



# Standard Guide for Sampling Waste and Soils for Volatile Organic Compounds<sup>1</sup>

This standard is issued under the fixed designation D 4547; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

## 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 D 4687.

1.5 *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.* See 7.2 and 8.1.1 for specific warnings.

## 2. Referenced Documents

### 2.1 ASTM Standards:

D 3550 Practice for Thick Wall Ring-Lined, Split Barrel, Drive Sampling of Soils<sup>2</sup>

D 4687 Guide for General Planning of Waste Sampling<sup>3</sup>

D 4700 Guide for Soil Sampling from the Vadose Zone<sup>2</sup>

D 5058 Test Methods for Compatibility of Screening Analysis of Waste<sup>3</sup>

D 5792 Practice for Generation of Environmental Data Related to Waste Management Activities: Development of Data Quality Objectives<sup>3</sup>

D 6051 Guide for Composite Sampling and Field Subsampling for Environmental Waste Management Activities<sup>3</sup>

D 6418 Practice for Using the Disposable En Core Sampler

for Sampling and Storing Soil for Volatile Organic Analysis<sup>3</sup>

D 6640 Practice for Collection and Handling of Soils Obtained in Core Barrel Samplers for Environmental Investigations<sup>3</sup>

E 856 Definitions of Terms and Abbreviations Relating to Physical and Chemical Characteristics of Refuse-Derived Fuel<sup>3</sup>

### 2.2 Federal Standard:

Title 49 Transportation, Code of Federal Regulations (CFR), Part 172, List of Hazardous Substances and Reportable Quantities<sup>4</sup>

## 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. **(E 856)**

3.2 *subsample, n*—a portion of a sample taken for the purpose of estimating properties or composition of the whole sample. **(D 6051)**

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 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 and headspace). The method of sample preparation for VOC analysis should be consistent with the data quality objectives (see Practice D 5792).

## 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

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<sup>2</sup> *Annual Book of ASTM Standards*, Vol 04.08.

<sup>3</sup> *Annual Book of ASTM Standards*, Vol 11.04.

<sup>4</sup> Available from Superintendent of Documents, U.S. Government Printing Office, Washington, DC 20402.

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 and Appendix X2. 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 D 5792). 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 D 5058) 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 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 or headspace analysis.

6.2.2 Advantages of methanol extraction are (1) large samples or composite samples, or both, can be collected to enhance representativeness (see Guide D 6051), (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

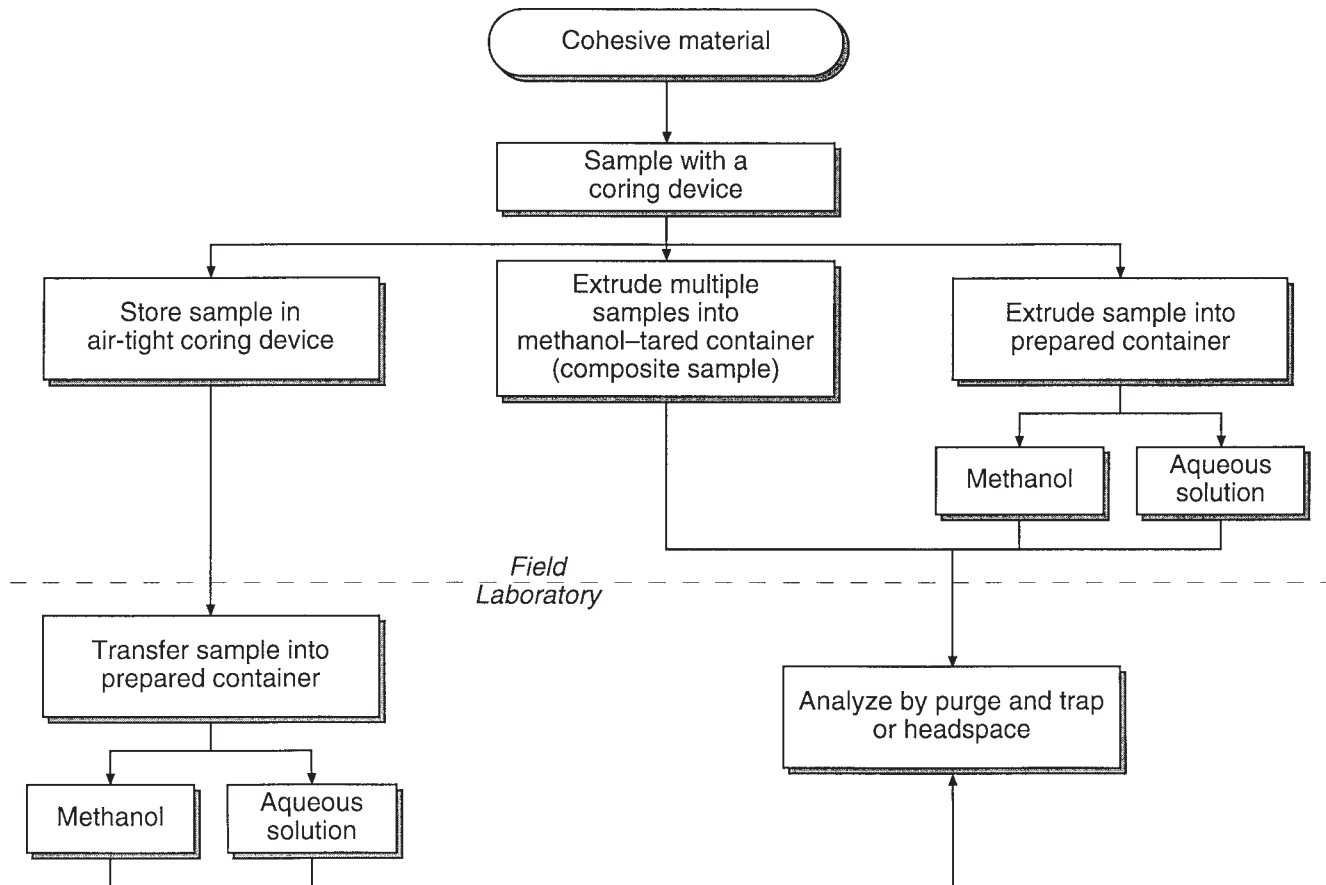


FIG. 1 Sample Handling Options for Cohesive Materials

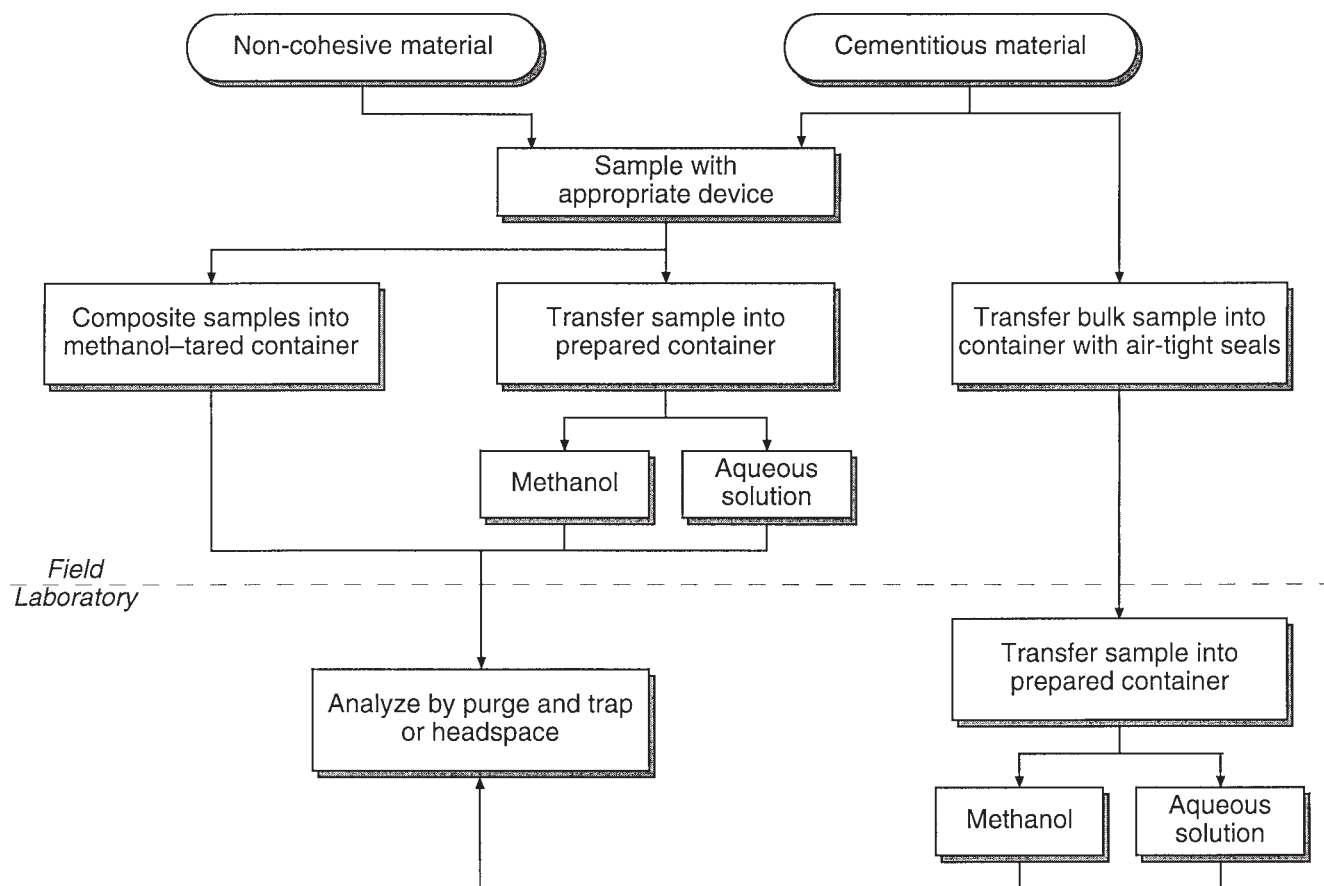


FIG. 2 Sample Handling Options for Non-Cohesive and Cementitious Materials

(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 or headspace. In both cases, the sample is placed into a tared volatile analysis (VOA) vial 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, 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 polytetrafluorethylene (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. 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 materials from subsurface regions. Most of the equipment used to obtain samples from the subsurface was originally developed for the geotechnical industry. These subsurface bulk sample retrieval systems are designed to obtain intact cylindrical cores of material, ranging anywhere from 1 to 4 in. in diameter, and 1 to several ft in length. Two commonly used collection devices for subsurface sample collection are the split-spoon corer that opens to expose the entire length of the material obtained for subsampling and core barrel liners (that is, ring-lined barrel sampling, see Practice D 3550) that typically are subsampled through the open ends. Core barrel liners fit snugly within a corer and come in a variety of lengths and materials (stainless steel, brass, PTFE, rigid plastics, etc.). Several liners, or a single long liner, can be placed within the core barrel, depending on the sampling plan (See **Warning** at the end of this paragraph). Additional information on the application and design of different types of subsurface collection systems available can be found in Guide D 4700. 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 of a bulk sample should occur within a couple minutes of its being brought to the surface (see 8.1 through 8.3 for additional sampling guidance). (**Warning**—Core barrel liners are not recommended for storage of samples intended for VOC analysis because they do not have airtight seals (see Appendix X1).)

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-cm<sup>3</sup>

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) for more than a few seconds, the main body should be constructed of materials that are nonreactive and have airtight seals that show limited sorption and penetration of VOCs. 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 10 mil.

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 D 4687). 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 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

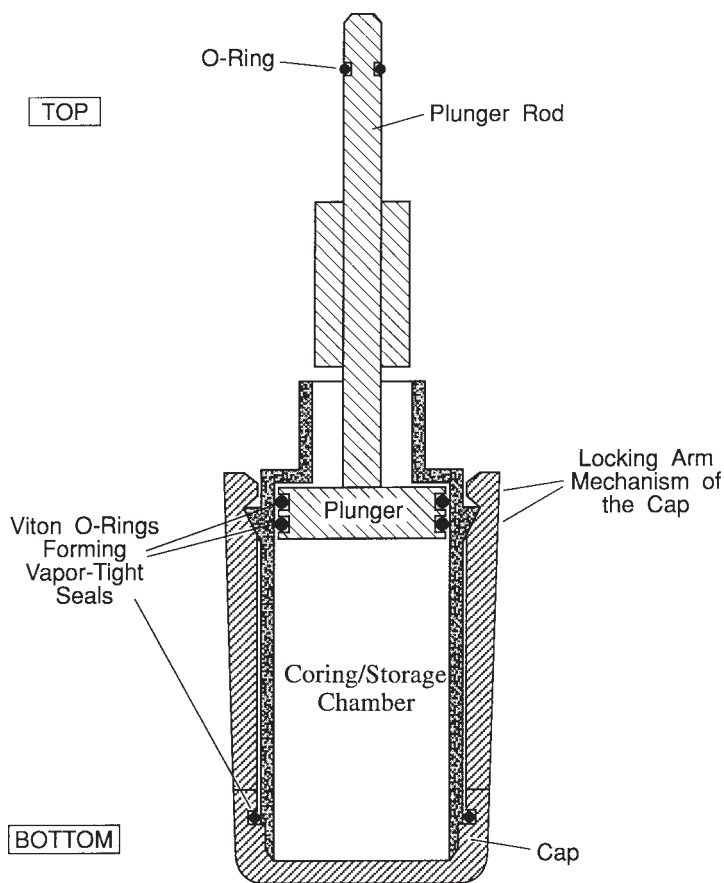


FIG. 3 Components of the En Core Sampler

use 44- (or 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 23-gage or smaller needle 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.)

## 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 an intact pit face or the relatively undisturbed contents of a split-barrel sampler or a core barrel liner. 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<sup>3</sup> volume would need to be collected (assuming the soil has density of 1.7 g/cm<sup>3</sup>). 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 (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 (see **Warning** at the end of this paragraph). 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 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. (**Warning**—This type of coring device is not appropriate for sample storage.)

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 is an En Core<sup>5</sup> sampler and it 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 compromise 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,

<sup>5</sup> En Core sampler, En Novative Technologies, Inc., 1241 Bellevue St, Green Bay, WI 54302. The En Core sampler is covered by a patent. Interested parties are invited to submit information regarding the identification of an alternative(s) to this patented item to the ASTM Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend.

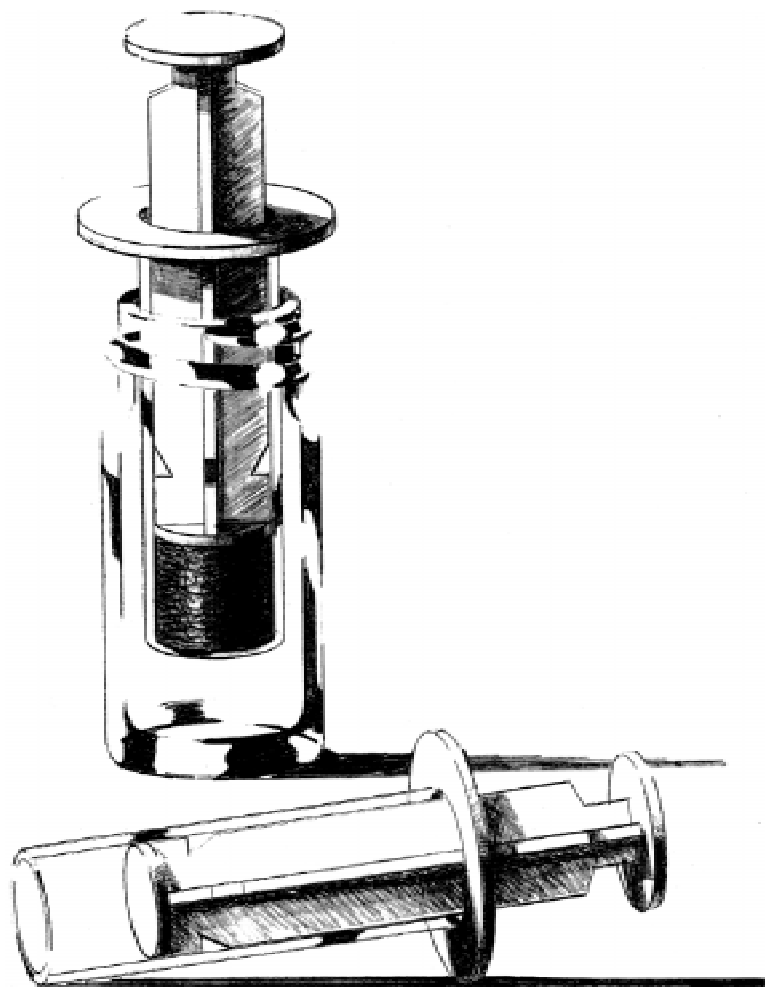


FIG. 4 A Coring Tool Made by Cutting the Tip Off a Plastic Syringe

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 can not 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  $4 \pm 2^\circ\text{C}$ .<sup>6</sup> For storage periods beyond 48 h, these air-tight containers (for example, VOA vial or En Core sampler [see Note 1]), should contain a chemical preservative or be held under conditions that ensure retention of the analytes of concern (see 9.2).

NOTE 1—The disposable En Core sampler is a coring device for collection, storage, and transfer of soil samples. This device meets the specifications discussed in 7.2.1 and 8.1.1. Guidance on the use of the En Core sampler is given in Practice D 6418.

### 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 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 the En Core sampler, the sample is extruded into a prepared VOA vial after low-temperature storage (see Practice D 6418).

**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

<sup>6</sup> SW-846, Method 5035, 3rd Update.

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 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 X3). 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  $40^\circ\text{C}$  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).<sup>7</sup>

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).

<sup>7</sup> The boldface numbers in parentheses refer to a list of references at the end of this standard.



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 2 or 3 mil (mil = 0.001 in.) 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).

## 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  $-12 \pm 5^\circ\text{C}$  (D 6418, 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  $-5^\circ\text{C}$ . 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  $-5^\circ\text{C}$  for up to 20 h (18). However, a shorter period of refrigeration below  $-5^\circ\text{C}$  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 can not be measured with conventional thermometers, since it is often below  $-20^{\circ}\text{C}$ . 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  $-5^{\circ}\text{C}$ . 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. TESTING FOR CARBONATES

X3.1 Soil or waste samples may contain carbonates that will generate carbon dioxide gas ( $\text{CO}_2$ ) when in contact with acid preservatives. The generation of  $\text{CO}_2$  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.

X3.1.1 Moisten approximately 1 g of sample material that has been placed on a watch glass or similar surface with water, than stir to remove any trapped air.

X3.1.2 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. 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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