GUIDANCE DOCUMENT FOR THE IMPLEMENTATION OF UNITED STATES ENVIRONMENTAL PROTECTION AGENCY METHOD 5035: METHODOLOGIES FOR COLLECTION, PRESERVATION, STORAGE, AND PREPARATION OF SOILS TO BE ANALYZED FOR VOLATILE ORGANIC COMPOUNDS

Department of Toxic Substances Control
California Environmental Protection Agency

November 2004

ACKNOWLEDGEMENTS

Preparation of this guidance document was achieved through the efforts of the following individuals at the Department of Toxic Substances Control:

Craig Christmann	Senior Engineering Geologist
Dan Gallagher	Senior Engineering Geologist
Theo Johnson	Senior Engineering Geologist
Greg Sweel	Senior Engineering Geologist
Fred Zanoria	Senior Engineering Geologist

Additional assistance was provided by Ruth Chang, Russ Chin and William Lum of the Hazardous Materials Laboratory at the Department of Toxic Substances Control. We thank them for their substantial contribution towards the completion of this guidance document.

TABLE OF CONTENTS

LIST OF TABLES AND FIGURES

1.0 INTRODUCTION

The United States Environmental Protection Agency (USEPA) Office of Solid Waste promulgated Method 5035, *Closed-System Purge-and-Trap Extraction for Volatile Organics in Soil and Waste Samples* in June 1997 in SW-846*, Test Methods for Evaluating Solid Waste, Physical / Chemical Methods, Update III* (Method 5035). More recently, in July 2002, USEPA updated the Method within SW-846 as Method 5035A[1]. Method 5035 describes procedures and protocols for the collection of three types of solid samples contaminated with volatile organic compounds (VOCs)[2]: low-concentration solids (i.e., soil, sludge and sediment), high-concentration solids, and solid samples with oily waste. For low-concentration samples, Method 5035 describes a "closed-system purge-and-trap" process to minimize the loss of VOCs due to sample collection and handling. For high-concentration samples, Method 5035 describes procedures for the collection and preservation of samples, but references Method 5030 (Revision 2, December 1996) for the actual analysis of the prepared sample extracts. Method 5030 remains as a part of Method 5035 and is applicable to the analysis of high-concentration soil and solid waste extracts prepared with Method 5035, as well as aqueous samples. As such, when USEPA promulgated Method 5035, there was no intention to make Method 5030 obsolete.

The procedures in Method 5035 should be used for the collection of soil samples at all sites in California contaminated with VOCs in order to comply with USEPA Region IX's Interim Policy and the California Code of Regulations. USEPA Region IX issued their Regional Interim Policy concerning Method 5035 on June 23, 1999. The Region IX Interim Policy requires the use of Method 5035, or an equally or more effective method, for the collection of VOC data for soil in California. The Region IX Interim Policy is included in this Guidance Document as Appendix D. The objective of the Interim Policy is to minimize VOC loss from volatilization and biodegradation during sample collection and handling. By minimizing soil sample transfer steps from sampling to analysis, VOC loss due to atmospheric volatilization is reduced. The use of chemical preservatives further minimizes microbial action, yielding soil samples that are more representative of site conditions. Likewise, the protocols of SW-846 are referenced within the California Code of Regulations as a mechanism to achieve representative samples of waste materials (Title 22, Chapter 11, Article 5, Appendix I).

2.0 PURPOSE

The Department of Toxic Substances Control (DTSC) has compiled this Guidance Document in order to provide assistance in the implementation of Method 5035 at sites regulated by the DTSC where VOCs are chemicals-of-concern. This Guidance Document is meant to supplement USEPA Method 5035 by summarizing the sampling options for the collection of soil samples for VOC analysis. It is DTSC's intent to provide the minimum requirements and minimum standards to prevent loss of VOCs during sample collection and handling. Thus**,** DTSC encourages all parties involved in site cleanup to read and understand SW-846 in conjunction with the use of this Guidance Document. This Guidance Document, along with SW-846 and the Region IX Regional Interim Policy, will provide technically defensible and consistent approaches for sampling VOCs in soils. However, while Method 5035 should always be implemented at sites in California

[1] Method 5035 and the associated 2002 update in SW-846 are collectively referred to as "5035" in this Guidance Document.

[2] The term "volatile organic compounds" refers to low molecular weight compounds which possess boiling points below 200°C, are insoluble or slightly soluble in water, and have been traditionally analyzed by purge-and-trap methods.

contaminated with VOCs, the procedures within this Guidance Document are recommendations only. Other technically equivalent procedures may exist that minimize VOC loss during soil sample collection, storage, preservation, and preparation, and the intent of this Guidance Document is not to exclude alternative sampling approaches as long as the alternative procedures are functionally equivalent to Method 5035. This Guidance Document addresses the collection and handling of soil samples. Sludge samples and sediment samples are not specifically addressed, although some of the procedures herein may apply. Likewise, this Guidance Document does not address the collection of solid samples contaminated with oily waste.

This Guidance Document does not address all aspects of VOC soil sampling and analysis. The focus of this Guidance Document is the field procedures associated with soil sample collection, storage, preservation, and preparation for VOC analysis, since most VOC loss during soil sampling occurs before the samples arrive at the laboratory. It is not the intent of this Guidance Document to provide specific instructions to stationary and mobile laboratories on how to perform the analysis of VOCs in soil samples, but rather to provide guidance on the collection of soil samples in the field.

3.0 SCOPE

The implementation of Method 5035 impacts multiple technical disciplines. Therefore, successful implementation of Method 5035 in the field will require increased communication, planning, and coordination among the project team responsible for site characterization. Method 5035 is more complex than previous soil sample preparation methods because it involves multiple soil preservation options for the project team, each suited for specific project objectives depending upon the action levels for the chemicals-of-concern and prior knowledge of the soil VOC concentrations. The final selection of sampling procedures will require input from all data users, such as project managers, geologists, chemists, risk assessors, and engineers. Items to consider before selecting the VOC sampling and analysis methods at a site are as follows:

- Compounds of interest
- Concentration range of the VOCs
- Potential compound interferences
- Data quality objectives
- Physical character of the soil
- Reactive character of the soil
- Chemical preservation techniques
- Laboratory equipment specifications

Accordingly, a high degree of coordination and planning is required between field and laboratory personnel before the start of field activities.

USEPA Method 5035 arranges the soil sampling options into three groups: low-concentration soil, high-concentration soil, and soil with oily waste. Sample preservation is then given within each group as a sub-option, followed by the appropriate type of sample container to use. This arrangement by USEPA emphasizes the systematic steps that are needed to determine the proper choice of VOC sampling methods, as follows: 1) determine target compounds and their concentration to select low concentration or high concentration methods; 2) select the preservation options that are best suited for the VOC target compounds and data quality objectives; and 3) determine the appropriate container or sampler for the sample collection.

In contrast, this Guidance Document does not emphasize a systematic approach for selecting a soil sampling technique within Method 5035. Rather, the Guidance Document groups the sampling options according to the sampling devices, followed with sub-options for low-concentration and high-concentration methods. The intent of this Guidance Document is to summarize the options available for the sampling of soils contaminated with VOCs and provide detailed field procedures for the use of each sampling approach. Nonetheless, the selection of a field sampling technique must be technically justifiable pursuant to the systematic steps within Method 5035. The technical justification for the selection of a particular sampling technique must be provided to DTSC for our approval within appropriate workplans. A sampling technique should not be selected based upon the availability of sample containers and convenience of use. Instead, the sampling and preservation options must meet the scientific requirements of the data quality objectives.

4.0 APPLICATION

This Guidance Document describes the field sampling and preservation procedures for soil samples subject to VOC analysis. The applicable analytical methods described in SW-846 to be used in conjunction with Method 5035 are as follows:

Method 8015A:	Non-halogenated Organics
Method 8021B:	Aromatic and Halogenated Volatiles
Method 8260B:	Volatile Organic Compounds

Accordingly, all soil samples collected at sites regulated by DTSC that are analyzed using the above methods should also be handled pursuant to the Method 5035 procedures described in this Guidance Document.

5.0 SUMMARY OF METHOD

Method 5035 soil sample collection and preparation procedures are dependent on the desired detection limits needed for the project. For the low VOC concentration method, the available options are summarized in Table 1. For the high VOC concentration method, the available options are summarized in Table 2. The selection of a preservation option must be a function of the data quality objectives as outlined above in Section 3.0. Soil samples with VOC concentrations below 200 micrograms per kilogram (μg/kg) are generally considered as "Low Level Analysis" and have a method detection limit of approximately 0.5 μg/kg. Soil samples with VOC concentrations above 200 μg/kg are generally considered as "High Level Analysis" and have a method detection limit of approximately 200 μg/kg.

The procedures for a Low Level Analysis utilize a hermetically-sealed sampling container and analysis of the sample by a closed-system purge-and-trap process. The Low Level Analysis method uses a direct purging of the VOCs from an aqueous medium. The aqueous medium can be either sodium bisulfate solution or reagent water. The sodium bisulfate solution acts both as a preservative and extractant medium whereas reagent water is strictly an extractant medium with minimal preservation benefit. The aqueous medium is introduced into the sampling container either in the field or at the laboratory. No sample dilution is involved, yielding detection limits of approximately 0.5 μg/kg.

The procedures for a High Level Analysis utilize a hermetically-sealed sampling container and analysis of the sample at the laboratory by Method 5030. The High Level Analysis method uses a

methanol solvent extraction technique. The methanol is introduced into the sampling container either in the field or at the laboratory. Detection limits of greater than 200 μg/kg occur due to dilution of the sample with methanol.

When designing and implementing a sampling program for VOC contaminated soil, the project team must consider the appropriate analytical detection limits needed for the site characterization. Ultimately, the detection limits should be a function of the end-use of the data. For example, if the objective of the sampling is to quantify the human health risk to exposure to VOCs where the action levels are very low, then nothing less than Low Level Analysis is acceptable for the project. Conversely, if the objective is waste classification where the regulatory concentration thresholds are relatively high, then High Level Analysis is warranted. Another case where High Level Analysis is appropriate is the delineation of non-aqueous phase liquid (NAPL) in soil for remedial system design.

5.1 Number of Samples Needed for Analysis

In contrast with past soil sampling practices, Method 5035 now requires, if necessary, that multiple soil samples be collected from each sampling location. If needed, both Low Level Analysis and High Level Analysis sample sets are collected with proper preservation at each sampling point. The need for multiple samples is pertinent to sites with unknown VOC concentrations and for the need to have the lowest possible detection limits.

If detection limits of approximately 0.5 μg/kg are needed for the soil at a site, three samples are collected pursuant to Method 5035. One sample is collected for High Level Analysis and two samples are collected for Low Level Analysis. First, the High Level Analysis sample is analyzed by the laboratory to determine if VOCs exist at the site in high concentrations. If this first sample yields VOC concentrations below the detection limit (<200 μg/kg), then a Low Level Analysis sample is analyzed. The second Low Level Analysis sample is available as a backup if the first Low Level Analysis run is unacceptable or re-analysis is warranted.

If detection limits of greater than 200 μg/kg are acceptable at a site, then only one sample is collected for High Level Analysis pursuant to Method 5035. As necessary, the laboratory can perform multiple dilutions on the methanol extract to meet the instrument's calibration range. However, under this scenario, Low Level Analysis cannot be performed after the High Level Analysis due to the lack of available soil. To assist in the determination of the number of samples needed for Method 5035, a soil sampling decision flowchart is provided in Figure 1.

A general overview of the sampling options with Method 5035 is summarized below. A more detailed description of the options is provided within the Appendices[3].

5.2 Option 1: Preserved VOA Vials (Field Chemical Preservation)

Tared and labeled VOA vials with polytetrafluoroethylene (PTFE)-lined septum caps are provided by the laboratory or a vendor with appropriate chemical preservatives. Typically, the VOA vials are

[3] The Appendices were written as stand-alone documents which could be detached from this Guidance Document and taken into the field as a resource for Method 5035 sampling; hence, the Appendices reiterates numerous procedures presented within the text of this Guidance Document. Likewise, the individual Appendices are repetitious due to the numerous commonalities of the sampling procedures.

40 milliliters in size. The preservation fluid is either methanol or another water-miscible solvent such as polyethylene glycol[4] (High Level Analysis), or sodium bisulfate solution[5] (Low Level Analysis). Also, for Low Level Analysis, the VOA vials can contain reagent-grade extractant water[6]. Magnetic stir bars should be added to the VOA vials for Low Level Analysis pursuant to the laboratory's requirements. The selection of the preservation fluid is based on the chemistry of the target compounds and the type of soil, along with the desired method detection limits. In the field, the pre-preserved VOA vials for High Level Analysis are re-weighed before use to verify no evaporative loss of methanol since last tared. Re-weighing of the VOA vials before use for Low Level Analysis is not necessary because sodium bisulfate solution and reagent water have no affect on the dilution calculation. The soil subcores are obtained from appropriate sample locations using a field coring device. Then the soil subcores of appropriate mass are placed into the VOA vials in the field and are capped, forming an airtight seal.

To avoid VOC loss, Low Level Analysis samples preserved with sodium bisulfate solution or placed into reagent-grade extractant water are never again opened throughout the entire storage, preparation, and analysis process. Thus, the physical dimensions of the VOA vials must be compatible with the laboratory's autosampler instrumentation since sample re-handling is not possible. At the laboratory, the capped VOA vials are re-weighed to obtain the weight of the soil samples. For Low Level Analysis samples preserved with sodium bisulfate solution or placed into reagent-grade extractant water, the samples are prepared and analyzed with the caps in-place. All surrogates, internal standards, and matrix spikes are introduced through the PTFE-lined septum caps either manually or mechanically. For samples preserved with methanol, the VOA vials may be opened pursuant to the procedures of Method 5030 but only after the soil subcore is completely immersed in methanol and shaken gently to completely capture the VOCs in the headspace.

There are five options available for sample collection, preservation, and analysis for preserved VOA vials, as follows.

Option 1A: Field Preservation with Methanol. After collecting the soil samples in tared VOA vials preserved with methanol, the vials are re-weighed in the field, and then are chilled at 4 ± 2°C in a cooler and shipped with adequate ice to ensure that 4 ± 2°C is maintained during transport to the laboratory. The samples must arrive at the laboratory within 48 hours of the sample collection time. The VOA vials are weighed again at the stationary laboratory to verify no methanol loss during transport. The laboratory must prepare and analyze the samples by Method 5030 within 14 days of the sample collection date. This technique applies only to High Level Analysis so it should be used if detection limits of greater than 200 μg/kg are warranted.

Option 1B: Field Preservation with Sodium Bisulfate Solution. After collecting the soil samples in tared VOA vials preserved with sodium bisulfate solution, the samples are kept chilled at 4 ± 2°C in a cooler and shipped with adequate ice to ensure that 4 ± 2°C is maintained during transport to the laboratory. The samples must arrive at the laboratory within 48 hours of the sample collection

[4] Ten milliliters of methanol or another water-miscible solvent is added to each VOA vial.

[5] A twenty percent sodium bisulfate solution is generally used for preservation. The solution is usually produced by adding one gram of sodium bisulfate to five grams of reagent water, thus producing a solution with a pH of less than two.

[6] Five milliliters of reagent-grade extractant water is added to each VOA vial.

time. The laboratory must prepare and analyze the samples within 14 days of the sample collection date. This preservation technique provides detection limits to approximately 0.5 μg/kg (Low Level Analysis). However, sample preservation with sodium bisulfate solution presents four potential problems. One, acid preservation may cause the chemical breakdown of certain reactive VOC compounds in the soil sample, specifically styrene, acrylonitrile, vinyl chloride, and 2-chloroethylvinyl ether. Two, in soil samples with a high proportion of organic material, acid preservation may generate acetone as a byproduct. Three, calcareous soil samples may effervesce upon contact with sodium bisulfate solution and cause VOC loss. Four, calcareous soil samples may increase the pH of the preservation fluid above 2.0, producing a sample in an unpreserved state. Accordingly, the soils at the site should be evaluated for potential problems prior to sampling activities. In cases where preservation by acid is a potential problem, an alternate sample collection method should be utilized.

Option 1C: Field Extraction into Reagent Water (Laboratory Freezing). After collecting the soil samples in tared VOA vials containing reagent-grade extractant water, the samples are kept chilled at 4 ± 2°C in a cooler and shipped with adequate ice to ensure that 4 ± 2°C is maintained during transport to the laboratory. The laboratory must receive and immediately freeze the sample vials to <-7°C within 48 hours of the sample collection time. During the freezing process, the VOA vials should be stored in a 45° angle to prevent water expansion from shattering the vials. The samples may be held at <-7°C for up to seven days prior to analysis from the sample collection date. The sample vials should not be frozen below -20°C due to potential problems with the vial seals. This technique applies to samples for Low and High Level Analysis.

Option 1D: Field Extraction into Reagent Water (Field Freezing). After collecting the soil samples in tared VOA vials containing reagent-grade extractant water, the samples are frozen to <-7°C in a cooler in the field and shipped with adequate dry ice[7] to ensure that <-7°C is maintained during transport to the laboratory. The sample vials should not be frozen below -20°C due to potential problems with the vial seals. A temperature blank should be included with the samples so that the laboratory can verify the temperature upon receipt and the arrival temperature of the samples should be annotated on the chain-of-custody form. During the freezing process, the VOA vials should be stored in a 45° angle to prevent water expansion from shattering the vials. To avoid potential rupture of the PTFE-lined septum caps, the dry ice should not directly contact the top of the VOA vials. The laboratory must immediately freeze the sample vials to <-7°C upon receipt. The samples may be held at <-7°C for up to seven days prior to analysis from the sample collection date. This technique applies to samples for Low and High Level Analysis. This option is used in the situations where it is difficult or impossible to deliver the samples to the laboratory within 48 hours of the sample collection time.

Option 1E: Field Extraction into Reagent Water; Analysis within 48 Hours. After collecting the soil samples in tared VOA vials containing reagent-grade extractant water, the samples are kept chilled at 4 ± 2°C in a cooler and shipped with adequate ice to ensure that 4 ± 2°C is maintained during transport to the laboratory. Upon receipt of the samples, the laboratory chills the tared VOA vials to 4 ± 2°C and analyzes the samples within 48 hours of the sample collection time. This technique applies to samples for Low and High Level Analysis.

[7] There two potential difficulties in using dry ice to achieve <-7°C in the field; 1) dry ice will only last about eight hours within a field cooler, and 2) dry ice may contain low concentrations of VOCs, such as acetone. Hence, care must be taken in overnight shipment of field coolers to insure proper freezing and trip blanks should always accompany coolers containing dry ice.

It should be noted that extruding soil samples into vials containing reagent-grade extractant water may have an adverse effect on sample results in that water may actually promote bacterial degradation of certain VOCs (See Section 6.3.1). Likewise, some VOCs may be unstable in reagent water, such as 1,1,2,2-tetrachloroethane. Accordingly, reagent water-filled VOA vials should only be used for chemicals that do not readily biodegrade or breakdown.

The field procedures for Options 1A, 1B, 1C, 1D and 1E are furthered discussed in Appendix A.

5.3 Option 2: Multi-Functional Sampling Devices (No Field Chemical Preservation)

Multi-functional sampling devices (MFSDs) act as both a coring tool and airtight storage container. Examples of MFSDs are the EnCore™ Sampler and the Core N' One™ Sampler[8]. In MFSDs, a small subcore of soil is collected directly into the volumetric storage chamber of the MFSD from a soil core or soil surface, filling it completely with zero headspace. The storage chamber is then capped to form an airtight seal. The intact MFSDs are placed into a plastic bag for transport to the laboratory at 4 ± 2°C. At the stationary laboratory, the soil content of the MFSD is extruded into a prepared VOA vial for analysis. The opening of the VOA vial must be sufficiently large to accept the soil content from the MFSD without obstruction. Since the VOA vial may be used directly for analysis, it must be compatible with the stationary laboratory's purge and trap apparatus to avoid further sample handling which might promote VOC loss. Field personnel should contact the laboratory for the required dimensions.

There are three options available for sample collection, preservation, and analysis for MFSDs, as follows.

Option 2A: The Subcore is Extruded into a VOA Vial Containing Chemical Preservative at the Laboratory. The field cooler is kept chilled at 4 ± 2°C and shipped with adequate ice to ensure that 4 ± 2°C is maintained during transport to the laboratory. The laboratory must receive the MFSDs and extrude the samples into VOA vials that contain appropriate extraction fluid within 48 hours of the sample collection time. For MFSDs for Low Level Analysis, the soil can be extruded, weighed, and preserved with sodium bisulfate solution. Also, for Low Level Analysis, the soil can be extruded into reagent-grade extractant water. For MFSDs for High Level Analysis, the soil must be extruded, weighed, and preserved with methanol. After extrusion of the soil into an appropriate extraction fluid, the sample may be held up to 14 days prior to analysis from the sample collection date.

Option 2B: The Subcore is Extruded into an Empty VOA Vial at the Laboratory. The field cooler is kept chilled at 4 ± 2°C and shipped with adequate ice to ensure that 4 ± 2°C is maintained during transport to the laboratory. The laboratory must receive the MFSDs and extrude the samples within 48 hours of the sample collection time. Upon receipt of the samples, the laboratory extrudes the subcores into empty VOA vials and then freezes the unpreserved VOA vials at <-7°C. The samples may be held at <-7°C for up to seven days[9] prior to analysis from the sample collection

[8] The mention of trade names or commercial products in this Guidance Document is for illustrative purposes only, and does not constitute an endorsement or exclusive recommendation for use at DTSC sites. Equipment other than that listed may be used provided that the resulting performance meets the project data quality objectives.

[9] The holding time of seven days from the sample collection date is consistent with guidance from the Los Angeles Regional Water Quality Control Board (General Laboratory Testing Requirements for Petroleum Hydrocarbon Impacted Sites, June 5, 2000)

date. For Low Level Analysis, the samples are prepared and analyzed with the VOA vial caps in-place. For High Level Analysis, the samples are handled pursuant to Method 5030.

Option 2C: The MFSD is Analyzed within 48 Hours. The field cooler is kept chilled at 4 ± 2°C and shipped with adequate ice to ensure that 4 ± 2°C is maintained during transport to the laboratory. Upon receipt of the samples, the laboratory chills the MFSDs to 4 ± 2°C until analysis. The laboratory must extrude and analyze the samples within 48 hours of the sample collection time. The samples may be subject to either High or Low Level Analysis.

The field procedures for Options 2A, 2B, and 2C are furthered discussed in Appendix B.

5.4 Option 3: Non-Preserved VOA Vials (Empty Vial Technique)

Empty, tared and labeled VOA vials with a PTFE-lined septum caps are taken into the field as provided by the laboratory. Likewise, these vials may be purchased as specially prepared vials from scientific suppliers or can be prepared by the field staff using empty VOA vials, certified clean to USEPA specifications. The VOA vials do not contain chemical preservatives, water-miscible solvents, or reagent water but may contain small magnetic stir bars as required by the laboratory. Soil cores of appropriate mass are placed into the VOA vials in the field and are capped, forming an airtight seal. For Low Level Analysis, the VOA vials are never again opened throughout the entire storage, preparation, and analysis process. Thus, the physical dimensions of the VOA vials must be compatible with the laboratory's autosampler instrumentation since sample re-handling is not possible. At the laboratory, the capped VOA vials are re-weighed to obtain the weight of the soil samples. For Low Level Analysis, the samples are prepared and analyzed with the caps in-place. All preservatives, surrogates, internal standards, and matrix spikes are introduced through the PTFE-lined septum caps either manually or mechanically and analyzed with a closed-system purge-and-trap process. For High Level Analysis, methanol is introduced through the septum and the resulting extract is analyzed with Method 5030.

There are three options available for sample collection, preservation, and analysis for non-preserved VOA vials, as follows.

Option 3A: Laboratory Freezing. After collecting the soil samples in tared VOA vials, the samples are kept chilled at 4 ± 2°C in a cooler and shipped with adequate ice to ensure that 4 ± 2°C is maintained during transport to the laboratory. The laboratory must receive the samples within 48 hours of the sample collection time and immediately freeze the sample vials to <-7°C upon receipt. The samples may be held at <-7°C for up to seven days prior to analysis from the sample collection date. The sample vials should not be frozen below -20°C due to potential problems with the vial seals and the samples may be subject to either High or Low Level Analysis.

Option 3B: Field Freezing. After collecting the soil samples in tared VOA vials, the samples are frozen to <-7°C in a cooler in the field and shipped with adequate dry ice[10] to ensure that <-7°C is maintained during transport to the laboratory. The sample vials should not be frozen below -20°C due to potential problems with the vial seals. A temperature blank should be included with the samples so that the laboratory can verify the temperature upon receipt and the arrival temperature

[10] There two potential difficulties in using dry ice to achieve <-7°C in the field; 1) dry ice will only last about eight hours within a field cooler, and 2) dry ice may contain low concentrations of VOCs, such as acetone. Hence, care must be taken in overnight shipment of field coolers to insure proper freezing and trip blanks should always accompany coolers containing dry ice.

of the samples should be annotated on the chain-of-custody form. During the freezing process, the VOA vials should be stored in a 45° angle to prevent sample expansion from shattering the vials. To avoid potential rupture of the PTFE-lined septum caps, the dry ice should not directly contact the top of the VOA vials. Upon receipt, the laboratory must commence with analysis. Otherwise, the laboratory must immediately freeze the sample vials to <-7°C upon receipt. The samples may be held at <-7°C for up to seven days prior to analysis from the sample collection date. The samples may be subject to either High or Low Level Analysis. This option is used in the situations where it is difficult or impossible to deliver the samples to the laboratory within 48 hours of the sample collection time.

Option 3C: Analysis within 48 Hours. After collecting the soil samples in tared VOA vials, the samples are kept chilled at 4 ± 2°C in a cooler and shipped with adequate ice to ensure that 4 ± 2°C is maintained during transport to the laboratory. Upon receipt of the samples, the laboratory chills the tared VOA vials to 4 ± 2°C and analyzes the samples within 48 hours of the sample collection time. The samples may be subject to either High or Low Level Analysis.

The field procedures for Options 3A, 3B, and 3C are furthered discussed in Appendix C.

6.0 CONDITIONS OF THE METHOD

6.1 Limitation of Methanol Preservation

The preservation and extraction of samples with methanol is not appropriate for soils with low VOC concentrations. The use of methanol as a preservative introduces a significant dilution factor that will raise the method detection limit beyond the operating range of the Low Level Analysis procedure. For gas chromatography, depending on the analytical method, methanol may also mask the elution of some VOCs. Accordingly, the potential for coelution should be discussed with the laboratory prior to sample collection. Potentially, these limitations could render the soil analytical results useless in evaluating sites for risk assessment purposes.

6.2 Subcoring Devices

With most standard drilling techniques, soil cores are retrieved from the subsurface during site characterization with a core barrel. When analyzing soil samples pursuant to Method 5035, the soil from the core barrels must be subcored and then these subcore samples must be placed into airtight containers. With Option 2, the MFSD acts as both a subcoring tool and airtight storage container. The MFSD is designed to collect, transport, and deliver intact soil sample subcores to the stationary laboratory. The coring body of the MFSD is pushed into a freshly exposed soil surface, obtaining a headspace-free subcore. The sample chamber is then sealed with the cap, becoming airtight. Once back at the laboratory, the sample subcore is extruded into a tared empty or preserved VOA vial, as appropriate. To aid in the extrusion of the subcore from the MFSD into the VOA vial, the opening of the VOA vial must be larger than the diameter of the subcore. Accordingly, the project planning team must contact the stationary laboratory to ensure that the MFSDs are compatible with the VOA vials used in the laboratory's autosampler instrumentation to avoid further sample handling which might promote VOC loss.

For Options 1 and 3, a subcoring device must be used to obtain the subcore soil samples. The subcoring device must have a diameter smaller than the opening of the VOA vial into which the subcore is extruded. Additionally, the project planning team must contact the stationary laboratory to ensure that the VOA vials used in the field are compatible with the laboratory's autosampler

instrumentation. The subcoring devices are used to obtain either five or ten grams of soil, as appropriate. Five grams is the preferred weight to minimize sample handling by the laboratory. Numerous subcoring devices are available for the collection of the soil subcores. The following list contains a description of three subcoring devices. However, any equivalent device may also be used.

- Disposable Plastic Syringe. A disposable plastic syringe can be easily converted to an inexpensive subcoring device. The "needle end" of the syringe barrel can be cut off, thus creating a blunt, even coring end. The end of the syringe should be cut with a knife or scissors rather than a saw so that the blunt end is smooth to prevent soil disaggregation upon collection. Prior to use, the plunger of the syringe must be in the “down position” so that its end directly contacts the soil, not allowing for any trapped air. The soil subcore is collected by pushing the cut end of the syringe into the freshly exposed soil surface until the soil column fills the inside of the syringe with five grams of soil, or as needed. The soil subcore is then removed from the syringe and extruded into the VOA vial using the syringe's plunger.

- EasyDraw Syringe™ and PowerStop Handle™. The soil subcore is obtained with the sampling device and transferred into a VOA vial in the field. The PowerStop Handle™ is reusable but a new syringe must be used for each sampling location. There are three 5 gram positions and three 10 gram positions on the PowerStop Handle™. The three positions are labeled light, medium, and heavy to correspond to low, medium and high soil densities. There is also one 13 gram position. In general, one of the 5 gram positions will be used to collect the soil subcores. The soil subcore is collected by pushing the EasyDraw Syringe™ into the freshly exposed soil surface until the soil column inside the syringe has forced the plunger to the stopping point.

- Lock N’ Load™ Soil Sampling Tool. The soil subcore is obtained with the sampling device and transferred into a VOA vial in the field. There are two settings, a 5 gram position and a 10 gram position, on the Lock N’ Load™ Soil Sampling Tool. In general, the 5 gram position will be used to collect the soil subcores. The Lock N’ Load™ Soil Sampling Tool is reusable but a new syringe must be used for each sampling location. The Lock N' Load syringe fits securely into the neck of a 40 milliliter glass vial and by turning the Lock N' Load handle, one can dispense the soil into a VOA vial without removing the syringe.

Section 6.10 provides guidance on the collection of samples from consolidated soil, such cemented soil, dense sand, stiff clay, or bedrock, where subcores cannot be obtained with a MFSD, disposable plastic syringe, EasyDraw Syringe™, Lock N’ Load™ Soil Sampling Tool, or other appropriate subcoring device.

6.3 Procedural Incompatibilities

6.3.1 Aromatic Hydrocarbons

Chemicals, such as aromatic hydrocarbons (AH), are subject to VOC loss by biodegradation under certain Method 5035 sampling procedures. Accordingly, to obtain AH soil concentrations that are representative of site conditions, only a subset of the available Method 5035 options are available for use. To reduce the biological activity in soil contaminated with AH, soil samples should be preserved with methanol or sodium bisulfate solution in the field, collected with MFSDs, or frozen in the field at <-7°C in non-preserved VOA vials. Under no circumstances should soil samples contaminated with AH be collected in the field with VOA vials containing reagent-grade extractant

water. The introduction of unpreserved water to the soil sample may enhance the biodegradation of the AH.

6.3.2 Chemical Reactions

Acid preservation of soil by sodium bisulfate solution, whether done in the field or in the stationary laboratory, may cause the chemical breakdown of certain compounds. Some olefins, ketones, esters, ethers, and sulfides may react under low pH conditions, yielding analytical results that are not representative of soil conditions. Hence, precaution should be taken when preserving soil samples with sodium bisulfate solution when these compounds are present. If the degree of potential chemical reaction is unknown, an alternative Method 5035 procedure should be used.

6.3.3 Calcareous Soil

Calcareous soil samples may react upon contact with sodium bisulfate solution, causing VOC loss through effervescence and potentially cause failure of the VOA vial septum through pressure build-up. Additionally, when soil samples are highly calcareous in nature, the sodium bisulfate preservative solution may not be strong enough to reduce the pH of the aqueous solution to below 2.0, potentially rendering the preservative useless. If carbon dioxide is generated due to carbonate reaction with the acid, the carbon dioxide in the VOA vial may interfere with the detector of the analytical equipment. Hence, precaution should be taken when preserving soil samples with sodium bisulfate solution when carbonates are present.

6.4 Selection of Appropriate Sampling Procedures

The selection of a Method 5035 sampling technique for a site should not be based upon on the availability of sample containers and convenience of use. Instead, the sampling and preservation options should be selected based upon the requirements of the data quality objectives for the project. Accordingly, this hierarchy of techniques is offered as a guide for users when evaluating the data quality needs for a project.

1) Option 1: Field Chemical Preservation. Chemical preservation of VOA vials in the field with sodium bisulfate solution (Low Level Analysis) or methanol (High Level Analysis) yields the best possible data quality for VOC analysis of soil. The introduction of these chemical preservatives in the field inhibits VOC loss by biodegradation. Also, VOC loss due to sample handling is minimized.

2) Option 2: Multi-Functional Sampling Devices. When the MFSDs are received by the stationary laboratory, the soil subcores within the MFSDs are extruded into VOA vials for analysis. As the soil subcores pass from the MFSDs to the VOA vials during the extrusion process, the soil subcores are open to ambient air and VOC loss could occur. This VOC loss could yield analytical results that are potentially biased low. Users of MFSDs must recognize this limitation when evaluating the data quality objectives for their project.

3) Option 3: Empty Vial Technique. The extractant fluid, whether methanol, sodium bisulfate solution, or reagent water, must be added by the stationary laboratory to the VOA vials after the soil has been sealed into the vials in the field. To do this, the PTFE-lined septum caps must be pierced for the introduction of the extraction fluid into the VOA vials. After the introduction of the extraction fluid, the vials must be stirred or sonicated to promote the partitioning of the VOCs into the extraction fluid. Upon completion of the stirring or sonication, the sample is then

analyzed for VOC concentration. During the stirring or sonication, VOCs can escape from the VOA vial through the pierced septum. Hence, the Empty Vial Technique may potentially yield analytical results that are biased low. Users of the Empty Vial Technique must recognize this limitation when evaluating the data quality objectives for their project.

Thus, the sampling options within Method 5035 do not potentially yield similar data quality results. Accordingly, for sites that require the highest quality analytical results, the soil subcores should be field preserved with methanol or sodium bisulfate solution.

For sites where the contaminants may react with the sodium bisulfate solution or where the soils may react with the sodium bisulfate solution due to high carbonate content, water may be substituted for the sodium bisulfate solution in the field in cases where chemical biodegradation is not a concern.

6.5 Field Screening

Not all soil samples collected from a borehole during site characterization are submitted to a stationary laboratory for analysis. Usually, the soil samples exhibiting the highest concentrations of VOCs through field screening techniques are submitted for analysis. Accordingly, to comply with the intent of Method 5035, care must be taken in the field to minimize VOC loss during the field screening process. Typically, during split-spoon sampling, cores are obtained within brass sleeves and one brass sleeve is field screened for VOC concentration. Meanwhile, another brass sleeve from the same depth interval is placed on ice in a sample cooler for possible laboratory analysis. Upon completion of the drilling, the soil samples for laboratory analysis are then selected. To comply with Method 5035, DTSC allows this style of procedure to continue but with minor modification. Brass sleeves can be held in a cooler filled with ice onsite awaiting subcoring for Method 5035 upon completion of borehole drilling if the following conditions are met:

1) The ends of the brass sleeve are covered with teflon sheeting, capped with tight-fitting plastic end-caps, and then placed into a resealable plastic (Ziploc™ type) bag.

2) No headspace exists within the brass sleeve.

3) The resealable plastic bag containing the brass sleeve is placed directly on ice within the shipping cooler.

4) No more than two hours transpire between core retrieval from the subsurface and the collection of the Method 5035 subcores from the brass sleeve.

5) The field log or boring log must reflect the time of core retrieval and the time of subcoring.

If the conditions listed-above are met, the brass sleeves can be held and subcored upon completion of the drilling of the borehole or within two hours of core retrieval, which ever is less. For Method 5035 sampling upon completion of borehole drilling, the brass sleeve is uncapped and the first inch of soil is removed from the brass sleeve with an appropriate instrument. The subcoring then takes place on the newly exposed surface as quickly as possible and as deep as possible within the brass sleeve. However, if the above conditions are not achieved in the field, all brass sleeves that might be subject to VOC analysis must be subcored immediately pursuant to Method 5035.

In some situations, acetate-lined core barrels are used rather than brass sleeves during the collection of subsurface soil samples. The above-mentioned approach applies to acetate-lined core samples where the cores would be manually sliced with a knife for field screening and subcoring.

Under no circumstances should brass sleeves or acetate-lined cores be submitted to a stationary laboratory for Method 5035 analysis. However, brass sleeves and acetate-lined cores can be hand-carried to an onsite mobile laboratory pursuant to the conditions referenced in Section 6.9 in this Guidance Document.

6.6 Dry Weight Determination

If the soil analytical results for a project must be reported on a dry weight basis, an additional soil sample must be collected from the sampling location in order to determine the dry weight of the soil. The soil sample submitted to the stationary laboratory specifically for dry weight determination does not need chemical preservation in the field and may be collected by conventional methods, such as in glass jars, brass sleeves, or acetate liners. However, the collection method should minimize sample handling, sample disaggregation, and moisture loss. As such, the sample containers used for the collection of these samples should have appropriate seals to prevent moisture loss and be clearly labeled to avoid confusion at the laboratory. Also, this sample for dry weight determination can be used by the laboratory to evaluate soil reactivity to sodium bisulfate solution.

6.7 Quality Assurance / Quality Control Samples

6.7.1 Trip Blanks

Soil samples can be contaminated by diffusion of VOCs through the septum on VOA vials or through the seal on MFSDs during shipment and storage. A trip blank prepared with laboratory-grade methanol, sodium bisulfate solution, or reagent water, dependent on the field methods, can be carried through sampling and handling protocols as a check on such contamination. DTSC recommends that, ideally, one trip blank should be used for each field sample cooler, but, at a minimum, one trip blank should be used per day.

6.7.2 Temperature Blanks

Temperature blanks should be used so that the laboratory can verify the temperature upon receipt of the samples. In the case of field freezing, the temperature blanks should be frozen upon arrival at the laboratory. The temperature of the samples upon arrival should be annotated on the chain-of-custody form and also mentioned in the laboratory narrative that accompanies the analytical results.

6.7.3 Matrix Spike and Matrix Spike Duplicate Samples

An important measure of the performance of an analytical method relative to the specific sample matrix of interest is the matrix spike and matrix spike duplicate (MS/MSD). The MS/MSD is an important aspect of an overall quality assurance program for a project. When soil sampling, a MS/MSD sample should be collected for each analytical method at a frequency of five percent of the field samples. The MS/MSD sample should be prepared in a fashion similar to the other samples pursuant to Method 5035. Samples taken for MS/MSD should be labeled as such and

specified on the chain-of-custody form. The primary purpose of MS/MSD analyses is to establish the applicability of the overall analytical approach to the specific sample matrix from the site.

6.7.4 Other Field Quality Control Samples

Field quality control samples to demonstrate the integrity of the field samples should also be collected. Field duplicates, field blanks, and equipment rinsate blanks should be collected at a frequency of five percent of the samples, or, at a minimum, one should be collected each day.

6.8 Bulk Soil Sampling

The collection of soil samples in bulk containers that would require laboratory subcoring is *not* an option pursuant to Method 5035. Large bottles, wide-mouthed jars, acetate liners, or brass sleeves from split-spoon samplers are not appropriate sample containers under Method 5035 for VOC analysis. However, with DTSC prior approval, these traditional, non-Method 5035 approaches can be used at sites for characterization purposes only, but VOC concentrations from these soil samples should never be used in fate and transport modeling or to quantify the risk associated with human and ecological exposure.

6.9 Mobile Laboratories

VOC analysis may be performed by a certified mobile field laboratory as long as their procedures and analytical equipment meet the performance standards of Method 5035. Tables 1 and 2 summarize the options available for sample preservation for both Low Level Analysis and High Level Analysis, respectively. Obviously, sample preservation for long holding times is not warranted with use of an onsite mobile laboratory. Accordingly, DTSC anticipates that soil samples for analysis by a mobile laboratory will be collected in a non-preserved manner. There are two options available for mobile laboratories for the analysis of soil samples pursuant to Method 5035, as follows:

1) Laboratory Subcoring. After the acquisition of soil cores from the subsurface, which are usually obtained within brass sleeves, the field geologist or technician covers the ends of one of the sleeves with teflon sheeting, caps the ends with tight-fitting plastic end-caps, and then places the sleeve into a resealable plastic bag. No headspace should exist within the brass sleeve. The brass sleeve is quickly brought to the mobile laboratory where the chemist can either carefully perform the subcoring of the brass sleeve and then immediately analyze the sample or the brass sleeve is placed into the mobile laboratory's freezer for later subcoring. A brass sleeve placed into the laboratory's freezer should only be held for two hours prior to analysis. Otherwise, the sample should be preserved pursuant to Method 5035 and then analyzed later as appropriate.

   At the mobile laboratory, the chemist performing the subcoring of the soil from the brass sleeve has two options for sample preparation and analysis. The soil subcore can be placed into either a VOA vial or a test tube for preparation and analysis. Prior to sample collection, the mobile laboratory chemist prepares pre-tared test tubes or VOA vials, with magnetic stir bars as needed. A subcoring device, such as a disposable plastic syringe, is used to remove a five gram sample plug from a newly exposed surface of the soil core. The barrel diameter of the disposable plastic syringe should be smaller than that of the test tube or VOA vial. The sample plug is immediately transferred to the test tube or VOA vial, which is then hermetically sealed. The test tube or VOA vial is then weighed to obtain the actual sample weight and the

test tube or VOA vial is loaded immediately on the closed system purge-and-trap for analysis. The time between removal of the sample plug from the soil core and the sealing of the test tube or VOA vial should be no more than two minutes. All surrogates, internal standards, and matrix spikes are introduced either through the PTFE-lined septum cap of the VOA vial or through the sampling value on the test tube cap.

2) Field Subcoring. Pre-tared, labeled VOA vials with PTFE-lined septum caps are taken into the field. The analytical instrumentation of the mobile laboratory should be capable of mechanically accepting the VOA vials. Magnetic stir bars are added to the VOA vials as necessary. Once a soil core is available from the drilling or sampling activities, a subcoring device, such as plastic syringe, is used to remove a five gram sample plug from a fresh surface of the soil core. The plastic syringe should be disposable with a barrel diameter that is smaller than the diameter of the VOA vial. Each sample subcore is immediately transferred to the VOA vial, which is then hermetically sealed. The time between removal of the soil core from the subsurface and hermetically sealing the VOA vial should be no more than two minutes. The sample is quickly brought to the mobile laboratory where the chemist immediately analyzes the sample. If the sample cannot be analyzed immediately, the sample is placed into the mobile laboratory's freezer for later analysis. The sample in the laboratory's freezer should only be held for two hours prior to analysis, otherwise the sample should be preserved pursuant to Method 5035 and then analyzed later as appropriate, either at the mobile laboratory or at a stationary laboratory.

The onsite mobile laboratory should process the samples immediately upon receipt. The chain-of-custody form should be checked and signed, the samples logged-in, and the samples should then be weighed as appropriate. For Low Level Analysis samples, the samples are prepared and analyzed with the caps in-place. All surrogates, internal standards, and matrix spikes are introduced through the septum, either manually or mechanically. For High Level Analysis, the VOA vials may be opened but only after the soil subcore is completely immersed in methanol, as introduced through the septum, and shaken gently to completely capture the VOCs in the headspace. All samples, while in the custody of either the field investigator or the mobile laboratory, should be chilled to 4 ± 2°C.

6.10 Sampling of Consolidated Soil

Some materials that require sampling may be too cohesive for subcoring tools to penetrate. Examples of such materials include cemented soil, dense sand, stiff clay, or bedrock. Samples of these materials can be collected by exposing a fresh surface and using an appropriate tool such as a clean chisel or spatula to generate aggregates of a size that can be placed into a VOA vial. When transferring the aggregates, care must be taken to prevent compromise of the sealing surfaces and threads of the VOA vials. The VOA vial should be handled and preserved pursuant to the data quality objectives for the site. When sampling under these conditions, field personnel should note the occurrence in their field logs. Although the inevitable disaggregation of the sample increases the possibility of VOC losses, there may be no alternative under these conditions. Therefore, caution should be used in the interpretation of the data obtained from this type of material.

TABLE 1: METHOD 5035 LOW LEVEL ANALYSIS
Low Concentrations of VOCs Are Anticipated in the Soil Samples
Sample Detection Limits are Approximately 0.5 μg/kg

Option	Sample Container	Field Preservation	Laboratory Activity	Holding Time [2]
1B	VOA Vial [1, 3]	Sodium bisulfate solution and cool to 4 ± 2°C	Cool to 4 ± 2°C until analysis	14 days
1C	VOA Vial [1, 5]	Water and cool to 4 ± 2°C	Freeze to <-7°C within 48 hours from sample collection	7 days
1D	VOA Vial [1, 5]	Water and freeze to <-7°C [4]	Freeze to <-7°C	7 days
1E	VOA Vial [1, 5]	Water and cool to 4 ± 2°C	Cool to 4 ± 2°C until analysis	48 hours
2A	Multi-Functional Sampling Device [3]	Cool to 4 ± 2°C	Extrude into sodium bisulfate solution within 48 hours of sample collection and cool to 4± 2°C	14 days
2B	Multi-Functional Sampling Device	Cool to 4 ± 2°C	Extrude into VOA vial within 48 hours of sample collection and freeze to <-7°C	7 days
2C	Multi-Functional Sampling Device [3]	Cool to 4 ± 2°C	Cool to 4 ± 2°C until analysis	48 hours
3A	VOA Vial [1]	Cool to 4 ± 2°C	Freeze to <-7°C within 48 hours from sample collection	7 days
3B	VOA Vial [1]	Freeze to <-7°C [4]	Freeze to <-7°C	7 days
3C	VOA Vial [1, 3]	Cool to 4 ± 2°C	Cool to 4 ± 2°C until analysis	48 hours

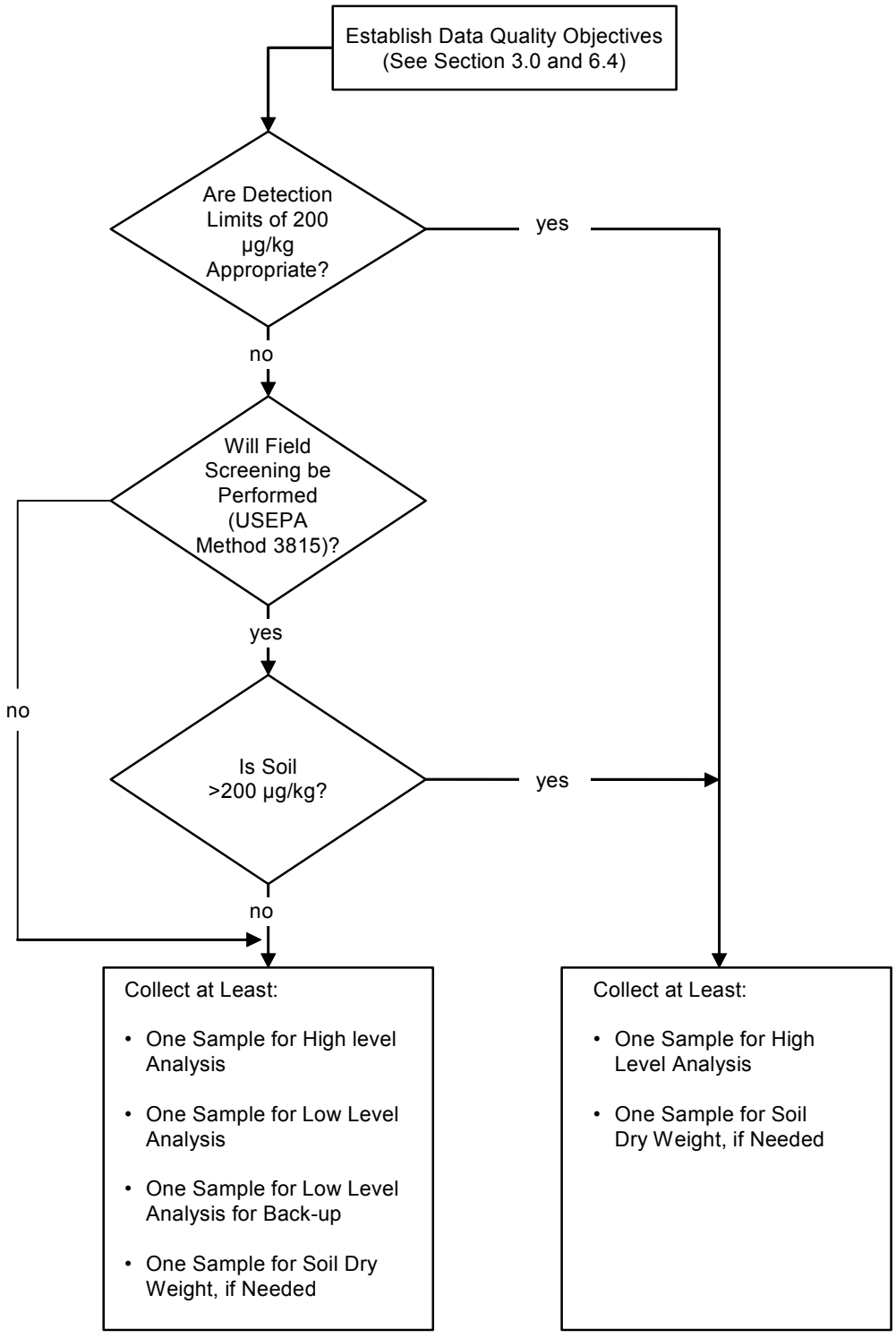
[1] VOA vials are never opened after being sealed in the field.
[2] Holding time is measured from the time of sample collection.
[3] Preferred method for aromatic hydrocarbons due to potential biodegradation.
[4] Field freezing is needed when the samples cannot be transported to the stationary laboratory within 48 hours of the sampling time.
[5] Water should be used as a replacement for sodium bisulfate solution when soils and contaminants are incompatible with low pH conditions.

TABLE 2: METHOD 5035 HIGH LEVEL ANALYSIS
High Concentrations of VOCs are Anticipated in the Soil Samples
Sample Detection Limits are Approximately 200 μg/kg

Option	Sample Container	Field Preservation	Laboratory Activity	Holding Time [2]
1A	VOA Vial [1, 3]	Methanol and cool to 4 ± 2°C	Cool to 4°C until analysis	14 days
1C	VOA Vial [1]	Water and cool to 4 ± 2°C	Freeze to <-7°C within 48 hours from sample collection	7 days
1D	VOA Vial [1]	Water and freeze to <-7°C [4]	Freeze to <-7°C	7 days
1E	VOA Vial [1]	Water and cool to 4 ± 2°C	Cool to 4 ± 2°C until analysis	48 hours
2A	Multi-Functional Sampling Device [3]	Cool to 4 ± 2°C	Extrude into methanol within 48 hours of sample collection and cool to 4 ± 2°C	14 days
2B	Multi-Functional Sampling Device	Cool to 4 ± 2°C	Extrude into VOA vial within 48 hours of sample collection and freeze to <-7°C	7 days
2C	Multi-Functional Sampling Device [3]	Cool to 4 ± 2°C	Cool to 4 ± 2°C until analysis	48 hours
3A	VOA Vial [1]	Cool to 4 ± 2°C	Freeze to <-7°C within 48 hours of sample collection	7 days
3B	VOA Vial [1]	Freeze to <-7°C [4]	Freeze to <-7°C	7 days
3C	VOA Vial [1, 3]	Cool to 4 ± 2°C	Cool to 4 ± 2°C until analysis	48 hours

[1] VOA vials are never opened after being sealed in the field.
[2] Holding time is measured from the time of sample collection.
[3] Preferred method for aromatic hydrocarbons due to potential biodegradation.
[4] Field freezing is needed when the samples cannot be transported to the stationary laboratory within 48 hours of the sampling time.

FIGURE 3: SOIL SAMPLING DECISION MATRIX
Selection of the Number of Soil Samples at a Sample Location Point



Note: The options for Low Level Analysis and High Level Analysis are shown in Tables 1 and 2.

Appendix A: Sampling Option 1

Sampling Options 1A, 1B, 1C, 1D, and 1E
Preserved VOA Vials

The stationary laboratory that will perform the soil analysis will provide preserved, tared, and labeled VOA vials that have PTFE-lined septum caps. Alternatively, VOA vials can be purchased from scientific suppliers that are certified clean to USEPA specifications. Typically, the VOA vials are 40 milliliters in size. The preservation fluid is either methanol or sodium bisulfate solution. Also, the VOA vials may contain reagent-grade extraction water. The methanol, sodium bisulfate solution, and reagent water must be laboratory-grade fluids. The fluids must be purge-and-trap grade, certified to be free of VOCs. The selection of the preservation fluid is based upon the desired method detection limits (Low Level Analysis or High Level Analysis) and the data quality objectives. In the field, the methanol-preserved VOA vials are re-weighed to verify no preservative loss due to volatilization. Re-weighing the VOA vials containing reagent water or sodium bisulfate solution is not necessary because these fluids have no affect on the dilution calculation. However, magnetic stir bars may be needed in VOA vials containing reagent water or sodium bisulfate solution pursuant to the laboratory's requirements. Soil subcores of appropriate mass are placed into the VOA vials in the field and are capped, forming an airtight seal. The soil samples preserved with methanol are re-weighed in the field to determine the soil sample weight. The soil samples in reagent water or sodium bisulfate solution are not reweighed in the field because the stationary laboratory determines the sample weight.

Usually, three co-located samples are taken and placed into their individual vials so that the laboratory has an appropriate sample volume. At the laboratory, the capped vials containing reagent water or sodium bisulfate solution are weighed to obtain the weight of the soil. The methanol-preserved samples are re-weighed to verify any preservative loss due to volatilization. For Low Level Analysis, the samples containing reagent water or sodium bisulfate solution are prepared and analyzed with the caps in-place. The vial caps are not removed throughout the entire storage, preparation, and analysis procedure. Hence, the VOA vials must be compatible with the laboratory's autosampler instrumentation to avoid further sample handling which might promote VOC loss. All surrogates, internal standards, extract aliquots and matrix spikes are introduced and removed through the septums, either manually or mechanically. For High Level Analysis, the methanol-preserved samples are analyzed by Method 5030.

Several coring devices are available for the collection of soil subcores, which can readily transfer the soil subcores into the relatively narrow opening of a VOA vial. These devices include the EasyDraw Syringe™ and PowerStop Handle™, the Purge-and-Trap Soil Sampler™, the Lock N' Load™ Soil Sampling Tool, and a cut plastic syringe. Any equivalent device may also be used after consultation with DTSC prior to sampling. The coring devices are usually disposable and should not be re-used. To expedite the soil sampling, numerous coring devices should be taken into the field.

A.1 Field Procedures at a Sample Location Point

1) On the day of the field activities, weigh the pre-tared methanol-preserved VOA vials to verify that no preservative has evaporated. All weights must be recorded to within 0.05 grams[11]. To the extent possible, field personnel should weigh the VOA vials in a protected environment to permit accurate weighing. The VOA vials containing reagent water or sodium bisulfate solution do not require weighing prior to sample collection.

2) Discard all methanol-preserved VOA vials with unacceptable preservative loss of greater than 0.05 grams.

3) Record the weight of the methanol-preserved VOA vials in the field log book.

4) Construct or assemble the subcoring device pursuant to the manufacturer's instructions.

5) Push the coring device into a freshly exposed soil surface. Continue pushing until the soil column inside the coring device has forced the device's plunger to the stopping point or until the appropriate amount of soil has been collected, usually five grams (two to three cubic centimeters).

6) Use a paper towel to quickly wipe the exterior of the coring device to remove excess soil.

7) Insert the end of the coring device into the pre-tared VOA vial and eject the soil sample into the vial by pushing on the plunger of the coring device. Avoid splashing the preservative out of the VOA vial by holding the VOA vial at an angle. The mouth of the coring device should not contact the preservative.

8) Use a paper towel to quickly wipe the VOA vial threads to remove excess soil and cap, hermetically sealing the vial. Note: Steps 5 – 8 should be done as quickly as possible, usually within two minutes, to prevent VOC loss.

9) Gently swirl the soil sample in the VOA vial to mix and break up the soil aggregate until the soil is covered with the preservative. The swirling of the VOA vial should not allow the soil to contact the PTFE septum. The PTFE septum must remain free of soil to allow for the analysis of the sample through the septum. Hence, do not vigorously shake the vial.

10) Re-weigh the methanol-preserved VOA vials to determine the weight of the soil sample. The VOA vials containing reagent water or sodium bisulfate solution do not require weighing after sample collection.

11) Using the pre-adhered label on the VOA vial, complete the label information as needed. The VOA vials as supplied from the laboratory or a certified vendor will be pre-labeled. Hence, no additional labeling of the VOA vials in the field should be done that might alter the weight of the sample container. If it is necessary to include another label, a label can be applied to the exterior of the plastic bag containing the vial.

[11] USEPA Method 5035 specifies that all weights should be recorded within 0.01 grams but most commercially available electronic balances only have the capacity to accurately measure within 0.05 grams; hence, 0.05 is used within this Guidance Document as the accuracy threshold.

12) Place the VOA vial into a resealable plastic bag and place the package into a cooler chilled to 4 ± 2°C or <-7°C, as needed. The VOA vials should be transported to the laboratory in an upright position whenever possible. However, VOA vials subject to freezing at <-7°C should be transported to the laboratory at a 45° angle to prevent vial breakage due to preservative expansion.

13) Repeat the procedure as necessary to obtain the required number of Method 5035 soil samples.

14) As needed, collect a soil sample for the measurement of the dry weight of the soil. The sample does not need chemical preservation and can be collected in either a sealable glass jar or empty VOA vial.

A.2 Field Considerations

a) Disposable plastic syringes can be easily converted into an inexpensive coring device. The "needle end" of the syringe barrel is cut-off with a sharp knife or scissors, creating a blunt, even coring end. The barrel diameter of the plastic syringe must be narrower than the diameter of the VOA vial for soil extrusion. Prior to field activities, the approximate volume associated with five grams of soil must be determined. Hence, it may be necessary to calibrate the syringe by collecting and weighing trial soil quantities with the plastic syringe to determine the length of soil in the syringe barrel that corresponds to 5.0 ± 0.5 grams.

b) Do not use or submit samples for analysis if the preservative has spilled or splashed from the VOA vial. Extra tared and preserved VOA vials should be taken into the field anticipating potential preservative loss due to evaporation or spillage. Methanol-preserved VOA vials should be weighed in the field prior to soil sample collection. A significant change in weight of the VOA vial indicates preservative loss and the VOA vial should not be used. Unacceptable preservative loss is 0.05 grams. After sample collection and before transport to the laboratory, the samples are reweighed to determine the weight of the samples.

c) Rough trimming of a sampling location's surface layer should be considered if the soil has been exposed to ambient air for more than two minutes. Removal of the surface layer can be accomplished by scraping the soil surface with a clean spatula, scoop, trowel, or knife.

d) The collection of numerous co-located subcores from a core sample may be difficult due to the small diameter of the core. Accordingly, care should be taken in obtaining all the necessary subcores. All subcores should be taken from a fresh surface. If a fresh surface is not available after the first or second co-located sample, the core sample should be slowly extruded from the core barrel and cut to expose additional subcore sampling areas.

e) Many core barrels are not entirely full upon retrieval from the subsurface. Hence, upon subcoring, these partially full core barrels will require bracing or support so that subcoring can occur without pushing the soil core into the interior of the barrel.

f) The collection of subsequent co-located subcores should not begin until the previous subcore is sealed in its vial.

g) Field personnel should wear powderless gloves during sample collection to avoid VOC exposure.

h) The threads of the VOA vials must be free of soil; otherwise the cap will not seal properly, compromising the integrity of the sample.

i) To maintain sample integrity, only two minutes should ideally transpire between core retrieval from the subsurface and subcoring by the coring device.

j) Soil samples with known high concentrations of VOCs should be separated from soil samples with low concentrations to prevent cross contamination. Ideally, the soil samples of differing VOC concentrations should be placed into different shipping bags and, if possible, placed into separate field coolers.

k) Calcareous soil samples may effervesce upon contact with sodium bisulfate solution and compromise the integrity of the sample. Off-gassing could result in VOC loss as the soil contacts the effervescing acid. Pressure build-up after sealing the VOA vial could cause the vial to shatter or the carbonates in the soil could buffer the acid, rendering sodium bisulfate solution ineffective as a preservative. Accordingly, the soils at the site should be evaluated for potential effervescence prior to sampling activities and the occurrence of effervescence should be reported to the laboratory. In cases where effervescence is a potential problem, an alternative sample collection method should be utilized.

l) Methanol is a toxic and flammable liquid, and must be handled with appropriate safety precautions. Inhalation of methanol vapors should be avoided. It should be handled in well ventilated areas and stored away from open flames and other ignition sources as well as extremely hot areas. Sodium bisulfate solution is a mineral acid and must be handled with appropriate safety precautions. Contact with skin and eyes should be avoided. Protective gloves and eye protection should be worn when handling vials containing sodium bisulfate solution.

m) Depending on the quantity and method of packaging, methanol and sodium bisulfate solution may be considered Department of Transportation (DOT) Hazardous Materials and subject to DOT hazardous materials regulations.

n) Consult the laboratory to determine if magnetic stir bars should be added to the VOA vials prior to hermetic sealing in the field. Soil samples subject to Low Level Analysis must be agitated during analysis to assist the VOC purge process. Agitation can be accomplished by either sonication or stirring with magnetic bars. Hence, if the stationary laboratory does not have the ability to sonicate the soil sample with their instrumentation, magnetic stir bars must be added to the VOA vials subject to Low Level Analysis.

A.3 Potential Field Equipment

- VOA Vials – Extra preserved VOA vials should be taken into the field due to potential breakage or expansion of the sampling program due to unanticipated field conditions. Typically, the VOA vials are 40 milliliters in size.

- Digital Field Scale – Used to weigh VOA vials to verify no methanol loss prior to sampling; if the field scale is a balance-type, calibrated weights must also be taken into the field. All

scales must have an accuracy of 0.05 grams. The field scale is also used to determine the volumetric amount of soil needed for five grams of sample.

- Coring Devices – Used to obtain the soil subcores; must have a diameter that is slightly smaller than the VOA vials.

- Gloves – Used for health and safety protection; powderless preferable.

- Paper Towels – Used to clean VOA vial threads for proper cap attachment.

- pH Test Strips – Used to verify that soil subcores are preserved to a pH of less than 2.0 in the VOA vials.

- Acid Preservative – Used as needed to reduce the pH in the VOA vials to less than 2 before adding the soil subcore to the vial; the addition of acid should only be done if the VOA vials were incorrectly preserved by the laboratory or vendor.

- Field Cooler – Insulated ice chest for sample storage and shipment; must be capable of cooling and maintaining the soil samples to 4 ± 2°C or <-7°C, as needed.

- Ice – Used to chill field cooler and samples to 4 ± 2°C. Wet ice preferred over blue ice for chilling to 4 ± 2°C. The wet ice should be double bagged to prevent filling the field coolers with water which may damage the labels on the samples. Dry ice, as needed, for chilling the field cooler to <-7°C.

- Field Blades – Clean spatula, scoop, trowel or knife used for exposing fresh soil surfaces before subcoring.

- Indelible Ink Pens – Labeling of the soil sample containers; pens that use VOCs, such as markers, are not recommended due to potential cross-contamination.

- Resealable Plastic Bags – Used as a secondary container to prevent moisture infiltration during sample transport.

- Glass Containers – Used to collect soil samples for dry weight determination. Samples for dry weight determination can also be collected in brass sleeves or acetate liners. These samples do not need preservation. However, the collection method should minimize sample handling, sample disaggregation, and moisture loss.

- Decontamination Equipment – Used to decontaminate the field blades and coring devices, for repeated use, as needed.

Appendix B: Sampling Option 2

Sampling Options 2A, 2B, and 2C
Multi-Functional Sampling Devices

Multi-functional sampling devices (MFSDs) are used which act as both a coring tool and airtight storage container. Examples of MFSDs are the EnCore™ Sampler and the Core N' One™ Sampler. The MFSDs collect a small sample subcore directly into a volumetric storage chamber, filling it completely with zero headspace. The soil sample size can be either five grams or 25 grams, dependent on the MFSD size[12]. MFSDs are to be used on cohesive but uncemented soils that will form a cohesive plug when sampled. The storage containers are then capped, forming an airtight seal. The intact samples are transported to the laboratory in the sealed device at 4 ± 2°C. Usually, three co-located samples are taken with the MFSDs so that the stationary laboratory has an appropriate sample volume; however, fewer number of samples may be taken pursuant to Figure 1 if the VOC concentrations can be quantified with high detection limits (200 μg/kg). At the stationary laboratory, the soil sample within the MFSD is transferred to a VOA vial. The diameter of the VOA vial must be sufficiently large to accept the soil sample from the MFSD without alteration and the VOA vial must be compatible with the laboratory's autosampler instrumentation.

B.1 Field Procedures at a Sample Location Point

1) Enter the preliminary sample identification information on the label of the MFSD package. Usually, each sampler is individually packaged in a resealable plastic bag with usage instructions attached. No pre-sampling container preparation is required.

2) Remove the sampler and cap from the package and assemble the MFSD pursuant to its instructions.

3) Push the coring body of the MFSD into a freshly exposed soil surface, filling the sampling chamber. The MFSD should be visually checked to verify that a headspace-free subcore has filled the chamber. Any excess soil extruding from the sample chamber should be carefully removed by trimming away the excess with a clean field blade.

4) Use a paper towel to quickly wipe the sampler head to remove excess soil from the exterior so that the cap can be tightly attached.

5) For an Encore™ Sampler, carefully push the cap on with a gentle twisting motion to firmly attach the cap to the chamber, taking care not to damage the o-ring seal on the sampler. For a Core N' One™ Sampler, the cap is gently treaded onto place on the sampling chamber, taking care to properly seat the sealing gasket on the chamber. Note: Steps 3 – 5 should be done as quickly as possible, usually within two minutes, to prevent VOC loss.

6) Complete the label information and attach label as needed or required. The label should be placed only on the exterior bag containing the MFSD and not on the MFSD itself.

[12] Generally, the 5 gram MFSDs are used for the determination of VOC concentrations in soil and the 25 gram MFSDs are used for Toxicity Characteristic Leaching Procedure (TCLP) testing. When conducting TCLP testing, usually two 25 gram samples are taken and submitted to the laboratory.

7) Place the MFSD back into its original package and place the package into a cooler chilled to 4 ± 2°C.

8) Repeat the procedure as necessary to obtain the required number of Method 5035 soil samples.

9) As needed, collect a soil sample for the measurement of the dry weight of the soil. The sample does not need to be collected within a MFSD and can be collected in either a sealable glass jar or empty VOA vial.

B.2 Field Considerations

a) The exterior surface of the MFSD must be free of soil; otherwise the cap will not seal properly, compromising the integrity of the sample.

b) Rough trimming of a sampling location's surface layer should be considered if the soil has been exposed to ambient air for more than two minutes. Removal of the surface layer can be accomplished by scraping the soil surface with a clean spatula, scoop, trowel, or knife.

c) The collection of numerous co-located subcores from a core sample may be difficult due to the small diameter of the core. Accordingly, care should be taken in obtaining all the necessary subcores. All subcores should be taken from a fresh surface. If a fresh surface is not available after the first or second co-located sample, the core sample should be slowly extruded from the core barrel and cut to expose additional subcore sampling areas.

d) Many core barrels are not entirely full upon retrieval from the subsurface. Hence, upon subcoring, these partially full core barrels will require bracing or support so that subcoring can occur without pushing the soil core into the interior of the barrel.

e) To maintain sample integrity, only two minutes should ideally transpire between core retrieval from the subsurface and subcoring by the MFSD.

f) The collection of subsequent co-located subcores should not begin until the previous subcore is sealed in its MFSD.

g) Soil samples with known high concentrations of VOCs should be separated from soil samples with low concentrations to prevent cross contamination. Ideally, the soil samples of differing VOC concentrations should be placed into different shipping bags and, if possible, placed into separate field coolers.

h) Field personnel must communicate the required detection limits of the soil samples to the stationary laboratory so that the proper extraction procedures can be followed.

i) A 25 gram MFSD is used to collect, store, and transfer soils for Toxicity Characteristic Leaching Procedure (TCLP) testing, and must not be subsampled by the laboratory into five gram aliquots for VOC analysis per Method 5035.

j) Field personnel should wear powderless gloves during sample collection to avoid VOC exposure.

k) The soil sample collected for measurement of dry weight will also be used by the laboratory to evaluate the soil for reactivity with sodium bisulfate solution prior to Low Level Analysis.

B.3 Potential Field Equipment

- Multi-Functional Sampling Devices – Extra MFSDs should be taken into the field due to potential MFSD breakage or expansion of the sampling program due to unanticipated field conditions.

- Gloves – Used for health and safety protection; powderless preferable.

- Paper Towels – Used to clean sampler head of the MFSD for proper cap attachment.

- Field Cooler – Insulated ice chest for sample storage and shipment; must be capable of cooling and maintaining the soil samples to 4 ± 2°C.

- Ice – Used to chill field cooler and samples to 4 ± 2°C. Wet ice preferred over blue ice for chilling to 4 ± 2°C. The wet ice should be double bagged to prevent filling the field coolers with water which may damage the labels on the samples.

- Field Blades – Clean spatula, scoop, trowel or knife used for exposing fresh soil surfaces before subcoring.

- Indelible Ink Pens – Labeling of the soil sample containers; pens that use VOCs, such as markers, are not recommended due to potential cross-contamination.

- Resealable Plastic Bags – Used as a secondary container to prevent moisture infiltration during sample transport.

- Glass Containers – Used to collect soil samples for dry weight determination. Samples for dry weight determination can also be collected in brass sleeves or acetate liners. These samples do not need preservation. However, the collection method should minimize sample handling, sample disaggregation, and moisture loss.

- Decontamination Equipment – Used to decontaminate the field blades, for repeated use, as needed.

Appendix C: Sampling Option 3

Sampling Options 3A, 3B, and 3C
Non-Preserved VOA Vials

Tared and labeled VOA vials with a PTFE-lined septum caps are taken into the field as supplied by the laboratory or certified vendor, cleaned to USEPA specifications. Typically, the VOA vials are 40 milliliters in size. The VOA vials do not contain chemical preservatives, water-miscible solvents, or reagent water. Soil cores of appropriate mass are placed into the VOA vials in the field and are capped, forming an airtight seal. However, magnetic stir bars may be needed in the VOA vials pursuant to the laboratory's requirements.

Usually, three co-located samples are taken and placed into their individual vials so that the laboratory has an appropriate sample volume. At the laboratory, the capped vials are weighed to obtain the weight of the soil. For Low Level Analysis, the samples are prepared and analyzed with the caps in-place. The vial caps are not removed throughout the entire storage, preparation, and analysis procedure. Hence, the VOA vials must be compatible with the laboratory's autosampler instrumentation to avoid further sample handling which might promote VOC loss. All surrogates, internal standards, extract aliquots and matrix spikes are introduced and removed through the septums, either manually or mechanically. For High Level Analysis, the samples are analyzed by Method 5030.

Several coring devices are available for the collection of soil subcores, which can readily transfer the soil subcores into the relatively narrow opening of a VOA vial. These devices include the EasyDraw Syringe™ and PowerStop Handle™, the Purge-and-Trap Soil Sampler™, the Lock N' Load™ Soil Sampling Tool, and a cut plastic syringe. Any equivalent device may also be used after consultation with DTSC prior to sampling. The coring devices are usually disposable and should not be re-used. To expedite the soil sampling, numerous coring devices should be taken into the field.

C.1 Field Procedures at a Sample Location Point

1) Obtain tared and labeled VOA vials from the laboratory or certified vendor.

2) Construct or assemble the subcoring device pursuant to the manufacturer's instructions.

3) Push the coring device into a freshly exposed soil surface. Continue pushing until the soil column inside the coring device has forced the device's plunger to the stopping point or until the appropriate amount of soil has been collected, usually five grams (two to three cubic centimeters).

4) Use a paper towel to quickly wipe the exterior of the coring device to remove excess soil.

5) Insert the end of the coring device into the pre-tared VOA vial and eject the soil sample into the vial by pushing on the plunger of the coring device.

6) Use a paper towel to quickly wipe the VOA vial threads to remove excess soil and cap, hermetically sealing the vial. Note: Steps 2 - 5 should be done as quickly as possible, usually within two minutes, to prevent VOC loss. Also, care should be taken so that the PTFE

septum remains free of soil to allow for the analysis of the sample through the septum. Hence, do not shake the vial.

7) Using the pre-adhered label on the VOA vial, complete the label information as needed. The VOA vials as supplied from the laboratory or a certified vendor will be pre-labeled. Hence, no additional labeling of the VOA vials in the field should be done that might alter the weight of the sample container. If it is necessary to include another label, a label can be applied to the exterior of the plastic bag containing the vial.

8) Place the VOA vial into a resealable plastic bag and place the package into a cooler chilled to 4 ± 2°C or <-7°C, as needed. The VOA vials should be transported to the laboratory in an upright position whenever possible. However, VOA vials subject to freezing at <-7°C should be transported to the laboratory at a 45° angle to prevent vial breakage due to sample expansion.

9) Repeat the procedure as necessary to obtain the required number of Method 5035 soil samples.

10) As needed, collect a soil sample for the measurement of the dry weight of the soil. The sample can be collected in a sealable glass jar or empty VOA vial.

C.2 Field Considerations

a) Disposable plastic syringes can be easily converted into an inexpensive coring device. The "needle end" of the syringe barrel is cut-off with a sharp knife or scissors, creating a blunt, even coring end. The barrel diameter of the plastic syringe must be narrower than the diameter of the VOA vial for soil extrusion. Prior to field activities, the approximate volume associated with five grams of soil must be determined. Hence, it may be necessary to calibrate the syringe by collecting and weighing trial soil quantities with the plastic syringe to determine the length of soil in the syringe barrel that corresponds to 5.0 ± 0.5 grams.

b) Rough trimming of a sampling location's surface layer should be considered if the soil has been exposed to ambient air for more than two minutes. Removal of the surface layer can be accomplished by scraping the soil surface with a clean spatula, scoop, trowel, or knife.

c) The collection of numerous co-located subcores from a core sample may be difficult due to the small diameter of the core. Accordingly, care should be taken in obtaining all the necessary subcores. All subcores should be taken from a fresh surface. If a fresh surface is not available after the first or second co-located sample, the core sample should be slowly extruded from the core barrel and cut to expose additional subcore sampling areas.

d) Many core barrels are not entirely full upon retrieval from the subsurface. Hence, upon subcoring, these partially full core barrels will require bracing or support so that subcoring can occur without pushing the soil core into the interior of the barrel.

e) The collection of subsequent co-located subcores should not begin until the previous subcore is sealed in its vial.

f) Field personnel should wear powderless gloves during sample collection to avoid VOC exposure.

g) The threads of the VOA vials must be free of soil; otherwise the cap will not seal properly, compromising the integrity of the sample.

h) To maintain sample integrity, only two minutes should ideally transpire between core retrieval from the subsurface and subcoring by the coring device.

i) Soil samples with known high concentrations of VOCs should be separated from soil samples with low concentrations to prevent cross contamination. Ideally, the soil samples of differing VOC concentrations should be placed into different shipping bags and, if possible, placed into separate field coolers.

j) Field personnel must communicate the required detection limits of the soil samples to the stationary laboratory so that the proper extraction procedures can be followed.

k) Consult the laboratory to determine if magnetic stir bars should be added to the VOA vials prior to hermetic sealing in the field. Soil samples subject to Low Level Analysis must be agitated during analysis to assist the VOC purge process. Agitation can be accomplished by either sonication or stirring with magnetic bars. Hence, if the stationary laboratory does not have the ability to sonicate the soil sample with their instrumentation, magnetic stir bars must be added to the VOA vials subject to Low Level Analysis.

l) The soil sample collected for the measurement of dry weight can also be used by the laboratory to evaluate the soil for reactivity with sodium bisulfate solution prior to Low Level Analysis.

C.3 Potential Field Equipment

- VOA Vials – Extra VOA vials should be taken into the field due to potential breakage or expansion of the sampling program due to unanticipated field conditions. Typically, the VOA vials are 40 milliliters in size.

- Coring Devices – Used to obtain the soil subcores; must have a diameter that is slightly smaller than the VOA vials.

- Gloves – Used for health and safety protection; powderless preferable.

- Paper Towels – Used to clean VOA vial threads for proper cap attachment.

- Digital Field Scale – Used to determine the volumetric amount of soil needed for five grams of sample.

- Field Cooler – Insulated ice chest for sample storage and shipment; must be capable of cooling and maintaining the soil samples to 4 ± 2°C or <-7°C, as needed.

- Ice – Used to chill field cooler and samples to 4 ± 2°C. Wet ice preferred over blue ice for chilling to 4 ± 2°C. The wet ice should be double bagged to prevent filling the field coolers with water which may damage the labels on the samples. Dry ice, as needed, for chilling to <-7°C.

- Field Blades – Clean spatula, scoop, trowel or knife used for exposing fresh soil surfaces before subcoring.

- Indelible Ink Pens – Labeling of the soil sample containers; pens that use VOCs, such as markers, are not recommended due to potential cross-contamination.

- Resealable Plastic Bags – Used as a secondary container to prevent moisture infiltration during sample transport.

- Glass Containers – Used to collect soil samples for dry weight determination. Samples for dry weight determination can also be collected in brass sleeves or acetate liners. These samples do not need preservation. However, the collection method should minimize sample handling, sample disaggregation, and moisture loss.

- Decontamination Equipment – Used to decontaminate the field blades and coring devices, for repeated use, as needed.

Appendix D: USEPA Interim Policy

United States Environmental Protection Agency
Region IX

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

June 23, 1999

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

June 23, 1999

MEMORANDUM

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

FROM: Nora McGee, Assistant Regional Administrator
USEPA Region 9

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

Purpose

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

Policy

Scope and Applicability

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

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

Time Frame for Implementation

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

Statement of Policy

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

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

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

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

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

---

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

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

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

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

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

Additional Considerations

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

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

Holding Times: The holding time for preserved soil samples should be interpreted as 14 days from the time of sample collection(stored at $4\pm2^{o}C$). Due to potential biodegradation losses, samples stored in sealed containers, but not chemically preserved, should not be stored for more than 48 hours. On a project/program specific basis, USEPA Region 9 will consider other alternatives to extend the holding time of soils that have not been chemically preserved (see Attachment A). Holding time will be considered as cumulative (see Attachment B for holding time examples). Exceptions should be documented in a QAPP or a SAP submitted to and approved by the Region 9 QA Office.

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

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

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

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

Background

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

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

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

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

References

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

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

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

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

Attachment A

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

> **Freezing of unpreserved samples:** It has been shown in several studies that freezing of unpreserved soils is an effective means of slowing the biodegradation process. At this time, USEPA Region 9 will accept freezing of unpreserved soils as a method to extend holding times up to seven days on a project specific basis. While there is some evidence that freezing for longer periods may also be acceptable for some data needs, USEPA Region 9 does not believe that the current scientific evidence supports a longer holding time for frozen samples in most cases. Samples should be frozen in containers that have an air tight seal and can maintain this seal while frozen. Because water expands in the freezing process, VOA vials with water or samples with extremely high moisture contents may rupture the storage container.
>
> **Preservatives**: Acids other than sodium bisulfate may be used to preserve low level samples. The choice of an alternative acid should be made in consultation with the USEPA Region 9 QA Office. In all cases the preserved sample pH should be 2.

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

> 1. A VOA vial with 5 mL of water without preservative and approximately 5 g of sample. Which must be analyzed within 48 hours of collection by closed system purge and trap.
>
> 2. A VOA vial with approximately 5 g of sample. Water must be introduced through the septa at time of analysis by closed system purge and trap. Sample must be analyzed within 48 hours of collection if stored at 4±2°C or 7 days if frozen. (This alternative must be approved on a project specific basis.)
>
> 3. An En Core™ sampler which is analyzed or preserved within 48 hours of collection if stored at 4±2°C or analyzed within 7 days if frozen. (Freezing of En Core™ samplers must be approved on a project specific basis.)

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

Attachment B Examples of Holding Time Policy

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

Sample must be analyzed within 48 hours of collection.

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

Sample must be analyzed within 48 hours of collection.

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

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

COMMENT SHEET
Method 5035 Guidance Document

As a user of this guidance document, your comments are important to the Department of Toxic Substances Control. Please use this sheet to inform us of any errors, deficiencies, or suggestions that may improvement this document. If you identify errors or technical deficiencies, please provide suggestions for their rectification.

Please send comments to:

Department of Toxic Substances Control
8800 Cal Center Drive
Sacramento, California 95826-3200
Attention: Geological Services Unit

Your name and address are optional, but if included, a written response will be provided.