TCEQ Remediation Division Guidance for USEPA SW-846 Method 5035A Closed System Purge-and-Trap and Extraction for Volatile Organics in Soil and Waste Samples

1.0 Introduction

A large body of evidence from both the federal and private sectors indicates using the traditional unpreserved bulk sample collection procedures to collect samples from solid matrices (e.g., soil) for volatile analysis can give results with a significant low bias due to loss of the volatile organic compounds (VOCs) during the sampling, handling, transporting, and/or analysis activities. Research has shown as much as three orders of magnitude in the loss of VOCs, e.g., 1000 microgram per kilogram (µg/kg) vs. 1 µg /kg, can be observed between a sample collected using bulk sampling techniques and analyzed on-site versus a split of that sample analyzed off-site by a fixed laboratory. These losses are attributed to 1) the disruption of the soil structure causing an increase in the surface area from which volatilization can occur and an increase in the amount of oxygen introduced into the solid matrix promoting microbial degradation; 2) loss of sample seal integrity; and/or 3) laboratory subsampling techniques.

Samples collected for VOC analysis must undergo preparation prior to analysis. The most common preparatory method for VOC analysis uses purge-and-trap technology. In 1997, the USEPA revised the SW-846 *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods* manual (SW-846) to remove the soil component from Method 5030 and to include the new Method 5035, *Closed-System Purge-and-Trap and Extraction for Volatile Organics in Soil and Waste Samples,* for preparing soil samples for purge-and-trap. With that revision to SW-846, the USEPA limited purge-and-trap preparation of solid samples to Method 5035 and limited purge-and-trap preparation of aqueous samples and sample extracts to Method 5030. Also, through Method 5035, the USEPA limited the use of bulk sample collection to only samples with high concentrations of VOCs, i.e., greater than 200 µg/kg. In 2002, the USEPA updated Method 5035 to Method 5035A.

Unlike most analytical methods published in SW846, implementation of Method 5035A impacts multiple technical disciplines. Successful implementation requires good communication among members of the project team, including the laboratory, and the final selection of sampling protocol requires input from all of the data users, data collectors, and data generators. Method 5035A, Appendix A, Section 2.0, outlines a project planning process to help in developing sampling and analytical protocols for a project.

2.0 Implementation

Beginning January 1, 2016, the TCEQ Remediation Division will require the use of Method 5035A, as amended, for collecting and preparing solid samples for VOC analysis using purge-and-trap technology. After December 31, 2015, the Remediation Division will reject VOC results from samples collected using another method when the intended use of the data is to demonstrate compliance with the rules in 30 Texas Administrative Code Chapter 334 subchapters D and F (Release Reporting and Corrective Action for Underground and Aboveground Storage Tanks), Chapter 335 Subchapter S (Risk Reduction Standards), and Chapter 350 (Texas Risk Reduction

Program). This requirement supersedes existing approvals on project plans unless otherwise specified in writing by the Remediation Division. Reconciliation of differences between the data generated from bulk samples prior to January 1, 2016, and the data generated from the use of Method 5035A will be resolved on a case-by-case basis based on the potential exposure at the site. No closed case will be reopened solely to confirm decisions made with samples collected in bulk. However, if a case is reopened after January 1, 2016 for other reasons and the concentrations of VOCs in solid matrices are in question, Method 5035A, as amended, will be used to collect confirmation samples.

3.0 Recommendations

Any of the procedures specified in Method 5035A for sample collection, preparation, and analysis can be used, but the Remediation Division recommends:

- Collecting soils via a closed-system using an open-bore syringe and 40-milliliter (mL) volatile organic analysis (VOA) vials without preservatives as described in Method 5035A, Appendix A, sections A.7.0 and A.8.2.2.

  NOTE: Samples collected in VOA vials can only be analyzed one time. Therefore, collect at least three separate vials at each sample location:

  - one vial for low-level concentration analysis,
  - one vial for low-level concentration reanalysis, if needed; and
  - one vial in the event of high levels of VOCs requiring methanol extraction.

  Collect an additional container (e.g., 40-mL vial or 4-ounce wide-mouth jar) for VOC screening and moisture determination.

- Wiping the threads of the vial clean prior to sealing the vial, then quickly sealing and chilling the vial and holding and shipping the vials at <6°C to the laboratory.
- Instructing the laboratory to analyze the sample within 48 hours from the time of collection or, to extend the hold time to 14 days, preserve the sample by freezing and storing the samples at <-7 °C.
  - If the sample is preserved with methanol, i.e., the VOC concentration is known or suspected to be high, the volume of methanol used in samples with a significant moisture content (>10%) must be corrected for sample moisture content as described in Section 11.5 of Method 5035A and Section 11.10.5 of Method 8000C.

This recommended collection procedure does not require the use of chemical preservatives in the field. The Remediation Division recommends collecting the samples with no chemical preservation, because soils in Texas can have significant levels of calcareous material that will react with acid preservatives to cause effervescence in the sample, and preservation with methanol increases the sample detection and quantitation limits the laboratory can achieve which can render non-detected results unusable. Collection of the sample using an approved coring device that serves as an intermediate hermetically sealed sample container can also be used to collect samples. This type of sampling device should be used according to the manufacturer's instructions and the specifications in Method 5035A, Appendix A. Organizations should have a copy of Method 5035A

(July 2002) as provided in SW846, or as amended, and the field and laboratory personnel should be familiar with the Method 5035A protocols prior to actual sample collection and analysis.

Additional guidance is available in the American Society Testing and Materials (ASTM) Method D4547-98, which is the ASTM standard practice for sampling waste, soils, and sediments for volatile organics. The ASTM Method D4547-98 describes field sampling of solid wastes for subsequent volatile organics analysis in the laboratory and considers both the collection of the sample and the method of containing the sample for shipment to the laboratory. The ASTM standard is consistent with the sample collection guidance in Method 5035A but is limited to only the field sampling methods; the standard does not cover laboratory preparation of containers or solutions or other laboratory techniques related to processing or analyzing the samples. The ASTM standard can be obtained directly from ASTM.

4.0 Sampling and Analysis Strategy

The selection of the appropriate analytical method depends upon the project objectives. These objectives include the analytical sensitivity requirements for the project and the identification of the chemicals of concern (COCs) known or reasonably anticipated to be associated with activities conducted at the site. When the nature of the contamination is not well known (e.g., during the initial assessment of the area of concern), method-specified target analyte lists are typically selected. Prior to sample collection and analysis, verify the COCs are included on the analyte list and the chemicals requiring low-level analyses are identified.

The method quantitation limit (MQL) for each analyte is established from the lowest calibration standard used in the initial calibration. The action levels used to guide assessments must be above the MQLs the laboratory can achieve. During the planning process, consult the laboratory regarding the project objectives to confirm the laboratory has the capability to perform the low-level preparation option and can quantify the VOCs below the action levels.

5.0 Other Considerations

For the recommended procedure, i.e., use of an open-bore syringe and a tared 40-mL VOA vial containing a stir bar, the field costs may increase slightly to cover the cost of additional sampling equipment needed, e.g., the coring device(s) and the tared 40-mL VOA vials with stir bars.

Field costs associated with collecting the sample in a coring device that can be used as a storage and transport container are dependent upon the cost of the coring device and the number of samples to be collected. Note: Using this sampling equipment, each aliquot at each sample location will require the use a sample transport container and each sample location will require collection of a minimum of 2 aliquots (the recommended number is 3 aliquots) up to a maximum 7 aliquots if the location is used for the matrix spike/matrix spike duplicate sample pair.

The use of field preservation is not recommended. However, if field preservation is used, the additional field costs associated with using methanol or sodium bisulfate can be significant, e.g., increase the time needed for the sample collection, additional field personnel needed to assist with checking the tare weights and packaging the samples for shipment, and additional shipping costs needed to comply with hazardous chemical regulations.