METHOD 3500A

ORGANIC EXTRACTION AND SAMPLE PREPARATION

1.0 SCOPE AND APPLICATION

1.1 The 3500 Methods are procedures for quantitatively extracting nonvolatile and semivolatile organic compounds from various sample matrices. Cleanup and/or analysis of the resultant extracts are described in Chapter Two, Sections 2.3.2 and 2.3.1, respectively.

1.2 Method 3580 describes a solvent dilution technique that may be used on non-aqueous nonvolatile and semivolatile organic samples prior to cleanup and/or analysis.

1.3 The 5000 Methods are procedures for preparing samples containing volatile organic compounds for quantitative analysis.

1.4 Refer to the specific method of interest for further details.

2.0 SUMMARY OF METHOD

2.1 3500 Methods: A sample of a known volume or weight is solvent extracted. The resultant extract is dried and then concentrated in a Kuderna-Danish apparatus (if necessary). Other concentration devices or techniques may be used in place of the Kuderna-Danish concentrator if the quality control requirements of the determinative methods are met (Method 8000, Section 8.0).

2.2 5000 Methods: Refer to the specific method of interest.

3.0 INTERFERENCES

3.1 Samples requiring analysis for volatile organic compounds, can be contaminated by diffusion of volatile organics (particularly chlorofluoro-carbons and methylene chloride) through the sample container septum during shipment and storage. A field blank prepared from organic-free reagent water and carried through sampling and subsequent storage and handling can serve as a check on such contamination.

3.2 Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or interferences to sample analysis. All these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required. Refer to Chapter One for specific guidance on quality control procedures.

3.3 Interferences coextracted from the samples will vary considerably from source to source. If analysis of an extracted sample is prevented due to interferences, further cleanup of the sample extract may be necessary. Refer to Method 3600 for guidance on cleanup procedures.

3.4 Phthalate esters contaminate many types of products commonly found in the laboratory. Plastics, in particular, must be avoided because phthalates are commonly used as plasticizers and are easily extracted from plastic materials. Serious phthalate contamination may result at any time if consistent quality control is not practiced.

3.5 Glassware contamination resulting in analyte degradation: Soap residue on glassware may cause degradation of certain analytes. Specifically, aldrin, heptachlor, and most organophosphorus pesticides will degrade in this situation. This problem is especially pronounced with glassware that may be difficult to rinse (e.g., 500 mL K-D flask). These items should be hand-rinsed very carefully to avoid this problem.

4.0 APPARATUS AND MATERIALS

4.1 Refer to the specific method of interest for a description of the apparatus and materials needed.

5.0 REAGENTS

5.1 Refer to the specific method of interest for a description of the solvents needed.

5.2 Organic-free reagent water. All references to water in this method refer to organic-free reagent water as defined in Chapter One.

5.3 Stock standards: Stock solutions may be prepared from pure standard materials or purchased as certified solutions.

5.3.1 Purgeable stock standards: Prepare stock standards in methanol using assayed liquids or gases, as appropriate. Because of the toxicity of some of the organohalides, primary dilutions of these materials should be prepared in a hood.

5.3.1.1 Place about 9.8 mL of methanol in a 10-mL tared ground-glass-stoppered volumetric flask. Allow the flask to stand, unstoppered, for about 10 min or until all alcohol-wetted surfaces have dried. Weigh the flask to the nearest 0.0001 g.

5.3.1.2 Using a 100-µL syringe, immediately add two or more drops of assayed reference material to the flask, then reweigh. The liquid must fall directly into the alcohol without contacting the neck of the flask.

5.3.1.3 Reweigh, dilute to volume, stopper, then mix by inverting the flask several times. Calculate the concentration in milligrams per liter (mg/L) from the net gain in weight. When compound purity is assayed to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

5.3.1.4 Transfer the stock standard solution into a Teflon-sealed screw-cap bottle. Store, with minimal headspace, at -10°C to -20°C and protect from light.

5.3.1.5 All standards must be replaced after 1 month, or sooner if comparison with check standards indicates a problem.

5.3.2 Semivolatile stock standards: Base/neutral and acid stock standards are prepared in methanol. Organochlorine pesticide standards are prepared in acetone.

5.3.2.1 Stock standard solutions should be stored in Teflon-sealed containers at 4°C. The solutions should be checked frequently for stability. These solutions must be replaced after six months, or sooner if comparison with quality control check samples indicate a problem.

5.4 Surrogate standards: A surrogate standard (i.e., a chemically inert compound not expected to occur in an environmental sample) should be added to each sample, blank, and matrix spike sample just prior to extraction or processing. The recovery of the surrogate standard is used to monitor for unusual matrix effects, gross sample processing errors, etc. Surrogate recovery is evaluated for acceptance by determining whether the measured concentration falls within the acceptance limits. Recommended surrogates for different analyte groups follow. However, these compounds, or others that better correspond to the analyte group, may be used for other analyte groups as well. Normally three or more standards are added for each analyte group.

5.4.1 Base/neutral and acid surrogate spiking solutions: The following are recommended surrogate standards.

Base/neutral	Acid
2-Fluorobiphenyl	2-Fluorophenol
Nitrobenzene-d_5	2,4,6-Tribromophenol
Terphenyl-d_{14}	Phenol-d_6

5.4.1.1 Prepare a surrogate standard spiking solution in methanol that contains the base/neutral compounds at a concentration of 100 mg/L, and the acid compounds at 200 mg/L for water and sediment/soil samples (low- and medium-level). For waste samples, the concentration should be 500 mg/L for base/neutrals and 1000 mg/L for acids.

5.4.2 Organochlorine pesticide/PCB surrogate spiking solution: The following are recommended surrogate standards for organochlorine pesticides/PCBs.

Organochlorine pesticides/PCBs

Dibutylchlorendate (DBC) (if available)
2,4,5,6-Tetrachloro-meta-xylene (TCMX)

5.4.2.1 Prepare a surrogate standard spiking solution at a concentration of 1 mg/L in acetone for water and sediment/soil samples. For waste samples, the concentration should be 5 mg/L.

5.4.3 Purgeable surrogate spiking solution: The following are recommended surrogate standards for volatile organics.

Purgeable organics

p-Bromofluorobenzene
1,2-Dichloroethane-d_4
Toluene-d_8

5.4.3.1 Prepare a surrogate spiking solution (as described in Section 5.3.1 or through secondary dilution of the stock standard) in methanol containing the surrogate standards at a concentration of 25 mg/L.

5.5 Matrix spike standards: Select five or more analytes from each analyte group for use in a spiking solution. The following are recommended matrix spike standard mixtures for a few analyte groups. These compounds, or others that better correspond to the analyte group, may be used for other analyte groups as well.

5.5.1 Base/neutral and acid matrix spiking solution: Prepare a spiking solution in methanol that contains each of the following base/neutral compounds at 100 mg/L and the acid compounds at 200 mg/L for water and sediment/soil samples. The concentration of these compounds should be five times higher for waste samples.

Base/neutrals	Acids
1,2,4-Trichlorobenzene	Pentachlorophenol
Acenaphthene	Phenol
2,4-Dinitrotoluene	2-Chlorophenol
Pyrene	4-Chloro-3-methylphenol
N-Nitroso-di-n-propylamine	4-Nitrophenol
1,4-Dichlorobenzene	

5.5.2 Organochlorine pesticide matrix spiking solution: Prepare a spiking solution in acetone or methanol that contains the following pesticides in the concentrations specified for water and sediment/soil. The concentration should be five times higher for waste samples.

Pesticide	Concentration (mg/L)
Lindane	0.2
Heptachlor	0.2
Aldrin	0.2
Dieldrin	0.5
Endrin	0.5
4,4'-DDT	0.5

5.5.3 Purgeable matrix spiking solution: Prepare a spiking solution in methanol that contains the following compounds at a concentration of 25 mg/L.

Purgeable organics

1,1-Dichloroethene
Trichloroethene
Chlorobenzene
Toluene
Benzene

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to the Organic Analyte Chapter, Section 4.1.

7.0 PROCEDURE

7.1 Semivolatile organic sample extraction: Water, soil/sediment, sludge, and waste samples requiring analysis for base/neutral and acid extractables and/or organochlorine pesticides must undergo solvent extraction prior to analysis. This manual contains four methods that may be used for this purpose: Method 3510; Method 3520; Method 3540; and Method 3550. The method that should be used on a particular sample, is highly dependent upon the physical characteristics of that sample. Therefore, review these four methods prior to choosing one in particular. Appropriate surrogate standards and, if necessary, matrix spiking solutions are added to the sample prior to extraction for all four methods.

7.1.1 Method 3510: Applicable to the extraction and concentration of water-insoluble and slightly water-soluble organics from aqueous samples. A measured volume of sample is solvent extracted using a separatory funnel. The extract is dried, concentrated and, if necessary, exchanged into a solvent compatible with further analysis. Method 3520 should be used if an emulsion forms between the solvent-sample phases, which can not be broken up by mechanical techniques.

7.1.2 Method 3520: Applicable to the extraction and concentration of water-insoluble and slightly water-soluble organics from aqueous samples. A measured volume of sample is extracted with an organic solvent in a continuous liquid-liquid extractor. The solvent must have a density greater than that of the sample. The extract is dried, concentrated and, if necessary, exchanged into a solvent compatible with further analysis. The limitations of Method 3510 concerning solvent-sample phase separation do not interfere with this procedure.

7.1.3 Method 3540: This is a procedure for extracting nonvolatile and semivolatile organic compounds from solids such as soils, sludges, and wastes. A solid sample is mixed with anhydrous sodium sulfate, placed into an extraction thimble or between two plugs of glass wool, and

extracted using an appropriate solvent in a Soxhlet extractor. The extract is dried, concentrated and, if necessary, exchanged into a solvent compatible with further analysis.

7.1.4 Method 3550: This method is applicable to the extraction of nonvolatile and semivolatile organic compounds from solids such as soils, sludges, and wastes using the technique of ultrasonic extraction. Two procedures are detailed depending upon the expected concentration of organics in the sample; a low concentration and a high concentration method. In both, a known weight of sample is mixed with anhydrous sodium sulfate and solvent extracted using ultrasonic extraction. The extract is dried, concentrated and, if necessary, exchanged into a solvent compatible with further analysis.

7.1.5 Method 3580: This method describes the technique of solvent dilution of non-aqueous waste samples. It is designed for wastes that may contain organic chemicals at a level greater than 20,000 mg/kg and that are soluble in the dilution solvent. When using this method, the analyst must use caution in determining the correct concentration of spike and surrogate solution to avoid diluting out these compounds when diluting the sample. The loss of surrogate and spike data should only occur in samples containing a high concentration of analytes which is unknown at the time of extraction or where sample interferences could not be eliminated following the best attempts at extract cleanup by the laboratory.

7.2 Volatile organic sample preparation: There are three methods for volatile sample preparation: Method 5030; Method 5040; and direct injection. Method 5030 is the most widely applicable procedure for analysis of volatile organics, while the direct injection technique may have limited applicability to aqueous matrices.

7.2.1 Method 5030: This method describes the technique of purge-and-trap for the introduction of purgeable organics into a gas chromatograph. This procedure is applicable for use with aqueous samples directly and to solids, wastes, soils/sediments, and water-miscible liquids following appropriate preparation. An inert gas is bubbled through the sample, which will efficiently transfer the purgeable organics from the aqueous phase to the vapor phase. The vapor phase is swept through a sorbent trap where the purgeables are trapped. After purging is completed, the trap is heated and backflushed with the inert gas to desorb the purgeables onto a gas chromatographic column. Prior to application of the purge-and-trap procedure, all samples (including blanks, spikes, and duplicates) should be spiked with surrogate standards and, if required, with matrix spiking compounds.

7.2.2 Method 5040: This method is applicable to the investigation of sorbent cartridges from volatile organic sampling train (VOST).

7.3 Sample analysis: Following preparation of a sample by one of the methods described above, the sample is ready for further analysis. For samples requiring volatile organic analysis, application of one of the methods described above is followed directly by gas chromatographic analysis (Methods 8010, 8011, 8015, 8020, 8021, 8030, 8240 and 8260). Samples prepared for semivolatile

analysis may, if necessary, undergo cleanup (See Method 3600) prior to application of a specific determinative method.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific guidance on quality control procedures.

8.2 Before processing any samples, the analyst should demonstrate through the analysis of a reagent water blank that all glassware and reagents are interference free. Each time a set of samples is processed, a method blank(s) should be processed as a safeguard against chronic laboratory contamination. The blank samples should be carried through all stages of the sample preparation and measurement.

8.3 Surrogate standards should be added to all samples when specified in the appropriate determinative method in Chapter Four, Section 4.3

8.4 A reagent blank, a matrix spike, and a duplicate or matrix spike duplicate must be performed for each analytical batch (up to a maximum of 20 samples) analyzed.

8.5 For GC or GC/MS analysis, the analytical system performance must be verified by analyzing quality control (QC) check samples. Method 8000, Section 8.0 discusses in detail the process of verification; however, preparation of the QC check sample concentrate is dependent upon the method being evaluated.

8.5.1 **Volatile organic QC check samples:** QC check sample concentrates containing each analyte of interest are spiked into reagent water (defined as the QC check sample) and analyzed by purge-and-trap (Method 5030). The concentration of each analyte in the QC check sample is 20 µg/L. The evaluation of system performance is discussed in detail in Method 8000, beginning with Paragraph 8.6

8.5.2 **Semivolatile organic QC check samples:** To evaluate the performance of the analytical method, the QC check samples must be handled in exactly the same manner as actual samples. Therefore, 1.0 mL of the QC check sample concentrate is spiked into each of four 1-L aliquots of reagent water (now called the QC check sample), extracted, and then analyzed by GC. The variety of semivolatile analytes which may be analyzed by GC is such that the concentration of the QC check sample concentrate is different for the different analytical techniques presented in the manual. Method 8000 discusses in detail the procedure of verifying the detection system once the QC check sample has been prepared. The concentrations of the QC check sample concentrate for the various methods are as follows:

8.5.2.1 Method 8040 - Phenols: The QC check sample concentrate should contain each analyte at a concentration of 100 mg/L in 2-propanol.

8.5.2.2 Method 8060 - Phthalate esters: The QC check

sample concentrate should contain the following analytes at the following concentrations in acetone: butyl benzyl phthalate, 10 mg/L; bis(2-ethylhexyl) phthalate, 50 mg/L; di-n-octylphthalate, 50 mg/L; and any other phthalate at 25 mg/L.

8.5.2.3 Method 8070 - Nitrosamines: The QC check sample concentrate should contain each analyte at 20 mg/L in methanol or some other water miscible solvent.

8.5.2.4 Method 8080 - Organochlorine pesticides and PCBs: The QC check sample concentrate should contain each single-component analyte at the following concentrations in acetone or some other water miscible solvent: 4,4'-DDD, 10 mg/L; 4,4'-DDT, 10 mg/L; endosulfan II, 10 mg/L; endosulfan sulfate, 10 mg/L; endrin, 10 mg/L; and any other single-component pesticide at 2 mg/L . If the method is only to be used to analyze PCBs, chlordane, or toxaphene, the QC check sample concentrate should contain the most representative multicomponent parameter at a concentration of 50 mg/L in acetone.

8.5.2.5 Method 8090 - Nitroaromatics and Cyclic Ketones: The QC check sample concentrate should contain each analyte at the following concentrations in acetone: each dinitrotoluene at 20 mg/L; and isophorone and nitrobenzene at 100 mg/L.

8.5.2.6 Method 8100 - Polynuclear aromatic hydrocarbons: The QC check sample concentrate should contain each analyte at the following concentrations in acetonitrile: naphthalene, 100 mg/L; acenaphthylene, 100 mg/L; acenaphthene, 100 mg/L; fluorene, 100 mg/L; phenanthrene, 100 mg/L; anthracene, 100 mg/L; benzo(k)fluoranthene, 5 mg/L; and any other PAH at 10 mg/L .

8.3.2.7 Method 8110 - Haloethers: The QC check sample concentrate should contain each analyte at a concentration of 20 mg/L in methanol or some other water miscible solvent.

8.5.2.8 Method 8120 - Chlorinated hydrocarbons: The QC check sample concentrate should contain each analyte at the following concentrations in acetone: hexachloro-substituted hydrocarbons, 10 mg/L; and any other chlorinated hydrocarbon, 100 mg/L.

8.3.2.9 Method 8140/8141 - Organophosphorus compounds: The QC check sample concentrate should contain each analyte in acetone at a concentration 1,000 times more concentrated than the selected spike concentration.

8.3.2.10 Method 8150 - Chlorinated herbicides: The QC check sample concentrate should contain each analyte in acetone at a concentration 1,000 times more concentrated than the selected spike concentration.

8.3.2.11 Method 8250/8270 - Semivolatile organics: The QC

check sample concentrate should contain each analyte in acetone at a concentration of 100 mg/L.

8.3.2.12 Method 8310 - Polynuclear aromatic hydrocarbons: The QC check sample concentrate should contain each analyte at the following concentrations in acetonitrile: naphthalene, 100 mg/L; acenaphthylene, 100 mg/L; acenaphthene, 100 mg/L; fluorene, 100 mg/L; phenanthrene, 100 mg/L; anthracene, 100 mg/L; benzo(k)fluoranthene, 5 mg/L; and any other PAH at 10 mg/L.

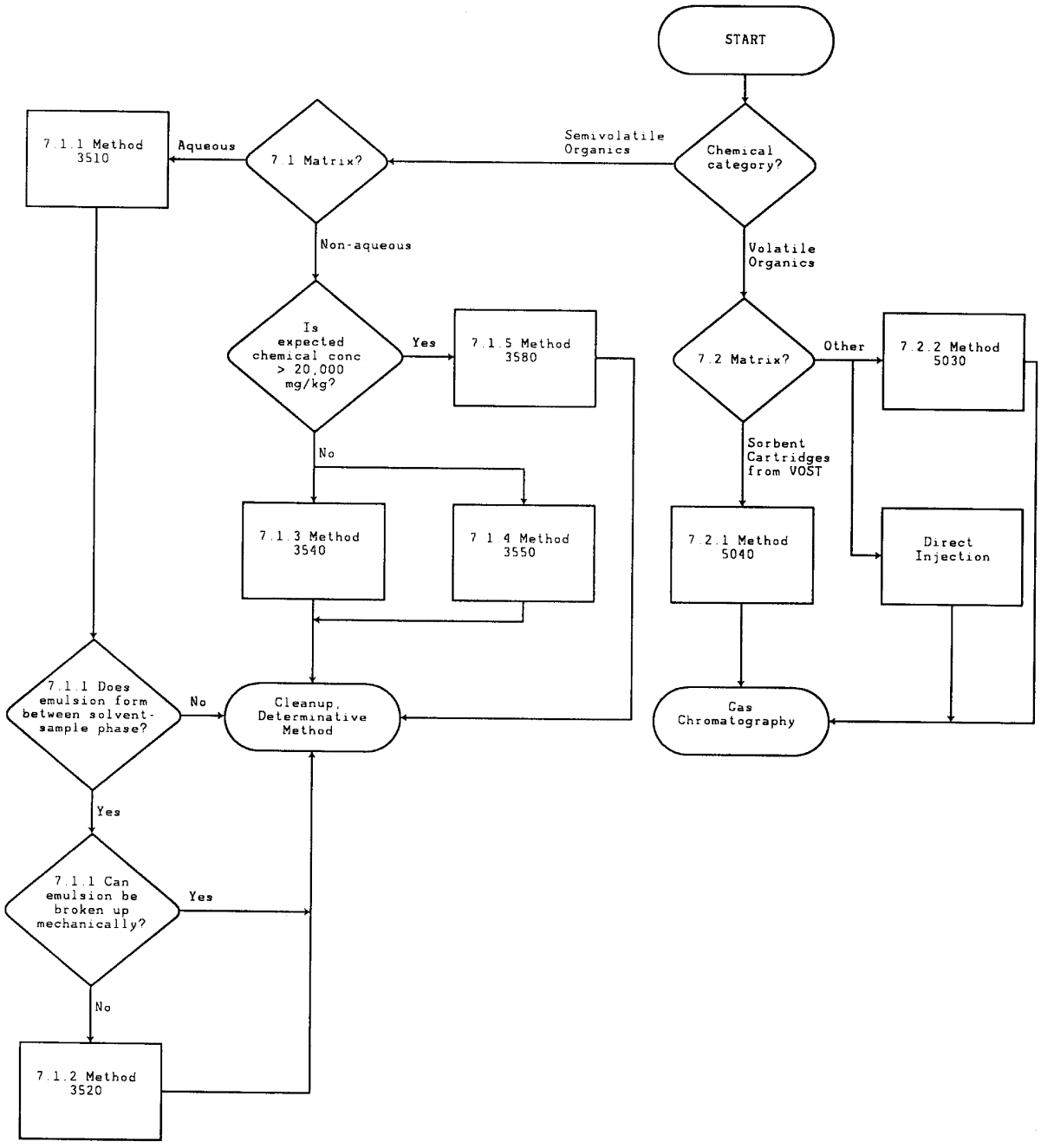
9.0 METHOD PERFORMANCE

9.1 The recovery of surrogate standards is used to monitor unusual matrix effects, sample processing problems, etc. The recovery of matrix spiking compounds indicates the presence or absence of unusual matrix effects.

9.2 The performance of this method will be dictated by the overall performance of the sample preparation in combination with the analytical determinative method.

10.0 REFERENCES

10.1 None required.


START
Chemical category?
Semivolatile Organics
Volatile Organics
7.1 Matrix?
Aqueous
Non-aqueous
7.1.1 Method 3510
Is expected chemical conc > 20,000 mg/kg?
Yes
No
7.1.5 Method 3580
7.1.3 Method 3540
7.1.4 Method 3550
7.2 Matrix?
Other
7.2.2 Method 5030
Sorbent Cartridges from VOST
7.2.1 Method 5040
Direct Injection
7.1.1 Does emulsion form between solvent-sample phase?
No
Yes
Cleanup, Determinative Method
Gas Chromatography
7.1.1 Can emulsion be broken up mechanically?
Yes
No
7.1.2 Method 3520