UNITED STATES
ENVIRONMENTAL PROTECTION AGENCY
REGION 9
Quality Assurance Office
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USEPA REGION 9 TECHNICAL GUIDELINES FOR ACCURATELY DETERMINING VOLATILE ORGANIC COMPOUND (VOC) CONCENTRATIONS IN SOIL AND SOLID MATRICES

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FINAL

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FOREWORD

The U.S. Environmental Protection Agency (EPA) is authorized to make decisions affecting public health and the environment. With the knowledge that there is an inviolable trust in the Agency, EPA mandated that environmental data collected by and for the Agency be of known quality, and, as appropriate, legally defensible in relation to the decisions to be made based on them. The Agency-Wide Quality System, EPA Order 5360.1 A1, EPA Quality Manual for Environmental Programs, May 2000, and EPA Order 5360.1 A2, Policy and Program Requirements for the Mandatory Agency-Wide Quality System, May 2000 (supersedes EPA Order 5360.1, 1984) defines this mandate. The Agency-Wide Quality System is intended to ensure that decision makers are provided the necessary knowledge and confidence on which to base their decisions.

The responsibility for planning, developing and implementing the EPA Region 9's Quality System resides with the Regional Quality Assurance Manager (RQAM) and the Quality Assurance Office (QA Office).

These guidelines have been developed by the RQAM/QA Office to support the mission of EPA Region 9.

These guidelines update and replace the EPA Region 9 "Regional Interim Policy for Determination of Volatile Organic Compound (VOC) Concentrations in Soil and Solid Matrices," June 23, 1999.

If you have any questions, please contact the Region 9 QA Office.

ACKNOWLEDGEMENTS

EPA Region 9 would like to thank all the technical reviewers, from the environmental testing and sampling industries and from State and Federal agencies, who provided input to this document and its predecessor.

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1.0 SUMMARY

These guidelines address methods for: (1) handling of samples as intact soil cores; (2) preserving samples; (3) storing samples in hermetically sealed containers; and (4) minimizing analyte losses due to direct volatilization (both in the field and the laboratory) and biodegradation. Region 9 believes that following these guidelines is an important part of ensuring that accurate concentrations of VOCs are measured. Therefore, the procedures by which data are generated for or by Region 9 should follow project and/or program specific methods for field sample collection and laboratory sample handling which adhere to these guidelines. Specific procedures should be included in a quality assurance project plan (QAPP) or sampling and analysis plan (SAP).

2.0 PURPOSE

EPA Region 9 has developed technical guidelines to help ensure that sampling and analyzing for Volatile Organic Compounds (VOCs) in soil and solid matrices are conducted in a manner that achieves accurate, technically defensible data. Region 9's guidelines, which are intended to apply whenever VOC sampling in and analysis of soil and solid matrices are conducted, are consistent with United States Environmental Protection Agency (USEPA) Office of Solid Waste test methods. These are included as part of a compendium of over 200 documents in "Test Methods for Evaluating Solid Wastes and Physical/Chemical Methods, SW-846" (hereafter "SW-846"), which are applicable when such sampling is conducted under the Resource Conservation and Recovery Act program. Region 9's guidelines provide greater flexibility than SW-846. These guidelines also have general applicability to other EPA programs where VOC data are collected for quantitative uses.

Region 9 recognizes that there may be methodologies other than those referenced in these guidelines that may also measure VOC concentrations in solid matrices. The use of alternative methods is acceptable, but only after credible method validation studies have been performed and documented.

These guidelines are based on the best scientific information available at this time, and therefore, are subject to further clarifications and additions as further peer reviewed and validated research or improved techniques become available.

3.0 BACKGROUND

In the 1990's, a number of studies were conducted to evaluate traditional VOC sampling and analysis techniques to determine whether they provided data that accurately reflected environmental conditions. At the time, the accepted, traditional sampling methodologies included methods such as the use of glass jars with minimal head space and/or sealed sampling sleeves. These studies determined that these techniques often resulted in inaccurately low measurements of VOCs due to volatilization and biodegradation losses from the sample media. These in turn may have lead to an underestimate of the risk posed by VOC contaminants to public health

and the environment. To address these technical deficiencies, USEPA's Office of Solid Waste, developed (as part of SW-846) Method 5035, "Closed-System Purge-and-Trap and Extraction for Volatile Organics in Soil and Waste Samples," and Method 5021, "Volatile Organic Compounds in Soils and Other Solid Matrices Using Equilibrium Headspace Analysis," to describe procedures and protocols for the collection and analysis of solid samples. (Method 5035 was updated to Method 5035A in July 2002. The update includes an Appendix, "The Collection and Preservation of Aqueous and Solid Samples for Volatile Organic Compound (VOC) Analysis," a useful reference for VOC sampling and analysis.). Soil was deleted as an option for Method 5030, "Purge-and-Trap for Aqueous Samples," (soil sample extracts and certain sample types still reference method 5030 for analysis).

4.0 SCOPE

Region 9 intends to follow the procedures set forth in these guidelines when it is determining VOC concentrations in soil and solid matrices. In order to help ensure that data generated are of known and appropriate quality and accurately reflect environmental conditions, Region 9 recommends that USEPA contractors and grantees, Federal Facilities, and other entities producing data for Region 9 decision-making follow the procedures set forth herein.

If methodologies that differ from those noted in these guidelines are followed, copies of documents which support the alternative methodology, including method validation studies, should be submitted with the data.

5.0 GUIDELINES

To help ensure accurate measurements, Region 9 recommends that these guidelines be followed whenever VOCs in soil or other solid matrices are sampled and analyzed. These guidelines address methods for: (1) handling of samples as intact soil cores; (2) preserving samples; (3) storing samples in hermetically sealed containers; and (4) minimizing analyte losses due to direct volatilization (both in the field and the laboratory) and biodegradation. Region 9 believes that following these guidelines is a scientifically important part of ensuring that accurate concentrations of VOCs are measured. Therefore, the procedures by which data are generated for or by Region 9 should follow project and/or program specific methods for field sample collection and laboratory sample handling referred to in these guidelines. These procedures should be documented in a quality assurance project plan (QAPP) or sampling and analysis plan (SAP).

Region 9's guidelines for measuring VOC concentrations in soil and other solid matrices include the following:

1. **Samples should be handled as intact soil cores until being transferred into methanol or into the container that will be used for analysis.**

Volatilization of VOCs can occur quickly from many matrix types. By preserving a cohesive matrix and minimizing surface area exposed to the atmosphere, VOC losses

can be minimized over a short duration of time. Therefore, Region 9 recommends that coring techniques be used which preserve soil integrity and cohesion.

However, these guidelines do not address the impact of drilling techniques on the collection of a representative VOC sample. Therefore, site/program QAPPs and SAPs should address the impact of all collection techniques on sample integrity and select those appropriate for the project data quality objectives (DQOs). Potential VOC losses due to drilling techniques include, but are not limited to: sample compression and loss of pore space; introduction of air into the sample matrix; mechanical heat introduced in the drilling process; and volatilization from prolonged periods in a non-hermetically sealed sampling apparatus.

Further, solid matrices that are not amenable to the use of a coring technique should be collected in such a way as to preserve their integrity. Transferring of these solids 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 (unexposed), soil at an adequate depth (representative of concentrations from the interior of the pile) should be sampled. Gravel or concrete samples may need to be manually transferred into VOC sampling containers quickly and in a condition and manner that minimizes VOC losses.

2. **Samples should be stored in containers which can be reliably sealed to prevent volatilization losses over the project specified analytical holding time.**

Significant volatilization has been shown to occur when samples are stored in jars, capped sleeves and other containers that do not provide reliable seals. Therefore, Region 9 recommends, consistent with the results of recent studies, that samples be stored in vials with sufficiently thick Teflon™/silicon septa as are commonly used for storage of water samples, to prevent VOC losses over the sample holding time.

3. **Samples should be analyzed or chemically preserved with acid or methanol, within 48 hours of collection.**

Soil samples stored in sealed vials have been shown to undergo significant biodegradation over time periods greater than 48 hours. Holding time guidelines for VOCs are given in SW846, Method 5035A, Appendix A, Table A.1 “Recommended VOC Sample Preservation Techniques and Holding Times.” The holding time for preserved soil samples should be interpreted as 14 days from the time of sample collection (stored at 4 ± 2^{o}C). Due to potential biodegradation, samples stored in sealed containers, but not chemically preserved, should not be stored for more than 48 hours prior to analysis or chemical preservation. On a project/program specific basis, Region 9 will consider other alternatives to extend the holding time of soils that have

not been chemically preserved. Holding time will be considered as cumulative. Exceptions should be documented in a QAPP or a SAP submitted to and approved by the Region 9 QA Office.

It should be noted that some soil types have been shown to exhibit significant degradation of aromatic VOCs in less than 48 hours (Hewitt, et. al., 1999, *Environmental Testing and Analysis*). Also, Sorini, et. al., (2002, *Soil Sediment & Water*) observed significant differences between samples that were extruded directly into methanol and samples where methanol was added at a later time to soil extruded into empty VOA vials (where methanol was added through the septum). Based on these findings, where project or program DQOs require a higher degree of accuracy soil samples may need to be chemically preserved in the field.

Care should be taken in choosing preservatives. For example, 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." Therefore, calcareous soils that effervesce on contact with the preservative solution, which is intended for low-level samples, should be preserved using an alternative technique.

As an alternative to chemical preservatives, several studies have shown that freezing of unpreserved soils, at -7 ^{o}C or less, is an effective means of slowing the biodegradation process. If freezing is determined to meet project or program DQOs, samples should be frozen in containers that have an air tight seal that can be maintained while frozen. Because water expands when frozen, samples extruded into water or samples with extremely high moisture content may rupture or compromise the seal of the storage container.

4. **Steps should be taken to minimize exposure of each sample core to the atmosphere in the field and laboratory.**

As noted by Hewitt and Lukash, "Uncontrollable volatilization losses occur within seconds of exposure for samples with a large surface / mass ratio. Thus, soils obtained in small diameter coring devices should be extruded directly into appropriately prepared analysis vials." (CRREL Special Report 96-5).

6.0 ADDITIONAL CONSIDERATIONS

Field Laboratories: The use of field laboratories to analyze samples within several hours of collection is an alternative to prevent loss of volatiles in transit and storage. The sample collection and analysis procedures should follow the guidelines above. Note that, for extremely short holding times, chemical preservation is not needed and sample storage containers may differ than those used for "fixed" laboratory analysis as long as these containers "prevent volatilization losses over the project specified analytical holding time." 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: It is best to add analytical surrogate and matrix spiking compounds into soils prior to sample extraction, using water or a solvent. Method 5035A does not incorporate the addition of these compounds prior to extraction in the field. Because this is an important control check on the analytical process, it may be appropriate to incorporate a procedure which adds surrogate and/or matrix spiking compounds prior to extraction for some project/program DQOs. This procedure should be implemented in consultation with the analytical laboratory.

Soil Gas: These guidelines are not intended to address data quality issues associated with collection of soil gas samples for VOCs in conjunction with, or as a substitute for, soil samples. Soil gas is the preferred data type to meet the quality objectives of some subsurface characterization activities. There are also scenarios where soil gas data are unacceptable for decision making (e.g., in excavated soils and when determining disposal or treatment options, or for determining concentrations of VOCs that have a high affinity for the soil matrix).

7.0 ADDITIONAL 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) resulting from volatilization (Hewitt, 1996) and biodegradation (Hewitt, 1994). Hewitt and Lukash (Hewitt, 1996) demonstrated that 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, in various matrix types, can have higher mobility than those tested, substantial losses may occur in a 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 (1994) noted that biodegradation of benzene and toluene in soil samples stored in sealed glass ampules at $4^{o}C$ for 14 days could be substantial, demonstrating a need for the use of chemical preservatives. Turriff and Reitmeyer (1998) observed that a variety of soil matrices could be held for 48 hours at $4^{o}C$, 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.

8.0 REFERENCES

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