SUBSTANTIVE POLICY STATEMENT

This Substantive Policy statement is advisory only. A substantive policy statement does not include internal procedural documents that only affect the internal procedures of the agency and does not impose additional requirements or penalties on regulated partied or include confidential information or rules made in accordance with the Arizona Administrative Procedure Act. If you believe that this substantive policy statement does impose additional requirements or penalties on regulated parties, you may petition the agency under Arizona Revised Statutes section 41-1033 for a review of the statement.

0170.000 IMPLEMENTATION OF EPA METHOD 5035 - SOIL PREPARATION FOR EPA METHODS 8015B, 8021B AND 8260B.

LEVEL TWO **Arizona Department of Environmental Quality**

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Authority: Arizona Revised Statutes (A.R.S.) §49-104(A)

I. PURPOSE

The EPA Office of Solid Waste promulgated Method 5035, ***Closed-System Purge-and-Trap Extraction for Volatile Organics in Soil and Waste Samples*** (Attachment 1), in June 1997 in SW-846, Update III. The Arizona Department of Health Services (ADHS) Office of Laboratory Licensure, Certification and Training adopted Method 5035 in May 1998 and Method 5035 became enforceable on March 1, 1999 in Arizona. The collection and analytical procedures for the approved method are flexible and, without further guidance, could result in multiple interpretations.

This policy establishes the sampling options and the preservation holding time requirements for individual programs within the ADEQ's Waste Programs Division. This policy is necessary to provide an understanding of the options set forth by the method and the limitations imposed on specific field sampling requirements. This policy does not eliminate the need to read and understand EPA Method 5035. The method, in conjunction with this policy, will provide a technically defensible and consistent approach to sampling for Volatile Organic Compounds (VOCs) in soils.

II. DEFINITIONS: (FOR PURPOSES OF EPA METHOD 5035 ONLY) -

1.	Sample Preservation:	The addition of methanol or sodium bisulfate to an unpreserved sample in the field or in the laboratory.
2.	Sample Extraction:	The addition of methanol to an unpreserved sample in the laboratory. After extraction, the methanol is transferred to a vial and can be stored at 4°C (± 2°C) until analysis.
3.	Hermetically Sealed:	For the purposes of this policy a hermetically sealed container shall be defined as a sample storage device that consistently shows less than 10% loss from volatilization over the intended storage holding time (usually 14 days) or a minimum of 48 hours for the compounds of concern at a given site.
4.	Sample Freezing:	A preservation technique in which the sample is frozen and stored at 0°C (32°F), or lower upon receipt at the laboratory. Blue ice is unacceptable.
5.	Calcareous Soil:	A soil whose content of carbonate is sufficient to cause effervescence when tested with hydrochloric acid. (Reference: Bates R. L. and Jackson J. A.. (1987). Glossary of Geology. (3rd ed.) Alexandria: American Geological Institute.)

III. POLICY

Method 5035 is structured as a 2-tier approach for low and high concentration sampling[1]. Preservation is recommended for both low and high contaminant concentrations as stated in the Method. Based upon program requirements, preservation can be conducted in the field or subsampled in an EnCore™ Sampler and the sample preserved in accordance with sample handling.

A. Sample collection options for low reporting limits (<200 µg/kg):

I. Methanol Preservation-

EPA has permitted the use of methanol preservation for low level analysis if the target analyte(s) can be quantitated below 200µg/kg. As a result, laboratories must demonstrate their ability to detect below 200 µg/kg to the client and ADHS. Samples preserved in the field with methanol using a 40 ml glass VOA vial with a plastic screw cap and a Teflon septa must be analyzed within 14 days from the time of sample collection.

ii. EnCore™ Sampler-

The sample can be collected using either a 5-gram or 25-gram EnCore™ Sampler. The sample must be stored at 4°C (±2°C) and preserved or extracted within 48 hours if not preserved. Approved preservatives include either methanol or sodium bisulfate. Once preserved, the sample must be analyzed within 14 days from the time of sample collection. The EnCore™ Sampler 48-hour preservation hold time as required in the method applies only to the EnCore™ Sampler option and is based on manufacturers' studies. Freezing the unpreserved sample in the EnCore™ Sampling device can extend the

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[1]Refer to EPA Method 5035 (Attachment 1) and Regional Interim Policy for Determination of Volatile Organic Compound (VOC) Concentrations in Soil and Solid Matrices, June 23, 1999 (Attachment 2).

holding time up to seven days (e.g., 48 hours unfrozen and 5 days frozen.)

iii. Sodium Bisulfate Preservation-

Samples preserved in the field with sodium bisulfate must be analyzed 14 days from the time of sample collection. This technique should be used if detection limits in the range of 2 - 5 μg/kg are desired. Calcareous samples, however, may effervesce upon contact with the sodium bisulfate preservative solution (thereby liberating the volatile gases) and compromise the integrity of the sample. In these instances, sodium bisulfate preservative solution cannot be utilized to attain the lower reporting levels and one of three alternative sample collection methods must be employed.

a) The sample can be collected in a VOA vial containing 10 ml of reagent grade water, sealed with a plastic screw cap containing a Teflon septa and stored at 4°C (±2°C.) This sample must be analyzed within 48 hours from the time of sampling using a closed system purge and trap.

b) The sample can be collected in a dry VOA vial, sealed with a plastic screw cap containing a Teflon septa and stored at 4°C (±2°C.) Once at the lab, water must be introduced through the septa and analyzed by closed purge and trap within 48 hours from the time of sample collection. Freezing the unpreserved sample can extend the holding time an additional 5 days for a total of 7 days from the time of sample collection.

c) The sample can be collected in an EnCore™ Sampler, stored at 4°C (±2°C) and analyzed within 48 hours from the time of sample collection. Freezing the unpreserved sample can extend the holding time up to seven days.

iv. Bulk Sampling-

The rationale for the collection of bulk samples must be clearly documented and approved by the appropriate program in a work or sampling plan or other written

communication with ADEQ. If samples are not preserved in the field, the reasons for not preserving must be clearly documented and approved by the relevant program.

ADHS rules require laboratories to flag data generated from samples that have not been preserved in the field or have not been collected in recommended containers if the reporting levels are below 200 µg/kg.

B. Sample collection options for high reporting limits (>200µg/kg):

I. Methanol Preservation-

This technique may be used if the reporting limits are above 200 µg/kg. Samples preserved in the field with methanol using a 40 ml glass VOA vial with a plastic screw cap and a Teflon septa must be analyzed within 14 days from the time of sample collection.

ii. EnCore™ Sampler-

The sample can be collected using an EnCore™ Sampler. Methanol must be added within the 48-hour period immediately following sample collection. The EnCore™ Sampler 48-hour preservation hold time as required in the method is applicable specifically only to the EnCore™ subcoring device and is based on the manufacturers' studies. After collection the sample must be stored on ice at 4°C (±2°C) until analyzed. Freezing the unpreserved sample in the EnCore™ Sampling device can extend the holding time up to seven days (e.g., 48 hours unfrozen and 5 days frozen.) Once the sample is preserved, it must be analyzed within 14 days from the time of sample collection.

iii. Bulk Sampling-

The rationale for collection of bulk samples must be clearly documented and approved by the

appropriate program in a work or sampling plan or other written communication with ADEQ. If samples are not preserved in the field or subsampled in EnCore™ Samplers, the reasons for not preserving must be clearly documented and approved by the relevant program.

Significant volatile loss occurs when samples are collected in glass jars and transported to a laboratory for analysis[2]. Therefore, **glass jars with Teflon™ -lined lids containing no preservative ARE NOT ACCEPTABLE** for the collection of soil for VOC analysis, unless otherwise specified in this policy (Program Specific Requirements) or prior approval has been received from the relevant program.

III. Program Specific Requirements[3]:

1. *WQARF, Hazardous Waste Compliance, Solid Waste Programs*

When utilizing the field preservation option of the 5035 method, samples must be preserved immediately after collection with minimal handling to be considered reliable compliance samples. Samples maybe collected and held on ice at 4°C (±2°C) for a maximum of 2 hours before preserving or analyzing the sample. This option of holding samples on ice for up to 2 hours is accepted, but not encouraged, due to the known volatile loss over time.

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[2]Siegrist, R.L., and P.D. Jennsen, 1990. Evaluation of Sampling Method Effects of Volatile Organic Compound Measurements in Contaminated Soil, *Environmental Science and Technology*, Vol.24, pp. 1387-1392.

[3]For specific programs, a sample collected in a brass/steel sleeve is acceptable under the conditions noted in Section IV. The brass or steel sleeves must have each end covered with a sheet of Teflon, aluminum foil (aluminum is optional, but preferred) and sealed with a plastic cap. The plastic caps must be secured and the capped sleeve should be placed in a plastic ziplock bag which is then taped to ensure the caps are secure. The use of tape to bind the cap to the end of the sleeve is discouraged. The length of time a sample can be held in this container is finite and subject to specific program requirements set forth in Section V.

Samples collected and preserved or analyzed after 2 hours will be considered bulk samples and not suitable for compliance purposes. Data generated from samples collected and transported to a laboratory in this manner has limited compliance value and may not be accepted by the above referenced programs.

2. ***Hazardous Waste Inspections and Emergency Response Programs***

For planned field sampling events, samples must be preserved immediately after collection, with minimal handling, to be considered compliance samples. The sample may be held on ice at 4°C (±2°C) for a maximum of 2 hours before preserving or analyzing the sample.

For unanticipated sampling events, where significant difficulties exist for preserving samples onsite, bulk soil samples may be collected and stored at 4°C (±2°C) but must be preserved within 72 hours with the approval of the program.

3. ***UST Program***

When site-specific sampling conditions prevent the use of appropriate sample collection and preservation techniques as defined in Section I or Section II, samples may be submitted in properly sealed brass sleeve containers maintained at 4°C (±2°C) for laboratory analysis of VOCs. The laboratory must document sample holding time and flag the associated analytical results if sample preservation or extraction exceeds 48 hours, regardless of the reporting limit. Reasons for lack of field preservation within the 48 hour period and submittal of bulk samples for laboratory analysis must be clearly documented.

IV. Quality Control for unpreserved samples:

Unpreserved samples submitted to the laboratory should have matrix spikes and surrogates added directly to an aliquot of the sample before extraction. The laboratory should be requested to provide a narrative describing

the procedures for sample spiking and flag all data in which the matrix was not directly spiked prior to extraction.

V. Example of Holding Time Calculations for Frozen Samples:

Example 1 Sample is placed in a vial without chemical preservative in the field and stored at 4°C (±2°C).

The sample must be analyzed within 48 hours of collection.

Example 2 The sample is collected in a hermetically sealed subcoring and storage device in the field, stored at 4°C (±2°C) and transferred into a vial without chemical preservative in the laboratory.

The sample must be analyzed within 48 hours of collection.

Example 3 The sample is collected in a hermetically sealed subcoring and storage device, transported/stored at 4°C (±2°C), frozen at the laboratory 18 hours after collection, thawed (at ambient temperature) after 4 days and transferred into a vial without a chemical preservative in the laboratory.

The sample must be analyzed within 30 hours from the time the sample is defrosted to 4°C (±2°C).

48 hours allowed before analysis - 18 hours before freezing = 30 hours allowed from thawing (at ambient temperature) to analysis.

Freezing can only extend the holding times for unpreserved samples. Freezing is an alternative to preserving samples in the field. Freezing can never extend the holding times of samples beyond the analytical methods required holding time. (Ex. Freezing cannot extend the holding time from 14 days to 19 days).

VI. RESPONSIBILITY

All staff in the respective Waste Programs Division programs are responsible for knowledge and implementation of this policy. Supervisors are responsible for ensuring that the information contained in this policy is consistently and equitably applied by all staff. It is the responsibility of the sampler to inform the laboratory receiving personnel which program requirements are appropriate for the sample.

0000.000 IMPLEMENTATION OF EPA METHOD 5035 - SOIL PREPARATION FOR EPA METHODS 8015B, 8021B, AND 8260B POLICY

LEVEL TWO: Waste Programs Division

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Issue Date:

Next Scheduled Review Date:

APPROVED BY:

Mark D. Charles for: 4/20/00

David Esposito, Date
Director
Waste Programs Division

4/20/00

Mark Santana Date
Administrative Counsel
Office of Administrative Counsel

The Policy Review Committee has posted, reviewed and accepted this policy by motion as of April 19, 2000.

Juanita Guidry Copeland 4/21/2000

Juanita Guidry Copeland Date
Acting Policy Coordinator

METHOD 5035

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.

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 negligible. 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 Method 5035 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 approximately ten times higher because of poor purging efficiency.

1.6 Method 5035, 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 Method 5035 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. 6.2.2).

1.9 This method is restricted to use by or under the supervision of trained 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 and soils and other solid samples with VOC concentrations in the range of 0.5 to 200 µg/kg.

Volatile organic compounds (VOCs) are determined by collecting an approximately 5-g sample, weighed in the field at the time of collection, and placing it in a pre-weighed vial with a septum-sealed screw-cap (see Sec. 4) that already contains a stirring bar and a sodium bisulfate preservative solution. The vial is sealed and shipped to a laboratory or appropriate analysis site. The entire vial is then placed, unopened, into the instrument carousel. 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 soil method - generally applicable to soils and other solid samples with VOC concentrations greater than 200 µg/kg.

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/EC, 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 a bulk sample in a vial or other suitable container without the use of the preservative solution described in Sec. 2.1. 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 5 mL of 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, some volatile constituents may be lost during handling.

2.2.2 The second option is to collect an approximately 5-g sample in a pre-weighed vial with a septum-sealed screw-cap (see Sec 4) that contains 5 mL of a water-miscible organic solvent (e.g., methanol). At the time of analysis, surrogates are added to the vial, then an aliquot of the solvent is removed from the vial, purged using Method 5030 and analyzed by an appropriate determinative method.

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.

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 INTERFERENCES

3.1 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 will be concentrated in the trap during the purge operation. These compounds will result in interferences or false positives in the determinative step.

3.2 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 organic-free reagent water and carried through sampling and handling protocols serves as a check on such contamination.

3.3 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 <u>not</u> present in the subsequent sample, then the analysis of organic-free reagent water is not necessary.

3.4 The laboratory where volatile analysis is performed should be completely free of solvents. Special precautions must be taken to determine 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 will also lead to random background levels and the same precautions must be taken.

4.0 APPARATUS AND MATERIALS

4.1 Sample Containers

The specific sample containers required will depend on the purge-and-trap system to be employed (see Sec. 4.2). 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 ny good quality glass vial that is large ugh 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.

4.2 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.

4.2.1 The purging device should be capable of accepting a vial sufficiently large 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 4.2.2).

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.

4.2.2 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 the 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), 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 is used. The primary criterion, as stated above, is that all target analytes meet the sensitivity requirements for a given project.

4.2.2.1 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.).

4.2.2.2 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.

4.2.2.2.1 2,6-Diphenylene oxide polymer - 60/80 mesh, chromatographic grade (Tenax GC or equivalent).

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

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

4.2.2.3 Trapping materials other than those listed above also may be employed, provided that they meet the specifications in Sec. 4.2.3, below.

4.2.3 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.

4.3 Syringe and Syringe Valves

4.3.1 25-mL glass hypodermic syringes with Luer-Lok (or equivalent) tip (other sizes are acceptable depending on sample volume used).

4.3.2 2-way syringe valves with Luer ends.

4.3.3 25-µL micro syringe with a 2 inch x 0.006 inch ID, 22° bevel needle (Hamilton #702N or equivalent).

4.3.4 Micro syringes - 10-, 100-µL.

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

4.4 Miscellaneous

4.4.1 Glass vials

4.4.1.1 60-mL, septum-sealed, to collect samples for screening, dry weight determination.

4.4.1.2 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.

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

4.4.3 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.

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

4.4.5 2-mL glass vials, for GC autosampler - Used for [illegible] waste samples extracted with methanol or PEG.

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

4.4.7 Disposable Pasteur pipettes.

4.4.8 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.

4.5 Field Sampling Equipment

4.5.1 Purge-and-Trap Soil Sampler - Model 3780PT (Associated Design and Manufacturing Company, 814 North Henry Street, Alexandria, VA 22314), or equivalent.

4.5.2 EnCore™ sampler - (En Chem, Inc., 1795 Industrial Drive, Green Bay, WI 54302), or equivalent.

4.5.3 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.

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

4.5.5 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.

5.0 REAGENTS

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

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

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

5.4 Low concentration sample preservative

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

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

5.5 See the determinative method and Method 5000 for guidance on internal standards and surrogates to be employed in this procedure.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

Refer to the introductory material in this chapter, Organic Analytes, Sec. 4.1, 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.

6.1 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.

6.1.1 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 Method 5035.

6.1.1.1 Add a clean magnetic stirring bar to each clean vial. If the purge-and-trap device (Sec. 4.2) 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.

6.1.1.2 Add preservative 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.

6.1.1.3 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.

6.1.1.4 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.

6.1.1.5 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).

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

6.1.1.7 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.

6.1.2 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. 4.4).

6.1.3 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.

6.1.3.1 Add 10 mL of methanol to each vial.

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

6.1.3.3 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).

6.1.3.4 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.

6.1.3.5 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.

6.1.4 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. 6.1.3, 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. 6.1.2.

6.2 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 ™, and a cut plastic syringe. Always wear gloves whenever handling the tared sample vials.

6.2.1 Low concentration soil samples

6.2.1.1 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.

6.2.1.2 Using the sample collection device, add about 5 g (2 - 3 cm) of soil to the sample vial containing the preservative solution. 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.

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 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 that do not contain the preservative solution.

6.2.1.3 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. 4.5.5). Record the weight of the sealed vial containing the sample to the nearest 0.01 g.

6.2.1.4 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.

6.2.1.5 As with the collection of aqueous samples for volatiles, collect <u>at least</u> two replicate samples. This will allow the laboratory an additional sample for reanalysis. 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.

6.2.1.6 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, dry weight 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 dry weight. 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 dry weight determination in a vial without either methanol or the low concentration aqueous preservative solution.

6.2.1 If samples are known or expected to co .n 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. 6.2.1.1. This aliquot may be used for those analytes that exceed the instrument calibration range in the 5-g analysis.

6.2.1.8 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.

6.2.1.9 The collection of low concentration soil samples in vials that contain methanol is <u>not</u> appropriate for samples analyzed with the closed-system purge-and-trap equipment described in this method (see Sec. 6.2.2).

6.2.2 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 <u>not</u> appropriate for use with the low concentration soil procedure described in this method.

<u>NOTE</u>: The use of methanol preservation has not been formally evaluated by EPA and analysts must be aware of two 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 1000, 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. The second problem is that the addition of methanol to the sample is likely to cause the sample to fail the ignitability characteristic, thereby making the unused sample volume a hazardous waste.

6.2.2.1 When samples are <u>known</u> 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.

6.2.2.2 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.

6.2.2.3 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.

6.2.2.4 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. 4.5.5). Record the weight of the sealed vial containing the sample to the nearest 0.01 g.

6.2.2.5 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.

6.2.2.6 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.

6.2.2.7 The collection of at least one additional sample aliquot is required for the determination of the dry weight, 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.

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

The collection of high concentration soil samples that are not preserved in the field generally follows similar procedures as for the other types of samples described in Secs. 6.2.1 and 6.2.2, 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 dry weight 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.

6.2.4 Oily waste samples

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

6.2.4.1 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. 6.1.4), using procedures similar to those described in Sec. 6.2.2.

6.2.4.2 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. 6.2.3, 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. 6.2.2. Otherwise, collect an unpreserved sample as described in Sec. 6.2.3.

6.3 Sample ha... ing 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.

6.4 Sample storage

6.4.1 Once in the laboratory, store samples at 4°C until analysis. The sample storage area should be free of organic solvent vapors.

6.4.2 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.

6.4.3 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 -10°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. 6.2.1.2 for additional information.

7.0 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.

7.1 Sample screening

7.1.1 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. 7.2), the high concentration (methanol extraction) method (Sec. 7.3), or the nonaqueous liquid (oily waste) methanol or PEG dilution procedure (Sec. 7.4).

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

7.1.2.1 Automated headspace (Method 5021) using a gas chromatograph (GC) equipped with a photoionization detector (PID) and an electrolytic conductivity detector (HECD) in series, or,

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

7.1.3 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.

7.1.4 Use the low concentration closed-system purge-and-trap method (Sec. 7.2) 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. 7.3), or the oily waste method (Sec. 7.4).

7.2 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.)

7.2.1 Initial calibration

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.

7.2.1.1 Assemble a purge-and-trap device that meets the specification in Sec. 4.2 and that is connected to a gas chromatograph or a gas chromatograph/mass spectrometer system.

7.2.1.2 Before initial use, a Carbopack/Carbosieve trap should be conditioned overnight at 245°C by backflushing 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 for 10 minutes at 245°C with backflushing. 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.

7.2.1.3 If the standard trap in Sec. 4.2.2.2 is employed, prior to initial use, the trap should be conditioned overnight at 180°C by backflushing 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 for 10 min at 180°C with backflushing. 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.

7.2.1.4 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.

7.2.1.5 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). 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.

7.2.1.6 Carry out the purge-and-trap procedure as outlined in Secs. 7.2.3. to 7.2.5.

7.2.1.7 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.

7.2.1.8 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.

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

7.2.1.8.2 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.

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

7.2.1.9 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 chamber after analysis normally corrects this. The newer purge-and-trap systems often overcome this problem with better bakeout of the system following the purge-and-trap process. Also, the charcoal traps retain less moisture and decrease the problem.

7.2.2 Calibration verification

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.

7.2.3 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.

7.2.3.1 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.

7.2.3.2 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.

7.2.3.3 For the sample selected for matrix spiking, add the matrix spiking solution described in Sec. 5.0 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 Sec. 8.0 of Method 8000.

7.2.3.4 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 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.

7.2.4 Sample Desorption

7.2.4.1 Non-cryogenic interface - After the 11 minute 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 . 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.

7.2.4.2 Cryogenic interface - After the 11 minute 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 Methods 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.

7.2.5 Trap Reconditioning

After desorbing the sample for 4 minutes, 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.

7.2.6 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. 6.2.1.7), 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 reported on a dry weight basis, proceed to Sec. 7.5

7.3 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 surrogates and, 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. 7.3.8).

The specific sample preparation steps depend on whether or not the sample was preserved in the field. Samples that were <u>not</u> preserved in the field are prepared using the steps below, beginning at Sec. 7.3.1. If solvent preservation was employed in the field, then the preparation begins with Sec. 7.3.4.

7.3.1 When the high concentration sample is <u>not</u> 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.

7.3.2 If the sample is from an unknown source, perform a solubility test before proceeding. Remove several grams of material from the sample container. 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. 7.3.3. If the sample is only soluble in hexadecane, proceed with Sec. 7.3.8.

7.3.3 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 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. Shake the vial for 2 min. If the sample was not soluble in methanol, but was soluble in PEG, employ the same procedure described above, but use 9.0 mL of PEG in place of the methanol. Proceed with Sec. 7.3.5.

NOTE: The steps in Secs. 7.3.1, 7.3.2, and 7.3.3 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.

7.3.4 For soil and solid waste samples that were collected in methanol or PEG (see Sec. 6.2.2), weigh the vial to 0.1 g as a check on the weight recorded in the field, add the surrogate spiking solution to the vial by injecting it through the septum, shake for 2 min, as described above, and proceed with Sec. 7.3.5.

7.3.5 Pipet approximately 1 mL of the extract from either Sec. 7.3.3 or 7.3.4 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.

7.3.6 The extracts must be stored at 4°C in the dark, prior to analysis. Add an appropriate aliquot of the extract (see Table 2) to 5.0 mL of organic-free reagent water and analyze by Method 5030 in conjunction with the appropriate determinative method. Proceed to Sec. 7.0 in Method 5030 and follow the procedure for purging high concentration samples.

7.3.7 If results are to be reported on a dry weight basis, determine the dry weight of a separate aliquot of the sample, using the procedure in Sec. 7.5, after the sample extract has been transferred to a GC vial and the vial sealed.

7.3.8 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 Sec. 7.0 of Method 3585.

7.4 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.

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 Sec. 7.0 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. 7.4.1. If methanol preservation was employed in the field, then the preparation begins with Sec. 7.4.3.

7.4.1 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.

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

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

7.4.2 Quickly add 1.0 mL of surrogate spiking solution 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 and then shake vigorously for 2 minutes.

7.4.3 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, add the surrogate spiking solution to the vial by injecting it through the septum. Swirl the vial to mix the contents and then shake vigorously for 2 minutes and proceed with Sec. 7.4.4.

7.4.4 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.

7.4.5 Add 10 - 50 µL of the methanol extract to 5 mL of organic-free reagent water for purge-and-trap analysis, using Method 5030.

7.4.6 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. 7.4.2 - 7.4.5. 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 Sec. 7.0 of Method 3585.

7.5 Determination of % Dry Weight

If results are to be reported on a dry weight basis, it is necessary to determine the dry weight of the sample.

NOTE: It is highly recommended that the dry weight 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 dry weight 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.

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

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

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

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

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures and Method 5000 for sample preparation QC procedures.

8.2 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.

8.3 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 Sec. 8.0 of Methods 5000 and 8000 for information on how to accomplish this demonstration.

8.4 Sample Quality Control for Preparation and Analysis - See Sec. 8.0 in 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.

8.5 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.

9.0 METHOD PERFORMANCE

9.1 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.

9.2 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.

10.0 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.

TABLE 1

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

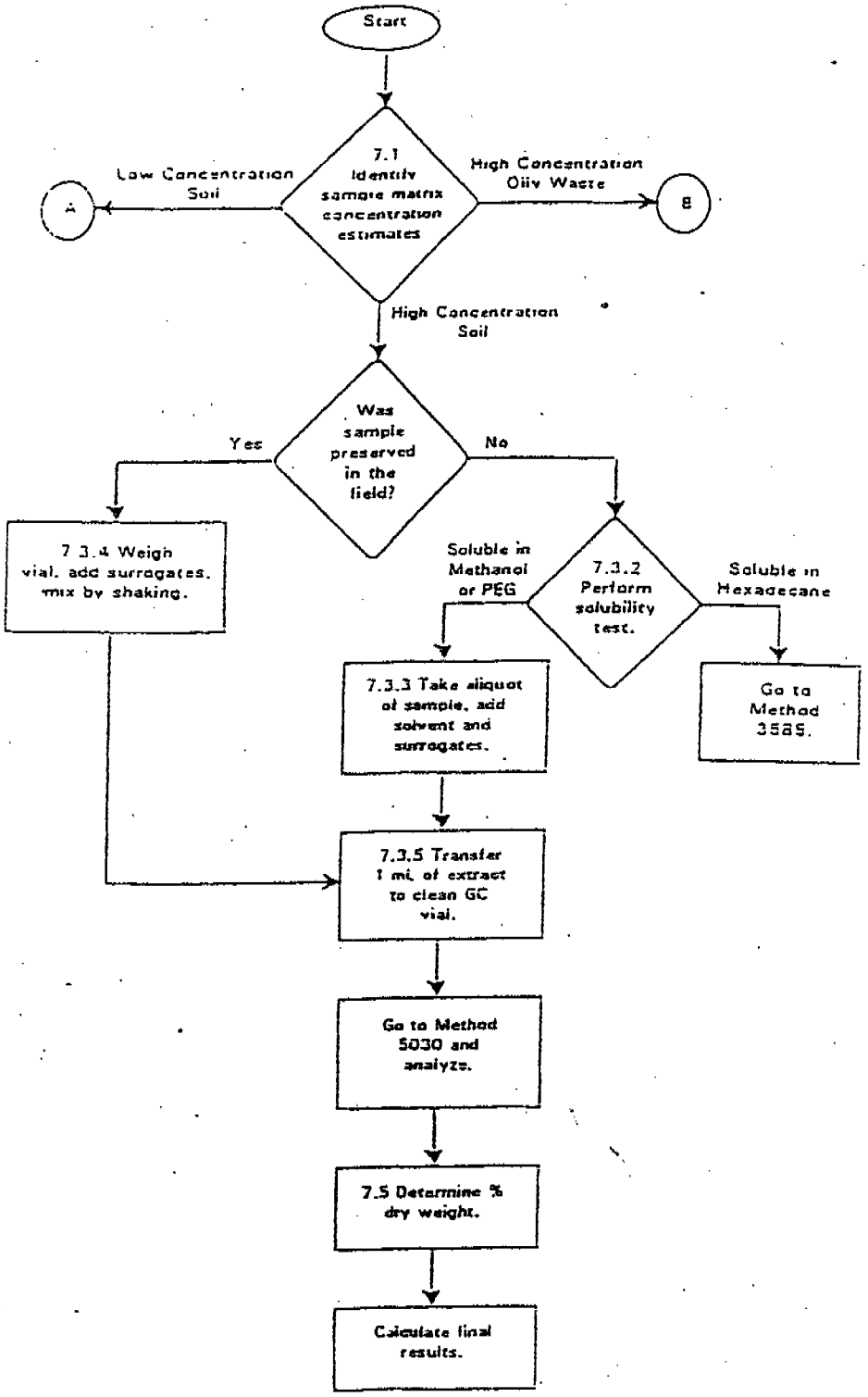
Approximate Concentration Range	Volume of Methanol Extract[a]
500 - 10,000 µg/kg	100 µL
1,000 - 20,000 µg/kg	50 µL
5,000 - 100,000 µg/kg	10 µL
25,000 - 500,000 µg/kg	100 µL of 1/50 dilution[b]

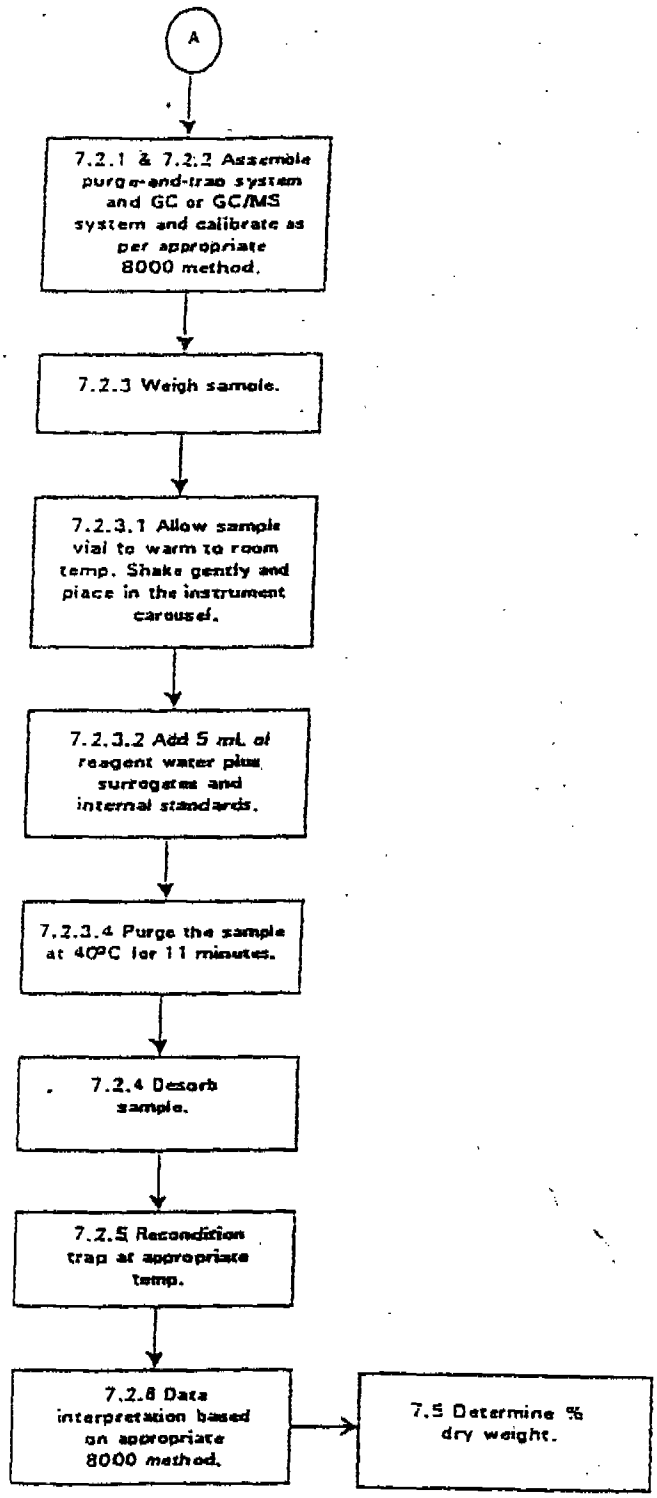
Calculate appropriate dilution factor for concentrations exceeding those in this table.

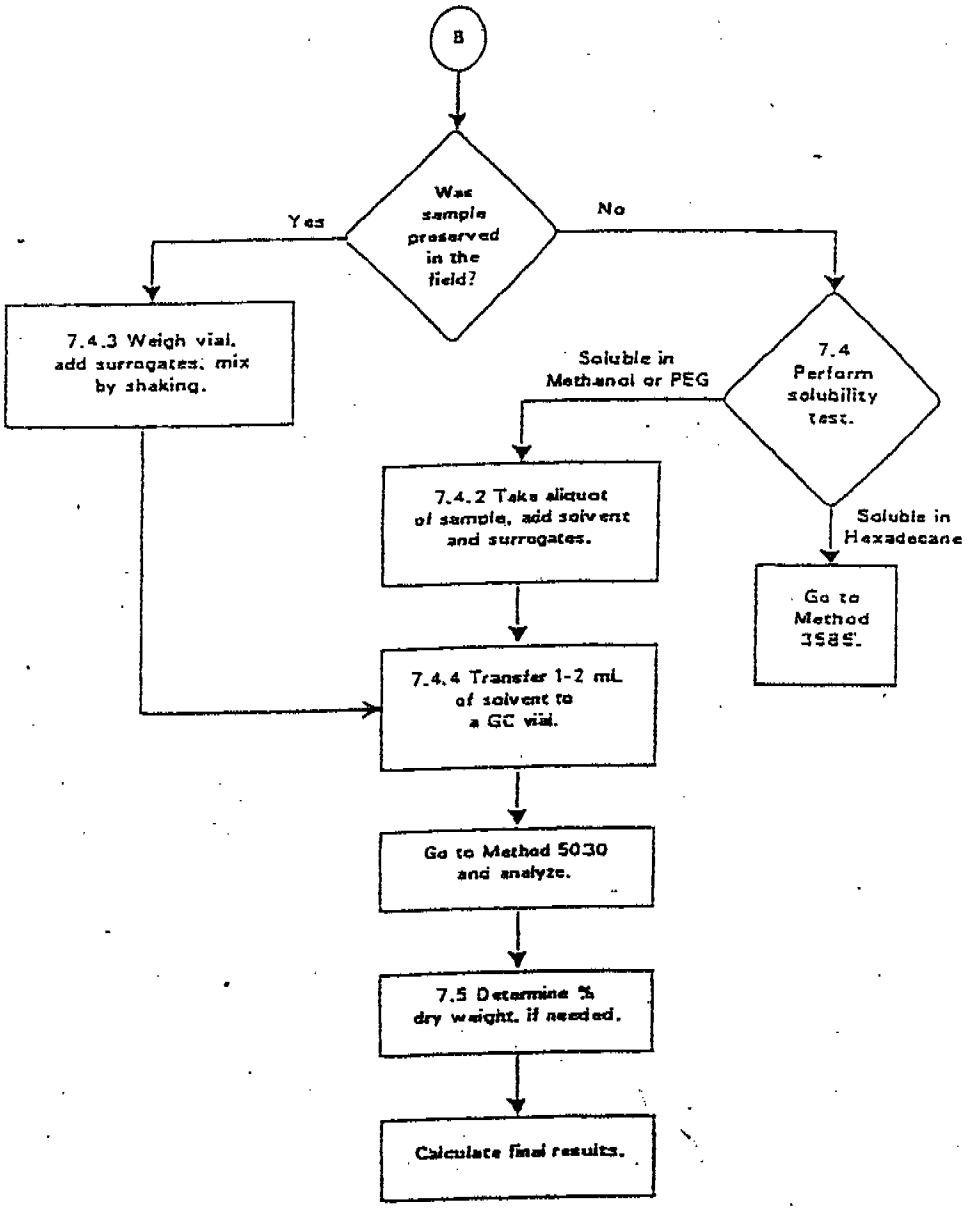
[a] The volume of methanol added to 5 mL of water being purged should be kept constant. Therefore, add to the 5-mL syringe whatever volume of methanol is necessary to maintain a total volume of 100 µL of methanol.

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

METHOD 5035
CLOSED-SYSTEM PURGE-AND-TRAP AND EXTRACTION
FOR VOLATILE ORGANICS IN SOIL AND WASTE SAMPLES




A
7.2.1 & 7.2.2 Assemble purge-and-trap system and GC or GC/MS system and calibrate as per appropriate 8000 method.
7.2.3 Weigh sample.
7.2.3.1 Allow sample vial to warm to room temp. Shake gently and place in the instrument carousel.
7.2.3.2 Add 5 mL of reagent water plus surrogates and internal standards.
7.2.3.4 Purge the sample at 40°C for 11 minutes.
7.2.4 Desorb sample.
7.2.5 Recondition trap at appropriate temp.
7.2.6 Data interpretation based on appropriate 8000 method.
7.5 Determine % dry weight.


B
Was sample preserved in the field?
Yes
No
7.4.3 Weigh vial, add surrogates, mix by shaking.
7.4 Perform solubility test.
Soluble in Methanol or PEG
Soluble in Hexadecane
7.4.2 Take aliquot of sample, add solvent and surrogates.
Go to Method 3585.
7.4.4 Transfer 1-2 mL of solvent to a GC vial.
Go to Method 5030 and analyze.
7.5 Determine % dry weight, if needed.
Calculate final results.

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
REGION IX
75 Hawthorne Street
San Francisco, CA 94105-3901

June 23, 1999

MEMORANDUM

SUBJECT: Regional Interim Policy for Determination of Volatile Organic Compound (VOC) Concentrations in Soil and Solid Matrices.

FROM: Nora McGee, Assistant Regional Administrator
USEPA Region 9

TO: USEPA Region 9 Personnel and Parties Collecting Environmental Measurements Under Regional Programs.

Purpose

Appropriate methodologies to minimize volatilization and biodegradation losses in solid matrices have not been consistently implemented throughout Region 9. This memorandum articulates the Region's policy on the adoption of sampling and laboratory methodologies for the collection of volatile organic compound (VOC) data from soil or solid matrices. USEPA SW-846, Update III, Method 5035, "Closed-System Purge-and-Trap and Extraction for Volatile Organics in Soil and Waste Samples," incorporating procedures to minimize VOC losses was finalized by USEPA in June 1997. This Region 9 policy requires the use of Method 5035, or an equally or more effective method, for the collection of representative and precise data for VOCs in soil and solid matrices. Additionally, this policy was developed to be consistent with the Agency's Data Quality Objectives (DQO) Process (outlined in "Guidance for the Data Quality Objectives Process," USEPA QA/G-4, September 1994) by allowing for a graded approach through the collection of representative data that meets project data quality needs.

Policy

Scope and Applicability

Environmental data collection activities performed under USEPA Region 9 programs for the determination of VOC concentrations in soil and solid matrices.

This policy is applicable to data collection activities conducted by USEPA staff and contractors, USEPA grantees, Federal Facilities, entities complying with USEPA regulatory requirements and/or other entities producing data for USEPA decision making. This includes data being collected under ongoing quality assurance plans and sampling plans.

INTERIM POLICY

Time Frame for Implementation

This policy should be adopted quickly and to the maximum practicable extent. Cases where it is not practicable to implement this policy should be brought to the attention of the USEPA Region 9 QA Office. This is being put forth as an interim policy, as USEPA is still evaluating technical information to further refine procedures for minimization of VOC losses. Please note, an amendment to this policy may be required.

Statement of Policy

Methods for the collection and analysis of VOCs in soil or other solid matrices must minimize volatile losses. Because USEPA SW-846 Method 5035 does not rigorously dictate specifics of field sample collection[1] and laboratory sample handling protocols, project specific procedures to minimize volatile losses must be developed and be included in the site/program quality assurance project plan (QAPP) or sampling and analysis plan (SAP). USEPA SW-846 Method 5021 "Volatile Organic Compounds in Soils and Other Solid Matrices Using Equilibrium Headspace Analysis," also incorporates procedures to minimize volatile losses. However, Method 5021 should be used with caution, as it can be reasonably interpreted and performed in a way which does not prevent loss of VOCs. USEPA Region 9 considers the following practices as minimum requirements to reduce volatile losses in soil samples:

1. Samples are handled as intact[2] soil cores in the field and laboratory.

2. Samples are stored in containers which can be reliably sealed to prevent volatilization losses[3] over the project specified analytical holding time.

3. Samples are analyzed or chemically, acid or methanol, preserved within 48 hours of collection, if any contaminant may undergo biodegradation.

4. Exposure of the sample core to the atmosphere in the field and laboratory should be minimized[4].

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1 ASTM Method D4547-98 "Standard Guide for Sampling Waste and Soils for VOCs," is a good reference for VOC sampling protocols.

2 Soils should always be collected and transferred using a coring device, such as a metal sleeve or cut off syringe. Use of transfer devices, such as spatulas, is not acceptable either in the field or laboratory.

3 Volatilization losses from sampling/storage containers must be less than what would be expected from a volatile organic analysis vial with a Teflon/silicon septa stored for 14 days, unless project DQOs require more stringent requirements.

4 Field sub-cores should be taken immediately upon exposing the soil core to ambient conditions. Sub samples should be directly extruded into the analysis containers. Total exposure of samples to ambient conditions should not be more than 15 seconds.

USEPA Region 9 will consider exceptions to this policy on a case-by-case basis. All deviations from procedures outlined in Method 5035 should be documented in a QAPP or a SAP which must be submitted to, and approved by, the Region 9 QA Office. Additionally, the party responsible for data collection must demonstrate that the methodologies proposed will result in data that meet project/program data quality objectives (DQOs).

Additional Considerations

Field Laboratories: The use of field laboratories, that analyze samples within several hours of collection, is an excellent choice to prevent loss of volatiles in transit and storage. However, the sample collection and analysis procedures used must prevent volatilization losses and comply with requirements 1 and 4 articulated in the Statement of Policy. Additionally, the quality control criteria and quality assurance system used by a field laboratory must be adequate for generation of data which will meet project DQOs.

Addition of Surrogates and Matrix Spiking Compounds in the Field: The most appropriate time for addition of analytical surrogate and matrix spiking compounds into soils is prior to sample extraction, by water or a solvent. Method 5035 does not incorporate the addition of the compounds prior to extraction in the field. Because this is an important control check on the analytical process, which begins at extraction, for some project/program DQOs it may be appropriate to incorporate a procedure which adds surrogate and/or matrix spiking compounds prior to extraction.

Holding Times: The holding time for preserved soil samples should be interpreted as 14 days from the time of sample collection(stored at 4±2°C). Due to potential biodegradation losses, samples stored in sealed containers, but not chemically preserved, should not be stored for more than 48 hours. On a project/program specific basis, USEPA Region 9 will consider other alternatives to extend the holding time of soils that have not been chemically preserved (see Attachment A). Holding time will be considered as cumulative (see Attachment B for holding time examples). Exceptions should be documented in a QAPP or a SAP submitted to and approved by the Region 9 QA Office.

Unconsolidated Solid Matrices: Solid Matrices that are not amenable to the use of a coring technique should be collected in such a way as to preserve the integrity of the sample matrix. Transferring of these soils with spatulas or similar devices into sampling containers is discouraged as this disrupts the sample pore spaces and greatly increases the sample surface area available for volatilization. For soil piles, fresh soil at an adequate depth should be sampled.

Calcareous Soils: Method 5035 notes that, "Soil samples that contain carbonate minerals (either from natural sources or applied as an amendment) may effervesce upon contact with the acidic preservative solution in the low concentration sample vial." Calcareous soils that effervesce on contact with the low-level preservative solution should be collected using an alternative preservation technique (see Attachment A).

Soil Gas: This policy is not intended to address the role of soil gas in the environmental decision making process. The Region recognizes that soil gas data is used extensively, in USEPA Region 9, for site decision making and in some cases soil gas is the preferred tool for gathering data on subsurface conditions. However, there are also scenarios where soil gas data are unacceptable for agency decision making (e.g., in excavated soils and when determining disposal options).

Drilling Techniques: This policy does not address the impact of drilling techniques on the collection of a representative VOC sample. Site/program QAPPs and SAPs should address the impact of all collection techniques on sample integrity and select those appropriate for the DQOs. Potential VOC losses due to drilling techniques include, but are not limited to: sample compression and loss of pore space; air introduction into the sample matrix; heat introduced in the drilling process; and volatilization from prolonged periods in a non-hermetically sealed sampling apparatus.

Background

Traditional practices for the sampling and analysis of volatile organic compounds (VOCs) in soil have been shown to have a significantly low bias of inconsistent magnitude (Grant, 1996) from volatilization (Hewitt, 1996) and biodegradation (Hewitt, 1994). Based on this and other research, the USEPA modified the methodology in SW846 for collection and analysis of volatiles in soil. Soil was deleted as an option from Method 5030 and Method 5035 and Method 5021 were added. These methods provide for handling of samples as intact soil cores, chemical preservation techniques, storage of samples in hermetically sealed containers and minimization of analyte losses due to direct volatilization (both in the field and the laboratory) and biodegradation.

"Traditional" collection techniques, such as transferring soils to a glass jar with minimal head space and collecting samples directly into a brass sleeve (e.g., CA Split Spoon) do not yield accurate or consistent results. It has been specifically demonstrated that capped brass sleeves show significant losses. Hewitt and Lukash (Hewitt, 1996) demonstrated capped sleeves can show substantial losses in less than one day. Hewitt and Lukash also demonstrated volatile losses in uncapped core liners of up to 90% in less than 40 minutes for trichloroethene (TCE). Because other analytes and matrix types can have higher mobility than those tested, substantial losses may occur in an even shorter period of time. Grant, Jenkins and Mudambi (Grant, 1996) examined split sampling results from a cross section of laboratories. For VOCs in soil they noted that, "The magnitude of this scatter [for a typical data comparison] is so large that it is

impossible to recommend effective limits of acceptability. Instead, we believe that steps are urgently needed to improve data quality." Hewitt noted (Hewitt, 1994) that biodegradation of Benzene and Toluene in soil samples stored in sealed glass ampules at 4 C for 14 days could be substantial, demonstrating a need for chemical preservatives. Turriff and Reitmeyer (Turriff, 1998) demonstrated that a variety of soil matrices could be held for 48 hours at 4 C, in sealed zero headspace containers, without substantial VOC losses. Additionally, Turriff and Reitmeyer demonstrated that freezing was an option to extend holding times of En Core™ sampling devices. Because volatile losses have been linked to disturbance of the soil matrix and exposure to the atmosphere, samples should be handled in intact soil cores and stored in hermetically sealed vessels in both the field and the laboratory.

This USEPA Region 9 policy is based on the best scientific information available at this time and is subject to further clarifications and additions as other research becomes available. If you have any questions please call Vance Fong at 415 744-1492 or Mathew Plate at 415 744-1493.

References

Hewitt, A.D. (1994) Concentration Stability of Four Volatile Organic Compounds in Soil Subsamples. US Army Cold Regions Research and Engineering Laboratory, Special Report 94-6.

Grant, C.L., T.F. Jenkins and A.R. Mudambi (1996) Comparison Criteria for Environmental Chemical Analyses of Split Samples Sent to Different Laboratories, Corps of Engineers Archived Data. US Army Cold Regions Research and Engineering Laboratory, Special Report 96-9.

Hewitt, A.D. and J.E. Lukash (1996) Obtaining and Transferring Soils for In-Vial Analysis of Volatile Organic Compounds. US Army Cold Regions Research and Engineering Laboratory, Special Report 96-5.

Turriff, D. Ph.D. and C. Reitmeyer (1998) Validation of Holding Times for the EnCore™ Sampler. En Novative Technologies, Inc.

Attachment A

Preservation Alternatives: The following are preservation alternatives that may be appropriate for some projects/programs and are subject to project/program specific approval by the USEPA Region 9 QA Office.

Freezing of unpreserved samples: It has been shown in several studies that freezing of unpreserved soils is an effective means of slowing the biodegradation process. At this time, USEPA Region 9 will accept freezing of unpreserved soils as a method to extend holding times up to seven days on a project specific basis. While there is some evidence that freezing for longer periods may also be acceptable for some data needs, USEPA Region 9 does not believe that the current scientific evidence supports a longer holding time for frozen samples in most cases. Samples should be frozen in containers that have an air tight seal and can maintain this seal while frozen. Because water expands in the freezing process, VOA vials with water or samples with extremely high moisture contents may rupture the storage container.

Preservatives: Acids other than sodium bisulfate may be used to preserve low level samples. The choice of an alternative acid should be made in consultation with the USEPA Region 9 QA Office. In all cases the preserved sample pH should be 2.

Sampling Containers: Currently the Region recognizes three sample collection/storage alternatives which can be used (other than acid/water or methanol, as specified in Method 5035).

1. A VOA vial with 5 mL of water without preservative and approximately 5 g of sample. Which must be analyzed within 48 hours of collection by closed system purge and trap.

2. A VOA vial with approximately 5 g of sample. Water must be introduced through the septa at time of analysis by closed system purge and trap. Sample must be analyzed within 48 hours of collection if stored at 4±2°C or 7 days if frozen. (This alternative must be approved on a project specific basis.)

3. An En Core™ sampler which is analyzed or preserved within 48 hours of collection if stored at 4±2°C or analyzed within 7 days if frozen. (Freezing of En Core™ samplers must be approved on a project specific basis.)

If requested, USEPA Region 9 QA Office will consider the applicability of other sampling containers/devices that have been demonstrated, with appropriate supporting documentation, to be adequate for collection and storage of VOCs.

Attachment B Examples of Holding Time Policy

Example 1 Sample is placed into a vial without chemical preservative in the field (due to effervescence) and stored at 4±2°C.

Sample must be analyzed within 48 hours of collection.

Example 2 Sample is collected into a hermetically sealed sub-coring and storage device in the field, stored at 4±2°C and transferred into a vial without chemical preservative in the laboratory.

Sample must be analyzed within 48 hours of collection.

Example 3 Sample is collected into a hermetically sealed sub-coring and storage device, transported/stored at 4±2°C, frozen at the laboratory 28 hours after collection, defrosted after 2 days and transferred into a vial without chemical preservative in the laboratory.

Sample must be analyzed within 20 hours from the time the sample is defrosted to 4±2°C.
48 (hours allowed) - 28 (hours before freezing) = 20 (hours allowed from defrosting to analysis)