



Standard Guide for Sampling Waste and Soils for Volatile Organic Compounds¹

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1. Scope

1.1 This guide describes recommended procedures for the collection, handling, and preparation of solid waste, soil, and sediment samples for subsequent determination of volatile organic compounds (VOCs). This class of compounds includes low molecular weight aromatics, hydrocarbons, halogenated hydrocarbons, ketones, acetates, nitriles, acrylates, ethers, and sulfides with boiling points below 200° Celsius (C) that are insoluble or slightly soluble in water.

1.2 Methods of sample collection, handling, storage, and preparation for analysis are described.

1.3 This guide does not cover the details of sampling design, laboratory preparation of containers, and the analysis of the samples.

1.4 It is recommended that this guide be used in conjunction with Guide [D4687](#).

1.5 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.6 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*²

[D1193](#) Specification for Reagent Water

[D1586](#) Test Method for Penetration Test (SPT) and Split-Barrel Sampling of Soils

[D3550](#) Practice for Thick Wall, Ring-Lined, Split Barrel, Drive Sampling of Soils

[D4687](#) Guide for General Planning of Waste Sampling
[D4700](#) Guide for Soil Sampling from the Vadose Zone
[D5058](#) Practices for Compatibility of Screening Analysis of Waste

[D5681](#) Terminology for Waste and Waste Management
[D5792](#) Practice for Generation of Environmental Data Related to Waste Management Activities: Development of Data Quality Objectives

[D6051](#) Guide for Composite Sampling and Field Subsampling for Environmental Waste Management Activities

[D6282](#) Guide for Direct Push Soil Sampling for Environmental Site Characterizations

[D6418](#) Practice for Using the Disposable En Core Sampler for Sampling and Storing Soil for Volatile Organic Analysis

[D6640](#) Practice for Collection and Handling of Soils Obtained in Core Barrel Samplers for Environmental Investigations

2.2 *Federal Standard:*

[Title 49](#) Transportation, Code of Federal Regulations (CFR), Part 172, List of Hazardous Substances and Reportable Quantities³

3. Terminology

3.1 *sample, n*—a portion of material taken from a larger quantity for the purpose of estimating properties or composition of the larger quantity. **(D5681)**

3.2 *subsample, n*—a portion of a sample taken for the purpose of estimating properties or composition of the whole sample. **(D6051)**

3.2.1 *Discussion*—A subsample, by definition, is also a sample.

4. Summary of Guide

4.1 This guide addresses the use of tools for sample collection and transfer, conditions for sample storage, sample preservation, and two common means of sample preparation for analysis. Special attention is given to each step from sample collection to analysis to limit the loss of VOCs by volatilization and biodegradation. The sample collected and analyzed should

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² For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

³ Available from Superintendent of Documents, U.S. Government Printing Office, Washington, DC 20402.

be representative of the matrix material sampled. The two methods cited for the preparation of samples for VOC analysis are methanol extraction and vapor partitioning (that is, purge-and-trap, headspace, and vacuum distillation). The method of sample preparation for VOC analysis should be consistent with the data quality objectives (see Practice D5792).

5. Significance and Use

5.1 This guide describes sample collection and handling procedures designed to minimize losses of VOCs. The principal mechanisms for the loss of VOCs from materials during collection, handling and storage are volatilization and biodegradation. Susceptibility of various VOCs to these two loss mechanisms is both compound and matrix specific. In general, compounds with higher vapor pressures are more susceptible to volatilization than compounds with lower vapor pressures. Also, aerobically degradable compounds are generally more susceptible to biodegradation than anaerobically degradable compounds. In some cases, the formation of other compounds not originally present in the material can occur. Loss or gain of VOCs leads to analytical results that are unrepresentative of field conditions.

5.2 Ancillary information concerning sample collection, handling and storage for VOC analysis is provided in Appendix X1, Appendix X2, and Appendix X3. These appendixes and cited references are recommended reading for those

unfamiliar with the many challenges presented during the collection, handling and storage of samples for VOC analysis.

6. Selection of Sample Preparation Method for VOC Analysis

6.1 Introduction:

6.1.1 Sample collection, handling, and preservation methods should be compatible with the method used to prepare the sample for VOC analysis, and meet the project's data quality objectives (see Practice D5792). Preparation of a sample for instrumental analysis can be initiated either in the field or laboratory. In either case, prior to analysis, the sample should be placed into a tared volatile organic analysis (VOA) vial or bottle meeting the specifications given in 7.3. When working with an uncharacterized solid waste, it is advisable to perform compatibility tests (see Test Methods D5058) between the sample material and the solution (see 6.2 and 6.3) into which it will be transferred in preparation for analysis. For instance, when collecting highly contaminated soils or waste of unknown composition, it is strongly recommended that preliminary testing be performed to adequately characterize the waste materials so that when the user applies the procedures cited in this guide, there will be no chemical reaction which may jeopardize the user's safety.

6.1.2 Figs. 1 and 2 are flow diagrams showing some

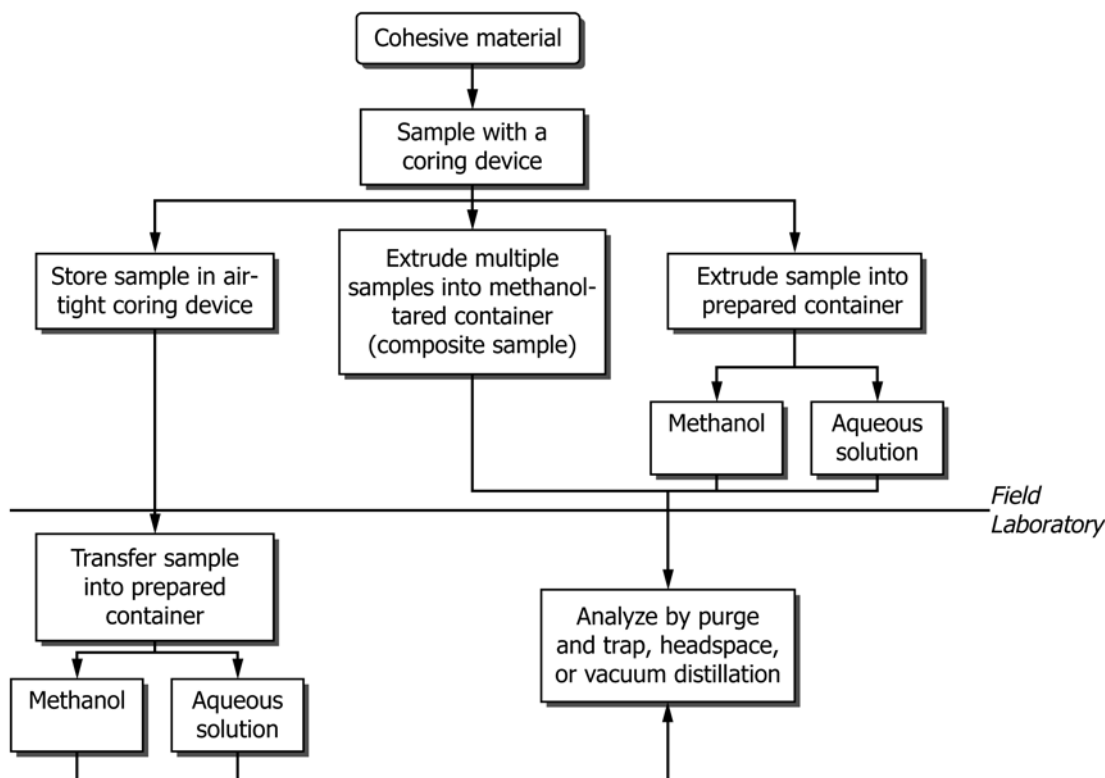


FIG. 1 Sample Handling Options for Cohesive Materials

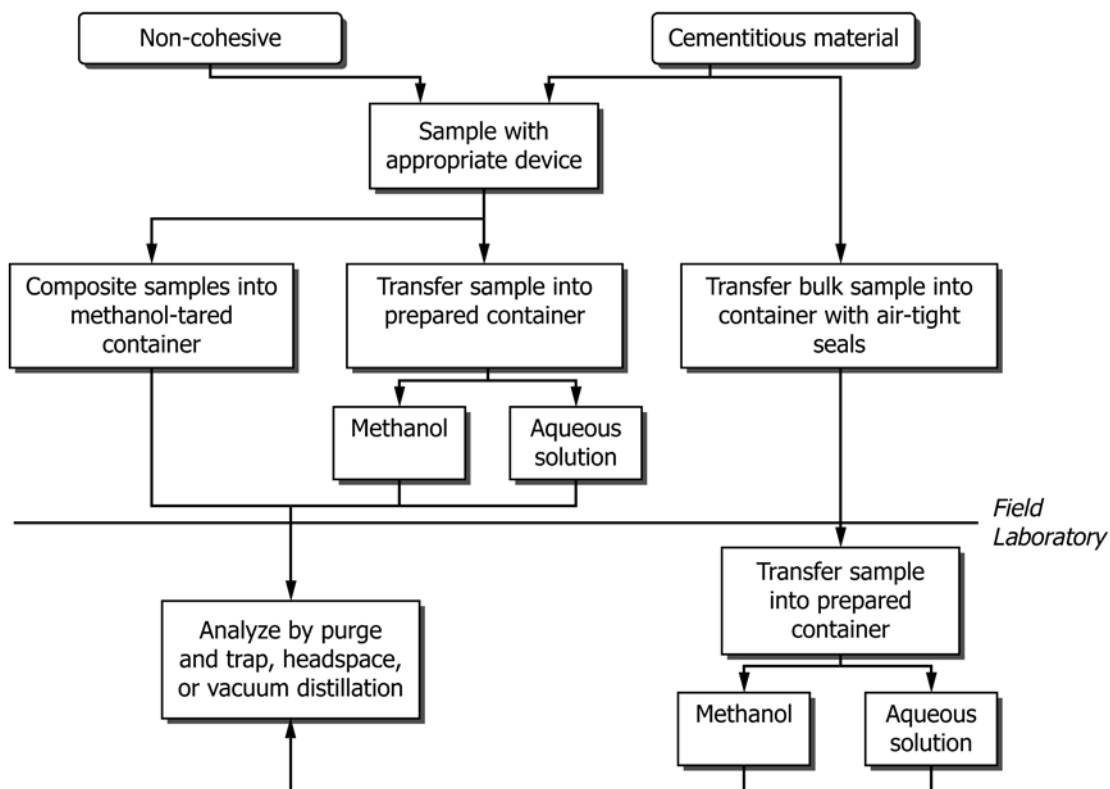


FIG. 2 Sample Handling Options for Non-Cohesive and Cementitious Materials

different options for combining sample collection, handling and preparation methods for instrumental analysis.

6.2 Methanol Extraction:

6.2.1 This method involves the extraction of VOCs from a sample with methanol and the subsequent transfer of an aliquot of the extract to water for either purge-and-trap, headspace analysis, or vacuum distillation.

6.2.2 Advantages of methanol extraction are (1) large samples or composite samples, or both, can be collected to enhance representativeness (see Guide D6051), (2) biodegradation is inhibited, (3) an efficient extraction of VOCs from the matrix materials can be achieved with methanol due to its strong affinity for these compounds and favorable wetting properties, (4) a subsample can be analyzed several times, and (5) sample extracts can be archived, if verified that VOC losses have not occurred (see 10.1.1).

6.2.3 The primary disadvantages of methanol extraction are (1) samples may have to be shipped as a flammable liquid depending on the amount of methanol present (for example, U.S. DOT reg. 49CFR§172.101), (2) hazards to personnel due to methanol’s toxicity and flammability, (3) detection limits are elevated due to analyte dilution, (4) possible interference of the methanol peak with VOCs of interest, (5) potential adverse impact of methanol on the performance of certain gas chromatograph/detector systems, and (6) samples extracted with methanol must be disposed of as a regulated waste.

6.2.4 Logistical challenges of performing these tasks in the field can be overcome by extracting samples with methanol once they have been received in a laboratory, provided that the samples are transported in an airtight container (see 7.3.2, 9.1

and 9.2). Furthermore, if VOC levels are unknown, a replicate sample can be obtained and screened to determine if methanol extraction is appropriate for the expected contaminant concentrations.

6.3 Vapor Partitioning:

6.3.1 Vapor partitioning involves the direct analysis of a sample by either purge-and-trap, headspace, or vacuum distillation. In each case, the sample is placed into a tared volatile analysis (VOA) vial or flask (for vacuum distillation) containing water or a preservative solution (for example, acidified water) from which the vapor is removed for analysis without the container being opened.

6.3.2 The principal advantages of this method are (1) it can offer lower detection limits than methanol extraction because no dilution is involved, (2) there are no organic solvent interferences, and (3) there is no use of regulated organic solvents, which may require special shipment, disposal, and field handling practices.

6.3.3 The disadvantages associated with vapor partitioning are (1) the VOA vial (VOA vials are different sizes for automated purge-and-trap and headspace instrumentation) or adapter used in conjunction with a VOA vial, or both, often are instrument specific, (2) sample size is limited (<10 g) by automated systems, (3) a matrix-appropriate method of preservation may be necessary (see Appendix X2), (4) vapor partitioning is less efficient at recovering VOCs from some materials than methanol extraction, and (5) when using purge-and-trap or vacuum distillation, only a single analysis of the same sample can be made; similarly only a single analysis may

be possible with headspace analysis unless concentrations allow for the use of a small injection volume.

6.3.4 Limitations imposed by vapor phase partitioning methods with regard to number of analyses that can be performed on a single sample can be addressed by taking replicate samples.

6.3.5 When employing vapor phase partitioning methods, the logistical challenges of performing sample preparation in the field (see 7.3.3) can be avoided by performing the preparation step in the laboratory, so long as the sample is transported to the laboratory in an airtight container (see 7.2.1). If VOC levels are unknown, a replicate sample can be obtained and screened to determine if it is appropriate to use a vapor partitioning method of sample preparation.

7. Sampling Tools and Containers

7.1 All sample handling devices and vessels used to collect and store samples for analysis should be constructed of nonreactive materials that will not sorb, leach or diffuse constituents of interest. Examples of materials that meet these criteria are glass, stainless steel, steel, and brass. Materials, such as polytetrafluoroethylene (PTFE) and many rigid plastics also can be used; however, it should be recognized that they may have some limited adsorptive properties or allow slow diffusive passage of some VOCs. Materials which show limited reactivity can be used when they have a very short period of contact with the sample or when they are necessary for making airtight (hermetic) seals. Collection tools and storage containers made of materials other than those cited in this section should only be used after they have demonstrated equivalency (see 7.2.1). All collection tools and storage containers should be cleaned in a manner consistent with their intended use.

7.2 *Tools*—There are often several steps to sampling, particularly if it involves obtaining bulk material from the subsurface. Most of the equipment used to obtain samples from the subsurface was originally developed for the geotechnical industry; however, several devices have been developed specifically for environmental sampling by direct push methods (Guide D6282). The subsurface bulk sampling systems are designed to obtain intact cylindrical cores of material, ranging anywhere from 2.5 to 10.2 cm in diameter and 30.5 cm or more in length. Two geotechnical tools that have been used for subsurface sample collection are the split-spoon sampler (Test Method D1586), which opens to expose the entire length of the material obtained for subsampling, and core barrel liners (ring-lined barrel sampling, see Practice D3550) that are typically subsampled through open ends. Core barrel liners should not be used for storage of samples intended for VOC analysis because they do not have airtight seals, see Appendix X1. Single tube and dual tube sampling devices have been developed for environmental applications (Guide D6282) and are usually operated by direct push methods. Sample liners used in the bulk sampling systems come in a variety of lengths and materials (stainless steel, brass, PTFE, rigid plastics, etc.). Additional information on the design and application of different types of subsurface collection systems that are available can be found in Guide D4700 and Guide D6282. Subsurface materials retrieved for VOC characterization should be

obtained (sampling tubes filled and brought to the surface) as quickly as possible and remain intact and undisturbed until they are subsampled (see Practice D6640). Subsampling a bulk sample should occur as quickly as possible after it is brought to the surface. It is important for subsampling to occur quickly because for bulk sample retrieval systems where the material is exposed directly to the atmosphere for a period of time during subsampling, there is an opportunity for VOC loss to occur. Suggested liner configurations and examples of sampling techniques for bulk soil samples collected by single tube direct push methods that provide limited exposure of the soil being sampled to the atmosphere, are described in Appendix X3 (see 8.1 through 8.3 for additional sampling guidance).

7.2.1 In addition to the coring devices which retrieve bulk quantities of material, there are smaller hand-operated coring tools for obtaining samples of the appropriate size (for example, coring devices capable of collecting 3- and 15-cm³ volumes, for collection of approximately 5- and 25-g samples, respectively) for analysis (see Fig. 3). If one of these smaller coring devices is used to store the sample (see 9.1.1), the main body shall be constructed of materials that are nonreactive and have airtight seals that show limited sorption and penetration of VOCs. Hand-operated coring devices that are used to store samples shall be evaluated using the procedure given in Appendix X4 to ensure that the device meets these criteria. Any alternate evaluation technique shall produce equal or better recoveries of the compounds stated in Appendix X4. When the coring device is only used to rapidly transfer the sample to a VOA vial, corer material requirements are less stringent.

7.3 *Containers*—VOA vials and bottles used for storage and preparation of samples for analysis should be made of glass and have airtight seals. To achieve an airtight seal, these containers should have a thick septum cushion between the sealing material (PTFE) and cap (rigid plastic screw cap or aluminum crimp top). PTFE-lined caps that do not have flexible septum backing often fail to achieve a liquid or airtight seal. Furthermore, the thickness of the PTFE used for a lined septum should be at least 0.254 mm.

7.3.1 *Preparation of VOA Vial or Bottle*—Record the tared weight of the VOA vial or bottle and cap prior to the sampling event. Moreover, depending on the method of sample preparation and analysis, the vessel may also contain a solvent, or VOC free water, and if required a PTFE or glass coated stir bar at the time of sample collection (see Section 9).

7.3.2 *Preparation of Containers for Methanol Extraction*—Container preparation applies to both field and laboratory sample preparation. The appropriate volume of analytical-grade methanol (high performance liquid chromatography, spectrographic or purge and trap) is added to the organic-free container by the laboratory that supplies the container, by the sample collector, or by a third party. The party that adds the methanol to the container should also be responsible for providing trip blanks (see Guide D4687). If methanol is present in the sample container in the field, this container should be opened only to add the sample(s). The tared weight of the container with methanol should be recorded prior to adding the sample to the container. A predetermined volume of sample

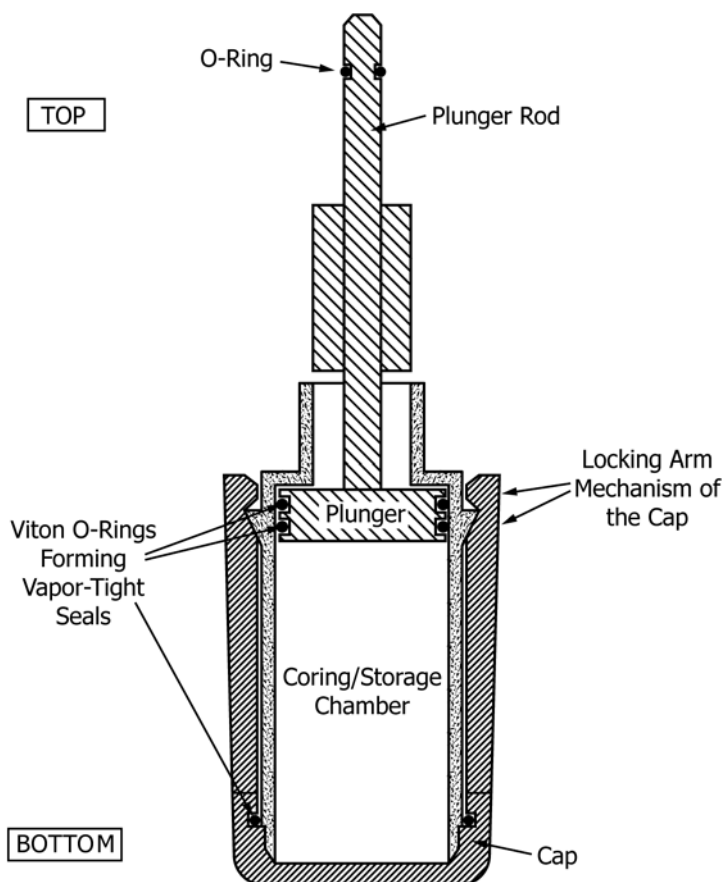


FIG. 3 Miniature Core Sampler

that corresponds to a weight in grams (g) that is equivalent to or less than the volume (mL) of methanol can then be introduced. The ratio (typically 1:1 to 10:1, methanol to material) between the two constituents should allow for formation of a clear layer of methanol over the sample after thorough mixing. The difference in weight of the container and cap, measured before and after the sample is introduced, is used to establish the sample's wet weight. Because of the water (moisture) present in most samples, calculation of the recovery of sample analyte concentrations should account for this source of dilution.

7.3.3 Preparation of Containers for Vapor Partitioning—Container preparation applies to both field and laboratory sample preparation. This method allows for the direct analysis of a sample by either purge-and-trap or headspace techniques. In both cases, the sample is placed into a VOA vial from which the vapor (only a portion for headspace analysis) is removed for analysis without the container being opened. Moreover, water that contains no detectable levels of VOCs and if required a PTFE or glass coated stir bar should be present in the VOA vial prior to introducing the sample. Current automated equipment for purge-and-trap and headspace systems typically use 40 and 22-mL VOA vials, respectively. The volume of water used for these two different systems is typically 10 mL or less. Furthermore, the tared weight of the container should be recorded prior to adding the sample. The

difference in weight of the container, measured before and after the sample is added, is used to determine the sample's wet weight.

7.3.4 Preparation of Samples Transported and Stored in Solventless VOA Vials or Bottles—When samples are held in a VOA vial or bottle, methanol can be added to the container by piercing the septum. In the case of a 5-g sample contained in a 40-mL VOA vial, 5.0 mL of methanol can be added without over pressurization. When larger samples and bottles, or both, are used, experimental trials should be performed to establish what volume of solution can be added. If performed manually, a 0.635 mm nominal outer diameter and 0.318 nominal inner diameter or smaller needle (see Note 1) should be used to add the methanol. After the methanol is introduced, the soil sample should be dispersed. If the sample is held beyond the laboratory-prescribed extraction and analysis period (typically 24 h or less), it is recommended that either the pierced septum be replaced with one that is intact or that an aliquot of the methanol be transferred to an appropriate vessel for storage. If the pierced septum is replaced, it should be replaced with one that is intact by replacing the cap of the vial or bottle with a cap having an intact septum. When the laboratory prescribed extraction method uses elevated temperatures, or sonication, or both, it is recommended that the pierced septum be replaced prior to this treatment. To limit the loss of VOCs when replacing the cap or transferring an aliquot of methanol, the

container should be cooled to $4 \pm 2^\circ\text{C}$, and these functions should be performed as quickly as possible. Cooling the sample lowers the vapor pressure of the analytes of interest and reduces the pressure created by adding the methanol. By having methanol present in the collection vessel prior to introducing the sample, the additional precautions associated with a pierced septum can be avoided. In addition, having methanol present in the collection vessel reduces the possibility of VOCs being lost during the transfer step (that is, extrusion of a plug of soil from the sampling tool into the empty vessel).

NOTE 1—This is a 23-gage needle.

8. Sample Collection

8.1 *General Sampling Guidance*—Using an appropriate sized coring tool (see below), collect samples from freshly exposed surfaces of the soil or waste with minimal disturbance. The soil or waste to be sampled may be from an intact pit face or the relatively undisturbed contents in a split-barrel sampler, a core barrel liner, or a liner from a single or double tube direct push sampling system. Before sampling, remove several centimeters of material to expose a fresh surface. Obtain a sample by pressing (or hammering in a few cases) the end of the coring tool into the pit face or into the end or side of a larger core

sample. Remove the coring tool. The optimum diameter of the coring tool depends on the following: size of the opening on the collection vial or bottle (tool should fit inside mouth), particle size of the solid materials (for example, gravel-size particles would require larger samplers), and volume of sample required for analysis. For example when a 5-g sample of soil is specified, only a single 3-cm^3 volume would need to be collected (assuming the soil has density of 1.7 g/cm^3). Larger sample masses or composite samples may be preferred as the heterogeneity of the material increases.

8.1.1 *Sampling of Cohesive but Uncemented Materials Using Devices Designed to Obtain a Sample Appropriate for Analysis*—Collect appropriate size sample for analysis using a metal or rigid plastic coring tool (see Figs. 3 and 4). For example, coring tools for the purpose of transferring a sample can be made from disposable plastic syringes by cutting off the tapered front end and removing the rubber cap from the plunger. Pre-fabricated plastic syringes/coring tools are available commercially. This type of coring device is not appropriate for sample storage. These smaller coring devices help maintain the sample structure during collection and transfer to the VOA vial or a larger bottle. When inserting a clean coring tool into a fresh surface for sample collection, air should not be

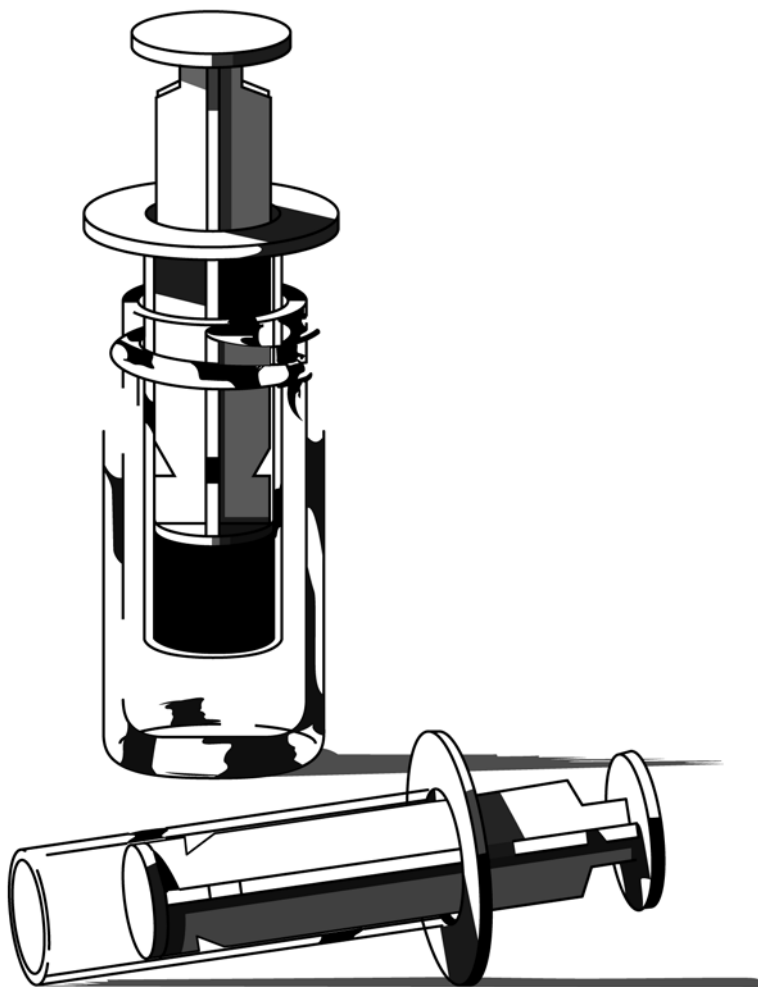


FIG. 4 A Coring Tool Made by Cutting the Tip Off a Plastic Syringe

trapped behind the sample. If air is trapped, it could either pass through the sampled material causing VOCs to be lost or cause the sample to be pushed prematurely from the coring tool. For greater ease in pushing coring tools into the solid matrix, their front edge can be sharpened.

8.1.2 Obtain an undisturbed sample by pushing the barrel of the coring tool into a freshly exposed surface and removing the corer once filled. Clean the exterior of the barrel by wiping with a clean disposable towel. If the coring tool sampler is used as a storage container, cap the open end after ensuring that the sealing surfaces are cleaned (see 9.1.1). If the device is solely used for collection and not storage, immediately extrude the sample into a tared VOA vial or bottle by gently pushing the plunger. During transfer of the sample into the container, care should be taken to prevent the sample from contacting the sealing surfaces which can comprise these surfaces and prevent an airtight seal. The volume of material collected should not cause excessive stress on the coring tool during intrusion into the material, or be so large that the sample easily falls apart during extrusion. Obtaining and transferring a sample should be done rapidly (<10 s) to reduce volatilization losses. If the vial or bottle contains methanol or another liquid, it should be held at an angle when extruding the sample into the container to minimize splashing. Just before capping, a visual inspection of the lip and threads of the sample vessel should be made, and any foreign debris should be removed with a clean towel, allowing an airtight seal to form.

8.2 *Devices That Can be Used for Sampling a Cemented Material*—Samples of hard or cementitious material may be obtained by fragmenting a larger portion of the material using a clean chisel to generate aggregate(s) of a size that can be placed into a tared VOA vial or bottle. When transferring the aggregate(s), precautions must be taken to prevent compromising the sealing surfaces and threads of the container. Losses of VOCs by using this procedure are dependent on the location of the contaminant relative to the surface of the material being sampled. Therefore, caution should be taken in the interpretation of the data obtained from materials that fit this description. As a last resort when this task can not be performed on-site, a large sample can be collected in a vapor-tight container and transported to the laboratory for further processing (see 9.1 and 9.2). Collecting, fragmenting, and adding the sample to a container should be accomplished as quickly as possible.

8.3 *Devices That Can be Used for Sampling a Noncohesive Material*—When sampling gravel, or a mixture of gravel and fines, that cannot be easily obtained or transferred using coring tools, as a last resort, a sample can be quickly transferred using a spatula or scoop (see discussion concerning the use of a spatula or scoop to collect samples for VOC analysis, in Appendix X1). If the tared collection vial or bottle contains methanol or an aqueous solution, transfer the sample to the vial or bottle with minimal splashing and without the spatula or scoop contacting the liquid contents. For some solids, a wide-bottom funnel or similar channeling device may be necessary to facilitate transfer to the container and prevent compromising of the sealing surfaces of the container. Caution should be taken in the interpretation of the data obtained from materials that fit this description. Losses of VOCs are likely

because of the nature of the sampling method and the noncohesive nature of the material exposes more surface area to the atmosphere than for other types of samples. Another potential source of error during the sampling process, is the separation of coarser materials from fines, which can bias the concentration data if the different particle sizes, which have different surface areas, are not properly represented in the sample.

8.4 *Sampling Location Physical Characteristics*—Collect a separate co-located sample within a couple of centimeters and from the same stratum and place in a suitable container for the determination of percent moisture content of the waste or soil. This sample should be collected in a container suitable for the retention of soil moisture. The location adjacent to where the sample for VOC analysis was collected should be inspected visually and its characteristics logged. This adjacent material can also be retained for determining other relevant properties, such as general appearance, color, presence of oils, other visible signs of contamination, grain-size distribution, organic carbon content, etc. Collection of these ancillary samples should be performed after the collection of samples for VOC analysis.

9. Sample Storage, Transportation, and Preservation

9.1 Sample Storage and Transportation:

9.1.1 *General Considerations*—During an initial 48 h storage and transportation period, all samples for VOC analysis should be held in air-tight containers and cooled to at least $4 \pm 2^\circ\text{C}$.⁴ For storage periods beyond 48 h, these air-tight containers should contain a chemical preservative or be held under conditions that ensure retention of the analytes of concern (see 9.2).

9.2 Sample Preservation Beyond 48 Hours:

9.2.1 Currently, it is recommended that samples stored in an air-tight container should be held for no longer than 48 h at $4 \pm 2^\circ\text{C}$ prior to analysis or preservation. Longer storage times at $4 \pm 2^\circ\text{C}$ can be applied if it can be demonstrated that the VOC concentrations are not affected or that the data generated at the time of analysis meets the data quality objectives. Extended sample storage can be achieved by using either physical or chemical methods of preservation. Sample preservation can be initiated at the time of sample collection or after arrival in a laboratory.

9.2.2 *Physical Preservation*—Samples contained in a VOA vial, a bottle, or coring device are physically preserved by low temperature storage (for example, preferably in a freezer set for $-12 \pm 5^\circ\text{C}$, or by using a temporary refrigerant, for example, a mixture of salt and ice or dry ice, see Appendix X2). Under this condition, sample storage (total time period starting at collection) can be extended up to 14 days. Longer periods of low temperature storage can be used provided it can be demonstrated that the VOC concentrations are not affected or that the data generated at the time of analysis meets the data quality objective. When low temperature storage is used for samples intended for analysis by vapor partitioning, VOC free water and if required a PTFE or glass coated stir bar should be

⁴ SW-846, Method 5035 A (July 2002), 3rd Update.

present prior to adding the sample in the field (see 7.3.3). Special precautions may be necessary, for example, positioning the sample vessel on its side, when using a low temperature condition with VOA vials smaller than 40 mL, or when more than 5 mL of water is present, because of the potential for breakage caused by the formation of ice. When the sample is intended to be prepared by methanol extraction, this solvent can be introduced through the septa of the storage vessel after low temperature storage (see 7.3.4). In either case, immediately following low temperature storage of samples in VOA vials or bottles, the caps should be checked and tightened, if necessary. For coring tools used as storage containers, the sample is extruded into a prepared VOA vial after low-temperature storage (see Practice D6418).

9.2.3 *Chemical Preservation*—Samples immersed in methanol are chemically preserved. Under this condition, storage (total time period starting at collection) at $4 \pm 2^\circ\text{C}$ can be extended for up to 14 days. Longer periods of methanol preservation can be used provided if it can be demonstrated that the VOC concentrations are not affected or that the data generated at the time of analysis meets the data quality objectives. A chemical preservation method for samples intended to be analyzed by vapor partitioning, is acidification to a pH of 2 or less with either sodium bisulfate or hydrochloric acid. However, VOC-contaminated samples containing carbonates should not be added to an acidic solution because of effervescence (for guidance on testing for carbonates and the use of these acids to preserve samples, see Appendix X5). Precautions must also be taken when preserving by acidification because certain compounds within the following classes; olefins, ketones, esters, ethers, and sulfides, will react under a low pH condition (see Appendix X2 for other potential problems). Acidified sample storage (total time period starting at collection) can be extended for up to 14 days at $4 \pm 2^\circ\text{C}$. Longer periods of acidified sample storage can be used provided it can be demonstrated that the VOC concentrations are not affected or that the data generated at the time of analysis meets the data quality objectives.

10. Sample Preparation

10.1 *Methanol Extraction*—Completely disperse samples in methanol, if possible, by shaking, vortexing or by sonication. Allow suspended particulates to settle so that an aliquot of

clear supernatant can be removed for analysis. Some materials will show a slow release of VOCs to methanol; therefore, the dissolved VOC concentration may increase with increasing extraction time (see Appendix X1). This increased extraction of VOCs over time may be particularly pronounced with cementitious materials or materials that strongly adsorb VOCs. Transfer of an aliquot for analysis should be performed using a clean liquid-tight syringe (composed of glass and metal) to withdraw the aliquot through the septum of the sample container. If necessary, the cap of the sample container can be removed, and an aliquot can be collected with either a clean syringe or pipette. However, the time that the cap is off the sample container should be minimized as much as possible to limit volatilization losses of solvent and VOCs. For purge-and-trap analysis, methanol aliquot volumes of less than 0.2 mL are typically transferred to a vessel containing 5 mL of organic-free water. For headspace analysis, methanol aliquot volumes as large as 1.0 mL, depending on the detector and analytes of concern, can be transferred to VOA vials containing 10 mL of organic-free water. When the re-analysis of the sample extract is a possibility, an aliquot of the extract should be archived by transferring it to an airtight vial (for example, 2 mL) with a PTFE-lined cap.

10.1.1 Periodic weighing of the sample container can be used to determine if a hermetic seal is being maintained, that is, no weight loss of methanol.

10.2 *Vapor Partitioning*—Completely disperse samples in water, if possible, by shaking, vortexing or by sonication. This mixing of the solid material with the aqueous solution not only helps prevent the plugging of the sparging needle used by purge-and-trap systems but also assists in attaining an equilibrium state by completely exposing the sample to the partitioning solution. To enhance partitioning into the vapor phase, automated purge-and-trap and headspace analysis systems warm the sample to a selected temperature (typically 40°C for purge-and-trap, this temperature or higher for headspace) prior to removing vapors for analysis.

11. Keywords

11.1 field sampling; methanol extraction; sample collection; sample handling; soil; solid wastes; vapor phase partitioning; volatile organic compounds

APPENDIXES

(Nonmandatory Information)

X1. ADDITIONAL INFORMATION CONCERNING SAMPLE COLLECTION AND HANDLING FOR VOC ANALYSIS

X1.1 Volatile organic compounds (VOCs) are among the most frequently identified soil contaminants at Superfund and other hazardous waste sites. Because some VOCs are potentially mutagenic, carcinogenic, and teratogenic, they often are key factors in the risk assessment process at these sites. These risk assessments and other remedial decisions depend upon an accurate understanding of the levels and extent of VOC contamination in soils and other materials.

X1.2 In most materials, VOCs coexist as gaseous, liquid, and solid (sorbed) phases. The VOC equilibrium that exists among these phases is controlled by physiochemical properties, material properties, and environmental variables (1, 2).⁵ Unaccounted loss of analytes from any phase may result in rendering the sample unrepresentative of the material from which it was taken. For this reason, sample collection, handling, and analysis must be performed under conditions that maintain the accountability of all phases present (3).

X1.3 In general, uncontrolled losses of VOCs from materials occur through two mechanisms: volatilization and biodegradation. Volatilization losses occur whenever gaseous molecules, which have diffusion coefficients up to four orders of magnitude greater than liquid diffusion coefficients, are allowed to move freely. Therefore, whenever a new surface is exposed, VOC losses are incurred. The extent to which VOCs are lost depends on the vapor phase concentration (analyte vapor pressure), surface area exposed, duration of exposure, porosity of matrix, and perhaps meteorological conditions (4).

X1.4 Biological degradation of VOCs in samples is usually dominated by aerobic processes because many conventional intrusive collection methods expose the sample to the atmosphere. The rate of this biological degradation is dependent on several factors, including the indigenous microbiological population, chemical properties of the VOC, and temperature. Provided that sufficient quantities of electron acceptors, nutrients, and moisture are present, indigenous microbes continue to aerobically degrade compounds even when stored at 4°C (5). Non-halogenated aromatic compounds are quite susceptible to this loss mechanism. To inhibit biodegradation of these compounds, the sample can be immersed in methanol, frozen (see Appendix X2), or acidified to a pH of 2 or less.

X1.5 One sampling procedure that fails to achieve accountability of all VOC phases is the collection of a bulk sample by using a spatula-type device to completely fill a bottle for sample storage and transportation (4, 6-10). Samples collected and transferred with spatula-type devices fail to control surface area exposure. Moreover, in the process of filling a bulk sample

bottle to capacity, the sealing surfaces often become compromised (dirty), preventing a vapor-tight seal during storage. For these reasons this procedure has been shown to result in concentrations that are less than 10 % of the in-situ contamination (6-9).

X1.6 Another procedure that often performs poorly is the use of core barrel liners covered with either PTFE or aluminum foil for sample transportation and storage, because these barriers fail to serve as air-tight seals (3, 11). Sheets of PTFE that are only 0.05 or 0.08 mm thick are easily penetrated by VOC vapors. Elastic formulations of PTFE (for example, white plumber's tape) show much greater rates of VOC penetration than non-elastic semi-translucent formulations. Aluminum foil fails because an airtight seal is often not achieved when this material is folded over the end of a core barrel liner and it sometimes corrodes allowing small holes to form. The addition of plastic caps and sealing tape does not improve the performance of either PTFE or aluminum foil, since pliable plastics sorb VOCs and sealing tapes often contain VOCs in the adhesive, which serves as a potential artifact source.

X1.7 The procedures discussed in this guide are designed to limit VOC losses by volatilization and biodegradation. This is accomplished by stressing that (1) samples be collected only from freshly exposed surfaces, (2) collection and transfer of a sample be performed quickly and with minimal disruption to its physical state, (3) samples be held under conditions that ensure retention of the analytes of interest, and, (4) in the case of samples collected for vapor partitioning methods of analysis (purge-and-trap or headspace), the VOA vial's airtight seal never be broken prior to analysis.

X1.8 An additional source of inaccuracy in VOC analyses is their incomplete extraction from the sampled material (12-17). This source of error can either be due to differences between sample preparation methods (that is, methanol extraction versus vapor partitioning) or the kinetics of the desorption processes. In general, as the indigenous total organic carbon content increases in a matrix, recoveries using vapor partitioning methods would be expected to decrease compared to methanol extraction, particularly for the more hydrophobic analytes (17). Heat or sonication, or both, have been shown to speed up desorption processes (that is, mass transfer of analyte from the sampled matrix to the vapor phase or methanol); therefore, these more aggressive extraction steps should be considered when a total VOC concentration is needed. In some instances, incomplete extraction due to either the method used or the kinetics associated with the release of VOCs from a given matrix can result in an under estimation (perhaps as much as an order of magnitude) of the total VOC concentration present in a sample (12, 14, 16, 17).

⁵ The boldface numbers in parentheses refer to a list of references at the end of this standard.

X2. INFORMATION ON THE PRESERVATION OF SAMPLES BY STORAGE UNDER LOW TEMPERATURE CONDITIONS

X2.1 Losses of VOCs due to biological degradation can be abated by storing samples at low temperatures, for example, in a freezer set at $-12 \pm 5^\circ\text{C}$ (D6418, 18, 19). This method of preservation offers several advantages over the recommended in-field chemical preservation option: no prior knowledge of the VOC concentrations is necessary, fewer Department of Transportation (DOT) regulatory requirements must be met, and field personnel don't have to handle chemical solutions or weigh samples. Moreover, freezing, rather than acidification, can be used to preserve VOCs in carbonaceous soils. An additional concern with sample acidification is that with some soil matrices, the formation of acetone, a regulated compound itself, has been observed.

X2.2 Low temperatures that will freeze a soil sample can be achieved with a freezer, by mixing table salt and ice together, or by using dry ice. It is recommended that a freezer be used in preference to these other temporary refrigerants, whenever possible. These other methods of achieving low temperatures that will freeze soil are intended for short term use (1 to 3 days), and should only be used when the following precautions are taken. When using salt and ice, this mixture should be contained in plastic bags, a high quality cooler should be used, and this refrigerant should be replaced when the cooler temperature reaches -5°C . Use a thick walled Styrofoam cooler packed so that about two thirds of its volume is filled with bags

containing a 1:3.6 weight ratio of NaCl to ice; initially establish a temperature of $-14 \pm 3^\circ\text{C}$, and keep below -5°C for up to 20 h (18). However, a shorter period of refrigeration below -5°C would most likely have resulted if the cooler had been opened frequently for adding or removing samples. If dry ice is used it should be placed below and above the sample containers while not coming into direct contact with them. This can be accomplished by placing the sample containers inside a cardboard box that is then placed inside the cooler with dry ice packed around the sample box. This precaution is necessary because when dry ice comes into direct contact with some plastic materials it can cause them to crack, or may cause the seal on a bottle to fail because materials (that is, glass and plastic) have different contractile properties. The temperature inside a cooler packed with dry ice usually cannot be measured with conventional thermometers, since it is often below -20°C . This extreme low temperature may affect the integrity of the seals of the sample container. There are also some special shipping concerns with the use of these two temporary refrigerants. For the salt and ice mixture, the shipping period and conditions should be closely tracked so that the cooler temperature remains below -5°C . When dry ice is used as a refrigerant, a placard must be placed on the outside of the cooler identifying the presence of this refrigerant and its weight.

X3. TECHNIQUES FOR SCREENING AND SUBSAMPLING SUBSURFACE SOIL CORES FOR VOC ANALYSIS

X3.1 The three techniques described below were developed to provide ways of screening and subsampling soil from the liners used in single tube direct push subsurface sampling systems to help reduce the potential for loss of VOCs during screening and sample collection. The techniques provide easy soil screening without violating the integrity of the soil that will be sampled for analysis. They maintain the integrity of the soil during sample collection and provide very short exposure time of the soil to the atmosphere during sampling.

X3.1.1 *Direct Subsurface Soil Sampling Technique*—For this technique, the liner, which is approximately 1-mm thick polyvinyl chloride (PVC) and has a series of circular perforations along a portion of its length that alternate in diameter, is wrapped in shrink wrap (see Notes X3.1 - X3.3). The perforations are spaced 4 cm apart (see X3.4). The location and number of the perforations in the liner should be such that the liner will be completely filled with soil over the length having the perforations for sample screening and collection. Any portion of the liner not completely filled with soil should not be screened or sampled. The diameter of the circular perforations that will be used for screening is 6 mm. The diameter of each circular perforation that will be used for sample collection is the dimension required for easy insertion of the hand-operated coring device that will be inserted into the hole to collect a sample (see Fig. X3.1). When a soil core is brought to the

surface and removed from the soil sampler tube, the shrink wrap is cut and removed to expose the 6-mm perforated circles for screening. The perforated circles in the liner are removed to expose the soil (see Note X3.5). The headspace above the exposed soil can be screened using a photoionization detector (PID) or other appropriate device to determine which adjacent larger perforated circles should be removed for soil collection for VOC analysis. For sample collection, the shrink wrap is removed to expose the larger perforated circle, the perforated circle is removed, and a hand-operated coring device is quickly inserted into the hole in the liner to collect the freshly exposed soil sample. If the sample is collected using a coring device designed for transferring the sample to a storage container, the sample should be immediately extruded into an appropriate container for storage and transportation to the laboratory. If the sample is collected in a coring device designed to store the sample, the open end of the device should be immediately capped after quickly ensuring that the sealing surfaces are clean (see 8.1.2 and 9.1.1).

NOTE X3.1—Preparation of sample liners, including cutting perforations into the liner or cutting the liner into sections followed by shrink wrapping the sample liners, occurs prior to the start of sample collection. The shrink-wrapped liners are at ambient temperatures when sample collection is started.

NOTE X3.2—Shrink wrap is applied to sample liners having perforations or cuts in them to prevent loss of VOCs and to prevent any fine-grained soil from going through the perforations or cuts and getting

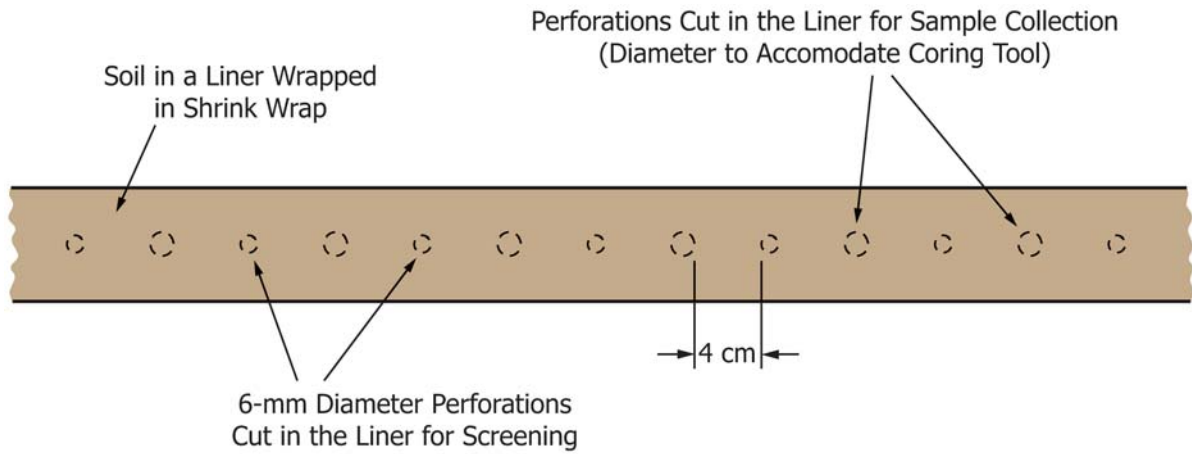


FIG. X3.1 Partial Liner Configuration for the Direct Subsurface Soil Sampling Technique (not to scale)

between the sample liner and the soil sampler tube. If this happens, it is difficult to remove the sample liner from the soil sampler tube. To prevent the shrink wrap from crinkling and potentially ripping when the shrink wrapped sample liner is inserted into the soil sampler tube, the shrink wrap is sized such that when it is shrunk around the liner, the fit is tight enough so the liner will slide into the soil sampler tube without interference from the shrink wrap. Instructions for shrink wrapping the sample liners can be obtained from the shrink wrap supplier.

NOTE X3.3—The shrink wrap that was used in the field testing described in X3.3 is flexible, thin-walled PVC heat shrinkable tubing, having a thickness of 0.1016 mm and a shrink temperature of 100°C.

NOTE X3.4—For the field work described in X3.3, the perforations were made using a hole saw.

NOTE X3.5—For the field work described in X3.3, perforations were

removed by cutting the remaining liner material using a razor knife. A tool, such as a flat-blade screwdriver could also be used to lift one side of the perforated circular section, and by rotating the screwdriver, the tabs attaching it to the sample liner could be broken.

X3.1.2 *Direct Subsurface Soil Sampling Technique Using a Cutting Tool*—For this technique, the liner, which is approximately 1-mm thick PVC, is intact and is not wrapped in shrink wrap. The soil core in the liner is brought to the surface, removed from the soil sampler tube, and placed in a metal rack for sub-sampling. A cutting tool powered by a portable drill is used to cut circles in the liner (see Fig. X3.2 and Note X3.6). Circles may be cut through the liner at the selected spacing

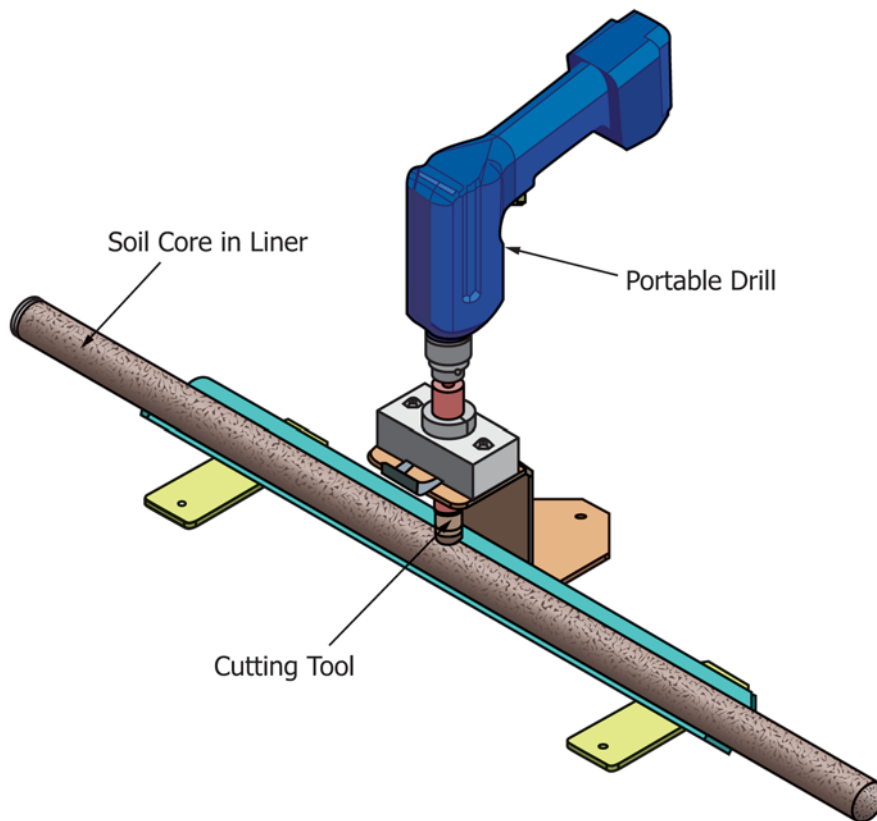


FIG. X3.2 Direct Subsurface Soil Sampling Technique Using a Cutting Tool

interval defined in the project sampling plan or based on field observation and experience. Circles can be cut in the liner over the length of the liner that is completely filled with soil for sample screening and collection. Any portion of the liner not completely filled with soil should not be screened or sampled. The diameter of each circle is the dimension required for easy insertion of the hand-operated coring device to be inserted into the hole resulting when the cut liner is removed for sample collection. The cut circles in the liner can be removed to expose the soil for screening. The headspace above the exposed soil can be screened using a PID or other appropriate device to determine which adjacent cut circles should be removed for soil collection for VOC analysis. For sample collection, the cut circle is removed and a hand-operated coring device is quickly inserted into the hole in the liner to collect the freshly exposed soil sample (see Note X3.7). If the sample is collected using a coring device designed for transferring the sample to a storage container, the sample should be immediately extruded into an appropriate container for storage and transportation to the laboratory. If the sample is collected in a coring device designed to store the sample, the open end of the device should be immediately capped after quickly ensuring that the sealing surfaces are clean (see 8.1.2 and 9.1.1).

NOTE X3.6—For the field work described in X3.3, the bit of the cutting tool was a stainless steel cylinder, 2.9 cm in length by 2.1 cm outer diameter. The upper half of the bit was equipped with a square fitting for attachment to the shaft of a conventional portable drill. 1.3 cm of the other end of the bit was hollow with the end milled to a sharp cutting edge. For discussion on the generation of heat from use of the powered cutting tool during field testing and the effect on VOC concentration, see X3.3.1.

NOTE X3.7—Because the sample liner is approximately 1-mm thick, only a small amount of cuttings are generated when circles are cut in the liner with the cutting tool. These cuttings tend to accumulate away from the soil core; however, if some cuttings fall onto the surface of the freshly exposed soil, they should be quickly removed before sample collection.

X3.1.3 *Sectioned Subsurface Soil Sampling Technique*—For this technique, a portion of the length of the liner is cut into alternating sections of suggested lengths of 8 cm and 5 cm (See Fig. X3.3). The location and number of the sections in the liner should be such so that the sections will be completely filled with soil for sample screening and collection. Any sections not completely filled with soil should not be screened or sampled. The 8-cm sections have a centered 6-mm perforated circle to

provide access for soil headspace screening (see Note X3.4). The liner with the cut sections and perforated circles is wrapped in clear shrink wrap (See Notes X3.1 - X3.3). When the soil core is brought to the surface and removed from the soil sampler tube, the shrink wrap is cut and removed to expose the 6-mm perforated circles for screening. The perforated circles in the liner are removed to expose the soil (see X3.5). The headspace above the exposed soil is screened using a PID or other appropriate device to determine which adjacent sections of soil should be sampled for VOC analysis. For sample collection, the shrink wrap is removed to expose the selected section for sampling. The soil in the cut liner section selected is immediately cut and the liner section with the soil is removed from the remaining soil core. The section is turned on one end and a hand-operated coring tool is used to collect a freshly exposed soil sample from the other end of the section. If the sample is collected using a coring device designed for transferring the sample to a storage container, the sample should be immediately extruded into an appropriate container for storage and transportation to the laboratory. If the sample is collected in a coring device designed to store the sample, the open end of the device should be immediately capped after quickly ensuring that the sealing surfaces are clean (see 8.1.2 and 9.1.1).

X3.2 A field study has shown that VOCs (Trichloroethene, 1,1,1-Trichloroethane, and cis-1,2-Dichloroethene) can be lost from coarse, sandy-type soils collected by a single tube direct push system when a horizontal strip of the soil core liner is removed for screening and subsampling. This is most likely due to exposure of the soil particles to the atmosphere during screening and sample collection and disruption of soil integrity during sample collection. The techniques discussed above provide easy soil screening without violating the integrity of the soil that will be sampled for analysis. These techniques maintain the integrity of the subsurface soil during sample collection and provide very short exposure time of the soil to the atmosphere during sampling. As a result, the potential for VOC loss from coarse, sandy soil types would be reduced by use of one of these techniques.

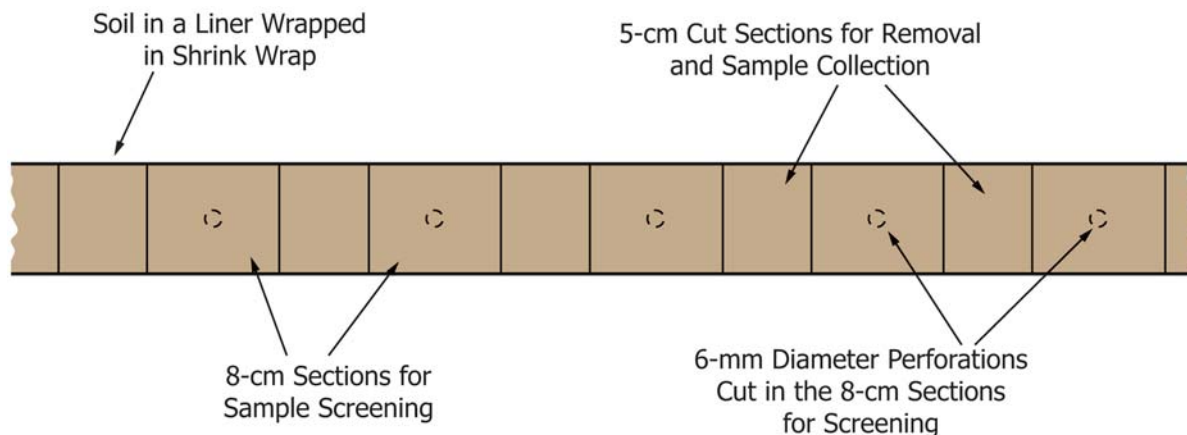


FIG. X3.3 Partial Liner Configuration for the Sectioned Subsurface Soil Sampling Technique (not to scale)

X3.3 A field study has shown that when a horizontal strip of the soil core liner is removed to expose soil for screening and subsampling tightly compacted clay-type soil collected using a single tube direct push system, there is statistically no difference at the 95 % confidence level in VOC (chloroform, carbon tetrachloride, trichloroethylene, benzene, ethylbenzene, and o-xylene) concentrations in the sample collected from the exposed soil and the samples collected using the three techniques described above. The outdoor temperatures during this study ranged from 28 to 33°C.

X3.3.1 Results from this field testing show that there is statistically no difference at the 95% confidence level in the concentrations of chloroform, carbon tetrachloride, trichloroethylene, benzene, ethylbenzene, and o-xylene in the samples collected using the three techniques for sampling

tightly compacted clay soil. These data indicate that no significant loss of the volatile compounds occurred due to generation of heat from use of the powered cutting tool for the direct subsurface soil sampling. In using the cutting tool, minimal heat was generated. The PVC liners are relatively thin at about 1-mm in thickness so the time to cut through the liner was less than 5 to 10 s. Coring bits must be changed or decontaminated between each circle that is cut so heat build-up due to long-term operation of the coring tool does not occur.

X3.4 The results discussed in X3.2 and X3.3 suggest for loose, coarse, sandy soil types, use of one of the techniques described above would be an additional precaution to help prevent VOC loss during subsampling. In turn, when sampling tightly compacted clay soils, the extra precaution does not seem to be needed based on current data.

X4. EVALUATING THE PERFORMANCE OF HAND-OPERATED CORING DEVICES TO STORE SOIL SAMPLES FOR VOC ANALYSIS

X4.1 Hand-operated coring devices that are used to store soil samples containing VOCs shall be evaluated using the procedure described below to ensure that the main body of the device is constructed of material that is nonreactive and that the device has airtight seals that show limited sorption and diffusive passage of VOCs. Any alternate evaluation technique shall produce equal or better recoveries of the compounds stated in this appendix.

X4.1.1 At least one soil type of known composition (that is, % sand, silt, clay, organic matter/carbon content, and moisture content) should be used in the evaluation.

X4.1.2 Sample storage in the hand-operated coring device at $4 \pm 2^\circ\text{C}$ for 48 h should be evaluated. See 9.1.

X4.1.3 The soil should be collected in a minimum of 10 coring devices. The coring devices containing the soil should be cooled to approximately 4°C prior to spiking to reduce the loss of VOCs during spiking. Gasoline-saturated water is recommended for preparing the spiking solution because it will hold VOCs better than water alone, so they will not be lost during the spiking procedure. An aqueous-based solution should be used to spike the soil samples, because an organic-based solution, such as a methanol solution, will have a very strong affinity for the VOCs and they may not be lost from the sampler even if it is constructed of a reactive material or does not have airtight seals, or both. A spiking solution consisting of pure water spiked with VOCs is difficult to use in this procedure because water has a low affinity for VOCs and the VOCs can be lost during the spiking procedure. Benzene and toluene are added to the spiked soil by the gasoline-saturated water. Ten other VOCs should be added to the spiking solution to give low-level VOC concentrations (<200 µg/Kg) in the spiked soil. The VOCs that are used should include petroleum-based and chlorinated solvent-based VOCs commonly found in VOC-contaminated soil. Recommended VOCs for evaluating the performance of hand-operated coring devices to store samples for VOC analysis are listed in Table X4.1 (see Practice D6418).

TABLE X4.1 Recommended Analytes for Evaluating the Performance of Hand-Operated Coring Devices to Store Samples for VOC Analysis

| |
|---|
| Vinyl Chloride |
| Methylene Chloride (MeCl ₂) |
| Methyl Tert-Butyl Ether (MTBE) |
| 1, 1-Dichloroethane |
| cis-1,2-Dichloroethylene (CDCE) |
| Chloroform |
| Benzene |
| Trichloroethylene (TCE) |
| Toluene |
| Tetrachloroethylene (PCE) |
| Ethyl Benzene |
| o-Xylene |

X4.1.4 Preparation of the Reagents:

X4.1.4.1 *Preparation of Gasoline-Saturated Water*—Add 250 µL of gasoline to approximately 80 mL of Type II reagent water (see D1193) in a 100-mL volumetric flask and dilute the solution to volume using Type II reagent water. Stir the mixture for 24 h, and then separate the gasoline from the water using a separatory funnel. Add approximately 39 mL of the gasoline-saturated water to a 40-mL VOA vial, so that the gasoline-saturated water fills the VOA vial, except for approximately 1 mL of headspace at the top of the vial.

X4.1.4.2 *Preparation of the Stock Solution*—Prepare a stock solution containing the analytes of interest, except for benzene and toluene, in methanol so that the concentration of each analyte in the solution is approximately 500 µg/mL. Benzene and toluene are added to the spiked soil by the gasoline-saturated water, and should not be added to the stock solution.

X4.1.4.3 *Preparing the Spiking Solution*—Inject 400 µL of the stock solution through the septum of the 40-mL VOA vial containing the gasoline-saturated water. Shake the VOA vial to mix the solution. Cool the spiking solution to approximately 4°C before using it to spike the soil samples. The spiking solution is cooled to reduce the loss of the VOCs from the solution during the spiking procedure.

X4.1.5 Sample Spiking, Storage, and Analysis:

X4.1.5.1 To evaluate hand-operated coring devices that are designed to collect approximately 5-g samples, spike the middle of each soil core in the coring devices with 100 μL of the spiking solution using a gas-tight syringe. Carefully and quickly remove the needle from the soil, wipe the sampler to remove any particles that will interfere with sealing, and cap the device. For evaluating hand-operated coring devices that are designed to collect approximately 25-g samples, 0.5 mL of spiking solution should be used to spike the samples as described above.

X4.1.5.2 Spiking the 5-g devices with 100 μL of spiking solution and the 25-g devices with 0.5 mL of spiking solution will give an approximate concentration of 100 $\mu\text{g}/\text{Kg}$ of each analyte of interest in the samples, with the exception of benzene, toluene, and possibly o-xylene and ethyl benzene. Because of their presence in the gasoline-saturated water, the concentrations of these compounds will most likely be greater than 100 $\mu\text{g}/\text{Kg}$.

X4.1.5.3 After the spiked samples are prepared, one half of the samples should be randomly selected for extrusion and analysis to give time-zero concentrations of the analytes of interest. The remaining samples should be stored at $4 \pm 2^\circ\text{C}$ for 48 h. The storage temperature should be monitored to ensure that the temperature is maintained at $4 \pm 2^\circ\text{C}$ during the storage time. After the samples are stored for 48 h, they must be extruded and analyzed using the same procedures that were used for the time-zero samples.

X4.1.6 Data Evaluation:

X4.1.6.1 To evaluate the data, the mean concentration of the analyte of interest calculated using the data from the stored samples should be compared to the mean concentration of the analyte of interest calculated using the data from the time-zero samples by calculating average percent recovery using [Eq X4.1](#).

$$\text{Ave. \% rec.} = (\bar{x}_{\text{stored}}/\bar{x}_{T=0}) 100 \% \quad (\text{X4.1})$$

where:

Ave. % rec. = average percent recovery of the analyte of interest from the stored sample,
 \bar{x}_{stored} = mean concentration of the analyte of interest in the stored samples, and
 $\bar{x}_{T=0}$ = mean concentration of the analyte of interest in the time-zero samples.

X4.1.6.2 Average percent recovery values for VOCs in soil stored in hand-operated coring devices must be 80 % or greater.

X4.1.6.3 The percent relative standard deviation of the concentration values in the time-zero and stored sample sets should also be calculated for each analyte of interest to show the variation between the concentration values used to calculate the mean concentration for each sample set. The percent relative standard deviation should be calculated using [Eq X4.2](#) and typically should be 10 % or less.

$$\% \text{ rel. std. dev.} = (s/\bar{x})/100 \% \quad (\text{X4.2})$$

where:

% rel. std. dev. = percent relative standard deviation of the concentration values in the sample set for the analyte of interest,
 s = standard deviation of the concentration values in the sample set for the analyte of interest, and
 \bar{x} = mean concentration of the sample set for the analyte of interest.

X5. TESTING FOR CARBONATES AND ACID PRESERVATION

X5.1 Soil or waste samples may contain carbonates that will generate carbon dioxide gas (CO_2) when in contact with acid preservatives. The generation of CO_2 may drive off VOCs and cause sample containers to fail due to increased pressures within the container. To determine whether carbonates are present in waste or soil, the following test should be performed.

X5.1.1 Moisten approximately 1 g of sample material that has been placed on a watch glass or similar surface with water, then stir to remove any trapped air.

X5.1.2 Add drop-wise a cold solution of 4N HCl to the moistened material while observing for effervescence using a hand lens. If effervescence (rapid formation of bubbles) is

observed, then preservation by acidification is not appropriate. If effervescence is not observed samples can be preserved by acidification.

X5.1.3 To determine the amount of hydrochloric acid or sodium bisulfate required to give a pH of 2 or less add the prescribed (usually 5 g) amount of sample material to a vessel containing 5 mL of water, mix thoroughly, then slowly add one of these acids while monitoring that pH. The volume or weight of acid determined to be necessary to achieve a pH of 2 or less should then be added to vials containing 5 mL of water, prior to adding samples of similar materials.

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