



Designation: **D4547–15** **D4547 – 20**

Standard Guide for Sampling Waste and Soils for Volatile Organic Compounds¹

This standard is issued under the fixed designation D4547; 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 (ϵ) 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 [D4687](#).

1.5 This guide offers an organized collection of information or a series of options and does not recommend a specific course of action. This document cannot replace education or experience and should be used in conjunction with professional judgment. Not all aspects of this guide may be applicable in all circumstances. This ASTM standard is not intended to represent or replace the standard of care by which the adequacy of a given professional service must be judged, nor should this document be applied without consideration of a project's many unique aspects. The word "standard" in the title of this document means only that the document has been approved through the ASTM consensus process.

1.6 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard. Reporting of test results in units other than SI shall not be regarded as nonconformance with this standard.

1.7 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~~ safety, health, and ~~health~~ environmental practices and determine the applicability of regulatory limitations prior to use.

1.8 This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.

2. Referenced Documents

2.1 *ASTM Standards:*²

¹ This guide is under the jurisdiction of ASTM Committee [D34](#) on Waste Management and is the direct responsibility of Subcommittee [D34.01.02](#) on Sampling Techniques. Current edition approved ~~Sept. 1, 2015~~ Sept. 1, 2020. Published ~~October 2015~~ September 2020. Originally approved in 1991. Last previous edition approved in ~~2009~~ 2015 as ~~D4547–09~~ D4547 – 15. DOI: ~~10.1520/D4547-15.10.1520/D4547-20.~~

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.

D1193 Specification for Reagent Water

~~D1586~~D1586/D1586M Test Method for Standard Penetration Test (SPT) and Split-Barrel Sampling of Soils

~~D3550~~D3550/D3550M 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

D6232 Guide for Selection of Sampling Equipment for Waste and Contaminated Media Data Collection Activities

~~D6282~~D6282/D6282M 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 (Withdrawn 2018)³

D6640 Practice for Collection and Handling of Soils Obtained in Core Barrel Samplers for Environmental Investigations

D8170 Guide for Using Disposable Handheld Soil Core Samplers for the Collection and Storage of Soil for Volatile Organic Analysis

2.2 *Federal Standard*:⁴

Title 49 Code of Federal Regulations (CFR), Title 49, Part 172 Transportation, Code of Federal Regulations (CFR), Part 172, List of Hazardous Substances and Reportable Quantities

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)

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3.1.2.1 *Discussion*—

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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, 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

³ The last approved version of this historical standard is referenced on www.astm.org.

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

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](#), [Appendix X3](#), [Appendix X4](#), [Appendix X5](#), [Appendix X6](#), [Appendix X7](#), [Appendix X8](#), [Appendix X9](#), [Appendix X10](#), [Appendix X11](#), [Appendix X12](#), [Appendix X13](#), [Appendix X14](#), [Appendix X15](#), [Appendix X16](#), [Appendix X17](#), [Appendix X18](#), [Appendix X19](#), [Appendix X20](#), [Appendix X21](#), [Appendix X22](#), [Appendix X23](#), [Appendix X24](#), [Appendix X25](#), [Appendix X26](#), [Appendix X27](#), [Appendix X28](#), [Appendix X29](#), [Appendix X30](#), [Appendix X31](#), [Appendix X32](#), [Appendix X33](#), [Appendix X34](#), [Appendix X35](#), [Appendix X36](#), [Appendix X37](#), [Appendix X38](#), [Appendix X39](#), [Appendix X40](#), [Appendix X41](#), [Appendix X42](#), [Appendix X43](#), [Appendix X44](#), [Appendix X45](#), [Appendix X46](#), [Appendix X47](#), [Appendix X48](#), [Appendix X49](#), [Appendix X50](#), [Appendix X51](#), [Appendix X52](#), [Appendix X53](#), [Appendix X54](#), [Appendix X55](#), [Appendix X56](#), [Appendix X57](#), [Appendix X58](#), [Appendix X59](#), [Appendix X60](#), [Appendix X61](#), [Appendix X62](#), [Appendix X63](#), [Appendix X64](#), [Appendix X65](#), [Appendix X66](#), [Appendix X67](#), [Appendix X68](#), [Appendix X69](#), [Appendix X70](#), [Appendix X71](#), [Appendix X72](#), [Appendix X73](#), [Appendix X74](#), [Appendix X75](#), [Appendix X76](#), [Appendix X77](#), [Appendix X78](#), [Appendix X79](#), [Appendix X80](#), [Appendix X81](#), [Appendix X82](#), [Appendix X83](#), [Appendix X84](#), [Appendix X85](#), [Appendix X86](#), [Appendix X87](#), [Appendix X88](#), [Appendix X89](#), [Appendix X90](#), [Appendix X91](#), [Appendix X92](#), [Appendix X93](#), [Appendix X94](#), [Appendix X95](#), [Appendix X96](#), [Appendix X97](#), [Appendix X98](#), [Appendix X99](#), and [Appendix X100](#). 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 Practices 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 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](#), [9.1.1](#), 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.

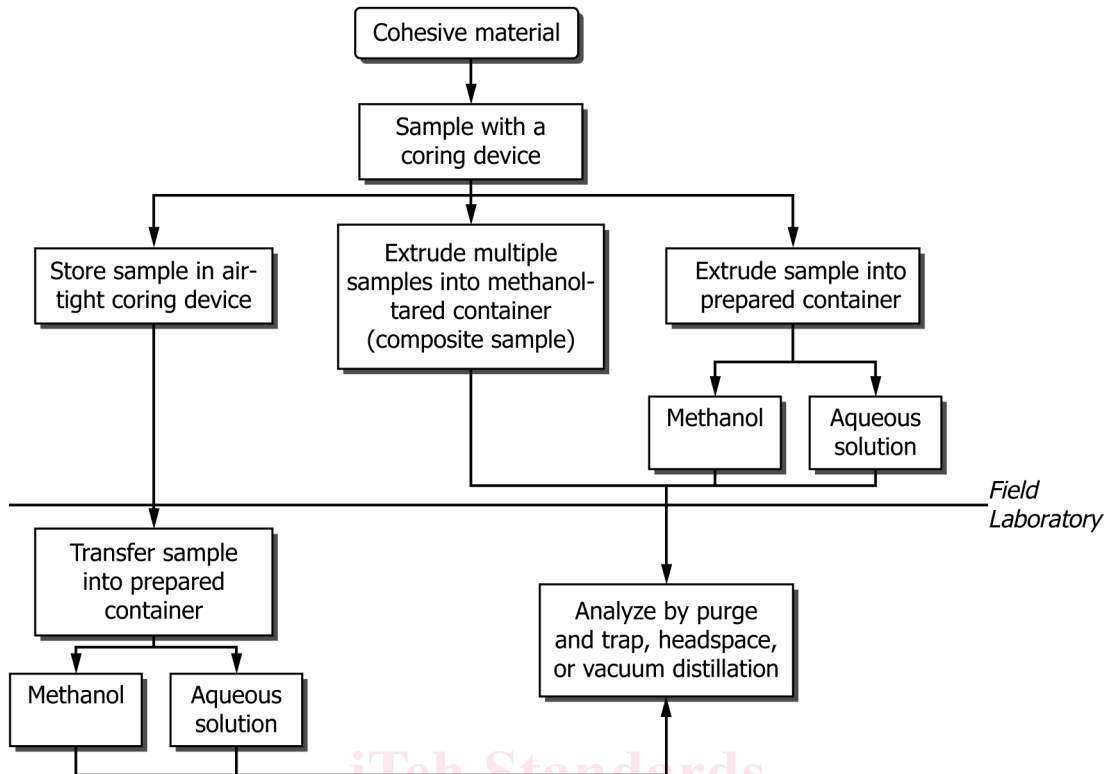


FIG. 1 Sample Handling Options for Cohesive Materials

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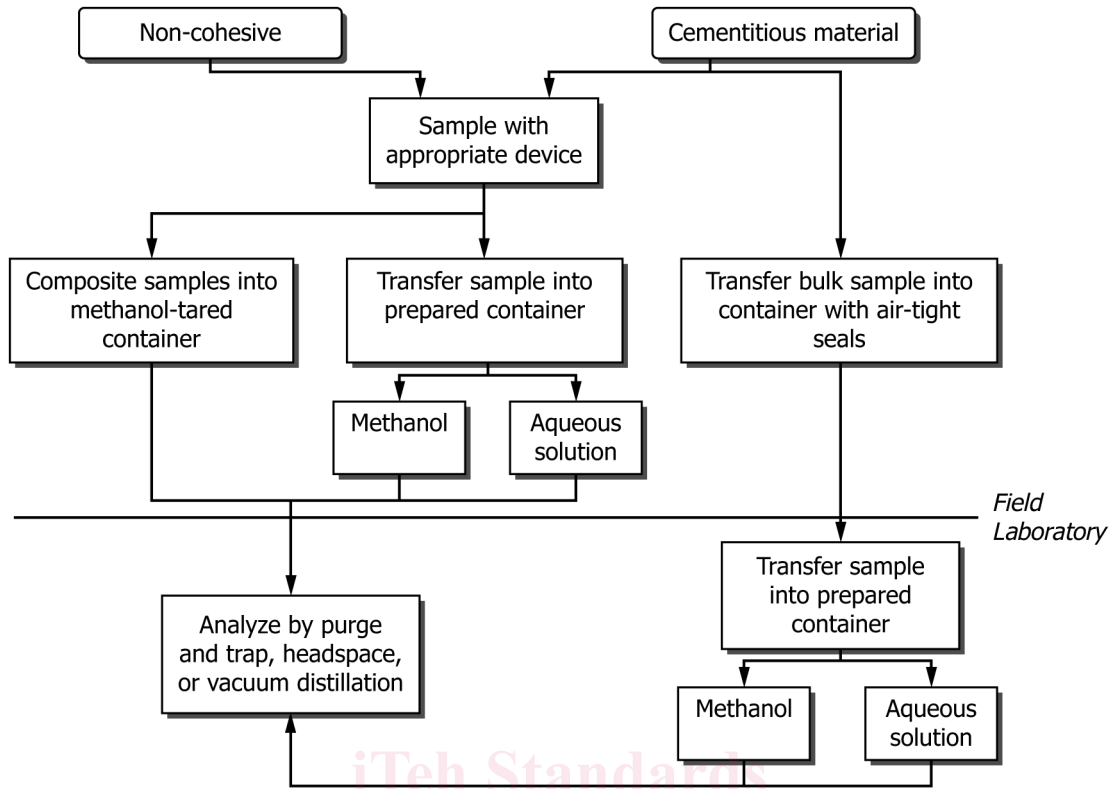


FIG. 2 Sample Handling Options for Non-cohesive and Cementitious Materials

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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~~ 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~~ 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,~~ 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/D6282M](#)). 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/D1586M](#)), which opens to expose the entire length of the material obtained for subsampling, and core barrel liners (ring-lined barrel sampling, see Practice [D3550/D3550M](#)) 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,~~ seals; see [Appendix X1](#). ~~Single-tube and dual-tube~~ Single-tube and dual-tube sampling devices have been developed for environmental applications (Guide [D6282/D6282M](#)) 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 [Guides D4700, D6232, and Guide D6282/D6282M](#). 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~~

single-tube direct push methods that provide limited exposure of the soil being sampled to the atmosphere, atmosphere are described in Appendix X3 (see 8.18.1 – 8.3 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 and Guide D8170). 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, solvent or VOC-free water and, if required, a PTFE or glass-coated 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) 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

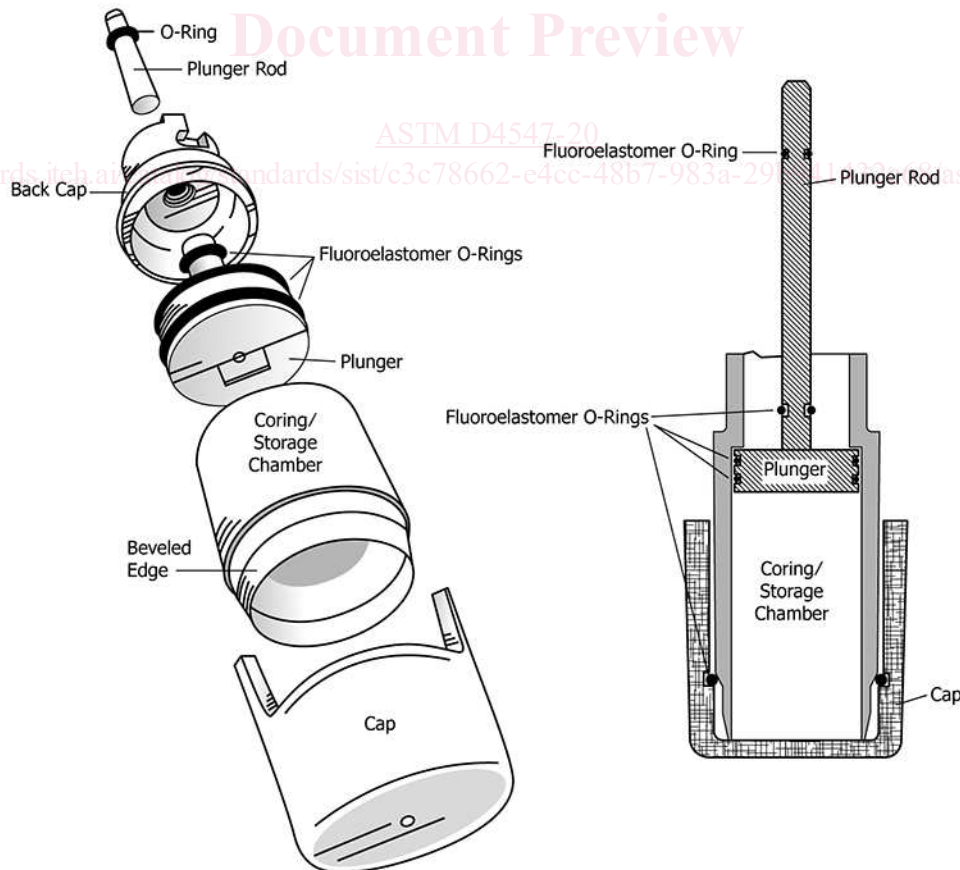


FIG. 3 Miniature Generic Disposable Handheld Soil Core Sampler

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 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~~. overpressurization. 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~~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~~ 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 $4 \pm 2^{\circ}\text{C}$; 2 °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). <https://standards.iteh.ai/catalog/standards/sist/c3c78662-e4cc-48b7-983a-29b941432c68/astm-d4547-20>

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~~ 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-cm³ volume would need to be collected (assuming the soil has density of 1.7 g/cm³). Larger sample masses or composite samples may be preferred as the heterogeneity of the material increases.

8.1.1 Sampling of Cohesive ~~but~~ 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 trapped behind the sample. If air is trapped, it could either pass through the sampled material causing

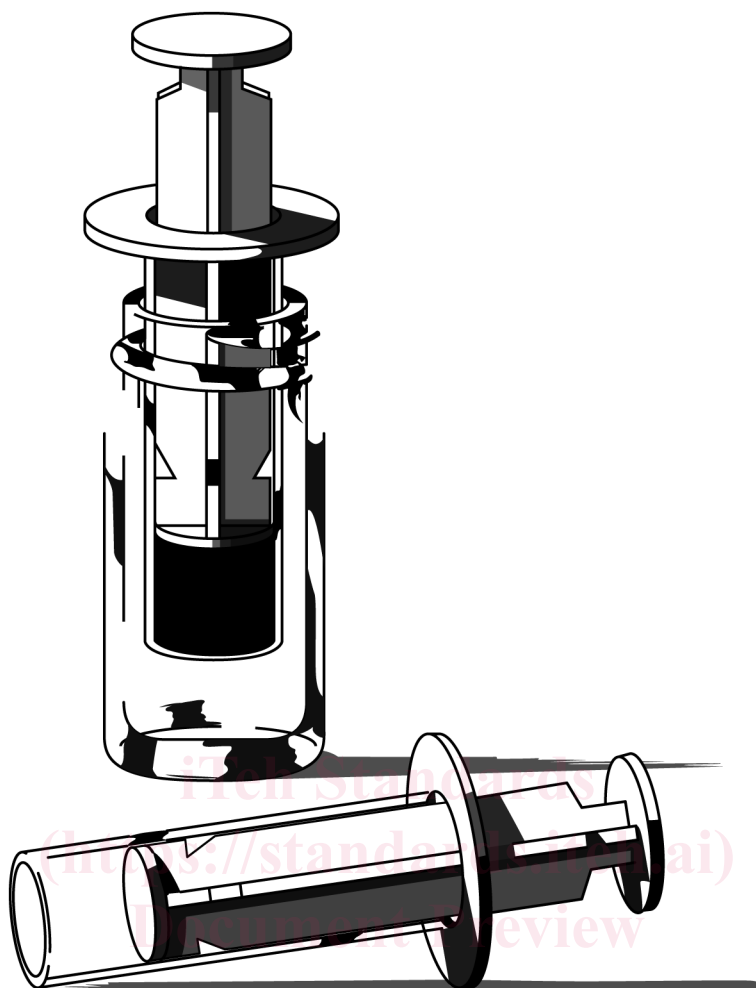


FIG. 4 A Coring Tool Made by Cutting the Tip Off a Plastic Syringe

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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, gravel~~ or a mixture of gravel and ~~finer, 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, 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, airtight~~ containers and cooled to at least $4 \pm 2^\circ\text{C}$.⁵ For storage periods beyond 48 h, these ~~air-tight, airtight~~ 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, airtight~~ 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, low-temperature~~ storage (for example, preferably in a freezer set for -12 – $-12 \pm 5^\circ\text{C}$, 5°C , or by using a temporary refrigerant, for example, a mixture of salt and ice or dry ~~ice, 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, 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, low-temperature~~ storage is used for samples intended for analysis by vapor partitioning, ~~VOC-free, VOC-free~~ water and, if required, a PTFE or ~~glass-coated, 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, 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, low-temperature~~ storage (see [7.3.4](#)). In either case, immediately following ~~low temperature, 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 Guide D6418D8170](#)).

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

⁵ SW-846, Method 5035 A (July 2002), 3rd Update.

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~~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~~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 $4 \pm 2^{\circ}\text{C}$ 2°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 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.