CHAPTER FOUR
ORGANIC ANALYTES

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 both liquid and solid matrices. 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.

At the time of analysis, the aliquot to be analyzed should be taken from the vial with a gas-tight syringe inserted directly through the septum of the vial. Only one analytical sample can be taken from each vial. If these guidelines are not followed, the validity of the data generated from the samples is suspect.

VOA vials for samples with solid or semi-solid matrices (e.g., sludges) should be completely filled as best as possible. The vials should be tapped slightly as they are filled to try and eliminate as much free air space as possible. 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 NOT 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 preceeding 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

Analyte Class	Container	Preservative	Holding Time
Volatile Organics			
Concentrated Waste Samples	125 mL widemouth glass container with Teflon lined lid	Cool, 4°C	14 days
Liquid Samples			
No Residual Chlorine Present	2 X 40 mL vials with Teflon lined septum caps	Cool, 4°C[1]	14 days
Residual Chlorine Present	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.[1] Cool, 4°C	14 days
Acrolein and Acrylonitrile	2 X 40 mL vials with Teflon lined septum caps	Adjust to pH 4-5; cool, 4°C	14 days
Soil/Sediments and Sludges	125 mL widemouth glass container sealed with a septum	Cool, 4°C	14 days

[1] Adjust pH <2 with H_2SO_4, HCl or solid $NaHSO_4$.

TABLE 4-1, Continued

Analyte Class	Container	Preservative	Holding Time
Semivolatile Organics/Organochlorine Pesticides/PCBs and Herbicides			
Concentrated Waste Samples	125 mL widemouth glass with Teflon lined lid	None	Samples must be extracted within 14 days and extracts analyzed within 40 days following extraction.
Water Samples			
No Residual Chlorine Present	1-gal. or 2 x 0.5-gal.,or 4 x 1-L, amber glass container with Teflon lined lid	Cool, 4°C	Samples must be extracted within 7 days and extracts analyzed within 40 days following extraction.
Residual Chlorine Present	1-gal. or 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.[2] Cool, 4°C	Samples must be extracted within 7 days and extracts analyzed within 40 days following extraction.
Soil/Sediments and Sludges	250 mL widemouth glass container with Teflon lined lid	Cool, 4°C	Samples must be extracted within 14 days and extracts analyzed within 40 days following extraction.

[2] Pre-preservation may be performed in the laboratory prior to field use.

4.2 SAMPLE PREPARATION METHODS

4.2.1 EXTRACTIONS AND PREPARATIONS

The following methods are included in this section:

Method 3500A:	Organic Extraction and Sample Preparation
Method 3510B:	Separatory Funnel Liquid-Liquid Extraction
Method 3520B:	Continuous Liquid-Liquid Extraction
Method 3540B:	Soxhlet Extraction
Method 3541:	Automated Soxhlet Extraction
Method 3550A:	Ultrasonic Extraction
Method 3580A:	Waste Dilution
Method 5030A:	Purge-and-Trap
Method 5040A:	Analysis of Sorbent Cartridges from Volatile Organic Sampling Train (VOST): Gas Chromatography/Mass Spectrometry Technique
Method 5041:	Protocol for Analysis of Sorbent Cartridges from Volatile Organic Sampling Train (VOST): Wide-bore Capillary Column Technique

4.2 SAMPLE PREPARATION METHODS

4.2.2 CLEANUP

The following methods are included in this section:

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

4.3 DETERMINATION OF ORGANIC ANALYTES

4.3.1 GAS CHROMATOGRAPHIC METHODS

The following methods are included in this section:

Method 8000A:	Gas Chromatography
Method 8010B:	Halogenated Volatile Organics by Gas Chromatography
Method 8011:	1,2-Dibromoethane and 1,2-Dibromo-3-chloropropane by Microextraction and Gas Chromatography
Method 8015A:	Nonhalogenated Volatile Organics by Gas Chromatography
Method 8020A:	Aromatic Volatile Organics by Gas Chromatography
Method 8021A:	Halogenated Volatiles by Gas Chromatography Using Photoionization and Electrolytic Conductivity Detectors in Series: Capillary Column Technique
Method 8030A:	Acrolein and Acrylonitrile by Gas Chromatography
Method 8031:	Acrylonitrile by Gas Chromatography
Method 8032:	Acrylamide by Gas Chromatography
Method 8040A:	Phenols by Gas Chromatography
Method 8060:	Phthalate Esters
Method 8061:	Phthalate Esters by Capillary Gas Chromatography with Electron Capture Detection (GC/ECD)
Method 8070:	Nitrosamines by Gas Chromatography
Method 8080A:	Organochlorine Pesticides and Polychlorinated Biphenyls by Gas Chromatography
Method 8081:	Organochlorine Pesticides and PCBs as Aroclors by Gas Chromatography: Capillary Column Technique
Method 8090:	Nitroaromatics and Cyclic Ketones
Method 8100:	Polynuclear Aromatic Hydrocarbons
Method 8110:	Haloethers by Gas Chromatography
Method 8120A:	Chlorinated Hydrocarbons by Gas Chromatography
Method 8121:	Chlorinated Hydrocarbons by Gas Chromatography: Capillary Column Technique
Method 8140:	Organophosphorus Pesticides
Method 8141A:	Organophosphorus Compounds by Gas Chromatography: Capillary Column Technique
Method 8150B:	Chlorinated Herbicides by Gas Chromatography
Method 8151:	Chlorinated Herbicides by GC Using Methylation or Pentafluorobenzylation Derivatization: Capillary Column Technique

4.3 DETERMINATION OF ORGANIC ANALYTES

4.3.2 GAS CHROMATOGRAPHIC/MASS SPECTROMETRIC METHODS

The following methods are included in this section:

Method 8240B: Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS)

Method 8250A: Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS)

Method 8260A: Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS): Capillary Column Technique

Method 8270B: Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS): Capillary Column Technique

Method 8280: The Analysis of Polychlorinated Dibenzo-p-Dioxins and Polychlorinated Dibenzofurans

Appendix A: Signal-to-Noise Determination Methods

Appendix B: Recommended Safety and Handling Procedures for PCDDs/PCDFs

Method 8290: Polychlorinated Dibenzodioxins (PCDDs) and Polychlorinated Dibenzofurans (PCDFs) by High-Resolution Gas Chromatography/High-Resolution Mass Spectrometry (HRGC/HRMS)

4.3 DETERMINATION OF ORGANIC ANALYTES

4.3.3 HIGH PERFORMANCE LIQUID CHROMATOGRAPHIC METHODS

The following methods are included in this section:

Method 8310: Polynuclear Aromatic Hydrocarbons

Method 8315: 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 8321: Solvent Extractable Non-Volatile Compounds by High Performance Liquid Chromatography/Thermospray/Mass Spectrometry (HPLC/TSP/MS) or Ultraviolet (UV) Detection

Method 8330: Nitroaromatics and Nitramines by High Performance Liquid Chromatography (HPLC)

Method 8331: Tetrazene by Reverse Phase High Performance Liquid Chromatography (HPLC)

4.3 DETERMINATION OF ORGANIC ANALYTES

4.3.4 FOURIER TRANSFORM INFRARED METHODS

The following method is included in this section:

Method 8410: Gas Chromatography/Fourier Transform Infrared (GC/FT-IR) Spectrometry for Semivolatile Organics: Capillary Column

4.4 MISCELLANEOUS SCREENING METHODS

The following methods are included in this section:

Method 3810:	Headspace
Method 3820:	Hexadecane Extraction and Screening of Purgeable Organics
Method 4010:	Screening for Pentachlorophenol by Immunoassay
Method 8275:	Thermal Chromatography/Mass Spectrometry (TC/MS) for Screening Semivolatile Organic Compounds