Required Use of Method SW846-5035

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Presentation Overview

- The TCEQ Remediation Division (REM) requires Method 5035 for determining volatile organic compounds (VOCs) in solids (e.g., soil, sludge, sediment)
- History & background – Why Method 5035 is required
- Planning the sample collection event for solids contaminated with VOCs
- Recommendations for collecting and preserving soil samples
- Special sampling considerations
- Answers to frequently asked questions.

Method SW846-5035 Requirement

Method 5035 (as amended) is required for solid samples collected for VOC analysis to demonstrate regulatory compliance with 30 Texas Administrative Code (TAC):

- Chapter 334
  - Subchapter D (*Release Reporting and Corrective Action*)
  - Subchapter F (*Aboveground Storage Tanks*)
- Chapter 335 Subchapter S (*Risk Reduction Standards*), and
- Chapter 350 (*Texas Risk Reduction Program*)

5035 Conditional Requirements

- No closed case will be reopened solely to confirm decisions made from samples collected using traditional bulk sampling procedures. However, if a case is reopened for other reasons, then 5035 is required if VOCs are chemicals of concern.

- The TCEQ recognizes other procedures technically equivalent to 5035 may be designed to minimize VOC loss during soil sampling and handling. These methods can be used with TCEQ approval provided documentation is available demonstrating the method generates data as good as or better than Method 5035.

History of Method 5035

Prior to 1997, solid samples were collected in bulk by repeatedly transferring soil to a jar until the jar was completely full.

During sample prep, the laboratory would open the jar to transfer a subsample to a tared 40-mL VOA vial, then would weigh the sample.

The vial was reopened to add water, surrogates, and internal standards, all of which allowed VOCs in the sample to volatilize.

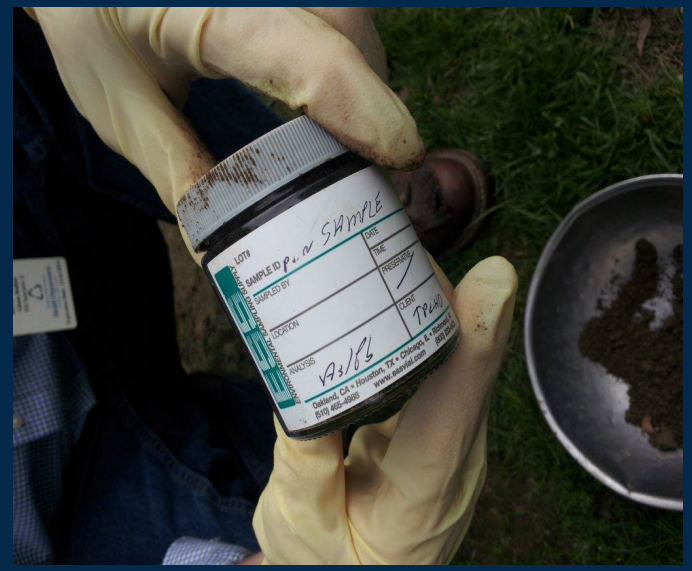
Key Point: Bulk sampling allows for significant loss of VOCs.

Illustration of VOCs Volatilizing During Bulk Sample Collection

VOCs are lost when soil is exposed to the atmosphere whether in the ground or in a container.

Key Point: Continual loss of VOCs during sampling activities results in inaccurate and biased low data.

Before Method 5035 - Soil Samples Collected in bulk for VOCs



SW-846 Method 5030 was used to prepare both water and soil samples. Soils were collected in bulk.

Key Point: Bulk sampling requires multiple transfers of soil to the jar allowing opportunity for loss of VOCs.

Laboratory Subsampling of Soil From Samples Collected in Bulk

Sample exposed to atmosphere when opened to:

- Transfer subsample into a VOA vial for VOC analysis;
- Transfer subsequent subsample to container for dry weight determination;
- Transfer subsample for other analyses, and
- Subsampling, if needed, for a rerun of VOC analysis.

Key Point: Method 5035 eliminates multiple soil transfers and laboratory subsampling from collection process.

Cause for VOC Loss from Soils

Significant volatilization often occurs during sample collection once soils are exposed to the atmosphere. Factors influencing the rate of volatilization include:

- Soil porosity/permeability;
- Soil temperature and moisture;
- Soil disturbance (disaggregation);
- Length of time of soil exposure;
- Leaking containers (not hermetically sealed); and
- Subsampling from bulk container.

Illustration of VOC loss if container not sealed

Cause for VOC Loss from Soils (cont'd)

Biodegradation – loss of VOCs, e.g., aromatic hydrocarbons such as benzene and toluene, consumed by microbes present in the environmental medium. The bulk sample collection process destroys the soil architecture introducing more air into the sample which can activate microbes. Some of the factors that influence the rate of biodegradation are:

- Number and type of indigenous microbes;
- Specific COCs (properties), e.g., aromatic vs. halogenated hydrocarbons;
- Total VOC concentration;
- Chemical properties of the environmental medium; and
- Temperature.

Technical Justification for 5035

Studies show bulk samples can lose >90% VOCs through volatilization and degradation. Reasons for the loss includes:

1. Exposure of soil to the atmosphere.
2. Soil disaggregation during sample collection; the soil structure is disrupted increasing the surface area from which volatilization can occur.
3. Oxygen is introduced triggering biodegradation. Non-halogenated VOCs, e.g., benzene and toluene, are highly susceptible to biodegradation; greater than 50% loss of benzene and toluene observed within five days in samples stored at 4°C.
4. Laboratory subsampling/manipulation recreates the conditions in 1 and 2, e.g., reopening jar and scooping out the subsample.

EPA Response to VOC Loss

In 1997 the USEPA Office of Solid Waste:

- Removed the soil/solid component from Method SW846-5030 preparation method.
- Introduced Method SW846-5035 for solids, a closed-system purge and trap and extraction process.
- Method 5035 includes sample collection requirements as part of the closed-system purge-and-trap process.

Key Point: Method 5035 is the only purge-and-trap preparation method for VOC analysis.

Planning VOC Sampling Events

The project team should read SW-846 chapters 1 and 4. Selecting the appropriate sampling protocol requires input from all project team members based on project objectives and consideration of the following:

1. Target COCs - concentration ranges, analytical sensitivity requirements;
2. Soil Characteristics - soil type, particle size, moisture content, microbial activity, pH, etc.;
3. Preservation techniques (in conjunction with soil characteristics);
4. Field collection strategies –Coring samplers, field balance, spoon, chisel, etc.;
5. Strategies for screening and subsampling cores - type of drilling, core liners, etc.; and
6. Sample holding times and coordination with the laboratory.

Examples of Coring Devices

Terra Core Sampler™

Easy Draw Sampler™

EnCore Sampler™

Reference to trade names or commercial products are for illustration purposes only and does not constitute an endorsement, disparagement, or recommendation by the TCEQ.

Sample Replicates and Sample Sizes

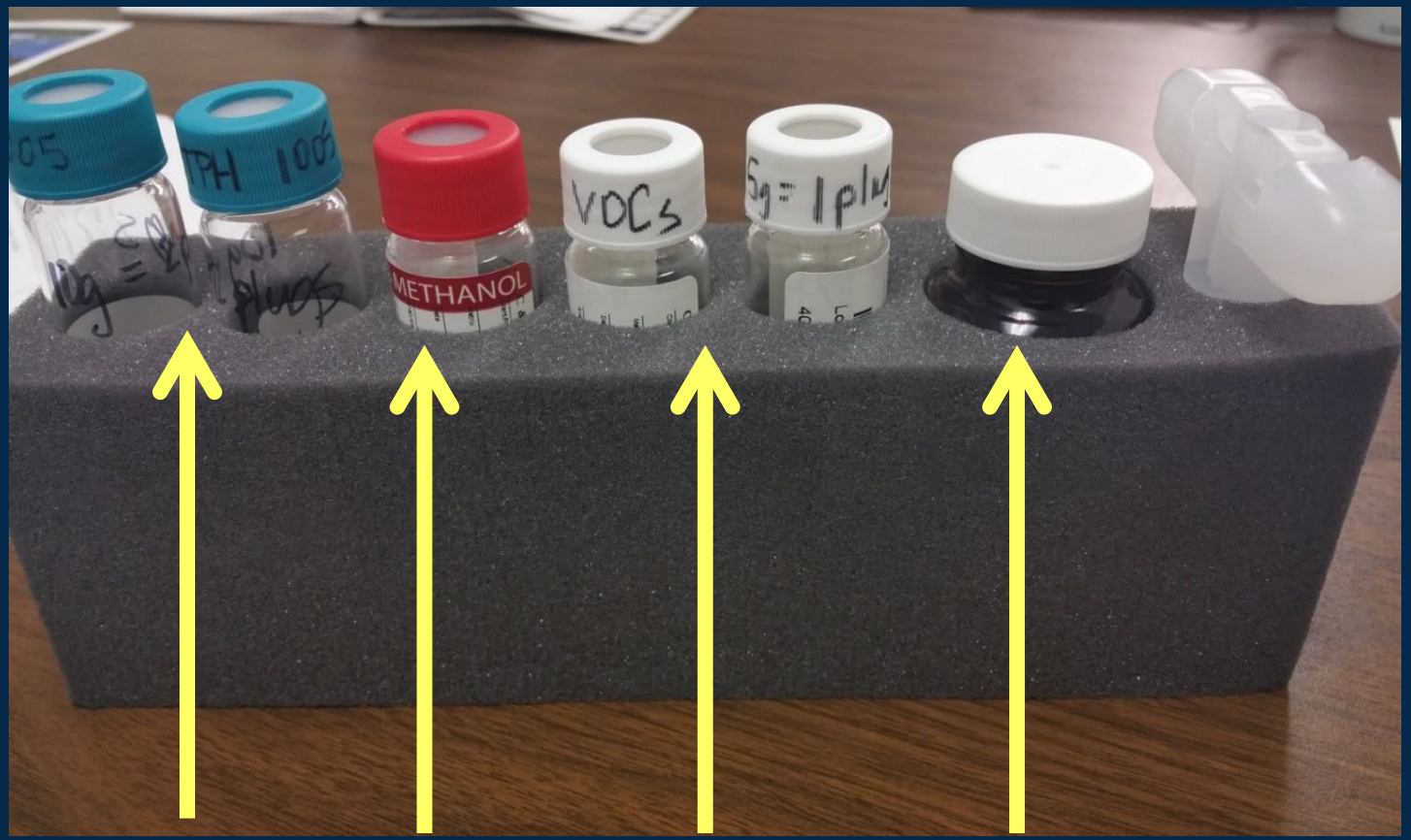
A closed system purge & trap soil sample, collected in a VOA vial, is analyzed only once. When reanalysis is needed, a replicate unopened vial is used. At a minimum, the field team should collect two low level and one high level replicates in VOA vials at each location plus a bulk sample for moisture determination and laboratory screening. Three additional replicates are collected for low level if matrix spike QC samples are required.

The sample size for most soils is 5.0 grams (g) if analyzing for VOCs and 10 g if collecting for TPH analysis by TCEQ Method 1005.

Note: There is an allowed exception of bulk sampling to determine the leaching potential of VOCs via SPLP by Method 1312 or TCLP by Method 1311. These methods are method defined parameters and must be followed as written.

SPLP - Synthetic Precipitation Leaching Procedure
TCLP – Toxicity Characteristic Leaching Procedure
TPH – Total Petroleum Hydrocarbons

Example of 5035 Sampling Kit



TPH High level Low level Bulk container

Vials with water & stir bars

Sample Preservation

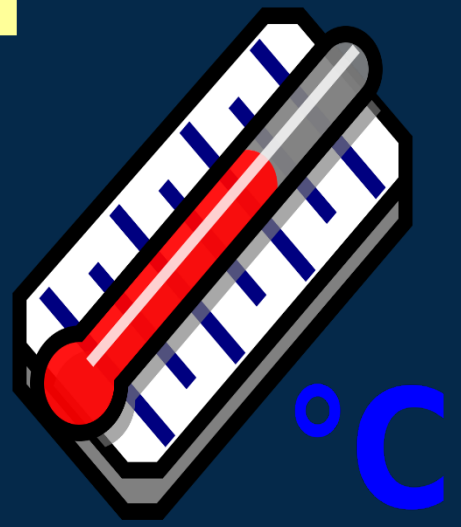
Thermal preservation and/or chemical preservation.

Each type of preservation can be used alone or in combination in the field or laboratory.

Key Point:

See Method 5035A Table A.1 Recommended Sample Preservation Techniques and Holding Times

Thermal Preservation



Thermal preservation lowers the sample temperature to slow down or stop chemical and biological processes.

- Cooling the sample to ≤ 6°C (but not frozen) slows chemical and biological processes.
- Freezing the sample to ≤ -7°C (but above -20°C) stops biological activity and further slows chemical processes.

Chemical Preservation

Adding a chemical biocide, e.g., methanol or sodium bisulfate.

- Methanol – stops biological processes. Note: Using methanol preservation can raise the detection/quantitation limit by 50X
- Sodium bisulfate – stops biological processes by lowering pH of sample to < 2, but use with caution when samples contain:
    - Highly reactive volatile COCs; e.g., styrene or vinyl chloride.
    - Carbonates; these calcareous soil types react with acid and effervesce.

Considerations When Chemically Preserving

If chemical preservation is used in the field, review:

- handling requirements,
- placarding requirements, and
- transportation limitations.

Minimizing VOC Loss

- Immediately upon exposing the soil to the atmosphere, collect the sample as an intact core with as little disaggregation as possible.
- Store samples in hermetically sealed vials.
- If VOC analysis cannot begin within 48 hours of collection, freeze the sample to ≤ -7°C but not below -20°C.

Minimizing VOC Loss (cont'd)

- Use closed system purge & trap procedures in Method 5035.
- Collect two low level samples, one high level sample, and one bulk sample for percent moisture determination. Note: Laboratories often use the bulk sample to also screen for high levels of VOCs.
- Use preservatives when soils are biologically active. Chemical preservatives are sodium bisulfate (for low level) and methanol (for high level). At a minimum, maintain sample on ice (≤6°C) until the sample is received by the laboratory.

Special Considerations – Unconsolidated Matrix

Highly unconsolidated matrix – Use a field balance to gauge the volume 5g would occupy in the vial. Then use a clean spatula to scoop approximately 5g of sample into a tared VOA vial.

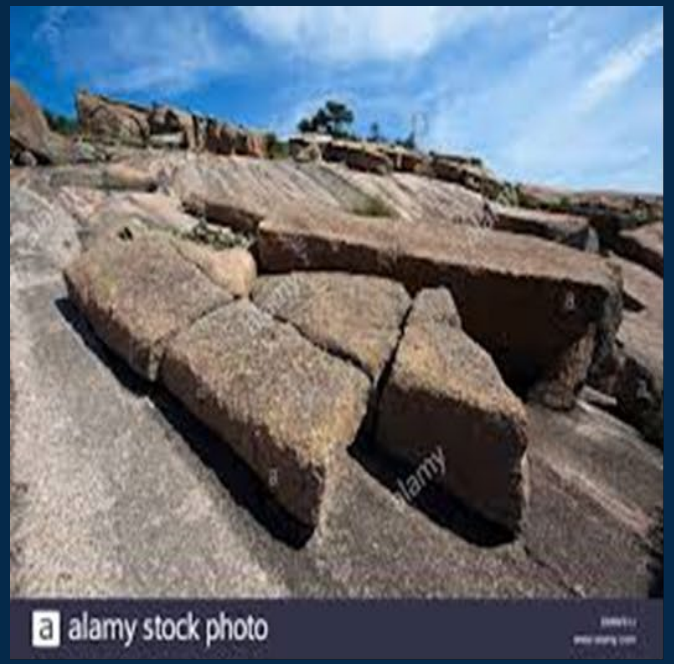
Pea Gravel

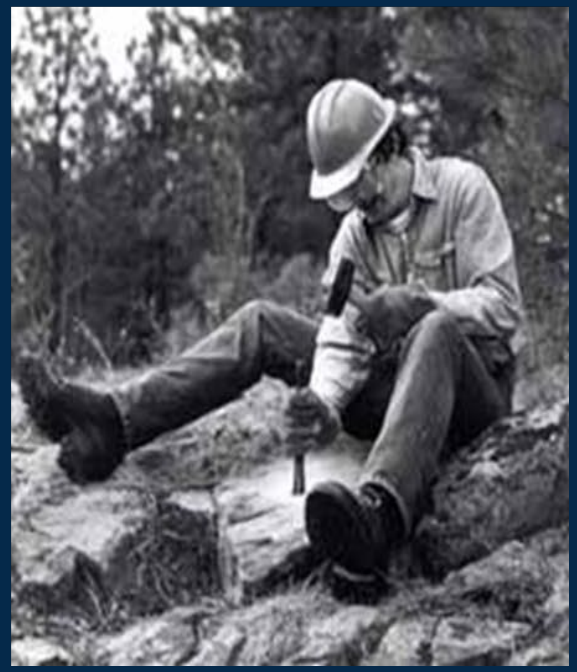
Caliche

Wood Mulch

Special Considerations – Consolidated Matrix

Highly consolidated matrix – Reduce the particle size to fit into a 40-mL vial. Use field balance to gauge the volume that 5g of particles will occupy in vial. Then quickly reduce the particle size and, using a clean spatula, transfer the ~5g sample to the vial.





Special Considerations – Safety/Accessibility

If the field team is unable to collect soil samples for VOCs directly in the pit due to safety issues, then samples may be safely collected using a backhoe to scoop a large area intact.

Subsamples for VOC analysis should be collected immediately from an undisturbed area after scraping several inches of soil off the top. A coring sampler must be used when possible.

Screening and Sampling Soil Cores

Planning a drilling event for VOC analysis:

1. Drilling techniques - do not use drilling methods that will severely strip VOCs from cores, e.g., direct air rotary, sonic drilling, or auger methods.
2. Core liners are highly recommended, e.g., acrylic, acetate, or polycarbonate liners.
3. Field VOC screening instruments, e.g., photoionization detector (PID); calibrate the instrument before the core is retrieved.

Screening and Sampling Soil Cores (cont'd)

Important: The driller needs to work at the pace of the sampling team. Multiple cores should not be stored to avoid VOC loss.

Two sampling team members are recommended to screen and collect soils for VOCs from cores.

No one size fits all conditions when screening for VOCs. The matrix is a determining factor for screening method.

Example 1: A compacted clayey soil can be screened by cutting the liner, then using a paint scraper to cut slits along the core at discreet intervals, and immediately collect three replicate samples near the location of the highest PID reading.

Screening and Sampling Soil Cores Continued

Example 2: A coarse, non-cohesive, or sandy soil type should be screened with the liner in place.

- To screen for VOCs, insert the PID probe where the liner has been pre-cut and take PID measurements.

- To collect the sample: drill larger holes or cut the liner (not pre-cut) next to the location with the highest PID reading and immediately collect replicate samples.

Guidance for VOC screening in soil:

- SW-846 method 3815
- ASTM Standard D4547-09, Appendix X3

Q & A #1:

Do tared vials received from a lab need to be re-weighed in the field?

- *If vial contains only a stir bar, then no.*
- *If the vials contain an aqueous solution, then yes, but only to spot check approximately 10% of the vials.*
- *If the vials contain methanol, then yes. Check the weight of every vial.*

The field balance should read to the nearest 0.05 gram. If the checked weight differs from the tare weight by more than 0.1 g, discard the vial.

Q & A #2:

If the samples have not been analyzed or frozen within 48 hours from collection, will data be rejected or a qualifier assigned to the results?

The data will be qualified. If the data indicate no action, the data may be qualified as rejected because of the potential low bias in the results. If data indicate action, data will be accepted.

Q & A #3:

Is 5035 applicable to TCEQ Method 1005?

Only when TCEQ Method 1005 data are used to evaluate risk associated with a total petroleum hydrocarbon mixture (TPH) under 30 TAC chapters 335 and 350. Section 6 of TCEQ Method 1005 requires the use of 5035 procedures when the TPH is known to contain hydrocarbons in the volatile range, i.e., nC_6 to nC_{12}, or when the composition of the TPH is not known. If the composition of the TPH is known not to contain volatile hydrocarbons, then TCEQ Method1005 allows for the collection of bulk samples.

Q & A #4:

If the sample for TPH is collected under the PST rules, is Method 5035 required?

> *No. The PST program does not evaluate TPH for compliance; TPH data are only used to determine if a polycyclic aromatic hydrocarbons (PAHs) analysis is required. For PST projects, the TPH samples can be collected using bulk procedures. (See Method 1005 introduction.)*

NOTE: PST samples for BTEX and MTBE and other volatiles must be collected using 5035 procedures.

Q & A #5:

If the sample is physically not amenable to the 5035 collection technique, what happens?

> *For VOC analysis using purge-and-trap, the sample must be transferred to a 40-mL VOA vial. If the sample is not collected in a 40-mL VOA vial, i.e., the sample is collected in bulk, then the lab must use the 5035 procedures to methanol extract the VOCs from the sample and transfer an aliquot of the extract into a 40-mL VOA vial.*

***Note**: Methanol extraction introduces a 50X dilution factor.*

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