USACE Sample Collection and Preparation Strategies for Volatile Organic Compounds in Solids
(October 1998)

Scope:

This document was generated to help implement sample collection and handling procedures that will minimize losses of volatile organic compounds (VOCs) in solid samples and thus obtain more representative VOC results for U.S. Army Corps of Engineers (USACE) environmental projects.[1] This document supplements existing guidance provided in SW-846 Method 5035 in order to resolve and clarify certain technical issues and deficiencies. This policy guidance does not address all facets of VOC sampling and analysis. For example, it does not address laboratory glassware cleaning procedures, the instrumental analysis of VOCs in the laboratory, and sampling design (e.g., how to obtain statistically representative samples of environmental populations). The document presents guidance for the selection of SW-846 methods for the analysis of VOCs in solid matrices and addresses select aspects of sample collection, handling, preparation, and shipment.

Unlike most analytical methods published in SW-846, implementation of Method 5035 impacts multiple technical disciplines. Therefore, successful implementation will require increased communication among members of the project planning team. The final selection of sampling protocol (e.g. field preservation versus EnCore™ sampler) will require input from all data users (e.g. project managers, risk assessors, regulatory specialists, etc.) as well as data implementors (e.g. chemists, geologists, etc). Data Quality Objectives (DQOs) for the project should determine which sampling protocol will be selected.

Introduction:

Traditionally, soils and other solid samples have been collected and analyzed for VOCs predominately using the "low-level" method described in SW-846 Method 5030 or 5030A (Update I). Samples were typically collected in 40 mL to 60 mL VOC vials with PTFE-lined septa using techniques that diminished the integrity of the samples. The physical disruption of the native soil structure that resulted during soil sampling exposed VOCs to open atmospheric conditions, giving rise to high analyte losses. In addition, the threads of vials and jars often became covered with small quantities of soil when the samples were being transferred. This prevented the formation of an air tight seal and gave rise to additional losses during storage. The samples were also transported and stored without any preservative measures other than to cool to 4 °C prior to being opened for subsampling in preparation for analysis by heated purge-and-trap analyses by GC or GC/MS. Because this storage temperature

[1] 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.

does not necessarily prevent biological degradation of aromatic VOCs, additional losses may have resulted for these and other compounds. To exacerbate matters, the sample handling procedures performed at the laboratory gave rise to additional VOC losses (e.g., the escape of headspace VOCs when the vials were opened at the laboratory and the losses arising from additional sample disaggregation when subsamples were taken for weighing and subsequent analysis). The samples were then analyzed directly by purge-and-trap.

A "high-level" method was also available (described in Methods 5030 and 5030A). For high-concentration samples, the laboratory could alternatively extract the samples with methanol (or another water-miscible extraction solvent), and subsequently analyze aliquots of the methanol extracts after aqueous dilution, using the purge-and-trap analysis procedure for aqueous samples. Methanol is an excellent preservative for VOCs. However, since methanol was not added in the field at the time of sample collection and the sample collection process was giving rise to high VOC losses (e.g., due to the disaggregation of samples during collection), the addition of methanol at the laboratory was ineffective in stemming VOC losses. Most of the VOCs were being lost before the samples even arrived at the laboratory. In addition, the analyses performed by methanol extractions typically represented a small fraction of the total VOC analyses performed.

A large body of evidence from both federal and private sectors indicated that the procedures described in Methods 5030 and 5030A were giving rise to unrepresentative results as analyte losses from sample collection and analysis were resulting in large negative biases (discrepancies were typically an order of magnitude or more). There were many incidents in which samples were shipped to the laboratory and subsequently reported to be "clean" when field personnel were confident that the samples had been collected from contaminated areas (based on sight or odor descriptions). Hence, alternative sampling techniques were occasionally implemented. The most common involved sleeves or liners (e.g., in the shape of cylindrical tubes) being placed inside sampling devices such as split spoons. The sleeves were then removed and the ends were sealed for transport to the laboratory. This reduced surface exposure. The soils were extruded from the sleeves in the laboratory prior to analysis. However, when the sleeves were only partially filled, headspace losses were problematic. Furthermore, when the sample containers arrived at the laboratory, it was necessary to weigh the samples after they were extruded, resulting in VOC losses.

To address significant problems with the VOC analyses, the methodology for the solid VOC analyses was dramatically revised in Update III of SW-846 (published in the June 13, 1997 Federal Register). In particular, Method 5030A was deleted for the low-level VOC solid analyses and was primarily replaced with Method 5035. A revised high-level method for solids was also presented in Method 5035. However, although the methodology described in Update III of SW-846 represents a significant improvement over that described in prior versions, there are still significant issues that need to be addressed and certain aspects of the methodology that needs to be clarified for USACE work. A higher degree of coordination is required between field and laboratory personnel. Samples must be handled differently from the onset of sample collection, depending upon the action levels for the project

and the anticipated concentrations of VOCs at the site.

Summary of Current Method 5035:

The two analytical techniques that will be addressed are methanol extraction and vapor partitioning. The new "low-level" method for VOCs is performed by vapor partitioning per Method 5035 (heated purge-and-trap). The new "high-level" VOC method is performed using methanol extraction per Method 5035. After the solid samples are extracted with methanol (or some other water miscible solvent), as described in Method 5035, the extracts are diluted with water and are analyzed essentially as aqueous samples per Method 5030A (purge-and-trap). From an analytical perspective, the low-level method is still a direct analysis method by vapor partitioning and the high-level method still involves solvent extraction followed by a vapor-partitioning analysis technique. The revised methods predominantly differ with respect to the manner in which solid samples are collected and prepared for analysis.

In order to minimize VOC losses, the sample collection and preparation procedures were dramatically modified for both the low-level and high-level methods. The revised sample collection techniques greatly reduce the time in which samples are exposed to atmospheric conditions. In order to help maintain the physical structure of samples for a cohesive granular material, a hand-operated coring device must be used to collect samples of appropriate size for laboratory analysis (e.g., cylindrical soil columns are extruded into vials using disposable plastic syringes with the tapered front ends removed). Chemical preservatives (e.g., sodium bisulfate solution or methanol) must be present in the collection vial prior to introducing the subsample for both the revised low-level and high-level methods. Field personnel transfer samples immediately into preweighed vials containing chemical preservatives. The vials are weighed in the field before use and are subsequently reweighed after the sample aliquots are added to obtain the net sample weights. Alternatively, in order to avoid weighing and preserving the samples in the field, samples for both the low-level and high-level methods may be collected and subsequently stored without preservation, for a maximum of 48 hours, in a coring device such as the EnCore™ [2] sampler (from En Chem, Inc.).

It should be noted that the sample vials for the low-level method are designed to be placed directly in the laboratory's instrument (e.g. auto sampler) so that they remain hermetically sealed until the VOCs are withdrawn during analysis. Therefore, it is critical that only the 40-mL VOC vial (and not the 60 mL VOC vial) that contain the magnetic stir bars be used for the low-level analysis. Recommend that disposable stir bars be used since memory effects have been reported with magnetic stir bars that have been re-used. The entire content of each vial is processed during instrumental analysis. Hence, when low-level VOC analyses of solids are required (as with the collection of aqueous samples for VOCs), it is necessary to collect at least two collocated samples. This gives the laboratory an opportunity to

[2] EnCore™ sampler, En Novative Technologies, Inc., 124 Bellevue St., Green Bay, WI 4302

perform an additional analysis should the first analysis be unacceptable. Furthermore, since the vials remain sealed, dilutions cannot be performed for high-concentration samples. Hence, when low-level VOC analyses are required, unless screening for VOCs is performed in the field (to determine whether the samples contain high VOC concentrations), a collocated sample for the high-level method must be collected with each set of low-level samples. Furthermore, since aqueous acidic solutions are used to preserve samples for the low-level analyses, low-level samples must be tested for carbonate interferences in the field before the samples are containerized. However, the high concentration method does not suffer from these complications. Carbonates are not problematic for methanol preservation and methanol sample extracts may be diluted in the laboratory when concentrations exceed the calibration range of the instrument. In addition, when samples are preserved with methanol, field personnel are not limited to single grab samples (as in the low-level method) but may subsample several locations in a core or split spoon.

Data Quality Objectives and Selection of Methodology:

The development of well defined DQOs during the planning stages of the project is vital to the selection of appropriate methodology. Prior to the selection of methodology, the potential contaminants of concern must be carefully identified. When the nature of the contamination is not well known (e.g., PA/SI), method-specified target analyte lists are typically selected by default. However, in many situations a target analyte list can be reduced based upon historic industrial process and waste disposal practices at the site. If there is no reason to suspect the presence of a contaminant it may be appropriate to omit them from the method analyte list. Since low-level analyses are usually more resource-intensive than high-level analyses, it recommended that rationale for the testing of the more toxic contaminants be carefully evaluated prior to analytical testing (since these contaminants will possess the lowest action levels).

Action levels should be established once the contaminants of concern have been identified (e.g., using regulatory and risk-based criteria). As an illustration, Table 1 lists U.S. EPA Region III Risk-Based Concentrations (RBCs) and Region IX Preliminary Remediation Goals (PRGs) for both residential or industrial sites. Individual states may also impose screening levels that are more restrictive than those listed in Table 1. In order to establish screening level for human-health risk assessment, the PRGs/RBCs listed in Table 1 are typically divided by 10 for noncarcinogenic endpoints (to allow for the presence of multiple contaminants and to ensure that the Hazard Index [HI] does not exceed unity). The Biological Technical Assistance Group (BTAG) RBCs were taken from the *Revised Region III BTAG Screening Levels*, 8-9-95. It is emphasized that these values are extremely conservative (they are based on toxicity to the most sensitive test species) and may not be appropriate for the ecological receptors found on a typical USACE hazardous, toxic, and radioactive waste site. Unfortunately, in the absence of a site-specific biota survey, combined with a literature search for receptor-specific toxicity values, this is the only screening-level information that is typically available. The proposed soil screening level (SSL) values are based upon extremely unrealistic assumptions (e.g., an infinite source of contaminant in constant contact with ground water) and are not recommended for screening

purposes. There are times, however, when screening against these values will be required by regulators.

Once action levels are established during the planning stages of the project, in order to select methodology with adequate sensitivity (i.e., to determine whether the low-level or high-level VOC analyses are more appropriate), the action levels must be compared to the quantitation limits of the laboratory that will be performing the actual analyses. Ideally, the action level for each target analyte should be at least two times greater than the laboratory's corresponding quantitation limits.

It is important to note that laboratories frequently fail to report scientifically valid quantitation limits. Quantitation limits have been generally defined as three to ten times the laboratory determined method detection limits. Quantitation limits should be established from the laboratory's lowest calibration standard and then adjusted for method-specific factors such as sample volume and dilutions. Laboratory detection limits are typically the method detection limits (MDLs) defined in 40 CFR, Part 136, Appendix B. The detection limits for the high-level method are typically 50 times higher than those for the low-level method due to sample dilution (100 uL methanol extract in 4.9 mL water). However, it should be noted that laboratory method detection limit studies are typically performed using "clean matrices" (e.g., sand) and may not reflect method sensitivity in actual environmental matrices of interest. Since, in general, the extraction efficiency for methanol is greater than that for vapor partitioning methods, if the MDL studies were to be performed in actual environmental matrices, the disparity between the detection limits would probably be less prominent (especially for matrices high in organic carbon).

Due to limited data available, a single laboratory's volatile organic compound list (method 8260B), method detection limits and quantitation limits for both the low-level and high-level methods are listed in Table 1. These should not be interpreted as "default" or contract-required compound list, detection and quantitation limits but are presented to illustrate how action levels, quantitation limits, and detection limits should be evaluated to select appropriate analytical methodology.

Sampling and Analysis Strategy:

In general, the selection of methodology—the low-level versus the high-level method—will not only be dependent upon the DQOs (as discussed above), but will also be dependent upon the VOC concentrations of the environmental matrices being sampled. This is illustrated in the flow chart shown at Figure 1. As shown in Figure 1, the high-level method is used when VOC action levels or site VOC concentrations are high. The low-level method is used when project action levels and site VOC concentrations are both low. Hence, when action levels are low, the selection of methodology will be dependent upon the level of site contamination; the high level method is typically required when VOC concentrations are greater than 200 ug/kg.

When action levels are low, both low-level *and* high-level samples must be collected or field screening

must be performed to determine whether low-level *or* high-level samples must be collected. The collection of both low-level and high-level samples for fixed-laboratory analyses constitutes the most conservative approach and is recommended (e.g., unless definitive on-site analyses are being performed). Furthermore, unless a field GC is being used to screen the samples, it is recommended that field screening be performed according to procedures described in "SOP for On-site Estimation of the Total Concentration at Sampling Locations," developed by the USACE Cold Regions Research and Engineering Laboratory.

Screening at the laboratory is recommended regardless of whether samples were screened in the field (although laboratory screening is more important when field screening is not performed). When both low-level and high-level samples are submitted to the laboratory, the laboratory must screen the samples prior to analysis or perform both low-level and high-level analyses on a "trial-and-error" basis. For example, if the laboratory does not perform screening, initially analyzes a sample using the high-level method, and VOCs are not detected or are detected below the quantitation limits, then the laboratory would be required to analyze the corresponding collocated low-level sample. Conversely, if the low-level sample is initially analyzed and exceeds the calibration range of the instrument, then the laboratory would be required to analyze the corresponding sample using the high-level method.

Regardless of the methodology employed, several collocated samples will generally be required for each sample location (e.g., for each sampling depth for a soil boring). The exact number of required collocated samples will be dependent upon a number of factors; these include the following: Analytical methodology (the high-level versus the low-level method), the field screening results when low-level analyses are required, the laboratory's protocols for screening of samples, and requirements for field QC samples (e.g., matrix spikes and duplicates). For example, when low-level analyses are required and site VOC concentrations are known to be low (e.g., from field screening results), at least two samples must be collected for analysis. When low-level analyses are required and the site VOC concentrations are unknown, at least two samples must be collected for potential low-level analysis and one sample must be collected for potential high-level analysis. However, if the laboratory plans to screen the samples, an aliquot may be taken from the high-level sample or an additional sample may be collected. In addition to the samples collected for instrumental (or potential instrumental) analysis, one collocated sample must be collected for a moisture content determination in order to report the VOC results on a dry-weight basis. Samples for moisture content determinations would not be chemically preserved and may be collected in conventional VOC vials. For quality control samples, one additional sample must be collected for the field duplicate and two additional samples for the matrix spike/matrix spike duplicate. Therefore, a site of unknown VOC concentration and a full set of QC would require a total of six samples; two for low-level analysis, one for high-level analysis, one for field duplicate, and two for matrix spike/matrix spike duplicate. However, given proper coordination with the laboratory and their screening process and batching sequence and the additional sample collected for the low-level analysis, the actual number could be reduced to five samples.

Sample Collection and Preparation Protocols:

All VOC sampling procedures for solid waste and soils material for VOC analysis should be compliant with the following criteria. It is important to note that Method 5035 describes laboratory analytical procedures as well as sample preparatory procedures performed in the field and laboratory. Samples analyzed by the low-level and high-level methods should be collected in the field using one of two possible sampling protocols[3] described below. Unless samples are being collected using sampling protocol 1, all soil samples should be chemically preserved in some manner.

Sampling Protocol 1:

This sampling protocol consists of a coring device that also serves as a shipping container. Presently, the EnCore™ sampler is the only commercially available coring device that was designed to collect, store and transfer soils with minimal loss of VOCs. The disposable EnCore™ sampler was designed to be a single use coring device that can also store soil in a sealed, headspace-free state without loss in sample integrity. Most soils that require sampling will consist of cohesive granular materials that allow use of such a coring device. EnCore™ currently has available a hand operated coring tool for obtaining 5-gram samples. A 25-gram sampler is also available for the purposes of Toxicity Characteristic Leaching Procedure testing. Note when a 25-gram sampler is used to collect, store and transfer soils from the field, it should not be subsampled in the lab into 5-gram aliquots.

The following is general guidance for the collection of a soil sample using the EnCore™ sampler (or other types of coring tools such as a disposable plastic syringe). After the split spoon is opened and a fresh surface is exposed to the atmosphere, the sample collection process should be completed in a minimal amount of time. Visual inspection and an appropriate screening method may be selected to determine the interval of the soil core to be sampled. Removing a sample from a material should be done with the least amount of disruption (disaggregation) as possible. Additionally, rough trimming of the sampling location's surface layers should be considered if the material may have already lost VOCs (been exposed for more than a few minutes) or if it may be contaminated by other waste, different soil strata, or vegetation. Removal of surface layers can be accomplished by scraping the surface using a clean spatula, scoop or knife. When inserting a clean coring tool into a fresh surface for sample collection, air should not be trapped behind the sample. An undisturbed sample is obtained by pushing the barrel of the coring tool into a freshly exposed surface and removing the corer once filled. Then the exterior of the barrel should be quickly wiped with a clean disposable towel to ensure a tight seal and the cap snapped on the open end. The sampler should be labeled, inserted into the sealable pouch, immediately cooled to 4 ± 2 °C and prepared for shipment to the lab. If samples are going to be shipped near the weekend or holiday, it is critical to coordinate with the receiving lab to ensure holding time of 48 hours for the EnCore™ sampler is met. Note that a coring device made from a disposable syringe cannot be used for storage or shipment. A separate collocated sample must be collected to

---

[3] It should be noted that the Engineer Manual does not identify the two sampling strategies as "sampling protocol 1" and "sampling protocol 2." This nomenclature was selected to conveniently describe the sampling strategies discussed in the manual.

determine moisture content.

Sampling Protocol 1 is advantageous because weighing and the addition of preservatives in the field are not required. Because sample preparation is performed at the laboratory, exposure hazards and DOT shipping issues arising from the field application of preservatives such as methanol are avoided. However, samples must be stored at 4 ± 2 °C and prepared for analysis within 48 hours of collection. The short holding time for sample preparation usually requires additional coordination with the analytical laboratory and may incur additional costs. Furthermore, the sampling protocol will not be applicable to all solid environmental matrices. Some geological materials are impossible to core (e.g., gravels and hard dry clays).

Sampling Protocol 2:

Unlike the first sampling protocol (which applies to only cohesive granular materials), Sampling Protocol 2 is applicable to all solid matrices. As in the first protocol, in order to minimize the physical disruption of the sample, a coring device (e.g., a disposable plastic syringe with the tapered front end cut off and the rubber cap removed from the plunger) is used to transfer cohesive material into the sample vials. Information on how to transfer non-cohesive materials is discussed later. However, all environmental samples must be weighed and chemically preserved immediately in the field rather than in the laboratory. For example (unless there are carbonates), when performing low-level analyses by Method 5035, samples must be preserved in an aqueous sodium bisulfate solution in the field.

VOC vials and bottles used to store samples should be prepared prior to transferring the sample to the container. That is, methanol (or other chemical preservative) and surrogate compounds should be present in the container, and the tared weight recorded prior to introduction of the sample. The difference in weight, measured before and after the sample is introduced, is used to establish the sample's wet weight. All of the containers used for the preparation of samples should be made of glass and have a thick septum cushion between the sealing material (PTFE) liner and cap (rigid plastic screw cap or aluminum crimp top). PTFE-lined caps for bottles should have flexible septum backing and be at least 10 mils thick to ensure a liquid or airtight seal. The appropriate volume and analytical-grade of methanol (or other chemical preservative) may be added by field personnel or the lab that supplies the containers. The lab should also be responsible for providing trip blanks, ambient blanks (e.g. methanol), and introducing the surrogate compounds. Once the methanol (or other chemical preservative) is placed in the vial, it should only be opened to add the subsample.

The sampling protocol for the collection of soil samples using the disposable plastic syringe should follow the same general description identified above for the EnCore™ sampler up until the coring device is removed from the freshly exposed surface being sampled. After this point, follow the steps identified below.

Each sample container should contain methanol (or other chemical preservative) prior to adding the

sample. Furthermore, the tared weight of the container should be recorded. If the containers are filled with methanol (or other chemical preservative) by the lab, the meniscus should be marked with a permanent marker to evaluate evaporation or accidental spillage in the field or during shipment. Any sample container that shows a loss of methanol (e.g. meniscus below the line marked by the lab) should be discarded. Since the vial or bottle contains methanol (or other chemical preservative), it should be held at an angle when extruding the sample into the container to minimize splashing. Just before capping, a visual inspection of the lip and threads of the sample vessel should be made, and any foreign debris should be removed with a clean towel, allowing an airtight seal to form. The vial should be gently tapped while holding in an upright position. The purpose of the agitation is to ensure that the preservative completely contacts the soil surfaces and disaggregate any large clumps. The sample vials should not be shaken vigorously or up and down. The weight of each container should be measures and entered into a permanent log book. The difference in weight of the container, measured before and after the sample is added, is used to determine the sample's wet weight. The samples should be placed immediately inside a cooler in an upright position and cooled to 4 ± 2 °C. Because of packaging constraints for shipping (e.g. need for inner receptacles), it is absolutely critical that samples be pre-chilled to 4 ± 2 °C prior to shipment. The samples should then be prepared for shipment to the laboratory following the criteria and regulatory considerations described at the end of this guidance. A separate collocated sample must also be collected to determine moisture content.

If soils are granular or wet enough to flow it may be necessary following the coring to cover the open end of the coring device with aluminum foil in a manner that will maintain sample integrity until the device is rotated up to prevent any losses of material. When sampling gravel, or a mixture of gravel and fines, that cannot be easily obtained or transferred using coring tools, as a last resort, a sample can be quickly transferred using a clean spatula or scoop. Typically the collection vial or bottle will contain methanol (or other chemical preservative), therefore, samples should be dislodged with minimal splashing and without the spatula or scoop contacting the liquid contents. For some solids, a wide-bottom funnel or similar channeling device may be necessary to facilitate transfer to the container and prevent compromising of the sealing surfaces of the container. Caution should be taken in the interpretation of the data obtained from materials that fit this description. Losses of VOCs are likely because of the nature of the sampling method and the noncohesive nature of the material exposes more surface area to the atmosphere than for other types of samples. Another potential source of error during the subsampling process, is the separation of coarser materials from fines, which can skew the concentration data if the different particle sizes, which have different surface areas, are not properly represented in the sample. Therefore, caution should be taken in the interpretation of the data obtained from noncohesive materials.

Some materials (e.g. cemented or noncohesive granular material) that require sampling may be to hard for coring tools to penetrate. Samples of such material can be collected by fragmenting a larger portion of the material using a clean chisel to generate aggregate(s) of a size that can be placed into a VOC vial or bottle containing methanol (or other chemical preservative). When transferring the aggregate(s), precautions must be taken to prevent compromising the sealing surfaces and threads of the container.

Losses of VOCs by using this procedure are dependent on the location of the contaminant relative to the surface of the material being sampled. Therefore, caution should be taken in the interpretation of the data obtained from materials that fit this description. As a last resort when this task cannot be performed onsite, a large consolidated sample can be collected in a vapor-tight container and transported to the laboratory for subsampling. Collection, fragmenting, and adding the sample to a container should be accomplished as quickly as possible.

Guidance for the Implementation of Method 5035:

Since it is anticipated that cohesive soils (and other aggregate granular material) will primarily be the matrices of interest and Method 5035 will primarily be used to perform both the low-level and high-level VOC analyses, the implementation of Method 5035 for cohesive soils will be discussed in additional detail (based upon this guidance and the guidance presented in SW-846). This section of document addresses several implementation problems that arise when samples are collected using sampling protocol 2.

Field Weighing:

When field personnel collect samples using the second sampling protocol, they essentially perform the following activities for both the low and high-level methods: Field personnel weigh the vials containing the liquid preservatives (e.g., aqueous sodium bisulfate and methanol for the low-level and high-level methods, respectively), collect the samples using some type of coring device (e.g., a syringe with its tip removed), extrude the sample cores into the vials, and reweigh the filled vials (to determine the exact weight of the sample added to the preservative).[4] A net sample weight of about five grams is required (assuming a soil density of 1.7 g/cm^3 this corresponds to a soil volume of about 3 cm^3).

The laboratory may add the chemical preservatives to the vials prior to shipping them to the field. Alternatively, field personnel may add the preservatives to the vials immediately prior to the addition of the sample cores.[5] According to Method 5035, all weights must be recorded to within ± 0.01 g. In addition, if methanol is added to the vials in the laboratory, Method 5035 states that the field personnel must verify the weights of the vials containing the methanol to within ± 0.01 g before the core samples are placed into the vials. Although it may be desirable to record weights to the nearest 0.01 g, weight verification to the nearest 0.01 g is often impractical under field conditions. To the extent possible under field conditions, samples should be collected in a "protected" environment to permit accurate

---

[4] According to Method 5035, after sample collection, the sample vials should also be weighed at the laboratory to verify the field weights.

[5] For the low-level method of Method 5035, the preservative consists of 1-gram of sodium bisulfate to 5 mL H_2O (the pH must be $\leq$ 2). For the high-level method, 5-grams of sample is added to 5 mL of methanol.

weighing. However, accuracy to within ± 0.01 g requires very controlled conditions available to only a limited number of sites (e.g., the weighing must be performed in a building or mobile laboratory). Weights should be recorded to the nearest 0.1 g and verified to the nearest 0.1 g (i.e., to within ± 0.15 g) for both the low-level and high-level analyses. The error associated with a 0.1 g mass discrepancy for a 5-gram sample will not be significant, relative to method analytical error (e.g., there is a 15% error tolerance for instrumental error alone).

Presence of Carbonates:

Since acidic preservatives are added to samples collected for low-level analyses, the presence of carbonates are problematic. When low-level samples are preserved in the field, all soil samples should be tested for carbonates prior to sample collection. If effervescence is observed, preservation by acidification is inappropriate. Samples that react with acid preservatives (i.e., effervesce) should be disposed as investigation derived waste (IDW) and not sent to the laboratory for analyses since the analytical results will not be representative of the VOC concentrations in the environmental matrix being sampled.

If carbonates are present, the following options should be considered: performing on-site analysis of the samples (e.g., using a field GC), collecting the samples using sampling protocol 1 and analyzing them at the laboratory within 48 hours of sample collection, or preserving the samples with methanol. Preliminary holding time studies on a reduced list of volatile organic compounds indicate that samples collected without chemical preservation using the EnCore™ sampler will maintain their integrity for up to 7 days when stored at 4 ± 2 °C and up to 14 days when stored at -12 ± 3 °C. However, the EnCore Sampler has not been demonstrated for compounds with boiling points less than 30 °C (e.g. bromomethane, chloroethane, chloromethane, or vinyl chloride). Additional guidance on extending the storage time will be provided as it becomes available. Field preservation with alternative chemical preservation (e.g., copper sulfate) can also be used. However, it should be noted that the techniques described are based upon limited data. As a consequence, in order to use these preservation techniques, regulatory approval and "additional demonstration of performance" would usually be required. For example, "additional demonstration of performance" may involve the collection of duplicates for a portion of the total number of site samples (e.g., 20% of the samples). For each duplicate pair, one sample would be collected using the EnCore™ sampler and analyzed within 48 hours. All the remaining samples would be preserved prior to analysis using one of the techniques described. If the duplicate results were comparable (i.e., within duplicate precision limits), then one would conclude that the protocols maintained integrity of the samples and that the results corresponding to these samples are acceptable (with respect to preservation and holdings times).

Contamination:

When samples are preserved with methanol in the field, it is especially critical to avoid the introduction of contamination from external sources such as vehicular emissions or dust. Hence, when samples are

preserved with methanol in the field, a methanol blank should be exposed to field conditions during the sample collection process.

Regulatory Considerations for Sample Shipping for Method 5035:

With the recent promulgation of EPA SW-846 Method 5035, a number of concerns and inquires have been made regarding the potential regulatory impacts to field personnel tasked with sampling, preserving, and shipping environmental samples using this method. When samples are collected using the second sampling protocol above, DOT shipping requirements (as well as health and safety issues) need to be taken into account for the preservatives. Depending on the quantity and method of packaging, sodium bisulfate and methanol may be DOT Hazardous Materials and may be subject to the DOT hazardous materials regulations. It should be noted that DOT regulations associated with the use of preservatives in the field may be avoided by using the first sampling protocol (e.g., EnCore™ core samples do not require chemical preservation in the field).

This section addresses specific aspects of the Department of Transportation (DOT) and International Air Transportation Association (IATA) regulations for the shipment of samples prepared in the field for laboratory analysis by Method 5035. When it is necessary to preserve samples in the field, there are three possible sample shipment scenarios: 1) small quantity exception; 2) limited quantity DOT hazardous material; or 3) fully regulated DOT hazardous material. These three options and associated requirements are outlined below.

Shipment as a Small Quantity Exception:

The recommended way to ship methanol or sodium bisulfate preserved samples is in accordance with 49 CFR 173.4 under the small quantity exception. If the criteria of this regulation as described below are met, shippers are not subject to the DOT Hazardous Materials Regulations or the associated personnel training. The Hazardous, Toxic, and Radioactive Waste Center of Expertise is coordinating with the Packaging, Storage, and Containerization Center at Tobbyhanna Army Depot, Tobbyhanna, PA to develop standard 49 CFR 173.4 tested and certified packaging to be used by field personnel.

Criteria:

Inner Container Limit: 30 mL {49 CFR 173.4(a)(1)(i)}
Total Net Quantity Outer Package Limit: 500 mL {IATA Dangerous Goods Regulations}
Package Certification: 49 CFR 173.4 (a)(10) Certification
Shipping Paper: Not Required, but Air waybill must be marked "Dangerous Goods in Excepted Quantities"
Marking: 49 CFR 173.4 (a)(10) Certification
Labeling: Not Required
Placarding: Not Required

DOT HMR Training: Not Required

NOTE: DOT considers the 30 mL inner container limit to include both methanol and soil because by definition the contents of the vial are a slurry containing free liquid. Therefore, in order to not exceed this 30 mL criteria and assuming a 1:1 ratio of methanol to soil, the recommended volume of methanol should not exceed 10 mL. The absolute volume would be 15 mL of methanol to 15 grams of soil.

Shipment as Limited Quantity Exception:

Methanol or sodium bisulfate preserved samples greater than 49 CFR 173.4 inner-container quantities (e.g. 30 mL) will void the 49 CFR 173.4 small quantity exception and samples should be shipped in accordance with the DOT Limited Quantity Exception.

Criteria:

Inner Container Limit: 49 CFR 172.101 Table, Column 8A criteria and for air transportation 49 CFR 172.101 Table, Column 9A/9B
Outer Container Limit: 49 CFR 172.101 Table, Column 8A criteria and for air transportation 49 CFR 172.101 Table, Column 9A/9B
Package Certification: 49 CFR 172.101 Table, Column 8A criteria
Shipping Paper: Required
Marking: PSN, UN#, orientation arrows, shipper name & address
Labeling: Required for air transportation 49 CFR 172.101 Table, Column 6
Placarding: Not required
DOT HMR Training: Required {49 CFR 172.700}

DOT Regulated Hazardous Materials Shipments, Fully Regulated:

If shippers *do not* take a limited quantity exception and their materials are regulated in commerce, they must have DOT specification packages and will have to consider the "cooler" a DOT overpack in accordance with 49 CFR 173.25.

Criteria:

Inner Container Limit: For air transportation 49 CFR 172.101 Table, Column 9A/9B
Outer Container Limit: For air transportation 49 CFR 172.101 Table, Column 9A/9B
Package Certification: UN Specification 49 CFR 172.101 Table, Column 8B criteria
Shipping Paper: Required
Marking: PSN, UN# orientation arrows, shipper name and address, inner packages comply with prescribed specifications 173.25(a)(4)

Labeling: As Required by 49 CFR 172.101 Table, Column 6
Placarding: As Required by 49 CFR 172.500
DOT HMR Training: Required

Site Safety:

Methanol is a toxic and flammable liquid. Therefore, methanol must be handled with all safety precautions related to toxic and flammable liquids. Inhalation of methanol vapors must be avoided. Vials would be opened quickly during the sample preservation procedure. Methanol must be handled in a ventilated area. Protective gloves should be worn when vials containing methanol are handled. Methanol should be stored away from open flames, areas of extreme heat, and other ignition sources. Vials containing methanol should be refrigerated (e.g., stored in coolers with ice).

Sodium bisulfate is a strong mineral acid and must be handled with all safety precautions related to acids. Contact with the skin and eyes should be avoided. Protective gloves and eye protection should be worn with vials containing sodium bisulfate.

Costs for Implementing Method 5035:

There will be additional costs associated with the implementation of Method 5035. The major laboratory cost associated with the new method is the $25,000.00 price tag for the auto-sampler. However, this cost is incurred no matter which sampling protocol is selected. The costs associated with the actual sampling process is discussed further. The cost of the EnCore™ containers is higher than conventional VOC vials. Assuming three cores will be required for each sampling location, the cost of the EnCore™ containers is approximately $25 dollars more than conventional containers (including the plastic syringes used to collect the samples). In addition to the containers, there is a one time cost for the stainless steel T-Handle and Extrusion tools ($125.00 and $175.00 respectively) needed to use the EnCore™ samplers. The alternative costs associated with performing preservation in the field is more significant. Preservation in the field may take up to an additional 50 percent of time to collect, preserve and weigh the sample vials because of the immediate need to both collect and preserve the soil samples. This in turn may require an additional person on site. The personnel responsible for preserving and weighing the samples should be experienced in analytical techniques. Since methanol acts as an absorbent to volatile vapors, ambient blanks will also be necessary at the cost of one volatile analysis. The cost to ship the Small Quantity Exception is equivalent to shipping the EnCore™ sampler. However, the surcharge to ship as Limited Quantity Exception can more than double the cost. Therefore, actual cost impact to a project is more significant for field preservation then shipment via the EnCore™ sampler.

The most significant issue that must be addressed is the collection of samples in a soil boring that will be analyzed based on field screening results. For example, in the case of 100 foot boring, samples may be collected every 10 feet with the stipulation that the three samples that exhibit the highest field screening

result will be submitted to the lab for analysis. While field screening will determine which samples are analyzed, the method 5035 protocol requires collection of all samples (e.g. EnCore™ or field preserved) immediately. The net result in both cases are seven sample intervals will be discarded. Samples collected by the EnCore™ samplers will result in an excess of 21 samples (a minimum of three samplers per interval). Samples collected and immediately field preserved will also result in excess of 21 sample containers. However, unlike the EnCore™ samplers that can be extruded and treated as IDW, the preserved samples must be managed as a hazardous waste (e.g. lab pack) unless excluded because it meets the criteria of a conditionally exempt small quantity generator's waste.

Possible Chemical Interactions:

Although not substantiated, there have been two occurrences with methanol and sodium bisulfate preservation that require some discussion. In the first case, soils that contain aluminum silicates may act as a catalyst causing the conversion of methanol to acetone. The possible mechanism for this interaction is being researched. In the second case, soils like lignite or peat contain a polymeric constituent known as humic acid that may also interact with sodium bisulfate to form acetone. Until either of these two mechanisms can be confirmed or denied, projects should evaluate the potential for acetone to be a site contaminant. For example, if acetone is not an analyte of concern, then the issue may not impact your project decisions. However, those projects that cannot remove acetone from the analyte list should be aware of these possible interactions and any acetone detects should be evaluated. A logical source of acetone contamination is the laboratory. Therefore, site specific sources should always be assessed and not necessarily attributed to one of the above interactions.

Alternative Storage Container for Soils:

A recent study (U.S. Analytical Laboratory - Kimberly, Wisconsin) has shown that soil samples may also be collected in conventional 40 ml VOA vials with teflon lined septa (e.g. vials generally used to collect water samples for VOA analysis). This soil sample collection procedure follows the generally accepted practice to generate a soil core of appropriate dimension from the freshly exposed surface being sampled. At this point, the soil core is extruded into an empty (e.g. no preservative), pre-weighed VOA vial (that may contain a cross shaped magnetic stir bar) and immediately closed. Although there is head space in the vial, the study demonstrated that there is little or no loss of volatiles from the vial (provided the septum remains in tact and is properly sealed). Once collected, the vial is then placed inside a cooler, chilled to 4 ± 2 °C and sent to the laboratory for analysis. The holding time study indicated that samples collected without chemical preservation will maintain their integrity for 5 to 7 days when stored at 4 ± 2 °C (in the 40 ml VOA vial). Therefore, upon receipt of samples from the field, the laboratory would have 5 to 7 days to add methanol or other preservative to the vials (by puncturing the septum with a 22-gauge needle or smaller). Note this study was performed with the full list of volatile organic compounds and not a subset of compounds (e.g. 63 compounds including compounds with boiling points less than 30 °C). Additional guidance on extending the storage time (for both pre- and post-preservation) for this procedure will be provided if it becomes available.

Like Sampling Protocol 1, this procedure is advantageous because weighing and the addition of preservatives (e.g. methanol) in the field are not required. In addition, sample preparation is performed at the laboratory, exposure hazards, and DOT shipping issues arising from the field application of preservatives such as methanol are avoided. Note, this is a closed-system that follows the intent of using a hermetically sealed vial as identified in method 5035. Prior to implementation regulatory approval would be recommended.

References:

Engineer Manual 200-1-3 Requirements for the Preparation of Sampling and Analysis Plans

Test Methods for Evaluating Solid Waste, SW-846 Final Update III, Method 5035 Closed System Purge-and-Trap and Extraction for Volatile Organics in Soil and Waste Samples. U.S. EPA, December 1996

U.S. Environmental Protection Agency, "Clarification Regarding Use of SW-846 Methods", Office of Solid Waste and Emergency Response, August 7, 1998.

Table 1: VOC soil screening levels versus method sensitivity for the low-level and high-level methods reported in units of mg/kg (ppm).

COMPOUND	LOW LEVEL		HIGH LEVEL		REGION IX		REGION III		BTAG[3]	SSL[4]
	MDL	QL*	MDL	QL**	IND.[1]	RES.[2]	IND.[1]	RES.[2]	RBC	
Acetone	na	na	0.160	0.5	8,800	2,100	200,000	7,800	na	8
Acrolein	na	na	0.100	0.5	0.34	0.1	41,000	1,600	na	na
Acrylonitrile	0.00056	0.005	0.02	0.25	0.47 c	0.19 c	11 c	1.2 c	na	na
Allyl chloride	0.00067	0.005	0.04	0.25	33,000	3,200	100,000	3,900	na	na
Benzene	0.0005	0.005	0.02	0.25	1.4 c	0.63 c	200 c	22 c	0.1 fa	0.02
Bromochloromethane	0.00032	0.005	0.020	0.25	na	na	na	na	na	na
Bromodichloromethane	0.0003	0.005	0.02	0.25	1.4 c	0.63 c	92 c	10 c	na	0.3
Bromoform	0.00056	0.005	0.024	0.25	240 c	56 c	720 c	81 c	na	0.5
Bromomethane	0.001	0.01	0.020	0.5	23	6.8	2,900	110	na	0.1
2-Butanone (MEK)	na	na	na	na	27,000	7,100	1,000,000	47,000	na	na
Carbon disulfide	0.00072	0.005	0.024	0.25	24	7.5	200,000	7,800	na	14
Carbon tetrachloride	0.00055	0.005	0.021	0.25	0.5 c	0.23 c	44 c	4.9 c	<0.3 fa	0.03
Chlorobenzene	0.00041	0.005	0.021	0.25	220	65	41,000	1,600	0.1 fa	0.6
Chlorodibromomethane	0.00028	0.005	0.020	0.25	23 c	5.3 c	68 c	7.6 c	na	0.2
Chloroethane	0.00035	0.005	0.020	0.25	na	na	820,000	31,000	na	33
2-Chloroethyl vinyl ether	0.00031	0.005	0.038	0.25	na	na	51,000	2,000	na	na
Chloroform	0.00075	0.01	0.024	0.5	0.53 c	0.25 c	940 c	100 c	<0.3 fa	0.3

COMPOUND	LOW LEVEL		HIGH LEVEL		REGION IX		REGION III		BTAG[3]	SSL[4]
	MDL	QL*	MDL	QL**	IND.[1]	RES.[2]	IND.[1]	RES.[2]	RBC	
Chloromethane	0.00053	0.005	0.025	0.25	2.6 c	1.2 c	440 c	49 c	na	0.007
1,2-Dibromo-3-chloropropane	0.00088	0.01	na	na	1.4 c	0.32 c	4.1 c	0.46 c	na	0.0006
1,2-Dibromoethane	0.00043	0.005	0.023	0.25	0.02 c	0.0049 c	0.067 c	0.0075 c	5 fl	0.0002
Dibromomethane	0.00055	0.005	0.023	0.25	na	na	na	na	na	na
1,2-Dichlorobenzene	0.00057	0.005	0.022	0.25	700 s	700 s	180,000	7,000	<0.1 fa	6
1,3-Dichlorobenzene	0.00062	0.005	0.024	0.25	860 s	500 s	180,000	7,000	na	na
1,4-Dichlorobenzene	0.00081	0.01	0.024	0.5	8.5 c	3.6 c	240 c	27 c	<0.1 fa	1
cis-1,4-Dichloro-2-butene [5]	na	na	0.080	0.25	0.017 c	0.0075 c	na	na	na	na
trans-1,4-Dichloro-2-butene [5]	0.00032	0.005	0.065	0.25	na	na	na	na	na	na
Dichlorodifluoromethane	0.00061	0.005	0.023	0.25	310	94	410,000	16,000	na	7.5
1,1-Dichloroethane	0.00037	0.005	0.025	0.25	17,000	5,000	200,000	7,800	<0.3 fa	11
1,2-Dichloroethane	na	na	0.020	0.25	0.55 c	0.25 c	63 c	7 c	870 fa	0.01
1,1-Dichloroethene	0.00056	0.005	0.023	0.25	0.08 c	0.037 c	9.5 c	1.1 c	na	0.03
trans-1,2-Dichloroethene	0.00059	0.005	0.025	0.25	270	78	20,000	780	<0.3 fa	0.2
1,2-Dichloropropane	0.00033	0.005	0.018	0.25	0.68 c	0.31 c	84 c	9.4 c	na	0.02
cis-1,3-Dichloropropene [6]	0.00020	0.005	0.025	0.25	0.55c	0.25 c	33 c	3.7 c	<0.3 fa	0.001
trans-1,3-Dichloropropene [6]	0.00026	0.005	0.024	0.25	na	na	na	na	na	na
Ethyl ether	0.00068	0.01	0.035	0.5	1,800 s	1,800 s	410,000	16,000	na	na
Ethylbenzene	0.00045	0.005	0.023	0.25	230 s	230 s	200,000	7,800	0.1fa	5

COMPOUND	LOW LEVEL		HIGH LEVEL		REGION IX		REGION III		BTAG[3]	SSL[4]
	MDL	QL*	MDL	QL**	IND.[1]	RES.[2]	IND.[1]	RES.[2]	RBC	
Hexachlorobutadiene	0.00072	0.01	0.024	0.5	24 c	5.7 c	73 c	8.2 c	na	0.1
2-Hexanone	0.00081	0.01	0.055	0.5	na	na	na	na	na	na
Iodomethane	0.00041	0.005	0.060	0.25	na	na	na	na	na	na
Isopropylbenzene	0.00072	0.01	0.020	0.5	na	na	na	na	na	na
Methylene chloride	na	na	0.025	0.25	18 c	7.8 c	760 c	85 c	<0.3 fa	0.01
4-Methyl-2-pentanone (MIBK)	0.00061	0.005	0.065	0.25	2,800	770	160,000	6,300	na	na
Naphthalene	0.00057	0.005	0.023	0.25	na	na	na	na	na	na
Styrene	0.00043	0.005	0.019	0.25	680 s	680 s	410,000	16,000	0.1 fa	2
1,1,1,2-Tetrachloroethane [7]	0.00042	0.005	0.021	0.25	5.4 c	2.4 c	220 c	25 c	<0.3 fa	na
1,1,2,2-Tetrachloroethane [7]	0.00036	0.005	0.020	0.25	1.1 c	0.45 c	29 c	3.2 c	<0.3 fa	0.001
Tetrachloroethene (PCE)	0.00078	0.01	0.022	0.5	17 c	5.4 c	110 c	12	<0.3 fa	0.04
Toluene	0.00054	0.005	0.022	0.25	880 s	790	410,000	16,000	0.1 fa	5
1,2,4-Trichlorobenzene [7]	0.0008	0.01	0.023	0.5	5,500 s	570	20,000	780	<0.1 fa	2
1,1,1-Trichloroethane [7]	0.00033	0.005	0.020	0.25	3,000 s	1,200	72,000	2,700	<0.3 fa	0.9
1,1,2-Trichloroethane [7]	0.00041	0.005	0.025	0.25	1.6 c	0.65 c	100 c	11 c	<0.3 fa	0.01
Trichloroethene (TCE)	0.00052	0.005	0.021	0.25	7.0 c	3.2 c	520 c	58 c	<0.3 fa	0.02
Trichlorofluoromethane	0.00068	0.005	0.022	0.25	1,800	380	610,000	23,000	na	13
1,2,3-Trichloropropane	0.00095	0.01	0.023	0.5	50	15	10,000	390	na	na
Vinyl acetate	na	na	0.085	0.25	2,600	780	1,000,000	78,000	na	84

COMPOUND	LOW LEVEL		HIGH LEVEL		REGION IX		REGION III		BTAG[3]	SSL[4]
	MDL	QL*	MDL	QL**	IND.[1]	RES.[2]	IND.[1]	RES.[2]	RBC	
Vinyl chloride	0.00053	0.005	0.018	0.25	0.035 c	0.016 c	3 c	0.34 c	0.3 fa	0.01
o-Xylene [7]	0.00051	0.005	0.022	0.25	320 s	320 s	1,000,000	160,000	<0.1 fa	na
m-Xylene [7,8]	0.00014	0.005	0.022	0.25	320 s	320 s	1,000,000	160,000	<0.1 fa	na
p-Xylene [7,8]	0.00014	0.005	0.022	0.25	320 s	320 s	na	na	<0.1 fa	na

FOOTNOTES / REMARKS:

1 Industrial Exposures
2 Residential Exposures
3 Biological Technical Assistance Group
4 Soil Screening Level
5 PRG/RBC is not isomer-specific
6 CASRNs identified in Method 5035 and the PRG/RBC table do not agree. Note also that the PRG/RBC tables do not specify cis or trans.
7 BTAG values are not isomer-specific.
8 MDLs apply to total m/p-xylene
The letter "c" denotes a carcinogenic endpoint.
The letter "m" indicates that the value is based on a non-risk "ceiling limit" of 10^5 mg/kg (or maximum).
The letter "s" indicates that the value is based on the EPA Region IX soil saturation equation

* Quantitation limits for the low level method were established as the typical lowest-level standard of the initial calibration.

** Quantitation limits for the high-level method were established by multiplying the on-column concentration of the typical lowest level initial calibration standard times 50 to account for dilution of the samples (100 uL in 4.9 mL water)

Note: Shading indicates compounds that have at least one soil screening criteria less than quantitation limit of high-level method

na - Information not available