassay
Method 4670:	Triazine Herbicides as Atrazine in Water by Quantitative 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 judgments necessary to meet the DQOs or needs for the intended use of the data.

The following methods are included in this section:

Method 3815:	Screening Solid Samples for Volatile Organics
Method 3820:	Hexadecane Extraction and Screening of Purgeable Organics
Method 8510:	Colorimetric Screening Procedure for RDX and HMX in Soil
Method 8515:	Colorimetric Screening Method for Trinitrotoluene (TNT) in Soil
Method 8535:	Screening Procedure for Total Volatile Organic Halides in Water
Method 8540:	Pentachlorophenol by UV-Induced Colorimetry
Method 9074:	Turbidimetric Screening Method for Total Recoverable Petroleum Hydrocarbons in Soil
Method 9078:	Screening Test Method for Polychlorinated Biphenyls in Soil
Method 9079:	Screening Test Method for Polychlorinated Biphenyls in Transformer Oil

4.6 REFERENCES

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Appendix A:
Summary of Updates/Changes in Chapter 4

1. The document format was updated to Microsoft Word .docx format.
2. The revision number was changed to five and the date published to July 2014.
3. Various editorial corrections were made throughout Section 4.1 to 4.5 to improve clarity.
4. Table 4-1 was reformatted and updated by removing the recommendation to collect a second set of samples without adding an acid preservative and analyze in a shorter time frame if vinyl chloride and styrene are analytes of concern for aqueous samples.
5. Methods 3511 and 3572 were added to Section 4.2.1. Various Method version letters were updated to the current version.
6. Methods 4025, 4430 and 4435 were added to Section 4.4
7. A references section was added as Section 4.6.