CLOSED-SYSTEM PURGE-AND-TRAP AND EXTRACTION FOR VOLATILE ORGANICS IN SOIL AND WASTE SAMPLES

1.0 SCOPE AND APPLICATION

1.1 This method describes a closed-system purge-and-trap process for the analysis of volatile organic compounds (VOCs) in solid materials (e.g., soils, sediments, and solid waste). While the method is designed for use on samples containing low levels of VOCs, procedures are also provided for collecting and preparing solid samples containing high concentrations of VOCs and for oily wastes. For these high concentration and oily materials, sample collection and preparation are performed using the procedures described here, and sample introduction is performed using the aqueous purge-and-trap procedure in Method 5030. These procedures may be used in conjunction with any appropriate determinative gas chromatographic procedure, including, but not limited to, Methods 8015, 8021, and 8260. The following compounds are appropriate for this sample preparation technique:

Compound	CAS No.[a]	Response	Stability
Acetone	67-64-1	ht	hs
Acetonitrile	75-05-8	pp	nd
Acrolein (Propenal)	107-02-8	pp	ms
Acrylonitrile	107-13-1	pp	hs
Allyl alcohol	107-18-6	ht	nd
Allyl chloride	107-05-1	c	ms
t-Amyl ethyl ether (TAEE)	919-94-8	c / ht	nd
t-Amyl methyl ether (TAME)	994-05-8	c / ht	hs
Benzene	71-43-2	c	hs
Benzyl chloride	100-44-7	c	nd
Bis(2-chloroethyl)sulfide	505-60-2	pp	nd
Bromoacetone	598-31-2	pp	nd
Bromochloromethane	74-97-5	c	hs
Bromodichloromethane	75-27-4	c	ms
Bromoform	75-25-2	c	hs
Bromomethane	74-83-9	c	hvs
n-Butanol	71-36-3	ht	nd
2-Butanone (MEK)	78-93-3	pp	hvs
t-Butyl alcohol	75-65-0	ht	nd
Carbon disulfide	75-15-0	pp	hvs
Carbon tetrachloride	56-23-5	c	hvs
Chloral hydrate	302-17-0	pp	nd
Chlorobenzene	108-90-7	c	hvs
Chlorodibromomethane	124-48-1	c	nd
Chloroethane	75-00-3	c	ms

(continued)

Compound	CAS No.[a]	Response	Stability
2-Chloroethanol	107-07-3	pp	nd
2-Chloroethyl vinyl ether	110-75-8	c	ls
Chloroform	67-66-3	c	hs
Chloromethane	74-87-3	c	hvs
Chloroprene	126-99-8	c	nd
Crotonaldehyde	4170-30-3	pp	nd
1,2-Dibromo-3-chloropropane	96-12-8	pp	ms
1,2-Dibromoethane	106-93-4	c	hs
Dibromomethane	74-95-3	c	hs
1,2-Dichlorobenzene	95-50-1	c	hs
1,3-Dichlorobenzene	541-73-1	c	ms
1,4-Dichlorobenzene	106-46-7	c	ms
cis-1,4-Dichloro-2-butene	1476-11-5	c	nd
trans-1,4-Dichloro-2-butene	110-57-6	pp	ls
Dichlorodifluoromethane	75-71-8	c	hs
1,1-Dichloroethane	75-34-3	c	hs
1,2-Dichloroethane	107-06-2	c	hs
1,1-Dichloroethene	75-35-4	c	hvs
cis-1,2-Dichloroethene	156-59-4	c	hs
trans-1,2-Dichloroethene	156-60-5	c	ms
1,2-Dichloropropane	78-87-5	c	hs
1,3-Dichloro-2-propanol	96-23-1	pp	nd
cis-1,3-Dichloropropene	10061-01-5	c	ls
trans-1,3-Dichloropropene	10061-02-6	c	ls
1,2,3,4-Diepoxybutane	1464-53-5	c	nd
Diethyl ether	60-29-7	c	nd
Diisopropyl ether (DIPE)	108-20-3	c / ht	hs
1,4-Dioxane	123-91-1	pp	nd
Ethylbenzene	100-41-4	c	hvs
Ethylene oxide	75-21-8	pp	nd
Ethyl methacrylate	97-63-2	c	ms
Ethyl *tert*-butyl ether (ETBE)	637-92-3	c / ht	hs
Hexachlorobutadiene	87-68-3	c	ms
2-Hexanone	591-78-6	pp	hvs
Iodomethane	74-88-4	c	nd
Isobutyl alcohol	78-83-1	ht / pp	nd
Isopropylbenzene	98-82-8	c	ms
Malononitrile	109-77-3	pp	nd
Methacrylonitrile	126-98-7	pp	hs
Methylene chloride	75-09-2	c	hs
Methyl methacrylate	80-62-6	c	ms
4-Methyl-2-pentanone (MIBK)	108-10-1	pp	ms
Methyl *tert*-butyl ether (MTBE)	1634-04-4	c / ht	hs
Naphthalene	91-20-3	c	ms
Nitrobenzene	98-95-3	c	nd

(continued)

Compound	CAS No.[a]	Response	Stability
2-Nitropropane	79-46-9	c	nd
N-Nitroso-di-*n*-butylamine	924-16-3	pp	nd
Paraldehyde	123-63-7	pp	nd
2-Pentanone	107-87-9	pp	nd
2-Picoline	109-06-8	pp	nd
1-Propanol	71-23-8	ht / pp	nd
2-Propanol	67-63-0	ht / pp	nd
â-Propiolactone	57-57-8	pp	nd
Propionitrile (ethyl cyanide)	107-12-0	ht	nd
n-Propylamine	107-10-8	c	nd
Styrene	100-42-5	c	hvs
1,1,1,2-Tetrachloroethane	630-20-6	c	hs
1,1,2,2-Tetrachloroethane	79-34-5	c	nd
Tetrachloroethene	127-18-4	c	ms
Toluene	108-88-3	c	hs
o-Toluidine	95-53-4	pp	nd
1,2,4-Trichlorobenzene	120-82-1	c	hs
1,1,1-Trichloroethane	71-55-6	c	ms
1,1,2-Trichloroethane	79-00-5	c	hs
Trichloroethene	79-01-6	c	ms
Trichlorofluoromethane	75-69-4	c	ls
1,2,3-Trichloropropane	96-18-4	c	ls
Vinyl acetate	108-05-4	c	ls
Vinyl chloride	75-01-4	c	hvs
o-Xylene	95-47-6	c	hvs
m-Xylene	108-38-3	c	hvs
p-Xylene	106-42-3	c	hvs

[a] Chemical Abstract Service Registry Number

c = Adequate response by this technique
ht = Method analyte only when purged at 80°C
pp = Poor purging efficiency resulting in high Estimated Quantitation Limits
nd = Not determined
hs = High stability in preserved water samples (> 60 days). Longer holding times may be appropriate, see Appendix A, Table A.1 footnote and ref. 47 for additional information
ms = Medium stability in preserved water samples (15 - 60 days). Longer holding times may be appropriate, see Appendix A, Table A.1 footnote and ref. 47 for additional information
ls = Low stability in preserved water samples (< 14 days), analyses should be performed as soon as possible.
hvs = Highly variable stability in preserved water samples. Longer holding times may be appropriate, see Appendix A, Table A.1 footnote and ref. 47 for additional information.

1.2 The low soil method utilizes a hermetically-sealed sample vial, the seal of which is never broken from the time of sampling to the time of analysis. Since the sample is never exposed to the atmosphere after sampling, the losses of VOCs during sample transport, handling, and analysis are minimized. The applicable concentration range of the low soil method is dependent on the determinative method, matrix, and compound. However, it will generally fall in the 0.5 to 200 µg/kg range.

1.3 Procedures are included for preparing high concentration samples for purging by Method 5030. High concentration samples are those containing VOC levels of >200 µg/kg.

1.4 Procedures are also included for addressing oily wastes that are soluble in a water-miscible solvent. These samples are also purged using Method 5030.

1.5 This method can be used for most volatile organic compounds that have boiling points below 200°C and that are insoluble or slightly soluble in water. Volatile, water-soluble compounds can be included in this analytical technique. However, quantitation limits (by GC or GC/MS) are significantly higher because of poor purging efficiency. The purging efficiency can be improved for water soluble analytes, e.g. ketones and alcohols, when purging at an elevated temperature of 80°C as compared to 20° or 40°C.

1.6 This method, in conjunction with Method 8015 (GC/FID), may be used for the analysis of the aliphatic hydrocarbon fraction in the light ends of total petroleum hydrocarbons, e.g., gasoline. For the aromatic fraction (BTEX), use this method and Method 8021 (GC/PID). A total determinative analysis of gasoline fractions may be obtained using Method 8021 in series with Method 8015.

1.7 As with any preparative method for volatiles, samples should be screened to avoid contamination of the purge-and-trap system by samples that contain very high concentrations of purgeable material above the calibration range of the low concentration method. In addition, because the sealed sample container cannot be opened to remove a sample aliquot without compromising the integrity of the sample, multiple sample aliquots should be collected to allow for screening and reanalysis.

1.8 The closed-system purge-and-trap equipment employed for low concentration samples is not appropriate for soil samples preserved in the field with methanol. Such samples should be analyzed using Method 5030 (see the note in Sec. 8.2.2).

1.9 Analysts should consult the disclaimer statement at the front of the manual and the information in Chapter Two for guidance on the intended flexibility in the choice of methods, apparatus, materials, reagents, and supplies, and on the responsibilities of the analyst for demonstrating that the techniques employed are appropriate for the analytes of interest, in the matrix of interest, and at the levels of concern.

In addition, analysts and data users are advised that, except where explicitly specified in a regulation, the use of SW-846 methods is *not* mandatory in response to Federal testing requirements. The information contained in this method is provided by EPA as guidance to be used by the analyst and the regulated community in making judgments necessary to generate results that meet the data quality objectives for the intended application.

1.10 Use of this method is restricted to use by, or under supervision of, appropriately experienced and trained laboratory analysts. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 Low concentration soil method - generally applicable to soils and other solid samples with VOC concentrations in the range of 0.5 to 200 µg/kg (refer to Appendix A for additional information).

Volatile organic compounds (VOCs) are determined by collecting an approximately 5-g sample and shipping to the laboratory or appropriate analysis site by the various methods outlined in Appendix A. To ensure minimal loss of volatile constituents prior to analysis the entire sample vial is placed, unopened with an unpierced septum, into the instrument auto sampler device. Immediately before analysis, organic-free reagent water, surrogates, and internal standards (if applicable) are automatically added without opening the sample vial. The vial containing the sample is heated to 40°C and the volatiles purged into an appropriate trap using an inert gas combined with agitation of the sample. Purged components travel via a transfer line to a trap. When purging is complete, the trap is heated and backflushed with helium to desorb the trapped sample components into a gas chromatograph for analysis by an appropriate determinative method.

2.2 High concentration method - generally applicable to soils and other solid samples with VOC concentrations greater than 200 µg/kg (refer to Appendix A for additional information).

The sample introduction technique in Sec. 2.1 is not applicable to all samples, particularly those containing high concentrations (generally greater than 200 µg/kg) of VOCs which may overload either the volatile trapping material or exceed the working range of the determinative instrument system (e.g., GC/MS, GC/FID, GC/ELCD, etc.). In such instances, this method describes two sample collection options and the corresponding sample purging procedures.

2.2.1 The first option is to collect an appropriate sample volume in a pre-weighed vial with a septum-sealed screw-cap (see Sec 6) that contains a water-miscible organic solvent (e.g., methanol). At the time of analysis, an aliquot of the solvent is removed from the vial and diluted into water along with the internal standards and surrogates, then purged using Method 5030 and analyzed by an appropriate determinative method.

2.2.2 The second option is to collect a bulk sample in a VOA vial without the use of a chemical preservative. A portion of that sample is removed from the container in the laboratory and is dispersed in a water-miscible solvent to dissolve the volatile organic constituents. An aliquot of the solution is added to reagent water in a purge tube. Surrogates and internal standards (if applicable) are added to the solution, then purged using Method 5030, and analyzed by an appropriate determinative method. Because the procedure involves opening the vial and removing a portion of the soil, a significant amount of volatile constituents may be lost during handling. (See Appendix A, Sec. 5.1 for additional details)

NOTE: Surrogate compounds may either be spiked into the solvent at the time of extraction or the reagent water containing an aliquot of the extract prior to analysis. Since the surrogate recovery data from these two options provides assurances of either extraction or analytical efficiencies, the decision as to when the surrogates are added depends on what questions need to be answered for a given sample matrix and the intended uses of the data.

2.3 High concentration oily waste method - generally applicable to oily samples with VOC concentrations greater than 200 µg/kg that can be diluted in a water-miscible solvent.

Samples that are comprised of oils or samples that contain significant amounts of oil present additional analytical challenges. This procedure is generally appropriate for such samples when they are soluble in a water-miscible solvent.

2.3.1 After demonstrating that a test aliquot of the sample is soluble in methanol or polyethylene glycol (PEG), a separate aliquot of the sample is spiked with surrogates and diluted in the appropriate solvent. An aliquot of the solution is added to 5 mL of reagent water in a purge tube, taking care to ensure that a floating layer of oil is not present in the purge tube. Internal standards (if applicable) are added to the solution which is then purged using Method 5030 and analyzed by an appropriate determinative method.

NOTE: Surrogate compounds may either be spiked into the solvent at the time of extraction or the reagent water containing an aliquot of the extract prior to analysis. Since the surrogate recovery data from these two options provides assurances of either extraction or analytical efficiencies, the decision as to when the surrogates are added depends on what questions need to be answered for a given sample matrix and the intended uses of the data.

2.3.2 Samples that contain oily materials that are not soluble in water-miscible solvents must be prepared according to Method 3585.

3.0 DEFINITIONS

Refer to Chapter One for a listing of applicable quality assurance/quality control (QA/QC) definitions.

4.0 INTERFERENCES

4.1 Impurities in the purge gas and from organic compounds out-gassing from the plumbing ahead of the trap account for the majority of contamination problems. The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by running method blanks. The use of non-polytetrafluoroethylene (non-PTFE) plastic coating, non-PTFE thread sealants, or flow controllers with rubber components in the purging device must be avoided, since such materials out-gas organic compounds which can be concentrated in the trap during the purge operation. These compounds can result in interferences or false positives in the determinative step.

4.2 Samples can be contaminated by diffusion of volatile organics (particularly methylene chloride and fluorocarbons) through the septum seal of the sample vial during shipment and storage. A trip blank prepared from an appropriate organic-free matrix and sample container, and carried through sampling and handling protocols, serves as a check on such contamination.

4.3 Contamination by carryover can occur whenever high-concentration and low-concentration samples are analyzed in sequence. Where practical, samples with unusually high concentrations of analytes should be followed by an analysis of organic-free reagent water to check for cross-contamination. If the target compounds present in an unusually concentrated sample are also found to be present in the subsequent samples, the analyst must demonstrate that the compounds are not due to carryover. Conversely, if those target compounds are not present in the subsequent sample, then the analysis of organic-free reagent water is not necessary.

4.4 The laboratory where volatile analysis is performed should be completely free of solvents. Special precautions must be taken when analyzing for methylene chloride. The analytical and sample storage area should be isolated from all atmospheric sources of methylene chloride, otherwise random background levels will result. Since methylene chloride will permeate through PTFE tubing, all GC carrier gas lines and purge gas plumbing should be constructed of stainless steel or copper tubing. Laboratory workers' clothing previously exposed to methylene chloride fumes during common liquid/liquid extraction procedures can contribute to sample contamination. The presence of other organic solvents in the laboratory where volatile organics are analyzed can also lead to random background levels and the same precautions must be taken.

5.0 SAFETY

This method does not address all safety issues associated with its 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 included in this method. A reference file of material safety data sheets (MSDSs) should be available to all personnel involved in these analyses.

6.0 EQUIPMENT AND SUPPLIES

6.1 Sample containers

The specific sample containers required will depend on the purge-and-trap system to be employed (see Sec. 6.2). Several systems are commercially available. Some systems employ 40-mL clear vials with a special frit and equipped with two PTFE-faced silicone septa. Other systems permit the use of any good quality glass vial that is large enough to contain at least 5 g of soil or solid material and at least 10 mL of water and that can be sealed with a screw-cap containing a PTFE-faced silicone septum. Consult the purge-and-trap system manufacturer's instructions regarding the suitable specific vials, septa, caps, and mechanical agitation devices. Additional information on sample containers can be found in Appendix A, Secs. 1.6, 3.0, 7.0 and 8.0.

6.2 Purge-and-trap system

The purge-and-trap system consists of a unit that automatically adds water, surrogates, and internal standards (if applicable) to a vial containing the sample, purges the VOCs using an inert gas stream while agitating the contents of the vial, and also traps the released VOCs for subsequent desorption into the gas chromatograph. Such systems are commercially available from several sources and shall meet the following specifications.

6.2.1 The purging device should be capable of accepting a vial sufficiently large enough to contain a 5-g soil sample plus a magnetic stirring bar and 10 mL of water. The device must be capable of heating a soil vial to 40°C and holding it at that temperature while the inert purge gas is allowed to pass through the sample. The device should also be capable of introducing at least 5 mL of organic-free reagent water into the sample vial while trapping the displaced headspace vapors. It must also be capable of agitating the sealed sample during purging, (e.g., using a magnetic stirring bar added to the vial prior to sample collection, sonication, or other means). The analytes being purged must be quantitatively transferred to an absorber trap. The trap must be capable of transferring the absorbed VOCs to the gas chromatograph (see 6.2.2).

NOTE: The equipment used to develop this method was a Dynatech PTA-30 W/S Autosampler. This device was subsequently sold to Varian, and is now available as the Archon Purge and Trap Autosampler. See the Disclaimer at the front of this manual for guidance on the use of alternative equipment.

6.2.2 A variety of traps and trapping materials may be employed with this method. The choice of trapping material may depend on the analytes of interest. Whichever trap is employed, it must demonstrate sufficient adsorption and desorption characteristics to meet the quantitation limits of all desired target analytes for a given project and the QC requirements in Method 8000 and the determinative method. The most difficult analytes are generally the gases, especially dichlorodifluoromethane. The trap must be capable of desorbing the late eluting target analytes.

NOTE: Check the responses of the brominated compounds when using alternative charcoal traps (especially Vocarb 4000, Supelco, Inc., Bellefonte, PA), as some degradation has been noted when higher desorption temperatures (especially above 240 - 250°C) are employed. 2-Chloroethyl vinyl ether is degraded on Vocarb 4000 but performs adequately when Vocarb 3000 (Supelco, Inc., Bellefonte, PA) is used. The primary criterion, as stated above, is that all target analytes meet the sensitivity requirements for a given project.

6.2.2.1 The trap used to develop this method was 25 cm long, with an inside diameter of 0.105 inches, and was packed with Carbopack/Carbosieve (Supelco, Inc., Bellefonte, PA).

6.2.2.2 The standard trap used in other EPA purge-and-trap methods is also acceptable. That trap is 25 cm long and has an inside diameter of at least 0.105 in. Starting from the inlet, the trap contains the equal amounts of the adsorbents listed below. It is recommended that 1.0 cm of methyl silicone-coated packing (35/60 mesh, Davison, grade 15 or equivalent) be inserted at the inlet to extend the life of the trap. If the analysis of dichlorodifluoromethane or other fluorocarbons of similar volatility is not required, then the charcoal can be eliminated and the polymer increased to fill 2/3 of the trap. If only compounds boiling above 35°C are to be analyzed, both the silica gel and charcoal can be eliminated and the polymer increased to fill the entire trap.

6.2.2.2.1 2,6-Diphenylene oxide polymer - 60/80 mesh, chromatographic grade (Tenax GC or equivalent).

6.2.2.2.2 Methyl silicone packing - OV-1 (3%) on Chromosorb-W, 60/80 mesh or equivalent.

6.2.2.2.3 Coconut charcoal - Prepare from Barnebey Cheney, CA-580-26, or equivalent, by crushing through 26 mesh screen.

6.2.2.3 Trapping materials other than those listed above also may be employed, provided that they meet the specifications as noted above.

6.2.3 The desorber for the trap must be capable of rapidly heating the trap to the temperature recommended by the trap material manufacturer, prior to the beginning of the flow of desorption gas. Several commercial desorbers (purge-and-trap units) are available.

6.3 Syringe and syringe valves

6.3.1 25-mL glass hypodermic syringes with Luer-Lok (or equivalent) tip (other sizes are acceptable depending on sample volume used).

6.3.2 2-way syringe valves with Luer ends.

6.3.3 25-µL micro syringe with a 2-inch x 0.006-inch ID, 22° bevel needle (Hamilton #702N or equivalent).

6.3.4 Micro syringes - 10-, 100-µL.

6.3.5 Syringes - 0.5-, 1.0-, and 5-mL, gas-tight with shut-off valve.

6.4 Miscellaneous

6.4.1 Glass vials

6.4.1.1 60-mL, septum-sealed, to collect samples for screening, moisture determination.

6.4.1.2 40-mL, screw-cap, PTFE lined, septum-sealed. Examine each vial prior to use to ensure that the vial has a flat, uniform sealing surface.

6.4.2 Top-loading balance - Capable of accurately weighing to 0.01 g.

6.4.3 Glass scintillation vials - 20-mL, with screw-caps and PTFE liners, or glass culture tubes with screw-caps and PTFE liners, for dilution of oily waste samples.

6.4.4 Volumetric flasks - Class A, 10-mL and 100-mL, with ground-glass stoppers.

6.4.5 2-mL glass vials, for GC autosampler - Used for oily waste samples extracted with methanol or PEG.

6.4.6 Spatula, stainless steel - narrow enough to fit into a sample vial.

6.4.7 Disposable Pasteur pipettes.

6.4.8 Magnetic stirring bars - PTFE- or glass-coated, of the appropriate size to fit the sample vials. Consult manufacturer's recommendation for specific stirring bars. Stirring bars may be reused, provided that they are thoroughly cleaned between uses. Consult the manufacturers of the purging device and the stirring bars for suggested cleaning procedures.

6.5 Field sampling equipment

6.5.1 Purge-and-trap soil sampler - Model 3780PT (Associated Design and Manufacturing Company, Alexandria, VA), or equivalent.

6.5.2 EnCore™ sampler - (En Novative Technologies, Inc., Green Bay, WI), or equivalent.

6.5.3 Terra Core™ sampler - (En Novative Technologies, Inc., Green Bay, WI), or equivalent.

6.5.4 EasyDraw™ syringe and PowerStop™ handle - (US Oil Company, Inc., Kimberly, WI), or equivalent.

6.5.5 Alternatively, disposable plastic syringes with a barrel smaller than the neck of the soil vial may be used to collect the sample. The syringe end of the barrel is cut off prior to sampling. One syringe is needed for each sample aliquot to be collected.

6.5.4 Portable balance - For field use, capable of weighing to 0.01 g.

6.5.5 Balance weights - Balances employed in the field should be checked against an appropriate reference weight at least once daily, prior to weighing any samples, or as described in the sampling plan. The specific weights used will depend on the total weight of the sample container, sample, stirring bar, reagent water added, cap, and septum.

6.5.6 Additional types of field sampling equipment and accessories are described in Appendix A, Secs. 1.6 and 7.0.

7.0 REAGENTS AND STANDARDS

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

7.2 Methanol, CH_3OH - purge-and-trap quality or equivalent. Store away from other solvents.

7.3 Polyethylene glycol (PEG), $H(OCH_2CH_2)_nOH$ - free of interferences at the detection limit of the target analytes.

7.4 Low concentration sample preservative

7.4.1 For determination as to whether sample preservation is necessary and for selection of appropriate preservation options, see Appendix A, Secs. 1.2, 1.3, 3.0 and 8.0.

7.4.2 Sodium bisulfate, $NaHSO_4$ - ACS reagent grade or equivalent.

7.4.3 The preservative, if necessary, should be added to the vial prior to shipment to the field, and must be present in the vial prior to adding the sample.

7.5 See the determinative method and Method 5000 for guidance on internal standards and surrogates to be employed in this procedure. The recommended surrogates are 4-bromofluorobenzene, 1,2-dichloroethane-d_4, and toluene-d_8. Other compounds may be used as surrogates, depending upon the analysis requirements and the specific target analytes. The recommended internal standards are chlorobenzene-d_5, 1,4-dichlorobenzene-d_4, and fluorobenzene. Other compounds may be used as internal standards as long as they have retention times similar to the target analytes being detected.

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

Refer to the introductory material in this chapter, Organic Analytes, Sec. 4.1, and Appendix A for general sample collection information. The low concentration portion of this method employs sample vials that are filled and weighed in the field and never opened during the analytical process.

As a result, sampling personnel should be equipped with a portable balance capable of weighing to 0.01 g.

8.1 Preparation of sample vials

The specific preparation procedures for sample vials depend on the expected concentration range of the sample, with separate preparation procedures for low concentration soil samples and high concentration soil and solid waste samples. Sample vials should be prepared in a fixed laboratory or other controlled environment, sealed, and shipped to the field location. Gloves should be worn during the preparation steps. More detailed information on additional options for the preparation of sample vials can be found in Appendix A, Secs. 3.0, 7.0, and 8.0.

8.1.1 Low concentration soil samples

The following steps apply to the preparation of vials used in the collection of low concentration soil samples to be analyzed by the closed-system purge-and-trap equipment described in this method.

8.1.1.1 Add a clean magnetic stirring bar to each clean vial. If the purge-and-trap device (Sec. 6.2) employs a means of stirring the sample other than a magnetic stirrer (e.g., sonication or other mechanical means), then the stir bar is omitted.

8.1.1.2 Add preservative, if necessary, (See Appendix A, Secs. 1.2, 1.3, 3.0 and 8.0) to each vial. The preservative is added to each vial prior to shipping the vial to the field. Add approximately 1 g of sodium bisulfate to each vial. If samples markedly smaller or larger than 5 g are to be collected, adjust the amount of preservative added to correspond to approximately 0.2 g of preservative for each 1 g of sample. Enough sodium bisulfate should be present to ensure a sample pH of ≤ 2.

8.1.1.3 Add 5 mL of organic-free reagent water to each vial. The water and the preservative will form an acid solution that will reduce or eliminate the majority of the biological activity in the sample, thereby preventing biodegradation of the volatile target analytes.

8.1.1.4 Seal the vial with the screw-cap and septum seal. If the double-ended, fritted, vials are used, seal both ends as recommended by the manufacturer.

8.1.1.5 Affix a label to each vial. This eliminates the need to label the vials in the field and assures that the tare weight of the vial includes the label. (The weight of any markings added to the label in the field is negligible).

8.1.1.6 Weigh the prepared vial to the nearest 0.01 g, record the tare weight, and write it on the label.

8.1.1.7 Because volatile organics will partition into the headspace of the vial from the aqueous solution and will be lost when the vial is opened, surrogates, matrix spikes, and internal standards (if applicable) should only be added to the vials after the sample has been added to the vial. These standards should be introduced back in the laboratory, either manually by puncturing the septum with a small-gauge needle or automatically by the sample introduction system, just prior to analysis.

8.1.2 High concentration soil samples collected without a preservative

When high concentration samples are collected without a preservative, a variety of sample containers may be employed, including 60-mL glass vials with septum seals (see Sec. 6.4). More detailed information on additional options for the preparation of sample vials can be found in Appendix A, Secs. 3.0, 7.0, and 8.0.

8.1.3 High concentration soil samples collected and preserved in the field

The following steps apply to the preparation of vials used in the collection of high concentration soil samples to be preserved in the field with methanol and analyzed by the aqueous purge-and-trap equipment described in Method 5030. See the water-miscible solvent dilution effect information in Sec. 11.5 and Method 8000 for guidance on correcting results for data reporting purposes. More detailed information on additional options for the preparation of sample vials can be found in Appendix A, Secs. 3.0, 7.0, and 8.0.

8.1.3.1 Add 10 mL of methanol to each vial.

8.1.3.2 Seal the vial with the screw-cap and septum seal.

8.1.3.3 Affix a label to each vial. This eliminates the need to label the vials in the field and assures that the tare weight of the vial includes the label. (The weight of any markings added to the label in the field is negligible).

8.1.3.4 Weigh the prepared vial to the nearest 0.01 g, record the tare weight, and write it on the label.

NOTE: Vials containing methanol should be weighed a second time on the day that they are to be used. Vials found to have lost methanol (reduction in weight of >0.01 g) should not be used for sample collection.

8.1.3.5 Surrogates, internal standards and matrix spikes (if applicable) should be added to the sample after it is returned to the laboratory and prior to analysis.

8.1.4 Oily waste samples

When oily waste samples are known to be soluble in methanol or PEG, sample vials may be prepared as described in Sec. 8.1.3, using the appropriate solvent. However, when the solubility of the waste is unknown, the sample should be collected without the use of a preservative, in a vial such as that described in Sec. 8.1.2.

8.2 Sample collection

Collect the sample according to the procedures outlined in the sampling plan. As with any sampling procedure for volatiles, care must be taken to minimize the disturbance of the sample in order to minimize the loss of the volatile components. Several techniques may be used to transfer a sample to the relatively narrow opening of the low concentration soil vial. These include devices such as the EnCore™ sampler, the Purge-and-Trap Soil Sampler ™, or any other sampling device listed in Sec. 6.5, or equivalent. Always wear gloves whenever handling the tared sample vials. More detailed information and additional sample collection options can be found in Appendix A, Sec. 7.0.

8.2.1 Low concentration soil samples

8.2.1.1 Volatile organic compounds (VOCs) are determined by collecting an approximately 5-g sample and shipping to the laboratory or appropriate analysis site by the various methods outlined in Appendix A. Using an appropriate sample collection device, collect approximately 5 g of sample as soon as possible after the surface of the soil or other solid material has been exposed to the atmosphere: generally within a few minutes at most. Carefully wipe the exterior of the sample collection device with a clean cloth or towel.

8.2.1.2 Using the sample collection device, add about 5 g (2 - 3 cm) of soil to the sample vial containing the preservative solution or other preservation options as discussed in Appendix A. Quickly brush any soil off the vial threads and immediately seal the vial with the septum and screw-cap. Store samples on ice at 4°C. Alternatively, samples can be collected into an empty vial or vial containing reagent water (with or without preservative) and stored frozen at < -7°C.

NOTE: Soil samples that contain carbonate minerals (either from natural sources or applied as an amendment) may effervesce upon contact with the acidic preservative solution option in the low concentration sample vial. If the amount of gas generated is very small (i.e., several mL), any loss of volatiles as a result of such effervescence may be minimal if the vial is sealed quickly. However, if larger amounts of gas are generated, not only may the sample lose a significant amount of analyte, but the gas pressure may shatter the vial if the sample vial is sealed. Therefore, when samples are known or suspected to contain high levels of carbonates, a test sample should be collected, added to a vial, and checked for effervescence. If a rapid or vigorous reaction occurs, discard the sample and collect low concentration samples in vials without chemical preservation.

8.2.1.3 When practical, use a portable balance to weigh the sealed vial containing the sample to ensure that 5.0 ± 0.5 g of sample were added. The balance should be calibrated in the field using an appropriate weight for the sample containers employed (Sec. 6.5.5). Record the weight of the sealed vial containing the sample to the nearest 0.01 g.

8.2.1.4 Alternatively, collect several trial samples with plastic syringes. Weigh each trial sample and note the length of the soil column in the syringe. Use these data to determine the length of soil in the syringe that corresponds to 5.0 ± 0.5 g. Discard each trial sample.

8.2.1.5 As with the collection of aqueous samples for volatiles, collect at least two replicate samples. This will allow the laboratory an additional sample for reanalysis, if needed. The second sample should be taken from the same soil stratum or the same section of the solid waste being sampled, and within close proximity to the location from which the original sample was collected.

8.2.1.6 In addition, since the soil vial cannot be opened without compromising the integrity of the sample, at least one additional aliquot of sample must be collected for screening, moisture determination, and high concentration analysis (if necessary). This third aliquot may be collected in a 60-mL glass vial or a third 40-mL soil sample vial. However, this third vial must *not* contain the sample preservative solution, as an aliquot will be used to determine % moisture. If high concentration samples are collected in

vials containing methanol, then two additional aliquots should be collected, one for high concentration analysis collected in a vial containing methanol, and another for the moisture determination in a vial without either methanol or the low concentration aqueous preservative solution.

8.2.1.7 If samples are known or expected to contain target analytes over a wide range of concentrations, thereby requiring the analyses of multiple sample aliquots, it may be advisable and practical to take an additional sample aliquot in a low concentration soil vial containing the preservative, but collecting only 1-2 g instead of the 5 g collected in Sec. 8.2.1.1. This aliquot may be used for those analytes that exceed the instrument calibration range in the 5-g analysis.

8.2.1.8 The EnCore™ sampler has not been thoroughly evaluated by EPA as a sample storage device. While preliminary results indicate that storage in the EnCore™ device may be appropriate for up to 48 hours, samples collected in this device should be transferred to the soil sample vials as soon as possible, or analyzed within 48 hours.

8.2.1.9 The collection of low concentration soil samples in vials that contain methanol is not appropriate for samples analyzed with the closed-system purge-and-trap equipment described in this method (see Sec. 8.2.2).

8.2.2 High concentration soil samples preserved in the field

The collection of soil samples in vials that contain methanol has been suggested by some as a combined preservation and extraction procedure. However, this procedure is not appropriate for use with the low concentration soil procedure described in this method.

NOTE: The use of methanol preservation has not been formally evaluated by EPA and analysts must be aware of three potential problems. First, the use of methanol as a preservative and extraction solvent introduces a significant dilution factor that will raise the method quantitation limit beyond the operating range of the low concentration direct purge-and-trap procedure (0.5-200 µg/kg). The exact dilution factor will depend on the masses of solvent and sample, but generally exceeds 100, and may make it difficult to demonstrate compliance with regulatory limits or action levels for some analytes. Because the analytes of interest are volatile, the methanol extract cannot be concentrated to overcome the dilution problem. Thus, for samples of unknown composition, it may still be necessary to collect an aliquot for analysis by this closed-system procedure and another aliquot preserved in methanol and analyzed by other procedures. Secondly, solid samples with a significant moisture content (>10%) that are extracted prior to analysis in a water miscible solvent such as methanol are diluted by the total volume of the solvent/water mixture. (see Sec. 11.5 and Method 8000) The final problem is that the addition of methanol to the sample is likely to cause the sample to fail the ignitability characteristic, or cause it to become a listed waste, thereby requiring the unused sample volume to be managed as a hazardous waste.

8.2.2.1 When samples are known to contain volatiles at concentrations high enough that the dilution factor will not preclude obtaining results within the calibration range of the appropriate determinative method, a sample may be collected and immediately placed in a sample vial containing purge-and-trap grade methanol.

8.2.2.2 Using an appropriate sample collection device, collect approximately 5 g of sample as soon as possible after the surface of the soil or other solid material has been exposed to the atmosphere: generally within a few minutes at most. Carefully wipe the exterior of the sample collection device with a clean cloth or towel.

8.2.2.3 Using the sample collection device, add about 5 g (2 - 3 cm) of soil to the vial containing 10 mL of methanol. Quickly brush any soil off the vial threads and immediately seal the vial with the septum and screw-cap. Store samples on ice at 4 °C.

8.2.2.4 When practical, use a portable balance to weigh the sealed vial containing the sample to ensure that 5.0 ± 0.5 g of sample were added. The balance should be calibrated in the field using an appropriate weight for the sample containers employed (Sec. 6.5.5). Record the weight of the sealed vial containing the sample to the nearest 0.01 g.

8.2.2.5 Alternatively, collect several trial samples with plastic syringes. Weigh each trial sample and note the length of the soil column in the syringe. Use these data to determine the length of soil in the syringe that corresponds to 5.0 ± 0.5 g. Discard each trial sample.

8.2.2.6 Other sample weights and volumes of methanol may be employed, provided that the analyst can demonstrate that the sensitivity of the overall analytical procedure is appropriate for the intended application.

8.2.2.7 The collection of at least one additional sample aliquot is required for the determination of the moisture content, as described in Sec. 6.2.1.6. Samples collected in methanol should be shipped as described in Sec. 6.3, and must be clearly labeled as containing methanol, so that the samples are not analyzed using the closed-system purge-and-trap equipment described in this procedure.

8.2.3 High concentration sample <u>not</u> preserved in the field

The collection of high concentration bulk samples, i.e., wastes containing percent level concentrations, that are not preserved in the field generally follows similar procedures as for the other types of samples described in Secs. 8.2.1 and 8.2.2, with the obvious exception that the sample vials contain neither the aqueous preservative solution nor methanol. However, when field preservation is not employed, it is better to collect a larger volume sample, filling the sample container as full as practical in order to minimize the headspace. Such collection procedures generally do not require the collection of a separate aliquot for moisture determination, but it may be advisable to collect a second sample aliquot for screening purposes, in order to minimize the loss of volatiles in either aliquot.

8.2.4 Oily waste samples

The collection procedures for oily samples depend on knowledge of the waste and its solubility in methanol or other solvents.

8.2.4.1 When an oily waste is <u>known</u> to be soluble in methanol or PEG, the sample may be collected in a vial containing such a solvent (see Sec. 8.1.4), using procedures similar to those described in Sec. 8.2.2.

8.2.4.2 When the solubility of the oily waste is <u>not</u> known, the sample should either be collected in a vial without a preservative, as described in Sec. 8.2.3, or the

solubility of a trial sample should be tested in the field, using a vial containing solvent. If the trial sample is soluble in the solvent, then collect the oily waste sample as described in Sec. 8.2.2. Otherwise, collect an unpreserved sample as described in Sec. 8.2.3.

8.3 Sample handling and shipment

All samples for volatiles analysis should be cooled to approximately 4°C, packed in appropriate containers, and shipped to the laboratory on ice, as described in the sampling plan. See Appendix A, Secs. 3.0, 7.0, and 8.0 for additional sample handling options.

8.4 Sample storage

8.4.1 Once in the laboratory, store samples at the recommended temperature until analysis (refer to Appendix A, Secs. 3.0 and 7.4 for additional sample storage information). The sample storage area should be free of organic solvent vapors.

8.4.2 All samples should be analyzed as soon as practical, and within the designated holding time from collection. Samples not analyzed within the designated holding time must be noted and the data are considered minimum values.

8.4.3 When the low concentration samples are strongly alkaline or highly calcareous in nature, the sodium bisulfate preservative solution may not be strong enough to reduce the pH of the soil/water solution to below 2. Therefore, when low concentration soils to be sampled are known or suspected to be strongly alkaline or highly calcareous, additional steps may be required to preserve the samples. Such steps include: addition of larger amounts of the sodium bisulfate preservative to non-calcareous samples, storage of low concentration samples at <-7°C (taking care not to fill the vials so full that the expansion of the water in the vial breaks the vial), or significantly reducing the maximum holding time for low concentration soil samples. Whichever steps are employed, they should be clearly described in the sampling and QA project plans and distributed to both the field and laboratory personnel. See Sec. 8.2.1.2 for additional information.

8.4.4 See Appendix A, Secs. 3.0, 7.0, and 8.0 for additional sample storage options.

9.0 QUALITY CONTROL

9.1 Refer to Chapter One for guidance on quality assurance (QA) and quality control (QC) protocols and Method 5000 for sample preparation QC procedures. Each laboratory should maintain a formal quality assurance program. The laboratory should also maintain records to document the quality of the data generated. All data sheets and quality control data should be maintained for reference or inspection. When inconsistencies exist between QC guidelines, method-specific QC criteria take precedence over both technique-specific criteria and those criteria given in Chapter One, and technique-specific QC criteria take precedence over the criteria in Chapter One.

9.2 Before processing any samples, the analyst should demonstrate through the analysis of an organic-free reagent water method blank that all glassware and reagents are interference free. Each time a set of samples is extracted, or there is a change in reagents, a method blank 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.

9.3 Initial demonstration of proficiency - Each laboratory must demonstrate initial proficiency with each sample preparation and determinative method combination it utilizes, by generating data of acceptable accuracy and precision for target analytes in a clean matrix. The laboratory must also repeat this demonstration whenever new staff are trained or significant changes in instrumentation are made. See the Quality Control Section of Methods 5000 and 8000 for information on how to accomplish this demonstration.

9.4 Sample quality control for preparation and analysis - See the Quality Control Section of Method 5000 and Method 8000 for procedures to follow to demonstrate acceptable continuing performance on each set of samples to be analyzed. These include the method blank, either a matrix spike/matrix spike duplicate or a matrix spike and duplicate sample analysis, a laboratory control sample (LCS), and the addition of surrogates to each sample and QC sample.

9.5 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

9.6 The laboratory should have quality control procedures to make sure that sample integrity is not compromised during the sample collection and sample handling process, e.g., making sure that septa and vial caps do not leak, etc. (See Appendix A, Secs. 1.6 and 7.1.1) In addition, it would be advisable for the laboratory to monitor the internal standard's (IS) area counts for the low concentration samples, since leaks attributed to a poor seal with the vial caps and septa will be evident by low IS area counts. Sample containers and data results for instances where low IS area counts are observed and leaks are suspected, should be discarded.

10.0 CALIBRATION AND STANDARDIZATION

Refer to the appropriate determinative method for calibration and standardization procedures.

11.0 PROCEDURE

This section describes procedures for sample screening, the low concentration soil method, the high concentration soil method, and the procedure for oily waste samples. High concentration samples are to be introduced into the GC system using Method 5030. Oily waste samples are to be introduced into the GC system using Method 5030 if they are soluble in a water-miscible solvent, or using Method 3585 if they are not.

11.1 Sample screening

11.1.1 It is highly recommended that all samples be screened prior to the purge-and-trap GC or GC/MS analysis. Samples may contain higher than expected quantities of purgeable organics that will contaminate the purge-and-trap system**,** thereby requiring extensive cleanup and instrument maintenance. The screening data are used to determine which is the appropriate sample preparation procedure for the particular sample, the low concentration closed-system direct purge-and-trap method (Sec. 11.2), the high concentration (methanol extraction) method (Sec. 11.3), or the nonaqueous liquid (oily waste) methanol or PEG dilution procedure (Sec. 11.4).

11.1.2 The analyst may employ any appropriate screening technique. Three suggested screening techniques employing SW-846 methods are:

11.1.2.1 Automated headspace (Method 5021) using a gas chromatograph (GC) equipped with an appropriate detector,

11.1.2.2 Screening with a portable photoionization detector (PID) (Method 3815) or,

11.1.2.3 Extraction of the sample with hexadecane (Method 3820) and analysis of the extract on a GC equipped with a FID and/or an ECD.

11.1.3 The analyst may inject a calibration standard containing the analytes of interest at a concentration equivalent to the upper limit of the calibration range of the low concentration soil method. The results from this standard may be used to determine when the screening results approach the upper limit of the low concentration soil method. There are no linearity or other performance criteria associated with the injection of such a standard, and other approaches may be employed to estimate sample concentrations.

11.1.4 Use the low concentration closed-system purge-and-trap method (Sec. 11.2) if the estimated concentration from the screening procedure falls within the calibration range of the selected determinative method. If the concentration exceeds the calibration range of the low concentration soil method, then use either the high concentration soil method (Sec. 11.3), or the oily waste method (Sec. 11.4).

11.2 Low concentration soil method (Approximate concentration range of 0.5 to 200 µg/kg - the concentration range is dependent upon the determinative method and the sensitivity of each analyte.)

11.2.1 Initial set-up

Prior to using this introduction technique for any GC or GC/MS method, the system must be calibrated. General calibration procedures are discussed in Method 8000, while the determinative methods and Method 5000 provide specific information on calibration and preparation of standards. Normally, external standard calibration is preferred for the GC methods (non-MS detection) because of possible interference problems with internal standards. If interferences are not a problem, or when a GC/MS method is used, internal standard calibration may be employed.

11.2.1.1 Assemble a purge-and-trap device that meets the specification in Sec. 6.2 and that is connected to a gas chromatograph or a gas chromatograph/mass spectrometer system.

11.2.1.2 Before initial use, a Carbopack/Carbosieve trap should be conditioned overnight at 245°C by baking out with an inert gas flow of at least 20 mL/minute. If other trapping materials are substituted for the Carbopack/Carbosieve, follow the manufacturers recommendations for conditioning. Vent the trap effluent to the hood, not to the analytical column. Prior to daily use, the trap should be conditioned by baking for 10 minutes at 245°C. The trap may be vented to the analytical column during daily conditioning; however, the column must be run through the temperature program prior to analysis of samples.

11.2.1.3 If the standard trap in Sec. 6.2.2.2 is employed, prior to initial use, the trap should be conditioned overnight at 180°C by baking out with an inert gas flow of at least 20 mL/min, or according to the manufacturer's recommendations. Vent the trap effluent to the hood, not to the analytical column. Prior to daily use, the trap should be

conditioned by baking for 10 min at 180°C. The trap may be vented to the analytical column during daily conditioning; however, the column must be run through the temperature program prior to analysis of samples.

11.2.1.4 Establish the purge-and-trap instrument operating conditions. Adjust the instrument to inject 5 mL of water, to heat the sample to 40°C, and to hold the sample at 40°C for 1.5 minutes before commencing the purge process, or as recommended by the instrument manufacturer.

11.2.1.5 Prepare a minimum of five initial calibration standards containing all the analytes of interest and surrogates, as described in Method 8000, and following the instrument manufacturer's instructions. The calibration standards are prepared in organic-free reagent water. The volume of organic-free reagent water used for calibration must be the same volume used for sample analysis (normally 5 mL added to the vial before shipping it to the field plus the organic-free reagent water added by the instrument). When the sodium bisulfate preservation technique is used, the calibration standards should also contain approximately the same amount of the sodium bisulfate preservative as the sample (e.g., ~1 g), as the presence of the preservative will affect the purging efficiencies of the analytes. The internal standard solution must be added automatically, by the instrument, in the same fashion as used for the samples. Place the soil vial containing the solution in the instrument carousel. In order to calibrate the surrogates using standards at five concentrations, it may be necessary to disable the automatic addition of surrogates to each vial containing a calibration standard (consult the manufacturer's instructions). Prior to purging, heat the sample vial to 40°C for 1.5 minutes, or as recommended by the manufacturer.

11.2.1.6 Carry out the purge-and-trap procedure as outlined in Secs. 11.2.3. to 11.2.5.

11.2.1.7 Calculate calibration factors (CF) or response factors (RF) for each analyte of interest using the procedures described in Method 8000. Calculate the average CF (external standards) or RF (internal standards) for each compound, as described in Method 8000. Evaluate the linearity of the calibration data, or choose another calibration model, as described in Method 8000 and the specific determinative method.

11.2.1.8 For GC/MS analysis, a system performance check must be made before this calibration curve is used (see Method 8260). If the purge-and-trap procedure is used with Method 8021, evaluate the response for the following four compounds: chloromethane; 1,1-dichloroethane; bromoform; and 1,1,2,2-tetrachloroethane. They are used to check for proper purge flow and to check for degradation caused by contaminated lines or active sites in the system.

11.2.1.8.1 Chloromethane is the most likely compound to be lost if the purge flow is too fast.

11.2.1.8.2 Bromoform is one of the compounds most likely to be purged very poorly if the purge flow is too slow. Cold spots and/or active sites in the transfer lines may adversely affect response.

11.2.1.8.3 Tetrachloroethane and 1,1-dichloroethane are degraded by contaminated transfer lines in purge-and-trap systems and/or active sites in trapping materials.

11.2.1.9 When analyzing for very late eluting compounds with Method 8021 (i.e., hexachlorobutadiene, 1,2,3-trichlorobenzene, etc.), cross-contamination and memory effects from a high concentration sample or even the standard are a common problem. Extra rinsing of the purge vessel after analysis normally corrects this. The newer purge-and-trap systems often overcome this problem with better bake-out of the system following the purge-and-trap process. Also, the charcoal traps retain less moisture and decrease the problem.

11.2.2 Calibration verification (see appropriate determinative method)

Refer to Method 8000 for details on calibration verification. A single standard near the mid-point of calibration range is used for verification. This standard should also contain approximately 1 g of sodium bisulfate if the samples are also preserved in this manner.

11.2.3 Sample purge-and-trap

This method is designed for a 5-g sample size, but smaller sample sizes may be used. Consult the instrument manufacturer's instructions regarding larger sample sizes, in order to avoid clogging of the purging apparatus. The soil vial is hermetically sealed at the sampling site, and MUST remain so in order to guarantee the integrity of the sample. Gloves must be worn when handling the sample vial since the vial has been tared. If any soil is noted on the exterior of the vial or cap, it must be carefully removed prior to weighing. Weigh the vial and contents to the nearest 0.01 g, even if the sample weight was determined in the field, and record this weight. This second weighing provides a check on the field sampling procedures and provides additional assurance that the reported sample weight is accurate. Data users should be advised on significant discrepancies between the field and laboratory weights.

11.2.3.1 Remove the sample vial from storage and allow it to warm to room temperature. Shake the vial gently, to ensure that the contents move freely and that stirring will be effective. Place the sample vial in the instrument carousel according to the manufacturer's instructions.

11.2.3.2 Without disturbing the hermetic seal on the sample vial, add 5 mL of organic-free reagent water, the internal standards, and the surrogate compounds. This is carried out using the automated sampler. Other volumes of organic-free reagent water may be used, however, it is imperative that all samples, blanks, and calibration standards have exactly the same final volume of organic-free reagent water. Prior to purging, heat the sample vial to 40°C for 1.5 minutes, or as described by the manufacturer.

11.2.3.3 For the sample selected for matrix spiking, add the matrix spiking solution described in the Reagents Section of Method 5000, either manually, or automatically, following the manufacturer's instructions. The concentration of the spiking solution and the amount added should be established as described in the Quality Control Section of Method 8000.

11.2.3.4 Purge the sample with helium or another inert gas at a flow rate of up to 40 mL/minute (the flow rate may vary from 20 to 40 mL/min, depending on the target analyte group) for the appropriate purge time (usually 11 minutes) while the sample is being agitated with the magnetic stirring bar or other mechanical means. The purged analytes are allowed to flow out of the vial through a glass-lined transfer line to a trap packed with suitable sorbent materials.

11.2.4 Sample desorption

11.2.4.1 Non-cryogenic interface - After the purge, place the purge-and-trap system in the desorb mode and preheat the trap to 245°C without a flow of desorption gas. Start the flow of desorption gas at 10 mL/minute for about four minutes (1.5 min is normally adequate for analytes in Method 8015). Begin the temperature program of the gas chromatograph and start data acquisition.

11.2.4.2 Cryogenic interface - After the purge, place the purge-and-trap system in the desorb mode, make sure that the cryogenic interface is at -150°C or lower, and rapidly heat the trap to 245°C while backflushing with an inert gas at 4 mL/minute for about 5 minutes (1.5 min is normally adequate for analytes in Method 8015). At the end of the 5-minute desorption cycle, rapidly heat the cryogenic trap to 250°C. Begin the temperature program of the gas chromatograph and start the data acquisition.

11.2.5 Trap reconditioning

After desorbing the sample, recondition the trap by returning the purge-and-trap system to the purge mode. Maintain the trap temperature at 245°C (or other temperature recommended by the manufacturer of the trap packing materials). After approximately 10 minutes, turn off the trap heater and halt the purge flow through the trap. When the trap is cool, the next sample can be analyzed.

11.2.6 Data interpretation

Perform qualitative and quantitative analysis following the guidance given in the determinative method and Method 8000. If the concentration of any target analyte exceeds the calibration range of the instrument, it will be necessary to reanalyze the sample by the high concentration method. Such reanalyses need only address those analytes for which the concentration exceeded the calibration range of the low concentration method. Alternatively, if a sample aliquot of 1-2 g was also collected (see Sec. 8.2.1.7), it may be practical to analyze that aliquot for the analytes that exceeded the instrument calibration range in the 5-g analysis. If results are to be corrected for moisture content, proceed to Sec. 11.5.

11.3 High concentration method for soil samples with concentrations generally greater than 200 µg/kg.

The high concentration method for soil is based on a solvent extraction. A solid sample is either extracted or diluted, depending on sample solubility in a water-miscible solvent. An aliquot of the extract is added to organic-free reagent water containing, if applicable, internal and matrix spiking standards, purged according to Method 5030, and analyzed by an appropriate determinative method. Wastes that are insoluble in methanol (i.e., petroleum and coke wastes) are diluted with hexadecane (see Sec. 11.3.8).

NOTE: Surrogate compounds may either be spiked into the solvent at the time of extraction or the reagent water containing an aliquot of the extract prior to analysis. Since the surrogate recovery data from these two options provides assurances of either extraction or analytical efficiencies, the decision as to when the surrogates are added depends on what questions need to be answered for a given sample matrix and the intended uses of the data.

The specific sample preparation steps depend on whether or not the sample was preserved in the field. Samples that were not preserved in the field are prepared using the steps below,

beginning at Sec. 11.3.1. If solvent preservation was employed in the field, then the preparation begins with Sec. 11.3.4.

11.3.1 When the high concentration sample is not preserved in the field, the sample consists of the entire contents of the sample container. Do not discard any supernatant liquids. Whenever practical, mix the contents of the sample container by shaking or other mechanical means without opening the vial. When shaking is not practical, quickly mix the contents of the vial with a narrow metal spatula and immediately reseal the vial.

11.3.2 If the sample is from an unknown source, perform a solubility test preferably using a sample container reserved for the % moisture determination before proceeding. Remove several grams of material from the sample container. If the sample material is obtained from a vial dedicated for analysis, quickly reseal the container to minimize the loss of volatiles. Weigh 1-g aliquots of the sample into several test tubes or other suitable containers. Add 10 mL of methanol to the first tube, 10 mL of PEG to the second, and 10 mL of hexadecane to the third. Swirl the sample and determine if it is soluble in the solvent. Once the solubility has been evaluated, discard these test solutions. If the sample is soluble in either methanol or PEG, proceed with Sec. 11.3.3. If the sample is only soluble in hexadecane, proceed with Sec. 11.3.8.

11.3.3 For soil and solid waste samples that are soluble in methanol, add 9.0 mL of methanol and 1.0 mL of the surrogate spiking solution, or 10.0 mL of methanol without surrogates to a tared 20-mL vial. Using a top-loading balance, weigh 5 g (wet weight) of sample into the vial. Quickly cap the vial and reweigh the vial. Record the weight to 0.1 g. See Appendix A, Sec. 6.2.1 for methanol contact time information. If the sample was not soluble in methanol, but was soluble in PEG, employ the same procedure described above, but use 9.0 or 10.0 mL of PEG in place of the methanol. Proceed with Sec. 11.3.5.

NOTE: The steps in Secs. 11.3.1, 11.3.2, and 11.3.3 must be performed rapidly and without interruption to avoid loss of volatile organics. These steps must be performed in a laboratory free from solvent fumes.

11.3.4 For soil and solid waste samples that were collected in methanol or PEG (see Sec. 8.2.2), weigh the vial to 0.1 g as a check on the weight recorded in the field. If desired, add the surrogate spiking solution to the vial by injecting it through the septum, and proceed with Sec. 11.3.5. See Appendix A, Sec. A.6.2.1 for methanol contact time information.

11.3.5 Pipet approximately 1 mL of the extract from either Sec. 11.3.3 or 11.3.4 into a GC vial for storage, using a disposable pipet, and seal the vial. The remainder of the extract may be discarded. Add approximately 1 mL of methanol or PEG to a separate GC vial for use as the method blank for each set of samples extracted with the same solvent.

11.3.6 The extracts must be stored at 4°C in the dark, prior to analysis. Add an appropriate aliquot of the extract (based on the approximate sample concentration as noted in the table below) to 5.0 mL of organic-free reagent water containing if applicable, surrogates, internal standards, and matrix spike compounds, and analyze by Method 5030 in conjunction with the appropriate determinative method. Proceed to the Procedure Section in Method 5030 and follow the procedure for purging high concentration samples.

QUANTITY OF METHANOL EXTRACT REQUIRED FOR ANALYSIS OF HIGH CONCENTRATION SOILS/SEDIMENTS

Approximate Concentration Range	Volume of Methanol Extract[a]
500 - 10,000 µg/kg	100 µL
1,000 - 20,000 µg/kg	50 µL
5,000 - 100,000 µg/kg	10 µL
25,000 - 500,000 µg/kg	100 µL of 1/50 dilution[b]

Calculate appropriate dilution factor for concentrations exceeding those in this table.

[a] The volume of methanol added to 5 mL of water being purged should be kept constant. Therefore, add to the 5-mL syringe whatever volume of methanol is necessary to maintain a total volume of 100 µL of methanol.

[b] Dilute an aliquot of the methanol extract and then take 100 µL for analysis.

11.3.7 If results are to be reported using a correction factor for moisture content, determine the moisture content of a separate aliquot of the sample, using the procedure in Sec. 11.5, after the sample extract has been transferred to a GC vial and the vial sealed.

11.3.8 For solids that are not soluble in methanol or PEG (including those samples consisting primarily of petroleum or coking waste) dilute or extract the sample with hexadecane using the procedures in the Procedure Section of Method 3585.

11.4 High concentration method for oily waste samples

This procedure for the analysis of oily waste samples involves the dilution of the sample in methanol or PEG. However, care must be taken to avoid introducing any of the floating oil layer into the instrument. A portion of the diluted sample is then added to 5.0 mL of organic-free reagent water, purged according to Method 5030, and analyzed using an appropriate determinative method.

NOTE: Surrogate compounds may either be spiked into the solvent at the time of extraction or the reagent water containing an aliquot of the extract prior to analysis. Since the surrogate recovery data from these two options provides assurances of either extraction or analytical efficiencies, the decision as to when the surrogates are added depends on what questions need to be answered for a given sample matrix and the intended uses of the data.

For oily samples that are not soluble in methanol or PEG (including those samples consisting primarily of petroleum or coking waste), dilute or extract with hexadecane using the procedures in the Procedure Section of Method 3585.

The specific sample preparation steps depend on whether or not the sample was preserved in the field. Samples that were not preserved in the field are prepared using the steps below, beginning at Sec. 11.4.1. If methanol preservation was employed in the field, then the preparation begins with Sec. 11.4.3.

11.4.1 If the waste was not preserved in the field and it is soluble in methanol or PEG, weigh 1 g (wet weight) of the sample into a tared 10-mL volumetric flask, a tared scintillation vial, or a tared culture tube. If a vial or tube is used instead of a volumetric flask, it must be calibrated prior to use. This operation must be performed prior to opening the sample vial and weighing out the aliquot for analysis.

11.4.1.1 To calibrate the vessel, pipet 10.0 mL of methanol or PEG into the vial or tube and mark the bottom of the meniscus.

11.4.1.2 Discard this solvent, and proceed with weighing out the 1-g sample aliquot.

11.4.2 Quickly add 1.0 mL of surrogate spiking solution, if desired, to the flask, vial, or tube, and dilute to 10.0 mL with the appropriate solvent (methanol or PEG). Swirl the vial to mix the contents. See Appendix A, Sec. 6.2.1 for methanol contact time information.

11.4.3 If the sample was collected in the field in a vial containing methanol or PEG, weigh the vial to 0.1 g as a check on the weight recorded in the field. If desired, add the surrogate spiking solution to the vial by injecting it through the septum. Swirl the vial to mix the contents and proceed with Sec. 11.4.4. See Appendix A, Sec. 6.2.1 for methanol contact time information.

11.4.4 Regardless of how the sample was collected, the target analytes are extracted into the solvent along with the majority of the oily waste (i.e., some of the oil may still be floating on the surface). If oil is floating on the surface, transfer 1 to 2 mL of the extract to a clean GC vial using a Pasteur pipet. Ensure that no oil is transferred to the vial.

11.4.5 Add 10 - 50 µL of the methanol extract to 5 mL of organic-free reagent water containing if applicable, surrogates and internal standards, followed by purge-and-trap analysis, using Method 5030.

11.4.6 If necessary, prepare a matrix spike sample by adding 10 - 50 µL of the matrix spike standard dissolved in methanol to a 1-g aliquot of the oily waste. Shake the vial to disperse the matrix spike solution throughout the oil. Then add 10 mL of extraction solvent and proceed with the extraction and analysis, as described in Secs. 11.4.2 - 11.4.5. Calculate the recovery of the spiked analytes as described in Method 8000. If the recovery is not within the acceptance limits for the application, use the hexadecane dilution technique in the Procedure Section of Method 3585.

11.5 Determination of % moisture

If results are to be reported using a correction factor for moisture content, it is necessary to determine the moisture content of the sample. Also note that solid samples with a significant moisture content (>10%) that are extracted prior to analysis in a water miscible solvent such as methanol are diluted by the total volume of the solvent/water mixture. (Ref. 51) In order to report this type of sample result on an "as received" basis, the detected concentration needs to be corrected by the solvent/water dilution factor. See Method 8000 for an explanation and the applicable calculations.

NOTE: It is highly recommended that the moisture content determination only be made after the analyst has determined that no sample aliquots will be taken from the 60-mL vial for high concentration analysis. This is to minimize loss of volatiles and to avoid sample contamination from the laboratory atmosphere. There is no holding time associated with the moisture content determination. Thus, this determination can be made any time prior to reporting the sample results, as long as the vial containing the additional sample has remained sealed and properly stored.

11.5.1 Weigh 5-10 g of the sample from the 60-mL VOA vial into a tared crucible.

11.5.2 Dry this aliquot overnight at 105°C. Allow to cool in a desiccator before weighing. Calculate the % moisture as follows:

$$\% \text{ moisture} = \frac{\text{g of sample} - \text{g of dry sample}}{\text{g of sample}} \times 100$$

WARNING: The drying oven should be contained in a hood or vented. Significant laboratory contamination may result from a heavily contaminated hazardous waste sample.

12.0 DATA ANALYSIS AND CALCULATIONS

There are no calculations explicitly associated with this extraction procedure. See the appropriate determinative method and Method 8000 for calculation of final sample results.

13.0 METHOD PERFORMANCE

13.1 Single laboratory accuracy and precision data were obtained for the method analytes in three soil matrices, sand, a soil collected 10 feet below the surface of a hazardous landfill, called the C-Horizon, and a surface garden soil. Each sample was fortified with the analytes at a concentration of 20 ng/5 g, which is equivalent to 4 µg/kg. These data are listed in tables found in Method 8260.

13.2 Single laboratory accuracy and precision data were obtained for certain method analytes when extracting oily liquid using methanol as the extraction solvent. The data are presented in a table in Method 8260. The compounds were spiked into three portions of an oily liquid (taken from a waste site) following the procedure for matrix spiking described in Sec. 7.4. This represents a worst case set of data based on recovery data from many sources of oily liquid.

14.0 POLLUTION PREVENTION

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity and/or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. The EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option.

14.2 For information about pollution prevention that may be applicable to laboratories and research institutions consult *Less is Better: Laboratory Chemical Management for Waste*

Reduction available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th St., N.W. Washington, D.C. 20036.

15.0 WASTE MANAGEMENT

The Environmental Protection Agency requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations. The Agency urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any sewer discharge permits and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management, consult *The Waste Management Manual for Laboratory Personnel* available from the American Chemical Society at the address listed in Sec. 12.2.

16.0 REFERENCES

1. Bellar, T., "Measurement of Volatile Organic Compounds in Soils Using Modified Purge-and-Trap and Capillary Gas Chromatography/Mass Spectrometry" U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Cincinnati, OH, November 1991.

2. Siegrist, R. L., Jenssen, P. D., “Evaluation of Sampling Method Effects on Volatile Organic Compound Measurements in Contaminated Soils”, Envir Sci Technol, 1990; 24; 1387-92.

3. Hewitt, A. D., Jenkins, T. F., Grant, C. L., “Collection, Handling and Storage: Keys to Improved Data Quality for Volatile Organic Compounds in Soil”, Am Environ Lab, 1995; 7(1); 25-8.

4. Liikala, T. L., Olsen, K. B., Teel, S. S., Lanigan, D. C., “Volatile Organic Compounds: Comparison of Two Sample Collection and Preservation Methods”, Envir Sci Technol, 1996; 30; 3441-7.

5. Lewis, T. E., Crockett, A. B., Siegrist, R. L., Zarrabi, K., “Soil Sampling and Analysis for Volatile Organic Compounds”, Envir Monitoring & Assessment, 1994; 30; 213-46.

6. Hewitt, A. D., “Enhanced Preservation of Volatile Organic Compounds in Soil with Sodium Bisulfate”, SR95-26, U. S. Army Cold Regions Research and Engineering Laboratory, Hanover, NH.

7. Hewitt, A. D., Lukash, N. J. E., “Sampling for In-Vial Analysis of Volatile Organic Compounds in Soil”, Am Environ Lab, 1996; Aug; 15-9.

8. Hewitt, A. D., Miyares, P. H., Sletten, R. S., “Determination of Two Chlorinated Volatile Organic Compounds in Soil by Headspace Gas Chromatography and Purge-and-Trap Gas Chromatography/Mass Spectrometry”, Hydrocarbon Contaminated Soils, 1993, 3; 135-45, Chelsea, MI, Lewis Publishers.

9. Hewitt, A. D., “Methods of Preparing Soil Samples for Headspace Analysis of Volatile Organic Compounds: Emphasis on Salting Out”, 12th Annual Waste Testing and Quality Assurance Symposium, Washington, DC, 1996, 322-9.

10. Hewitt, A. D., Miyares, P. H., Leggett, D. C., Jenkins, T. F., “Comparison of Analytical Methods for Determination of Volatile Organic Compounds”, Envir Sci Tech, 1992; 26; 1932-8.

APPENDIX A

THE COLLECTION AND PRESERVATION OF AQUEOUS AND SOLID SAMPLES FOR VOLATILE ORGANIC COMPOUND (VOC) ANALYSIS

FOREWORD

The information provided in this Appendix is based on EPA's evaluation of currently available data and technology as applied to the most appropriate sample handling and preservation procedures in order to minimize the loss of volatile organic compounds (VOCs) during the collection and analysis of aqueous and solid materials, such as groundwater, wastewater, soils, solid waste, or sediments. These procedures are designed to minimize the losses of VOCs through the two most common mechanisms, volatilization and biodegradation. The intended users of this Appendix guidance are those individuals and organizations involved in the collection and preparation of samples for VOC analyses during the characterization of solid materials under the Resource Conservation and Recovery Act (RCRA). The procedures and techniques described in this Appendix are not presented in any preferential order nor do they represent EPA requirements, but rather they are intended solely as guidance and should be selected and utilized based on the stated project-specific data quality objectives.

This Method 5035 Appendix was developed under the direction of Mr. Barry Lesnik, U.S. EPA, Office of Solid Waste (OSW), Methods Team in collaboration with Mr. David Payne, U.S. EPA, Region 5, Mr. Alan Hewitt, U.S. ACE CRREL, and the SW-846 Organic Methods Workgroup Members. The Methods Team is the focal point within OSW for expertise in analytical chemistry and characteristic testing methodologies, environmental sampling and monitoring, and quality assurance. The Methods Team provides technical support to other OSW Divisions, EPA Program Offices and Regions, state regulatory agencies, and the regulated community.

DISCLAIMER

The U.S. Environmental Protection Agency's Office of Solid Waste (EPA or the Agency) has prepared this Method 5035 Appendix to provide guidance to those individuals involved in the collection and preparation of samples for volatile organic compounds (VOCs) analysis during the characterization of aqueous and solid materials under the Resource Conservation and Recovery Act (RCRA). This Appendix provides guidance for selecting an appropriate sample collection and preservation technique that may be suitable for VOC analyses in order to meet the data quality requirements or objectives for the intended use of the results.

EPA does not make any warranty or representation, expressed or implied with respect to the accuracy, completeness or usefulness of the information contained in this report. EPA does not assume any liability with respect to the use of, or for damages resulting from the use of, any information, apparatus, method or process disclosed in this report. Reference to trade names or specific commercial products, commodities, or services in this report does not represent or constitute an endorsement, recommendation, or favoring by EPA of the specific commercial product, commodity, or service. In addition, the policies set out in this Appendix are not final Agency action, but are intended solely as guidance. They are not intended, nor can they be relied upon, to create any rights enforceable by any party in litigation with the United States. EPA officials may decide to follow the guidance provided in this Appendix, or to act at variance with the guidance, based on an analysis of specific site or facility circumstances. The Agency also reserves the right to change this guidance at any time without public notice.

CONTENTS

Tables

A.1.0 PURPOSE AND OVERVIEW

This Appendix provides guidance in sample collection and preservation procedures that may be suitable for use during the characterization of volatile organic compounds (VOCs) in solid materials, such as soils, solid wastes, or sediments and aqueous samples or leachates from solid matrices.

A.1.1 What are VOCs?

VOCs are a class of organic compounds that includes low molecular weight aromatics, hydrocarbons, halogenated hydrocarbons, ketones, acetates, nitriles, acrylates, ethers, and sulfides with sufficiently low boiling points to give them appreciable vapor pressures at 1 atmosphere of pressure. Although EPA has never defined a strict boiling point cut-off for this compound class, most VOCs of concern to EPA have boiling points below 150°C, while some members of this class may have boiling points as high as 200°C.

The solubilities of the individual VOCs in water vary widely, from insoluble to soluble, with many of the oxygenated compounds (ketones and ethers) at the soluble end of the range and the hydrocarbons and substituted hydrocarbons at the insoluble end of the range.

Given that water may be present to varying degrees in such solid materials of environmental significance as soils, solid wastes, and sediments, the water solubility of an individual VOC may in fact control its "solubility" in solid samples.

A.1.2 What is sample preservation?

The sample collection procedures described in EPA analytical methods are designed to ensure that at the time of analysis, the chemical composition of the small volume of material collected from the parent bulk material is representative of the chemical composition of the original material. Considerations regarding sample support and sampling design (discussed in Chapter Nine of the SW-846 manual) ensure that the physical aspects of sample collection (e.g., sample volume and orientation, numbers and distribution of samples) produce data estimates that are representative of the bulk material subject to regulatory decision-making, perhaps millions of gallons a day of discharged wastewater, or thousands of kilograms of solid material. Once collected, a sample should be maintained in a manner that preserves the relationship between it and the bulk material, e.g., the chemical composition of the sample should not change by virtue of being collected. Maintaining that relationship between the sample and the bulk material is referred to as sample preservation.

Several types of sample preservation are employed in EPA methods. The most common method of preservation is to cool the sample to 4 ± 2°C. Cooling may be applied to many types of sample matrices, including water, soil, sediments, and solid wastes. The temperature of 4 ± 2°C is used because it represents the temperature at which pure water exhibits its maximum density, hence its minimum volume. However, if aqueous samples are cooled below 0°C, the water expands significantly as it freezes and may crack the sample container.

By lowering the temperature of the sample, many of the physical, chemical, and biological processes that may cause environmental contaminants to leave the sample (e.g., loss of volatiles to the air) or be transformed into other compounds (e.g., chemical breakdown or biodegradation) are greatly slowed. However, even if the rates of biodegradation are reduced by physical preservation, many environmental matrices of interest contain large numbers of microorganisms that may break down contaminants. Examples include wastewaters from sewage

treatment, surface waters, and surface soil. In these types of matrices, simply reducing the rate at which biodegradation occurs may not be enough to maintain the condition of the original sample.

The most practical way in which to reduce this biological activity in aqueous samples is through the use of chemical preservatives that act as biocides. Historically, this has included preservatives such as sodium bisulfate or hydrochloric acid to adjust the pH for aqueous samples to less than pH 2, at which point, virtually all biological activity ceases.

Adjusting the pH of a solid sample such as a soil, sediment, or solid waste presents a number of other difficulties. In particular, samples containing carbonates should not be acidified due to the potential for effervescence which may result in loss of volatile compounds. Precautions should also be taken when preserving by acidification since certain compounds within the olefins, ketones, esters, ethers, and sulfides classes may react under low pH conditions and possibly not be representative of the material as sampled. Additionally, acidification of solid wastes may evolve toxic gases that may be harmful to field and laboratory personnel. **It is therefore recommended that when collecting wastes of unknown composition, preliminary screening and characterization of potential sample contents should be performed prior to use of acidification as a means to chemically preserve samples designated for determinative analyses.**

Sample collection and preservation procedures should be carefully selected in order to minimize VOC losses prior to sample preparation and determination in the laboratory. Although this guidance discusses some traditional approaches to VOC sample collection and preservation, its main purpose is to provide guidance regarding newer approaches, such as freezing the samples, which may particularly decrease VOC loss in some materials. For additional information regarding the challenges associated with collecting and handling VOC samples, recommended reading includes the "Standard Guide for Sampling Waste and Solids for Volatile Organic Compounds" (ASTM D 4547-98), published by the American Society for Testing and Materials (ASTM). (Ref. 15)

Currently, **it is recommended that VOC solid samples are to be collected, while maintaining a closed-system approach to prevent constituent losses, using an appropriate coring device and immediately transferred to the VOA vial to be used for analysis and should be stored for no longer than 48 hours at 4 ± 2°C prior to analysis or preservation.** Longer storage times at 4 ± 2°C may be appropriate if it can be demonstrated that the VOC concentrations are not adversely affected or that the data generated at the time of sample analysis meets the project-specific data quality objectives. Extended sample storage, up to 14 days from sample collection, may be obtained by either physical or chemical preservation techniques as noted in this Appendix guidance. These preservation techniques can be initiated at the time of sample collection or after arrival in a laboratory. Refer to Table A.1 for a summary of the recommended preservation techniques and analytical holding times.

A.1.3 Do all VOA samples need to be chemically preserved?

No. Only samples that contain analytes that are subject to biological degradation prior to analysis need to be preserved. Samples where aromatic hydrocarbons are target analytes, which are most subject to biological degradation, need to be preserved, unless they are to be analyzed immediately on-site, even if other VOA compound classes are present. Preservation may be inappropriate for highly reactive compounds, e.g., styrene, vinyl chloride, since it may accelerate loss by polymerization or other rapid chemical reaction. Samples for which chlorinated aliphatic hydrocarbons are the only target analytes generally do not need to be preserved. However, all aqueous samples containing free chlorine must be preserved with a dechlorinating agent in order to prevent formation of trihalomethanes and other possible chemical reactions.

A.1.4 Who is the intended audience for this Appendix?

VOCs are frequently Resource Conservation and Recovery Act (RCRA) Program analytes of concern, and thus waste management decisions are often based on characterization of the VOC levels. The intended users of this Appendix guidance are those individuals involved in any way in the collection and preparation of samples for VOC analysis during the characterization of solid materials under RCRA. This may include:

- field sampling personnel
- laboratory analysts
- environmental project managers, whether at a facility regulated under RCRA, or working for a regulatory agency
- Federal, state, and local regulators with oversight responsibilities for sample collection activities
- quality assurance personnel
- data quality assessors.

A.1.5 What does this guidance *not* cover?

This Appendix does *not* provide detailed guidance regarding sampling design or the actual steps in sample preparation and VOC determination in the laboratory. For such guidance, users of this manual should refer to Chapter Nine of SW-846 and the preparation and determinative methods that are selected for analysis as part of the planning process in order to meet the intended data quality objectives.

A.1.6 What equipment is needed?

The site-specific Sampling and Analysis Plan should clearly list the required sample collection equipment necessary to ensure that the loss of volatile constituents will be minimized during the sample collection process. As with all environmental sampling applications, the analytical data usability and representativeness will be affected by improper sample collection techniques. Sampling personnel will be responsible for ensuring that VOA vials are sealed properly using a septum of sufficient thickness without any punctures. The improper vial sealing (i.e., due to excess sample retained on the vial threads) and tightening of caps are the primary factors in the loss of volatiles due to sample collection activities. Care should also be exercised in the selection of approved pre-cleaned and certified VOA vials absent of burrs on the glass. Procedures should be in place for the selection and appropriate use of sample collection devices (i.e., bailer, coring tool, etc.) along with the required decontamination measures. It is also recommended to store one trip blank per cooler when collecting volatile samples in order to assess possible field induced contamination.

A.1.7 How is the guidance organized?

This Appendix is organized as follows:

Section A.2.0 - Project Planning -- Provides an overview of the data quality objectives (DQOs) process as related to the suggested project planning activities prior to sample collection.

Section A.3.0 - Aqueous Sample Matrices and Volatile Organic Compounds – Outlines the appropriate sampling and preservation strategy for aqueous sample matrices.

Section A.4.0 - Solid Materials/Cohesive Soils and Volatile Organic Compounds -- Describes the two most common mechanisms (volatilization and biodegradation) for potential VOC losses during the sample collection process.

Section A.5.0 - History of Practices in the Sampling and Preparation of Solid Materials for VOC Analysis – Provides a summary of the common historical VOC loss mechanisms and discusses the improvements and new developments in sample collection techniques.

Section A.6.0 - Overview of Vapor Partitioning and Methanol Extraction Technologies – Discusses the two most commonly used methods for the laboratory preparation of soils for VOC analysis.

Section A.7.0 - Sample Collection – Describes the sample collection and storage process for various solid matrices.

Section A.8.0 - Approaches to Sample Preparation -- Provides examples of several sample preparation techniques that may be appropriate based on the intended use of the data.

Section A.9.0 - Summary of Findings – Lists the key highlights as discussed in Sections A.2.0 through A.8.0.

Section A.10.0 - References

A.2.0 PROJECT PLANNING

The EPA requires that a systematic planning process such as, but not limited to, the Data Quality Objectives (DQOs) Process be used for all EPA environmental data collection activities. Systematic Planning is necessary to define the type, quantity, and quality of data a decision maker needs before collecting or generating environmental data. As part of the DQO process, questions such as "what are the possible sample matrices?," "why is the sample being collected?," and "what are the appropriate analytical methods?" can be answered based on the intended use of the data. The Systematic Planning process should also include the preparation of a Quality Assurance Project Plan (QAPP) along with a site-specific Sampling and Analysis Plan (SAP) prior to any sample collection activities. Refer to *Guidance for the Data Quality Objectives Process* (G-4) (August 2000, EPA/600/R-96/055), *Guidance for Quality Assurance Project Plans* (G-5) (February 1998, EPA/600/R-98/018) and Chapter Nine of SW-846 for guidance on how to perform the DQO process and planning guidance associated with RCRA waste sampling and analysis.

During the project planning period it is important to stress to all interested parties that any samples identified as a result of the planning process must be representative of the material subject to investigation, and that each sample handling activity can affect sample integrity and representativeness up through analysis (e.g., VOCs can be lost if samples are not appropriately collected and preserved [See Sec. A.1.3]).

The EPA encourages the use of a performance-based measurement system (PBMS) during selection of sample collection and preparation approaches. The EPA defines PBMS as "a set of processes wherein the data quality needs, mandates or limitations of a program or project are specified, and serve as criteria for selecting appropriate methods to meet those needs in a cost effective manner." The PBMS process permits the use of any appropriate method that demonstrates the ability to meet established criteria while complying with specified data quality needs. In addition, analysts must generate initial and continuing method performance data that demonstrate that the selected approaches were appropriate. Implementation of PBMS does not negate the need for or use of standard or consensus methods. It only eliminates the mandate that they be used exclusively. The following are typical items that should be considered during selection of approaches to VOC sample collection and preservation:

1. VOC concentration range.

2. VOC constituents of interest.

3. Physical characteristics of material, i.e., water content and particle size distribution.

4. Chemical and biological characteristics of material, i.e., acid/base properties, chlorine residual, carbonate content, and microbial activity.

5. Compatibility with selected preparation method.

6. Holding time constraints.

7. Data quality requirements.

A.3.0 AQUEOUS SAMPLE MATRICES AND VOLATILE ORGANIC COMPOUNDS

All environmental aqueous samples are physically preserved at 4 ± 2°C immediately after collection in order to improve the overall VOC stability prior to analysis. This preservation process alone has been shown to be effective in preventing the degradation of most constituents for up to seven days from the sample collection date. Depending on the project required VOC constituents, an aqueous sample stability or holding time period can be extended to fourteen days with the use of chemical preservatives such as sodium bisulfate or hydrochloric acid. The chemical preservatives act as acidifying agents to lower the sample pH and thereby inhibit microbial activity which may cause biological degradation of aromatic hydrocarbons. However, since reactive compounds such as 2-chloroethyl vinyl ether are unstable at low pHs, if these analytes are to be determined, the collection of a second set of samples without acid preservatives is necessary. In addition, aqueous samples containing methyl *tert*-butyl ether and other fuel oxygenate ethers should not be acidified if high temperature sample preparative methods (Methods 5021, 5030, 5032) are used. (Refs 48,49) (NOTE: if the aromatic constituents such as benzene, toluene, ethylbenzene, and xylenes (BTEX) are among the analytes of interest, acidification is required for biologically active samples because it has been demonstrated that losses can occur within four hours of sample collection).

The presence of free chlorine in aqueous samples must be monitored and controlled in order to prevent the possible formation of trihalomethanes and reaction with certain compounds such as styrene after sample collection. Therefore, samples containing residual chlorine should be treated with a 10% sodium thiosulfate solution or ascorbic acid prior to acidification in order to reduce the chlorine to unreactive chloride.

Details of procedures and protocols for sample collection must be identified in an approved sampling plan. Aqueous samples for volatile constituents should be collected in vials or containers specifically designed to prevent loss of analytes. In most cases, containers should be provided by the laboratory conducting the analysis. If chemical preservation is required and the laboratory has not pre-preserved the containers, add the appropriate preservative prior to sample collection. Store empty VOC containers on ice in order to reduce potential volatilization while they are being filled. During the sample collection process do not rinse the container before filling and take care to minimize sample overflow that may dilute the preservative. The container should be filled until the water sample forms a positive meniscus at the brim. At this point the container is capped immediately to prevent bubbles and headspace. After the sample has been collected and the container capped, the formation of bubbles can be verified by inverting and lightly tapping the side of the container. Sometimes it is not possible to collect a sample without air bubbles, particularly if the water is aerated. In these cases, the field personnel should record the problem and account for the probable cause. (NOTE: dechlorinating agents should not be mixed with the acid preservative prior to sample collection).

During transport and prior to analysis, samples should be stored in a cooler or refrigerator maintained at 4 ± 2°C and care should be taken to prevent freezing of the sample and possible container breakage. The sampling plan should indicate how sample shipment will occur along with method of packaging, shipping, and the time schedule relative to sample collection and analytical holding times. Refer to Table A.1 for a summary of the recommended preservation techniques and analytical holding times.

A large number of water VOC sample holding time and stability studies have been performed to determine the degree of degradation which may occur at a variety of concentrations, preservation, and storage conditions. Data from these studies have been reviewed by the Oak Ridge National Laboratory (ORNL) in order to develop an approach for assessing the data

confidence from analyses completed beyond the regulatory holding time of 14 days. This approach is based on methodology, referred to as "Practical Reporting Times," that were developed by ORNL in the early 1990's, and described in a summary report listed in Ref. 47. Users may find the data provided in Tables 2 and 3 of this referenced report to be helpful in estimating the post-holding time degradation of VOCs in water and for determining the potential data impact from analyses completed beyond the required holding time. However, the user is cautioned that the holding times provided in this report are estimations based on actual analytical data, and the true values are relative to the on-site sample matrix conditions. See the footnote following Table A.1 regarding holding time extensions.

A.3.1 Alternative Considerations for Sample Holding Time Criteria

Recognition that holding times for environmental contaminants are analyte-specific and highly variable is not new. (Refs. 52,53,54). Environmental contaminants may be short-lived, destroyed by preservation, or highly resistant to degradation. Understanding and applying historical knowledge (Table A.1) can be important and valuable. (Ref. 55) Therefore, we encourage consideration of alternative holding times for several reasons:

1. Project planning,

2. Performance based data review processes,

3. Analytical method selection,

4. Streamlined verification of unexpected or suspect analytical results, and

5. Design of alternative quality control procedures.

Specific examples of how to implement the information incorporated in Table A.1 include the following: During project/systematic planning, field measurement or quick-turn-around analyses must be identified as critical if particular contaminants of concern for a project are easily lost or destroyed. Currently, data review guidelines suggest samples analyzed within 2 weeks of collection be accepted as uniformly reliable, and analyses completed >2 weeks after sample collection are uniformly assessed as unacceptably uncertain. This review judgement is not technically defensible. Many of the most common contaminant decision drivers listed in Table A.1 are important, because they are stable over time, e.g., chlorinated solvents. For these contaminants, cooperative Inter-Agency research has demonstrated no significant change in results from analyses performed at 30 days, often as long as 96 days, after collection and preservation. *NOTE: this extension assumes preservation of samples as identified in Table A.1.* In addition, longer holding times than those specified in Table A.1 may be appropriate if it can be demonstrated that the reported VOC concentrations are not adversely affected from preservation, storage and analyses performed outside the recommended holding times.

The resistance to degradation of these frequent environmental drivers offers additional process improvement opportunities. Utilization of a second VOA sample analyzed beyond the recommended holding time is a mechanism to verify or independently determine unexpected results or correct laboratory errors that cannot be addressed within the current 2-week window. With no significant loss of confidence in the results, this approach eliminates the schedule delays and expense of sampling crew mobilization.

In addition, the use of site-specific performance evaluation material is recognized as a high confidence mechanism to ensure reliability of project data. However, the historical perception of short shelf-life for volatile organics in water eliminates implementation of this approach as a viable

quality control/quality assurance system component for water monitoring programs. Table1 and the associated references contain documentation of appropriate analytes and procedures to develop and implement these alternatives.

Table A.1
Recommended VOC Sample Preservation Techniques and Holding Times

Sample Matrix	Preservative	Holding Time	Comment
Aqueous Samples With No Residual Chlorine Present	Cool to 4 ± 2°C.	7 days	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. If aromatic and biologically active compounds are analytes of interest, acid preservation is necessary and the holding time is extended to 14 days.
Aqueous Samples With No Residual Chlorine Present	Cool to 4 ± 2°C and adjust pH to less than 2 with HCl or solid $NaHSO_4$.	14 days[1]	Reactive compounds such as 2-chloroethylvinyl ether readily break down under acidic conditions. If these types of compounds are analytes of interest, collect a second set of samples without acid preservatives and analyze as soon as possible.
Aqueous Samples With Residual Chlorine Present	Collect sample in a pre-preserved container containing either 25 mg ascorbic acid or 3 mg of sodium thiosulfate per 40-mL of chlorinated sample volume containing less than 5 mg/L of residual chlorine. Cool to 4 ± 2°C.	7 days	Samples containing greater than 5 mg/L of residual chlorine may require additional amounts of dechlorinating agents. 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. If aromatic and biologically active compounds are analytes of interest, acid preservation is necessary and the holding time is extended to 14 days.
Aqueous Samples With Residual Chlorine Present	Collect sample in a pre-preserved container containing either 25 mg ascorbic acid or 3 mg of sodium thiosulfate per 40-mL of chlorinated sample volume containing less than 5 mg/L of residual chlorine. Cool to 4 ± 2°C and adjust pH to less than 2 with HCl or solid $NaHSO_4$	14 days[1]	Samples containing greater than 5 mg/L of residual chlorine may require additional amounts of dechlorinating agents. Reactive compounds such as 2-chloroethylvinyl ether readily break down under acidic conditions. If these types of compounds are analytes of interest, collect a second set of samples without acid preservatives and analyze as soon as possible. Caution: never add acid preservative directly to a dechlorinating agent prior to sample collection.
Solid Samples[2]	Sample is extruded into an empty sealed vial and frozen on-site to < -7°C.	14 days[1]	Sample vials should not be frozen below -20°C due to potential problems with vial seals and the loss of constituents upon sample thawing.

Table A.1 (Continued)

Sample Matrix	Preservative	Holding Time[1]	Comment
Solid Samples[2]	Sample is extruded into an empty sealed vial and cooled to 4 ± 2°C for no more than 48 hours then frozen to < -7°C upon laboratory receipt.	14 days[1]	Analysis must be completed within 48 hours if samples are not frozen prior to the expiration of the 48 hour period. Sample vials should not be frozen below -20°C due to potential problems with vial seals and the loss of constituents upon sample thawing.
	Sample is extruded into an empty sealed vial and cooled to 4 ± 2°C for no more than 48 hours then preserved with methanol upon laboratory receipt.	14 days[1]	Analysis must be completed within 48 hours if samples are not preserved with methanol prior to the expiration of the 48 hour period.
	Sample is extruded into an empty sealed vial and cooled to 4 ± 2°C.	48 hours	
	Cool to 4 ± 2°C the coring tool used as a transport device	48 hours	The holding time may be extended to 14 days if the sample is extruded to a sealed vial and either frozen to < -7°C or chemically preserved. Coring tools should not be frozen below -20°C due to potential problems with tool seals and the loss of constituents upon sample thawing.
	Freeze to < -7°C the coring tool used as a transport device	48 hours	The holding time may be extended to 14 days if the sample is extruded to a sealed vial and either frozen to < -7°C or chemically preserved. Coring tools should not be frozen below -20°C due to potential problems with tool seals and the loss of constituents upon sample thawing.
	Sample is extruded into a vial containing reagent water and frozen on-site to < -7°C.	14 days[1]	Sample vials should not be frozen below -20°C due to potential problems with vial seals and the loss of constituents upon sample thawing.
	Sample is extruded into a vial containing reagent water and cooled to 4 ± 2°C for 48 hours or less then frozen to < -7°C upon laboratory receipt.	14 days[1]	Analysis must be completed within 48 hours if samples are not frozen prior to the expiration of the 48 hour period. Sample vials should not be frozen below -20°C due to potential problems with vial seals and the loss of constituents upon sample thawing.

Table A.1 (Continued)

Sample Matrix	Preservative	Holding Time[1]	Comment
Solid Samples[2]	Sample is extruded into a vial containing reagent water and 1 g $NaHSO_4$ and cooled to 4 ± 2°C.	14 days[1]	Reactive compounds such as 2-chloroethylvinyl ether readily break down under acidic conditions. If these types of compounds are analytes of interest, collect a second set of samples without acid preservatives and analyze as soon as possible.
	Sample is extruded into a vial containing methanol and cooled to 4 ± 2°C.	14 days[1]	Additional methanol extract storage time beyond 14 days may be acceptable if the desired VOC constituent stability can be demonstrated from appropriate performance data.

[1] A longer holding time may be appropriate if it can be demonstrated that the reported VOC concentrations are not adversely affected from preservation, storage and analyses performed outside the recommended holding times.

[2] For biologically active soils, immediate chemical or freezing preservation is necessary due to the rapid loss of BTEX compounds within the first 48 hours of sample collection.

During the selection of VOC sample collection and preservation approaches, it is important to understand the mechanisms of VOC loss inherent to solid materials and VOCs. In general, uncontrolled losses occur through both volatilization and biodegradation. However, for some compounds, e.g., vinyl chloride, acrylonitrile, 2-chloroethylvinyl ether, and styrene, rapid losses can occur through chemical reaction, as well. (Ref. 46)

In most solid materials, VOCs coexist in gaseous and liquid phases, as well as sorbed to the solid particles. The molecular diffusion coefficients of VOCs in the gaseous phase are high enough to allow for the immediate volatilization of those VOCs from a freshly exposed sample surface, resulting in a loss to the surrounding atmosphere. If the sample matrix is porous, these losses will continue as VOCs below the surface diffuse outward. Furthermore, once the gaseous phase is lost, the dynamic equilibrium between the gaseous phase and the liquid and sorbed VOC phases will result in rapid transformations of the liquid and sorbed VOCs to the gaseous phase, where they can continue to be lost to the atmosphere. (Ref. 4) Thus, the primary goal of preservation is to minimize or eliminate the loss of the compounds of concern through direct volatilization to the atmosphere.

The biodegradation of VOCs usually involves compound loss by biological processes mediated by naturally-occurring micro- and macro-organisms found in solid environmental samples such as soils and sediments. Aerobic processes are often of greatest concern, but anaerobic organisms in some sediments and soils can also result in significant losses of VOCs. Biodegradation may be of concern in waste samples, particularly those that may have been stored outdoors.

Most soil sample collection procedures involve intrusive sampling operations that can create or enhance aerobic conditions within a sample. Aerobic conditions can occur by disaggregation of the particles in the solid, or by simple exposure of the sample to air (e.g., collection of a sediment sample from under standing water). Soil samples should be collected immediately or as soon as practical after exposure of the soil during such activities as tank removal or excavation in order to minimize VOC losses from uncontrolled aerobic processes. Unless precautions as noted in this Appendix are employed, aerobic conditions will then persist during handling and storage of the sample.

The rate of biodegradation is dependent on several factors, including the indigenous microbes, the chemical properties of the individual VOC, the total VOC concentration, the chemical properties of the solid matrix, and temperature. In general, the biodegradation mechanism for soil VOCs is not as large a source of determinate error as volatilization. Volatilization losses of an order of magnitude can occur in minutes to hours, whereas losses of a similar magnitude due to biodegradation usually take days to weeks.

Biodegradation is compound selective whereby, under aerobic conditions, the biological mechanisms favor the degradation of aromatic hydrocarbons over the loss of halogenated (chlorinated) hydrocarbons. (Refs. 1,2,4) Aromatic hydrocarbons such as benzene, toluene, ethyl benzene, and xylenes (collectively referred to as BTEX) can be lost in days from samples stored at $4 \pm 2^{\circ}$ C, while losses of chlorinated hydrocarbons by biodegradation over the same period can be relatively insignificant. Major benzene and toluene biodegradation losses (50% or more) have been observed when soils are stored at room temperature (22°C) for five (5) days and near complete concentration reduction when stored for fourteen (14) days at 4°C. (Refs. 1,2,4,6,11,17) For extremely biologically active soils this can occur in less than five days. (Ref. 11)

Due to the above mechanisms, attempts are made from the beginning to maintain sample integrity and representativeness. In doing so, approaches often use various combinations of chemical (e.g., methanol) and physical (e.g., freezing) preservation procedures and collection (e.g., single transfer to air-tight vial) and storage practices (e.g., holding times) to minimize VOC loss. Some of these approaches are presented within this guidance.

A.5.0 HISTORY OF PRACTICES IN THE SAMPLING AND PREPARATION OF SOLID MATERIALS FOR VOC ANALYSIS

A.5.1 Traditional Practices

Over the past 20 years, solid samples obtained for VOC analysis were collected using a spatula -type device to completely fill a container for transfer off-site before the introduction of certain preparation steps and analysis within a 14-day holding time. VOC sampling procedures recommended the use of clean stainless steel utensils to completely fill either 40-mL to 250-mL glass containers. The containers were then closed with polytetrafluoroethylene (PTFE)-lined caps. Sample containers were stored in coolers at 4 ± 2° C and shipped to field or off-site support laboratories for subsampling (usually with 1 to 5 g aliquots) and subsequent analysis. The common holding time for these bulk soil samples, held at 4 ± 2°C, was 14 days.

During the 1990s, research efforts demonstrated that the above VOC bulk sampling procedure is inaccurate and produces VOC results that are biased low. (Refs. 3,8,10,16,30,31,32,33,34) The studies showed that bulk samples can lose 90% or more of their VOC content prior to analytical measurement. (Refs. 3,8,10,16,29,31,32,33) Reasons identified for these losses include:

1. Volatilization from exposure of the solid surface near the time of collection. (Refs. 3,8)

2. Volatilization from intermediate storage containers (e.g., core barrel liners, plastic bags, etc.). (Refs. 4,10,13,17,30)

3. Volatilization from disaggregation of the solid during collection. (Refs. 3,8)

4. Volatilization from failed seals on the PTFE-lined caps of the bottles or volatile organic analyte (VOA) vials (can be caused by soiling of cap and bottle ring closures during filling of containers). (Refs. 3,8)

5. Volatilization during laboratory subsampling of the bulk samples. (Refs. 3,8)

6. Biodegradation (principally of aromatic hydrocarbons, especially benzene and toluene) during storage (probably hastened by disaggregation of soils during sampling). (Refs. 3,8,11)

7. Reaction of chemically reactive compounds during sample storage.

8. Pressure changes during sample collection and transport.

A.5.2 Improvement of Sample Collection Techniques

Due to concerns regarding the loss of VOCs, particularly in samples containing low concentrations of VOCs (<200 µg/kg) during traditional sampling practices, the scientific community investigated other approaches to VOC sample collection and preparation. A closed-system purge-and-trap technique was developed and tested for the analysis of low-level concentrations of VOCs in solids. The methanol extraction option for high concentrations (>200 µg/kg) and oily wastes remained unchanged. The Office of Solid Waste promulgated Method 5035 as part of Update III to the Third Edition of SW-846 on June 13, 1997. (Ref. 38) As an active participant in these studies in conjunction with OSW, the American Society for Testing and Materials (ASTM) published the

"Standard Guide for Sampling Waste and Soils for Volatile Organic Compounds" (ASTM D 4547-98). (Ref. 15)

These documents include the immediate in-field transfer of the sample (by a coring tool of 2 to 5 g capacity) into a tared VOA vial (of 22 to 40 mL capacity) that contains acidified reagent water (most often acidified by 1g $NaHSO_4$ per 5g of soil) so that a vapor partitioning preparation procedure (see Sec. A.6.0 of this Appendix) can be performed by the laboratory on the sample without reopening the vial. A second in-field transfer to a tared VOA vial containing 5 to 10 mLs of methanol is used for VOC soil concentrations larger than 200 µg/kg.

Another technique described is the immediate in-field collection and maximum 48 hour storage in an air-tight coring device/container (such as the EnCore™ sampler) so that the laboratory preservation and preparation procedures described for the closed-system purge-and-trap (Method 5035) or headspace (Method 5021) can be performed. (Ref. 39) (An EnCore™ sampler is a device that can be used for both sample collection and as the sample transport and storage device. See Sec. A.8.0)

Both documents recommend similar approaches to sample preservation and preparation in order to minimize VOC loss and address the collection of cohesive solids whereby a coring tool collects a relatively undisturbed sample by compression, and then extrudes the sample into an appropriate VOA vial. The documents also provide guidance for the collection of cemented materials and non-cohesive materials (e.g., dry sand, mixtures of gravel and fines) and collectively address factors that must be considered when selecting the most appropriate approach for VOC sample preservation and preparation, including expected concentrations of VOCs (high versus low). A screening method for determining whether a sample contains high or low concentrations of VOCs (Method 3815) is available for making these determinations on-site. (Ref. 40)

A.5.3 New Developments

Since the publication of the new VOA sampling techniques for solids, the scientific community has continued to investigate additional techniques to further improve sample collection and preservation to minimize VOC loss. For example, studies were conducted regarding the freezing of samples without the use of chemical preservatives (see Sec. A.8.0), use of "empty VOA vials," and more information was gained regarding acidification of samples, as discussed below. (Refs. 4,19)

Current practice recommends the use of $NaHSO_4$ to acidify reagent water in VOA vials prior to addition of the sample when preservation is necessary. (Ref.1) This acidification is one means used to minimize loss of VOC due to biodegradation. However, acidification is not recommended for solids or aqueous samples with significant levels of carbonates, because the acidification can cause effervescence and the loss of VOCs. In 1998 and 1999, other adverse effects of acid preservation of soils were discovered i.e., chemical breakdown of certain classes of compounds. Additionally, certain VOC components such as 2-chloroethylvinyl ether are lost by the acidification. An artifact is sometimes observed for acetone in that acidification of certain soils may cause the formation of acetone. (Refs. 4,37)

The approaches recommended in Sec. A.8.0 of this guidance incorporate the new developments in solid sample preparation for VOC analysis.

A.6.0 OVERVIEW OF VAPOR PARTITIONING AND METHANOL EXTRACTION TECHNOLOGIES

Vapor partitioning and methanol extraction are the two most commonly used methods for the laboratory preparation of soils for VOC analysis. This section briefly discusses these two procedures, and their relative advantages and disadvantages. For further information, ASTM D 4547-98 (Ref. 15) discusses the merits of vapor partitioning relative to the use of methanol extraction; and Method 5035 relates concerns regarding the use of methanol.

Selection of the preparation technology should be made during the systematic planning process prior to sample collection given that the selection will dictate subsequent sample collection and preservation practices. One technology may be preferred based on the project data quality objectives and target analytes, and the sample collection and handling approaches need to be compatible with the chosen technology.

Each preparation technology involves use of a VOA vial for sample collection and transport. Approaches for preparation of the vials (with and without preservatives), often based on the technology to be used, will be discussed in a section to follow.

A.6.1 Vapor Partitioning

One means of vapor partitioning involves the direct analysis of a sample by purge-and-trap (Method 5035). This technique is routinely used for the analysis of volatiles in environmental samples and is considered more sensitive than the headspace technique. By purging samples at higher temperatures, higher molecular weight compounds can be detected. However, the purge-and-trap technique requires more time for sample preparation.

Another means of vapor partitioning involves the direct analysis of a sample by equilibrium headspace (Method 5021). This technique is most suited for the analysis of very light molecular weight volatiles in samples that can be efficiently partitioned into the headspace gas volume from the liquid or solid matrix sample. Higher boiling point volatiles are not detected with this technique due to their low partition rate in the gas headspace volume. In addition, the technique is generally less sensitive than purge-and-trap, however, it is preferred for the analysis of gases, highly water-soluble compounds, and very light molecular weight volatiles which may not be analyzed using the purge-and-trap technique.

For both vapor partitioning techniques, the vapor is removed for analysis without opening the container. Heat and water are usually used to assist in the direct partitioning of VOCs from the solid matrix. Vapor partitioning is applicable to VOC soil concentrations of 2 to 200 ppb. Methods 5021 or 5035 commonly require 2- to 5-g soil aliquots collected in individual 20- to 40-mL VOA vials, depending on the specific instrumentation used in the selected purge-and-trap or headspace method. Only one analysis per VOA vial can be done using purge-and-trap or headspace (Methods 5035 or 5021).

Vapor partitioning can offer lower detection limits than methanol extraction because no dilution is involved. In addition, there are no organic solvent interferences and no use of regulated organic solvents (e.g., methanol), which requires special handling and disposal practices. Use of methanol may generate a flammable waste that is hazardous based on the ignitability characteristic (40 CFR § 261.21) or a listed waste (40 CFR § 261, Appendix VII).

A.6.2 Methanol Extraction

Methanol extraction involves the extraction of VOCs from a sample with methanol, and the subsequent transfer of an aliquot of the extract to water (dilution) for either purge-and-trap or headspace analysis. After extraction with methanol (anywhere from 1:1 methanol to soil to a 10:1 methanol to soil ratio); the extract typically receives a 50-fold dilution. Methanol extracts must be diluted to minimize adverse effects of methanol on analytical instrumentation. However, solid samples with a significant moisture content (>10%) that are extracted prior to analysis in a water miscible solvent such as methanol are diluted by the total volume of the solvent/water mixture. (Ref. 51) The total mixture volume can only be calculated based on the sample moisture present as determined by the % moisture determination. Therefore, in order to report results for samples containing significant moisture contents on an "as received" basis, the detected concentration needs to be corrected by the solvent/water dilution factor. See Method 8000 for an explanation and the applicable calculations.

One advantage of a methanol extract is it may be tested more than once. Methanol extracts of soil are applicable to a wide range of high to low concentrations, e.g., 50 ppb to several ppm. Once a methanol extract is obtained, it can be stored at 4 ± 2 °C for two weeks, and sufficient volume is present for multiple VOC determinations. Additional extract storage time beyond two weeks may be acceptable if the desired VOC constituent stability can be demonstrated from appropriate performance data.

As noted above, concerns exist regarding the use of methanol extraction. The information to follow provides recent observations regarding the use of methanol for VOC analysis.

A.6.2.1 Contact Time Effect

Methanol extraction can provide more robust, larger or accurate values for VOCs when compared to vapor partitioning results. (Refs. 5,9,16,27,29,30,32,33,41,42) However, methanol extract results tend to increase with time as the sample contact time increases. (Refs 27,33) State agencies implementing methanol extraction for soil VOCs often require either a minimum contact time of one day, or the soil is to be sonicated for 20 to 30 minutes at 40° C with the methanol prior to analytical measurement of VOCs. The actual contact time should be sufficient enough to efficiently extract all VOC constituents of interest and to allow for the complete breakdown of agglomerated solid materials.

Particularly volatile VOCs (e.g., benzene, dichloroethene) in sandy soils are not expected to show this effect of contact time. The less volatile VOCs (e.g., xylenes) in an organic rich soil or clay can be expected to demonstrate higher results with increased contact time. (Refs. 5,9,27,33)

A.6.2.2 Safety and Hazardous Waste Generation Concerns

A primary disadvantage of methanol extraction is that it poses hazards to personnel due to its toxicity and flammability. Finally, the addition of methanol to a sample is likely to cause the sample to fail the ignitability characteristic or to become a listed waste, thereby making the unused sample volume a hazardous waste.

A.7.0 SAMPLE COLLECTION

A.7.1 Collection of Samples for Analysis

After a fresh surface of the solid material is exposed to the atmosphere, the subsample collection process should be completed in the least amount of time in order to minimize the loss of VOCs due to volatilization. Removing a subsample from a material should be done with the least amount of disruption (disaggregation) as possible. Additionally, rough trimming of the sampling location's surface layers should be considered if the material may have already lost VOCs (been exposed for more than a couple of minutes) or if it may be contaminated by other waste, different soil strata, or vegetation. Removal of surface layers can be accomplished by scraping the surface using a clean spatula, scoop, knife, or shovel. (Refs. 15,51)

A.7.1.1 Subsampling of Cohesive Granular but Uncemented Materials Using Devices Designed to Obtain a Sample Appropriate for Analysis

Subsamples of the appropriate size for analysis should be collected using a metal or rigid plastic coring tool. For example, coring tools for the purpose of transferring a subsample can be made from disposable plastic syringes by cutting off the tapered front end and removing the rubber cap from the plunger or can be purchased as either plastic or stainless steel coring devices. These smaller coring devices help to maintain the sample structure during collection and transfer to the VOA vial as do their larger counterparts used to retrieve subsurface materials. When inserting a clean coring tool into a fresh surface for sample collection, air should not be trapped behind the sample. If air is trapped, it could either pass through the sampled material causing VOCs to be lost or cause the sample to be pushed prematurely from the coring tool. The commercially available EasyDraw Syringe™ and Powerstop Handle™ and Terra Core™ sampler coring devices are designed to prevent headspace air above the sample contents. For greater ease in pushing into the solid matrix, the front edge of these tools can be sharpened. The optimum diameter of the coring tool depends on the following: size of the opening on the collection vial or bottle (tool should fit inside mouth), dimensions of the original sample, particle size of the solid materials (e.g., gravel-size particles would require larger samplers), and volume of sample required for analysis. For example when a 5-g subsample of soil is specified, only a single 3-cm^3 volume of soil has to be collected (assuming the soil has density of 1.7 g/cm^3). Larger subsample masses or more subsample increments are preferred as the heterogeneity of the material increases. After an undisturbed sample has been obtained by pushing the barrel of the coring tool into a freshly exposed surface and then removing the corer once filled, the exterior of the barrel should be quickly wiped with a clean disposable towel. The next step varies, depending on whether the coring device is used for sample storage and transfer or solely for transfer. If the coring tool is used as a storage container, cap the open end after ensuring that the sealing surfaces are cleaned. If the device is to be solely used for collection and not for storage, immediately extrude the sample into a VOA vial or bottle by gently pushing the plunger. The volume of material collected should not cause excessive stress on the coring tool during intrusion into the material, or be so large that the sample easily falls apart during extrusion. Obtaining and transferring a sample should be done rapidly (<10 seconds) to reduce volatilization losses. If the vial or bottle contains methanol or another liquid, it should be held at an angle when extruding the sample into the container to minimize splashing. Just before capping, a visual inspection of the lip and threads of the sample vessel should be made, and any foreign debris should be removed with a clean towel, allowing an airtight seal to form.

A.7.1.2 Devices that Can be Used for Subsampling a Cemented Material

The material requiring sampling may be so hard that even metal coring tools cannot penetrate it. Subsamples of such materials can be collected by fragmenting a larger portion of the material using a clean chisel to generate aggregate(s) of a size that can be placed into a VOA vial or bottle. When transferring the aggregate(s), precautions must be taken to prevent compromising the sealing surfaces and threads of the container. Losses of VOCs by using this procedure are dependent on the location of the contaminant relative to the surface of the material being sampled. Therefore, caution should be taken in the interpretation of the data obtained from materials that fit this description. As a last resort when this task can not be performed onsite, a large sample can be collected in a vapor-tight container and transported to the laboratory for subsampling. Collecting, fragmenting, and adding the sample to a container should be accomplished as quickly as possible.

A.7.1.3 Devices that Can be Used for Subsampling a Non-cohesive Granular Material

As a last resort, gravel, or a mixture of gravel and fines that can not be easily obtained or transferred using coring tools, can be quickly sampled using a stainless steel spatula or scoop. If the collection vial or bottle contains methanol or an aqueous solution, samples should be transferred with minimal splashing and without the spatula or scoop contacting the liquid contents. For some solids, a wide-bottom funnel or similar channeling device may be necessary to facilitate transfer to the container and prevent compromising of the sealing surfaces of the container. Caution should be taken in the interpretation of the data obtained from materials that fit this description. Losses of VOCs are likely because the nature of the sampling method and the noncohesive nature of the material expose more surface area to the atmosphere than other types of samples. During the sampling process, noncohesive materials also allow for the separation of coarser materials from fines, which can skew the concentration data if the different particle sizes, which have different surface areas, are not properly represented in the sample.

A.7.2 Use of the EnCore™ Sampler (or Equivalent) for Sample Transport and Storage

The EnCore™ sampler is a sampling device that can be used as both a simultaneous coring tool for cohesive soils and a transport device to a support laboratory (field or off-site). The EnCore™ sampler is intended to be a combined sampler-storage device for soils until a receiving laboratory can initiate either immediate VOC analysis, or preserve extruded soil aliquots for later VOC analysis. It is meant to be disposed after use. The commercially available device is constructed of an inert composite polymer. It uses a coring/storage chamber to collect either a 5 g or 25 g sample of cohesive soils. It has a press-on cap with hermetically vapor tight seal and locking arm mechanism. It also has a vapor tight plunger for the nondisruptive extrusion of the sample into an appropriate container for VOC analysis of soil.

An individual disposable EnCore™ sampler (or equivalent) is needed for each soil aliquot collected for vapor partitioning or methanol sample preparation. Upon soil sample collection, the EnCore™ sampler is stored at 4 ± 2°C until laboratory receipt within 48 hours. Upon laboratory receipt, soil aliquots are extruded to appropriate tared and prepared VOA vials.

Validation data have been provided to support use of the EnCore™ sampler for VOC concentrations in soil between 5 and 10 ppm, for two (2) sandy soils, with a 2-day holding time at 4 ± 2°C. Preliminary data (Ref. 25) demonstrate an effective 2-day (48-hour) holding time at 4 ±

2°C for three sandy soil types with VOC concentrations at 100 ppb (benzene and toluene at 300 ppb), as well as an effective 1 or 2 week holding time at -12°C (freezing temperature). Recent published work (Ref. 43) neither definitively supports or shows the EnCore™ device to be ineffective for sample storage at these preservation temperatures. Soils stored in the EnCore™ device for 2 calendar days at 4 ± 2°C are subject to loss of BTEX compounds by biodegradation if the soil is an aerated, biologically active soil (e.g., garden soil) (Ref. 24), but this BTEX loss is eliminated for up to 48 hours under freezing conditions. (Ref. 2)

Further details on the EnCore™ sampler can be found in ASTM D4547-98 (Ref. 15) or other publications.

A.7.3 Concerns Regarding Use of Core Barrel Liners

One geotechnical technique for retrieval of bulk soil from subsurface regions is ring-lined barrel samples. Core barrel liners fit snugly within a corer and can be constructed of steel or brass (which is inert to VOCs). Cylindrical cores of subsurface soil can be obtained anywhere from 1 to 4 inches in diameter of varying lengths in feet.

Core barrel liners have been used as both a sample collection and storage device for VOC soil samples. Upon retrieval with subsurface soil, the core barrel liner (brass) is covered on both ends with a thin sheet of PTFE or with aluminum foil. Plastic caps are pressed over the ends to hold the PTFE/aluminum in place. The core barrel liner sample is maintained at 4 ± 2°C during shipment and storage at a laboratory. Sample preparation for VOC analysis is initiated by opening the core barrel coverings and sub-sampling the soil with a coring tool for analyses by either the vapor partitioning or methanol extraction options.

Experimental work has demonstrated that the core barrel transport and storage procedure is ineffective for a 2-day storage and holding time. (Refs. 4,10,13,16, 36) PTFE coverings (0.02 mm and 0.05 mm thickness) and aluminum foil will not prevent losses of 30-90% for certain volatile compounds (dichloroethene, benzene and trichloroethene). Therefore, the core barrel liners should be used as sample collection and transfer devices only with the least amount of elapsed time as possible prior to sample preparation.

A.7.4 After Collection -- Sample Handling and Storage

A.7.4.1 Holding Times

Published holding times should be followed, unless performance data can be produced to support longer time periods.

This guidance assumes a 48-hour holding time, unpreserved at 4 ± 2°C, between sample collection and analysis or preservation of VOC soil aliquots in VOA vials. Most validation data provided to support or justify an approach listed the holding time as 48 hours. The 48-hour holding time results for VOC in soil can provide average recoveries of 80% or more. However, recoveries from samples stored for 5 days are less successful. Little data exists on the impact of holding times between 48 hours and 5 days.

Implementing a 48-hour holding time can be difficult when transporting VOC soil samples (via overnight air carrier) from the field to an off-site support laboratory. All interested parties i.e., field and laboratory personnel need to be cognizant that the 48 hour holding time begins **from the time of sample collection**. If the VOC analysis cannot be completed prior to the expiration of the initial 48 hour period, other

preservation measures (i.e., freezing, chemical preservation, and methanol extraction) are required in order to extend the analysis holding time to 14 days from the time of sample collection.

A.7.5 Quality Control

Quality control checks to be employed during field sampling activities should include the collection, preparation, and analysis of the various QC samples discussed below:

Note: The exact specifications and need for the following QC samples should be outlined in the project planning documents.

1. Field duplicate: A field duplicate may be prepared at a frequency of one per day per matrix. The field duplicate is an independent sample which is collected as close as possible to the same point in time and space as the primary field sample. Field duplicates are used to estimate the reproducibility (precision) of the sampling process.

2. Trip blank: Trip blanks should be prepared at a frequency of one per day of sampling during which samples will be collected for VOCs. Trip blanks are prepared using reagent water (see Chapter One for definition) prior to the site visit at the time sample containers and kits are transported to the site. The trip blank will accompany the field samples throughout all sample collection and transport operations. This blank will not be opened during sampling activities and will be used to assess sample contamination originating from sample transport, shipping, or site conditions.

3. Field blank: A field blank conversely is prepared on-site during the sample collection activities using the same reagent water source used to prepare the trip blank. The field blank should be collected and preserved in the same manner as the environmental samples. The results from this analysis are used to assess sample contamination originating predominantly from field sampling conditions.

4. Equipment rinsate: An equipment rinsate blank should be collected from sample collection devices used for each distinct sample matrix. The equipment blanks are obtained either prior to or during sample collection activities. The results from these analyses are used to assess possible sample contamination from sampling equipment.

5. Temperature blank: A temperature blank prepared with a water-filled vial or a suitable thermometer, should be included with each cooler of samples designated for transport. Upon sample receipt, the laboratory will use the temperature blank or thermometer to determine the internal temperature of each cooler. Acceptable temperatures are $4 \pm 2\,^{\circ}C$ for refrigerated aqueous and solid samples and $< -7\,^{\circ}C$ for frozen solid samples.

6. Matrix spike and matrix spike duplicate: Additional sample aliquots should be collected when matrix spike and matrix spike duplicate analyses are required. Matrix spikes are aliquots of environmental samples to which known concentrations of certain target analytes have been added before sample manipulation from the preparation, cleanup, and determinative procedures have been implemented. The matrix spike analysis is used to assess the performance of the method by measuring the effects of interferences caused by

the sample matrix and reflects the accuracy of the method for the particular matrix in question.

7.6 Interferences / Artifacts of Analysis

When aqueous and solid samples are acidified it can lead to losses of highly reactive compounds such as 2-chloroethylvinyl ether through chemical reaction. Additionally, acidification of certain soils with sodium bisulfate may produce a false positive acetone artifact of 100-200 ppb, or more. (Refs. 4,37) Furthermore, *meta*- and *para*-xylene co-elute on most analytical columns and need to be reported as an isomeric pair. Acid preservation of samples to be analyzed for methyl *tert*-butyl ether (MTBE) should be avoided because use of a high temperature sample preparation method (Methods 5021, 5030, or 5032) can cause degradation of the MTBE to *tert*-butyl alcohol (TBA) during the high temperature sample preparation step. (Refs. 49,50)

Since aqueous samples containing residual chlorine must be dechlorinated to prevent the formation of trihalomethanes and other chlorinated compounds, the sample should be added to the dechlorinating agent prior to acid preservation. The addition of sodium thiosulfate to an acidified sample will generate sulfur dioxide which may interfere with the determination of gaseous VOC constituents of interest.

The project chemist should research and review historical data pertaining to the use of VOCs at the site under investigation. If previous data indicates that tetrachloroethylene or trichloroethylene were used at the site and their daughter products dichloroethene and dichloroethane are present, then vinyl chloride may also be present. In this scenario acid preservation would not be appropriate due to the reactive nature of vinyl chloride.

If the sampling location is known to contain polymers that were manufactured from monomers, then both vinyl chloride or styrene could be present. For this situation, due to the potential for reactive compounds present, acid preservation would not be necessary.

Pre-testing of a representative soil sample, prior to collection, with acid or bisulfate may show effervescence if carbonaceous materials are present. If bubbling occurs during chemical preservation, samples should not be collected with acid or bisulfate preservative. If the soil sample is a loamy material or contains a high proportion of decayed matter then acid preservation may generate acetone as a byproduct. The sampling personnel should examine and pre-test the soils to be collected prior to actual collection in order to make the proper determination for the correct preservation technique.

The laboratory should fully document whenever sample matrix interferences are suspected and can be attributed to poor analytical method quality control data. It is also important for the laboratory area where volatile analyses are performed to be completely free of solvents. Special precautions must be taken for the analysis of methylene chloride, since random background levels will result if the analytical and storage areas are not isolated from all sources of atmospheric methylene chloride.

A.8.0 APPROACHES TO SAMPLE PREPARATI0N

This section provides examples of approaches to sample preparation that include prepared vials (e.g., chemical preservation approaches) and use of empty vials (other means such as freezing used for preservation). Complete validation data is not available for all approaches. Analysts are responsible for showing that any given approach is appropriate for the intended use of the data.

Typically, as part of these procedures, a cohesive soil subsample (2 to 5g) from a freshly exposed sampling trench, geotechnical coring device/probe, etc., using a coring tool such as a cut-off syringe or purchased device (e.g., EasyDraw Syringe™ and Powerstop Handle™ or EnCore™), is extruded immediately to either a tared empty VOA vial or to a tared prepared VOA vial. Precautions with handling tared vials i.e., not applying additional labels, markings, and seals are necessary to ensure an accurate sample weight. Once filled with sample, the VOA vials are then capped (with PTFE-lined septa) until VOC sample preparation. Three or more replicate VOA vials (e.g., two for vapor partitioning and additional ones for any matrix spike QC analysis) are utilized by either technique, as well as one more soil aliquot for a percent moisture determination. One coring tool (disposable or reusable) can be used at each soil sampling location by providing co-located cores for the replicate VOA vials. The same coring tool can be used to collect an additional co-located soil for the percent moisture determination typically required by the laboratory preparation procedures. If the coring tool can be properly capped to prevent moisture loss, the coring tool can be used as a storage container for percent moisture. Note: should freezing be used as a means to preserve samples in the field, the aliquot reserved for percent moisture determination should not be frozen.

The preparation of samples for VOC analysis can be initiated either in the field at the time of collection using the prepared VOA vials, or at either an on- or off-site support laboratory using either the empty VOA vials (note the manual puncture of septa to introduce reagent water prior to analysis is not recommended) or a coring tool (e.g., the EnCore™ sampler) that can also serve as a sample transport device. A separate EnCore™ sampler is required for each replicate VOA vial used for VOC analysis.

When determining VOCs over the complete concentration range of ppb to several ppm, four (4) or more VOA vials may be required for each sampling point. For example, at least one VOA vial is necessary for methanol extraction when selected to analyze high VOC concentrations, while at least two vials are necessary for when vapor partitioning is to be used because low VOC concentrations (<200 ppb) are expected. A fourth VOA vial may be necessary for percent moisture determination so that VOC concentrations can be corrected for moisture content and/or methanol dilution factor, if required. A set of replicates for a single investigative soil sample are often composed of the following:

1. Two (2) 40-mL VOA vials for direct vapor partitioning measurement. These are needed for the most sensitive measurements - one is kept in reserve for any necessary repeat analysis. The upper concentration value of the vapor partitioning method's calibration range limits the usability of these direct measurements.

2. One (1) 40-mL VOA vial for methanol extraction of soil aliquot prior to vapor partitioning. Once a methanol extract is obtained, an aliquot of this extract is diluted fifty-fold (50) or more with water and is tested by vapor partitioning as a water matrix. The 50-fold dilution is necessary to minimize interferences in vapor partitioning measurements of water matrices. Methanol extracts have no

upper limit of measured VOC concentration since the extract can be sub-aliquoted for different dilutions.

3. One (1) 60-mL VOA vial for any percent moisture determination to report VOC results on a moisture corrected basis, if necessary. Also note that solid samples with a significant moisture content (>10%) that are extracted prior to analysis in a water miscible solvent such as methanol are diluted by the total volume of the solvent/water mixture. (Ref. 51) The total mixture volume can only be calculated based on the sample moisture present as determined by the % moisture determination. Therefore, in order to report this type of sample result on an "as received" basis, the detected concentration needs to be corrected by the solvent/water dilution factor. See Method 8000 for an explanation and the applicable calculations. The physical preservation (4 ± 2 °C) of this vial is not as critical as for the VOC analytes in soil.

4. VOA vials for any QC audits such as duplicates, matrix spikes, etc.

Please note that a VOA vial should always be collected for methanol extraction unless it is known in advance that VOCs will not exceed the upper usable concentration values for direct vapor partitioning measurements.

Before presenting the different approaches using empty or prepared vials, a discussion is included regarding the study of the preservation of soils by freezing. As noted, this was studied using empty VOA vials. Some of the empty VOA vial approaches that follow in Sec. A.8.2 use freezing as a preservative.

A.8.1 Overview of Empty Vial Technique

Hewitt (Refs. 2, 4, 7,10) and Ricker (Refs. 19, 20, 21) independently developed “empty vial” techniques. Using a coring tool (Hewitt’s cut-off syringe or Ricker’s commercially available syringe and 5- to 13-g sample) a 5-g aliquot of undisturbed soil is transferred to a tared empty VOA vial and capped with a PTFE-lined septa (PTFE of 0.25 mm thickness). The two "empty vial" techniques were evaluated using methanol extraction (Method 5035) measurements.

The sealed vial with the soil aliquot is maintained either frozen (< -7 °C), or at 4 ± 2 °C until laboratory receipt and analysis. Multiple VOA vials can be collected, as necessary based on the sample preparation technique to be used. Sample vials should not be frozen below -20 °C due to potential problems with vial seals and the loss of constituents upon sample thawing.

Upon laboratory receipt of VOA vials maintained at 4 ± 2 °C (within 48 hours of sample collection), one “empty VOA vial” is selected for methanol extraction and the methanol reagent is added through the septum using a glass syringe equipped with a 23-gage Luer Lock needle. The methanol is mixed with the soil and any pressure can be relieved by cracking the VOA vial’s cap once. The methanol extract, stored at 4 ± 2 °C or less, has a shelf life of up to two weeks. Upon laboratory receipt of frozen VOC samples, a vial may be thawed and methanol added through the septa as described above.

To determine VOCs by vapor partitioning, “empty VOA vials” should have 10 mLs of reagent water added, either through the septa liner by a laboratory’s automated sampler at the time of analysis, or be present in the vial prior to sample collection (see Sec. A.8.3) when Method 5035 is used. For VOC samples maintained at 4 ± 2 °C this must be done within 48 hours of sample collection. Experimental work by En Novative Technologies, Inc., and Hewitt (Refs. 44, 45) indicates that VOCs are slowly lost through the pierced septa after reagent water is manually added to an

"empty VOA vial," prior to Method 5035 purge and trap measurements. To avoid any clogging of the needle of an automated purge-and-trap system, reagent water or the sodium bisulfate solution can be present in the VOA vial (Sec. A.8.3) prior to sample collection, thereby, allowing the soil/solid to be dispersed prior to the purge-and-trap analysis.

Ricker and Hewitt in their experimental work demonstrated that the empty VOA vial, with a suitable PTFE-lined septa cap, has integrity for several days. Significant VOC losses do not occur at 4 ± 2°C through the septum of the sealed VOA vial. A 48-hour holding time for soils, at 4 ± 2 °C storage of samples, has been found effective with the “empty VOA vial” for most target VOCs studied, except for aromatic compounds in biologically active, aerated garden soils (Refs. 2, 20). Hewitt studied freezing of soils (< -7°C) as a preservative for soils, in conjunction with the “empty VOA vial” technique and found it effective for all target VOCs studied, including aromatic compounds, so long as freezing starts at the time of collection.

When soils are maintained at 4 ± 2°C for 48 hours until freezing starts, the same condition or stability is found for the VOCs except for benzene in biologically active soil. Use of freezing at the time of lab receipt of empty VOA vials can therefore simplify sample handling of soil materials. ASTM D 4547-98 (Ref. 15) and Method 5035 briefly mention freezing, but do not endorse it because data were not available at the time of their publication to support preservation by freezing. With this approach, chemical preservatives are not needed. VOA vials, maintained at < -7°C, need only be thawed on the day of analysis, whether it be by vapor partitioning or by methanol extraction.

A.8.2 Preservation Approaches Using Empty VOA Vials

This section provides five examples of approaches to sample preparation using empty VOA vials -- no preservatives or solutions are added to the vials.

A.8.2.1 Preservation by freezing (< -7°C)

Upon collection, the soil is added to replicate empty vials and frozen at < -7°C until thawed for analysis. The design of newer vials makes it possible to freeze the contents in an upright position, however, it may be advisable to place the vials on their side during the freezing process to prevent breakage. Freezing has been found effective to preserve both aromatic and chlorinated hydrocarbon VOCs in soil for two weeks at all VOC concentrations studied. (Refs. 2,4,11) Sample vials should not be frozen below -20°C due to potential problems with vial seals and the loss of constituents upon sample thawing.

The on- or off-site support laboratory thaws a VOA vial when needed and either adds 5 or 10 mLs of methanol through the PTFE-lined septum using a 23-gage Luer lock syringe for methanol extraction and preservation. (Refs. 4,21,22) Addition of 5-10 mLs of water to the vial through the septum should not be performed, since this technique will create a punctured septum capable of producing VOC losses prior to purge-and-trap analysis.

This technique is unpopular for vapor partitioning because a prepared VOA vial with reagent water fits the operations of Methods 5021/5035 better than the empty VOA vial.

This technique can be undesirable when soil samples are transported to a support laboratory because dry ice, gel packs or salt-ice mixtures can be required to

maintain sub-zero temperature conditions during shipment. This technique has merit when freezers are available at a field site or on a sampling vessel.

A.8.2.2 Refrigerate VOA vials at 4 ± 2°C for 48 hours or less, then preserve by freezing at < -7°C upon laboratory receipt

Upon laboratory receipt, replicate soil VOA vials are frozen (< -7°C) then thawed as needed for preparation by methanol extraction, or if possible by vapor partitioning. Sample vials should not be frozen below -20°C due to potential problems with vial seals and the loss of constituents upon sample thawing. The 48-hour time period prior to freezing is practical and can be supported by the studies:

1. The chlorinated hydrocarbon volatiles that were studied have been found to be stable for two weeks at 4°C, with dichloroethene isomers not being as stable as other chlorinated compounds studied. (Refs. 1,2,4,7,11,16)

2. For spiked (at 5 ppm) typical soils, aromatic hydrocarbons demonstrate major losses at room temperature (22°C) after 5 days of storage. (Refs. 1,2,4) When these soil types are stored at 4°C, major losses occur between 10 and 14 days for aromatic hydrocarbons (e.g., benzene) spiked at 5 ppm. (Refs. 1,2,4) When these soil types are spiked at 30-40 ppb with aromatic hydrocarbons, major losses for benzene and toluene occur at 3-5 days of storage. (Refs. 2,4)

3. Aromatic hydrocarbons (such as benzene or toluene) when spiked into biologically active soil (aerated garden soil or fertilized soil) and stored at 4°C demonstrate losses of 20-30% within 48 hours. (Refs. 2,16,17,19,20). Limited disruption sampling techniques in conjunction with a maximum holding time of 48 hours can minimize this loss, but not eliminate it. Soils containing manure exhibited a major loss of aromatic hydrocarbons within one day while soil sterilization eliminated this loss. (Ref. 16)

4. Observed losses of aromatic or dichloroethene volatile compounds in soil, stored at 4°C, cease when soil is frozen at < -7°C. (Refs. 2,4).

A.8.2.3 Refrigerate VOA vials at 4 ± 2°C for 48 hours or less, then preserve with methanol upon laboratory receipt

Upon laboratory receipt, the volume of methanol necessary for methanol extraction sample preparation is added to one of the replicate VOA vials through the PTFE-lined septum cap, using a 23-gage needle on a Luer lock syringe. Methanol will preserve VOCs in soil for 2 weeks if stored at 4 ± 2°C. See Sec. A.8.2.2 above for discussion on initial ≤ 48-hour transport at 4 ± 2°C. Certain PTFE-lined septa caps were found to be effective seals for 10 days prior to the addition of methanol. (Refs. 19,20,21)

When methanol is added through the septum cap to a soil aliquot core in an empty VOA vial, the mixture is swirled to provide contact with the soil and methanol, to wet the head space, and dissolve gaseous and sorbed VOC compounds into the methanol. At this point, there can be a pressure build-up within the vial that can be removed by cracking the VOA vial cap and immediately resealing it. (Ref. 4) There is believed not to be significant VOC loss so long as the methanol remains in contact with

the soil material. The methanol extraction efficiency can be improved by sonicating and heating the mixture at 40°C for 30 minutes followed by centrifuging and transferring the supernatant to a disposable, screw-top glass centrifuge tube. (Ref. 33)

A.8.2.4 Refrigerate VOA vials at 4 ± 2°C for 48 hours or less and complete VOC analysis (Method 5021/5035) within 48 hours

VOC sample preparation by vapor partitioning is completed within 48 hours from sample collection. See Secs. A.8.2.2 and A.8.2.3 above for further details.

A.8.2.5 Refrigerate/freeze coring tool used as transport device for 48 hours or less (Refs. 15,26)

Each replicate soil aliquot is collected by a suitable coring device, (e.g., EnCore™) that is used as a transport device to the laboratory. Upon laboratory receipt, soil aliquots from each replicate transport device are extruded into individual empty or prepared tared VOA vials as noted in Secs. A.8.2.2 to A.8.2.4. Upon cap closure, the vial is weighed again and the wet sample weight is determined by difference.

For spiked soils characteristic of a waste site, some VOC losses were observed in 2 days for soils stored at 4 ± 2°C and losses continued further at a 5-day and 12-day storage time period. Losses during the first 2 days for aromatics and dichloroethene, were equivalent to the empty vial techniques as noted in Sec. A.8.2.2. (Ref. 4) Also, sampling of TCE contaminated soil showed reasonable agreement between the EnCore™ and cut-off syringe/empty vial techniques. (Ref. 4) Significant losses after 2 days at 4°C have been observed for the EnCore™ for biologically active soils. (Refs.16,24).

The EnCore™ sampler has been systematically evaluated for three sandy soil types (at high VOC concentrations (5 -10 ppm) and at low VOC concentrations (100 ppb). (Refs. 22,23,24,25). The EnCore™ was effective as a 2-day transport device when stored at 4 ± 2°C, for the above studies, and storage could be extended from 1 week to 12 days further under freezing conditions (< -7°C) during the low VOC concentration study. (Ref. 25) The EnCore™ was ineffective for one soil type using high concentration spikes, because the soil was non-cohesive (dry clumped sand) - any coring device could be ineffective. (Refs. 15,22) The three soils exhibited little biodegradation of aromatic hydrocarbons discussed above.

For the original EnCore™ of stainless steel construction, it was found to be the only sampling/storage device that was as effective as the original single vial technique (Dynatech vial of January 1995 draft Method 5035). (Ref. 16)

A.8.3 Preservation Approaches Using Prepared VOA Vials

This section provides four examples of preservation approaches using prepared VOA vials. During sample collection, a coring tool is used to extrude the collected sample into a VOA vial containing methanol. Co-located soil cores are extruded into replicate VOA vials containing reagent water, or reagent water acidified with 1 g $NaHSO_4$ per 5 mLs water.

Coordination between field and laboratory personnel is required so specific vials and reagents are consistent with laboratory instrumentation and reagents. Vials with reagents, and any magnetic stirring bars (e.g., for Method 5035) need be tared prior to field use. If prepared VOA vials contain methanol or water they must be tared with the septum caps and the added reagent. Once

methanol or water reagent is added, a meniscus level of the liquid in the VOA vial can be marked. This allows field personnel to note any apparent liquid loss (especially methanol) during shipment to the field. If field personnel are concerned with reagent weight loss during shipment to the field and return, individual vials can be periodically weighed after initial tare or after addition of cored soil aliquot.

A.8.3.1 Collection with reagent water, preservation by freezing (< -7°C) and analysis by vapor partitioning

Extrude collected soil from a coring device into a VOA vial containing 5 mLs water (Method 5035), turn vial on its side and freeze contents. It may be problematical to freeze 10 mLs of water in the 22 ml vial used for Method 5021. Maintain at < -7°C until thawed for analysis. Sample vials should not be frozen below -20°C due to potential problems with vial seals and the loss of constituents upon sample thawing. Few published data exist to validate this preservation technique, but its effectiveness is inferred from Sec. A.8.2.1, and should be demonstrated by appropriate performance data results. (Ref. 28)

A.8.3.2 Collection with reagent water, preservation by refrigeration at 4 ± 2°C for 48 hours or less and immediate laboratory analysis or freezing storage at < -7°C for subsequent vapor partitioning

Sample is collected as in Sec. A.8.3.1 but transported to the laboratory within 48 hours at 4 ± 2 °C for:

1. Immediate analysis by vapor partitioning within 48 hours of sample collection.

2. Freezing at < -7°C upon laboratory receipt for vapor partitioning analysis within 2 weeks from sample collection. Sample vials should not be frozen below -20°C due to potential problems with vial seals and the loss of constituents upon sample thawing.

One investigator has found that a spiked hazardous waste site soil provided the same results one week after freezing with water as the initial spiked soil results. (Ref 28). Another investigator used headspace techniques with soil added to 10 mLs of reagent water to develop justification for certain variables discussed in Sec. A.8.3.2 for the initial 48-hour holding time. (Refs. 6,12) Sec. A.8.2.2 should be consulted for biodegradation effects for aromatic hydrocarbons. This technique allows the laboratory to observe the dispersion of soils in water and take any corrective action prior to purge-and-trap analysis. This technique is also most consistent with automated purge-and-trap samplers where stirring occurs prior to the purge cycle.

A.8.3.3 Collection with 5 mLs of water and 1 g of $NaHSO_4$ and analysis by vapor partitioning

Extrude collected soil from a coring device into a VOA vial containing 5 mLs of reagent water and 1 g of $NaHSO_4$ for vapor partitioning by Method 5035. For a spiked soil, $NaHSO_4$ was found to preserve the aromatic hydrocarbons at room temperature for more than 2 weeks. (Refs.1,11) The same soil showed major losses of aromatic hydrocarbons (5-10 ppm) when stored at room temperature for 5 days or at 4 ± 2°C after 10 days when no $NaHSO_4$ was present. (Ref. 1) The studied chlorinated hydrocarbons demonstrated insignificant losses during these storage conditions. The

use of $NaHSO_4$ with sample acidification to pH 2 or less eliminates the biodegradation of the important aromatic hydrocarbon volatile compounds.

1 g of $NaHSO_4$ will acidify 5 g of soil with an alkaline content (as $CaCO_3$) of 5%. It is insufficient to neutralize a soil with an alkaline content of 10%. This technique has been found to be somewhat problematic since publication of Method 5035. Carbonaceous soils cause effervescence of the acidic soil slurry with loss of volatiles and even cause failure of the septa VOA vial cap or even the VOA vial itself. Upon acidification, certain soils exhibit a false positive acetone artifact of 100-200 ppb, or more. (Refs. 4,37) The $NaHSO_4$ corrosive vapors may cause increased purge-and-trap maintenance by laboratories due to creation of active sites on the trapping material. A very few target compounds such as styrene, vinyl chloride, and 2-chloroethylvinyl ether react under acidic conditions and are not detected. Note that the sodium chloride matrix modifying reagent of Method 5021 was found to be as effective as $NaHSO_4$ for inhibiting biodegradation of aromatic hydrocarbons in soil and may be more advantageous to use with calcareous soils, since the inhibitory agent is not dependent on the concentration of hydrogen ion present. (Ref. 1)

A.8.3.4 Collection and preservation with methanol at 4 ± 2° C

Extrude collected soil from a coring device into a VOA vial containing 5 -10 mLs of methanol. Larger volumes of methanol may be used if compositing of soils is required. Methanol preservation is effective for 2 weeks if stored at 4 ± 2 °C. Also, one investigator has found methanol preservation of a sand spiked with gasoline to be effective when traditional techniques were ineffective. (Ref. 36)

A.9.0 SUMMARY OF FINDINGS

1. An aqueous sample holding time period can be extended to fourteen days with the use of chemical preservatives such as sodium bisulfate or hydrochloric acid, however, since reactive compounds such as 2-chloroethylvinyl ether are unstable at low pHs, if these types of analytes are to be determined, the collection of a second set of samples without acid preservatives is necessary. Aqueous samples containing methyl *tert*-butyl ether and other fuel oxygenate ethers should not be acidified if high temperature sample preparative methods (Methods 5021, 5030, 5032) are used. (Refs. 49,50) (Sec. A.3.0)

2. The solid material to be characterized should be sampled with limited disruption (e.g., by a coring device for cohesive soils) and single transfer to an air tight VOA vial (PTFE-lined septa cap) that will be used for storage and preparation for VOC analysis. (Sec. A.7.1)

3. Data have been published or presented to validate different storage devices, procedures, preservative reagents and techniques for the VOC analysis of aqueous and solid samples. A wide range of recovery results have been observed. Acceptable devices, procedures, preservatives, and techniques should provide an average recovery of greater than 80% for important volatile contaminants such as benzene, dichloro- and trichloroethanes/ethenes. A recovery of 80% may be difficult for gaseous VOC contaminants such as vinyl chloride and chloroethane; however, the acceptability of a procedure should not be solely based on the less volatile VOCs such as chlorobenzene, xylenes, and trimethyl benzene. (Secs. A.2.0, A.6.0, A.7.0 and A.8.0)

4. VOCs in solids can be successfully sampled using coring tools (usually 5-g aliquots but can be 2 to 25 g) if the material is cohesive. Sampling procedures are not available to prevent VOC loss during sampling of non-cohesive soil material (dry sand, gravel, liquid sediment) or cemented material. (Secs. A.4.0 and A.7.0)

5. The following two techniques have been found accurate (minimal VOC loss) for preparation of soils for VOC analysis; however, they are not without problems:

   a. Soil is added to empty VOA vials at time of collection and is frozen at < -7°C until thawed for analysis. Validation data have not been provided yet, but it is believed that a prepared VOA vial with reagent water only is also acceptable for low concentration VOC in soil (<200 ppb) if frozen at < -7°C at time of collection.

   b. Soil is added to a prepared VOA vial, with methanol reagent, at time of collection and stored at 4 ± 2°C until time of analysis. This is applicable only to VOC in soil concentrations greater than 50 ppb. (Sec. A.6.2) (See comments below regarding use of methanol.)

6. The following techniques have been found to be the most practical, currently available alternatives for preparation of soil for VOC analysis. Validation data are not available to fully support their use for all types of soil or to fully differentiate them in accuracy relative to each other. The techniques rely on transport of sealed VOA vials or coring tools, at 4 ± 2°C, to a support laboratory within 48

hours where they are preserved/stored appropriately or immediately tested for VOCs. As more validation data and experience occur with time, their relative worth will become more apparent. The techniques listed below are superior to the traditional procedures of ten years ago.

a. Soil is added to tared replicate "empty VOA vials" at time of collection, preserved, refrigerated at 4 ± 2°C until laboratory receipt within 48 hours, and then preserved by freezing (< -7°C). Individual vials are thawed prior to sample preparation within 14 days of collection. A thawed vial must be processed within 24 hours by either screening using methanol extraction or analysis by vapor partitioning. At time of laboratory receipt, laboratories have the option of immediately testing a soil by vapor partitioning where the required reagent water is added through the PTFE-lined septa cap using the automated instrument sampling devices after weighing an "empty VOA vial" and obtaining wet sample weight by difference. In addition at time of laboratory receipt, laboratories have the option of immediately preparing a soil for methanol extraction by weighing an "empty VOA vial," obtaining the wet sample weight by difference, then adding methanol reagent through the PTFE-lined septa cap using a 23-gage needle on a Luer lock syringe. The sample-methanol mixture is shaken for 15 seconds to wet the vial's head space. The vial cap is opened once to vent pressure and then closed for the extraction process. (Sec. A.8.0)

b. For carbonate-containing soils (or soils suspected as such), ASTM D4547-98 (Ref. 15) provides for adding 2 to 5 g of soil (using coring tool) to tared, replicate prepared VOA vial containing 5 mLs of reagent water. Prepared VOA vials are maintained at 4 ± 2°C until laboratory receipt within 48 hours, and immediately tested for VOCs by vapor partitioning. This approach offers the advantage of mixing and dispersing the soil into the water and to observe any problematic samples prior to vapor partitioning analysis. Alternatively, the reagent water prepared VOA vials may be preserved by freezing (< -7°C) by placing vials in horizontal position. This technique is an alternative or fall-back from the prepared VOA vial with acidified reagent water; however, little or no data are available to validate its use. (Sec. A.5.3)

c. Soil is collected in replicate "Coring Tool Used as Transport Device" (e.g., the EnCore™ sampler), maintained at 4 ± 2 °C until laboratory receipt within 48 hours, then extruded into individual "Empty VOA Vials" for preservation by freezing (< -7°C) or into prepared VOA vials for immediate analysis by vapor partitioning or for sample preparation by methanol extraction. (Sec. A.7.2)

d. For known non-carbonate soils, a coring tool soil aliquot for BTEX type VOC analysis is added to a tared prepared VOA vial containing 5 mLs reagent water acidified with 1g $NaHSO_4$. The prepared VOA vial is maintained at 4 ± 2°C for BTEX testing by vapor partitioning within 14 days of sample collection. Acidified reagent water has been problematic when applied to a wide range of soil types for a large analyte list; however, it is effective for the volatile BTEX compounds in known non-carbonate soils. It is a specialized, preservation technique that minimizes aromatic VOC losses from biodegradation at 4 ± 2 °C.

Acetone artifacts are sometimes observed in soil samples preserved with $NaHSO_4$.

7. Use of a prepared VOA vial with acidified ($NaHSO_4$) reagent water is not recommended as a primary preservation technique for all soil types and a broad VOC analyte list. This technique is applicable to volatile aromatic hydrocarbons in soils known not to contain carbonates as discussed above.

8. A longer holding time may be appropriate if it can be demonstrated that the reported VOC concentrations are not adversely affected from storage and analyses performed outside the recommended holding times.

A.10.0 REFERENCES

1. Hewitt, A.D., "Chemical Preservation of Volatile Organic Compounds in Soil," *Environmental Science & Technology*, 31, pp. 67-70 (1997).

2. Hewitt, A.D., "Frozen Storage of Soil Samples for VOC Analysis,"*Environmental Testing & Analysis*, 8 (5), pp. 18-25, 46 (1999).

3. Hewitt, A.D., T.F. Jenkins, and C.L. Grant, "Collection, Handling and Storage: Keys to Improved Data Quality for Volatile Organic Compounds in Soil,"*American Environmental Laboratory*, (February 1995).

4. Hewitt, A.D., "Storage and Preservation of Soil Samples for Volatile Compound Analysis; Special Report 99-5," Hanover, NH; U.S. Army Cold Regions Research and Engineering Laboratory, 1999.

5. Hewitt, A.D., "Comparison of Sample Preparation Methods for the Analysis of Volatile Organic Compounds in Soil Samples: Solvent Extraction vs Vapor Partitioning," *Environmental Science & Technology*, 32, pp.143-149 (1998).

6. Hewitt, A.D., "Concentration Stability of Four Volatile Organic Compounds in Soil Samples; Special Report 94-6," Hanover, NH; U.S. Army Cold Regions Research and Engineering Laboratory, 1994.

7. Hewitt, A.D., "Freezer Storage of Soil Samples Containing Volatile Organic Compounds," *Proceedings of the 15th Annual Waste Testing and QA Symposium,* U.S. EPA, Washington, D.C. pp. 125-128, 1999.

8. Hewitt, A.D., "Losses of Trichloroethylene from Soil During Sample Collection, Storage and Laboratory Handling, Special Report 94-8," Hanover, NH; U.S. Army Cold Regions Research and Engineering Laboratory, 1994.

9. Hewitt, A.D., "Preparing Soil Samples for Volatile Organic Compound Analysis; Special Report 97-11," Hanover, NH; U.S. Army Cold Regions Research and Engineering Laboratory, 1997.

10. Hewitt, A.D., and N.J.E. Lukash, "Obtaining and Transferring Soils for In-Vial Analysis of Volatile Organic Compounds; Special Report 96-5," Hanover, NH; U.S. Army Cold Regions Research and Engineering Laboratory, 1996.

11. Hewitt, A.D., "Determining Volatile Organic Compound Concentration Stability in Soil," *Proceedings of the 11th Annual Waste Testing and QA Symposium,* U.S. EPA, Washington, D.C. pp. 173-183, 1995.

12. Hewitt, A.D., "Evaluation of Methanol and $NaHSO_4$ for Preservation of Volatile Organic Compounds in Soil Subsamples," *American Environmental Laboratory*, pp. 16-18 (1995).

13. Hewitt, A.D., and N.J.E. Lukash, "Sampling for In-Vial Analysis of Volatile Organic Compounds in Soil," *American Environmental Laboratory*, pp. 15-19, (1996).

14. Hewitt, A.D., "A Tool for the Collection and Storage of Soil Samples for Volatile Organic Compound Analysis," *American Environmental Laboratory*, 9, (10) pp. 14-16, 1997.

15. ASTM D 4547-98; "Standard Guide for Sampling Waste and Soils for Volatile Organic Compounds."

16. Turriff, D. and C. Klopp, "Studies of Sampling, Storage and Analysis of Soils Contaminated with Gasoline and Diesel," PUBL-SW-513-95, Wisconsin Department of Natural Resources, 1995.

17. Turriff, D., "Comparison of Alternatives for Sampling and Storage of VOCs in Soil," *Proceedings of the 11th Annual Waste Testing and QA Symposium*, U.S. EPA, Washington, D.C. pp. 51-58, 1995.

18. Turriff, D., "A New Soil Sampling and Soil Storage System for Volatile Organic Compound Analysis," *Proceedings of the 11th Annual Waste Testing and QA Symposium*, U.S. EPA, Washington, D.C. pp. 95-96, 1995.

19. Ricker, M.J., "Determining Volatiles in Soils: A New Sampling Procedure," *Environmental Testing & Analysis*, July/August, pp. 13-16, 1999.

20. Ricker, M.J., "An Easy, Cost-Effective Solution for Sampling Volatile Organic Compounds in Soil," *Proceedings of the 15th Annual Waste Testing and QA Symposium*, U.S. EPA, Washington, D.C. pp. 134-162, 1999.

21. Ricker, M.J., "Validation of a New Sampling Procedure for Determining Volatiles in Soils," Report to the Wisconsin Department of Natural Resources, U.S. Oil Company, Kimberly, WI, 1998.

22. Soroni, S.S. and J.F. Schabron, "Validation of a New Soil VOC Sampler: Development of a Standard Practice for Using the Disposable En Core Sampler for Sampling and Storing Soil for Volatile Organic Analysis," Topical Report WRI-99-R003; Laramie, WY; Western Research Institute, 1999.

23. Soroni, S.S. and J.F. Schaborn, "Development of a Standard Practice for Using the Disposable En Core Sampler for Sampling and Storing Soil for Volatile Organic Analysis," Laramie, WY; Western Research Institute, 1999.

24. Soroni, S.S. and J.F. Schaborn, "Performance of the Disposable En Core Sampler for Storing Soil for Volatile Organic Analysis," *Proceedings of the 15th Annual Waste Testing and QA Symposium,* U.S. EPA, Washington, D.C. pp. 129-134, 1999.

25. Soroni, S.S., J.F. Schaborn and J.F. Rovani, "Validation of a New Soil VOC Sampler: Performance of the En Core Sampler for Storage of Low VOC Concentrations and EPA Method 1311 Volatile Organic Analytes," Topical Report WRI-01-R005; Laramie, WY; Western Research Institute, 2001.

26. ASTM D6418-99; "Standard Practice for Using the Disposable En Core Sampler for Sampling and Storing Soil for Volatile Organic Analysis."

27. Phillips, J.H., A.D. Hewitt and J.P. Glaser, "Recovery of VOCs from Soils With and Without Methanol Preservation," *Proceedings of the 15th Annual Waste Testing and QA Symposium,* U.S. EPA, Washington, D.C. pp. 163-169, 1999.

28. Severn Trent Services, "Method 5035 EnCore Holding Time Study," Denver, CO, April 2000.

29. Minnich, M.M., B.A. Schumacher, and J.H. Zimmerman, "Comparison of Soil VOCs Measured by Soil Gas, Heated Headspace, and Methanol Extraction Techniques," *Journal of Soil Contamination*, 6 (2), pp. 187-203, (1997).

30. Siegrist, R.L. and P.D. Jenssen, "Evaluation of Sampling Method Effects on Volatile Organic Compound Measurements in Contaminated Soils," *Environmental Science & Technology*, 24, pp. 1387-1392, (1990).

31. Urban, M.J., J.S. Smith & R.K. Dickinson, "Volatile Organic Analysis for a Soil, Sediment or Waste Sample," *Proceedings of the 5th Annual Waste Testing and QA Symposium*, U.S. EPA, Washington, D.C. pp. II-87-II-101, 1989.

32. Liikala, T.L., K.B. Olsen, S.S. Teel and D.C. Lanigan, "Volatile Organic Compounds: Comparison of Two Sample Collection and Preservation Methods," *Environmental Science & Technology*, 30, pp. 3441-3447, (1996).

33. Askari, M.D.F., M.P. Maskarinec, S.M. Smith, P.M. Beam and C.C. Travis, "Effectiveness of Purge-and-Trap for Measurement of Volatile Organic Compounds in Aged Soils," *Analytical Chemistry*, 68, pp. 3431-3433, (1996).

34. Voice, T.C. and B. Kolb, "Static and Dynamic Headspace Analysis of Volatile Organic Compounds in Soils," *Environmental Science & Technology*, 27, pp. 709-713, (1993).

35. Vitale, R.T., "Report: Comparison of Volatile Organic Compound Results Between Method 5030 and Method 5035 on a Large Multi-State Hydrocarbon Investigation; Poster Session - WTQA Symposium 1998 or 1999.

36. King, P.H., "Evaluation of Sample Holding Times and Preservation Methods for Gasoline in Fine-Grained Sand," Report to - National Symposium on Measuring and Interpreting VOCs in Soils: State of the Art and Research Needs, 1993.

37. Uhlfelder, M.M., "Study of Acetone Production in SW-846 Method 5035 (Low Level) Associated with Various Preservation Techniques and Storage Conditions," *Proceedings of the 16th Annual Waste Testing and QA Symposium*, U.S. EPA, Washington, D.C. p. 13, 2000.

38. USEPA Method 5035, "Closed-System Purge-and-Trap and Extraction for Volatile Organics in Soil and Waste Samples," *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods*," EPA Publication SW-846, Third Edition, as amended by Updates I, II, IIB, and III, finalized in the Federal Register on June 13, 1997.

39. USEPA Method 5021, "Volatile Organic Compounds in Soils and Other Solid Matrices Using Equilibrium Headspace Analysis," *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods*," EPA Publication SW-846, Third Edition, as amended by Updates I, II, IIB, and III, finalized in the Federal Register on June 13, 1997.

40. USEPA Method 3815, "Screening Solid Samples for Volatile Organics," *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods*," EPA Publication SW-846, Third Edition, Draft Update IVB, listed in the Federal Register on November 27, 2000.

41. Minnich, M.M., J.H. Zimmerman and B.A. Schumacher, "Extraction Methods for Recovery of volatile Organic Compounds from Fortified Dry Soils," *Journal of AOAC International*, Vol. 79, No. 5, 1996.

42. Sawhney, B.L., J.J. Pignatello and S.M. Steinberg, "Determination of 1,2-Dibromoethane (EDB) in Field Soils: Implication for Volatile Organic Compounds," *Journal of Environmental Quality*, Vol. 17, No. 1, pp. 149-152, 1988.

43. USEPA OERR, "Multi-Laboratory Study on the Effects of Temperature and Sample Container on Volatile Organic Compounds from Time of Sampling to Time of Analysis - Final Report," April 24, 2001.

44. En Novative Technologies, Inc., Personal Communication to D. Payne, USEPA Region 5, October 5, 2000.

45. Hewitt, A. D., Personal Communication to D. Payne, USEPA Region 5, August 9, 2001.

46. Solomons, Graham, T.W., *Fundamentals of Organic Chemistry*, 3rd ed., pp 403, 505, 1990.

47. Oak Ridge National Laboratory, "Summary Report - Evaluation of the Impact of post-Holding Time Analyte Degradation on Regulatory Decision-Making -VOCs in Water," May 2001.

48. Oak Ridge National Laboratory, "Summary Report - Method for Preparing Performance Evaluation Water Samples for Volatile Organic Compounds," May 2001.

49. USEPA OSW, "Development and Evaluation of Methods for the Analysis of MTBE," September 17, 2001.

50. USEPA OUST, *Environmental Fact Sheet: Analytical Methods for Fuel Oxygenates,* EPA 510-F-02-001, May, 2002, www.epa.gov/OUST/mtbe/.

51. Hewitt, A.D., and K.F. Myers, "Sampling and On-Site Analytical Methods for Volatiles in Soil and Groundwater - Field Guidance Manual; Special Report 99-16," Hanover, NH; U.S. Army Cold Regions Research and Engineering Laboratory, 1999.

52. Maskarinec, M.P., L.H. Johnson, S.K. Holladay, R.L. Moody, C.K. Bayne, and R.A. Jenkins, “Stability of Volatile Organic Compounds in Environmental Water Samples during Transport and Storage,” *Environmental Science & Technology*, 24(11) pp1665-1670, 1990.

53. Bottrell, D.W., J.F. Fisk, G.L. Robertson, J.D. Dempsey, C.H. Petty, and M.L Bartling, “Holding Times of Volatile Organics in Water,” *Waste Testing and Quality Assurance: Third Volume, ASTM STP 1075*, C.E. Tatsch, Ed., American Society for Testing and Materials, Philadephia, PA, 1991.

54. Bottrell, D.W., “Suggested Modification of Pre-Analytical Holding Times - Volatile Organics in Water Samples,” *Proceddings of the 11th Annual Waste Testing and Quality Assurance Symposium*, U.S. EPA, Washington D.C. pp. 507-516, 1995.

55. Bayne, C.K., D.D. Schmoyer, and R.A. Jenkins, ”Practical Reporting Times for Environmental Samples,” *Environmental Science & Technology*, 28 (8) pp1430-1436, 1994.