

EPA Method 5035

Proper Collection and Analysis of Soil Samples for Volatile Organics



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- **History and Justification of Method 5035**
- **Application of Method 5035 Requirements**
- **Frequently Asked Questions**



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History and Justification of Method 5035

- Prior to 1997 and publication of SW846 Update III, Volatile Organics for all matrices were collected and analyzed using Method 5030.
- Update III of SW846 (pub Dec. 1996), soil matrices were removed from Method 5030 and a new Method (5035) was published
- In 2002, USEPA updated to Method 5035A, removing bulk collection as an option for samples with high concentrations of VOCs



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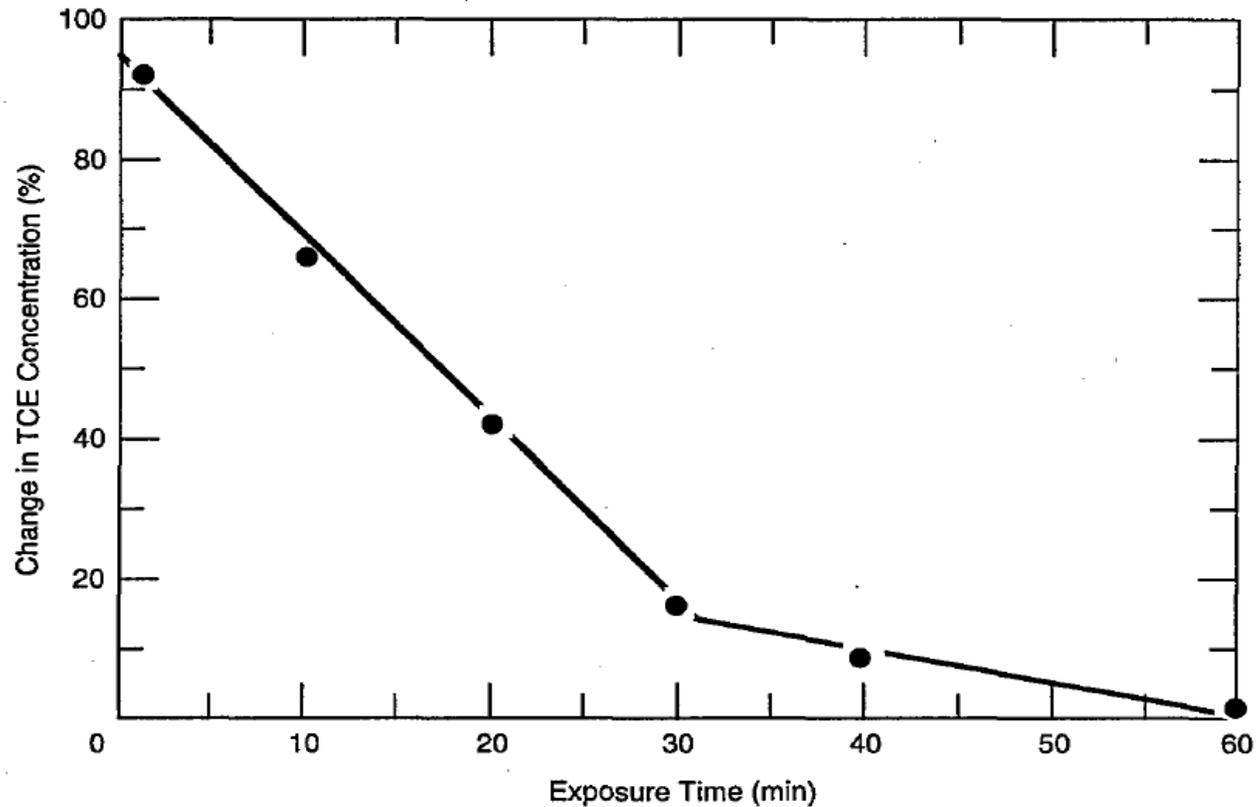
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Effect of Volatilization on Bulk Soils VOC Concentrations

- In soils and solid waste materials, VOCs coexist in gaseous, liquid, and solid phases.
 - Initial concern is in retention of the gaseous phase
 - As the gaseous phase dissipates from the sample, the liquid and solid phases volatilize to maintain equilibrium
 - Loss of TCE was investigated in a narrow mouth container completely filled with sample and held at ambient temperature for 1 hour in the field



Effect of Volatilization on Bulk Soils TCE Concentrations



Alan D. Hewitt, USACE, May 1999



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Effect of Volatilization on Bulk Soils VOC Concentrations

- Nearly 100% of the TCE was lost to evaporation within 1 hour of collection
- Change in loss rate indicative of phase change from liquid or solid (adsorbed) states after initial loss of gaseous TCE in maintenance of equilibrium



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Effects of Aerobic Microbial Degradation on VOC Concentrations

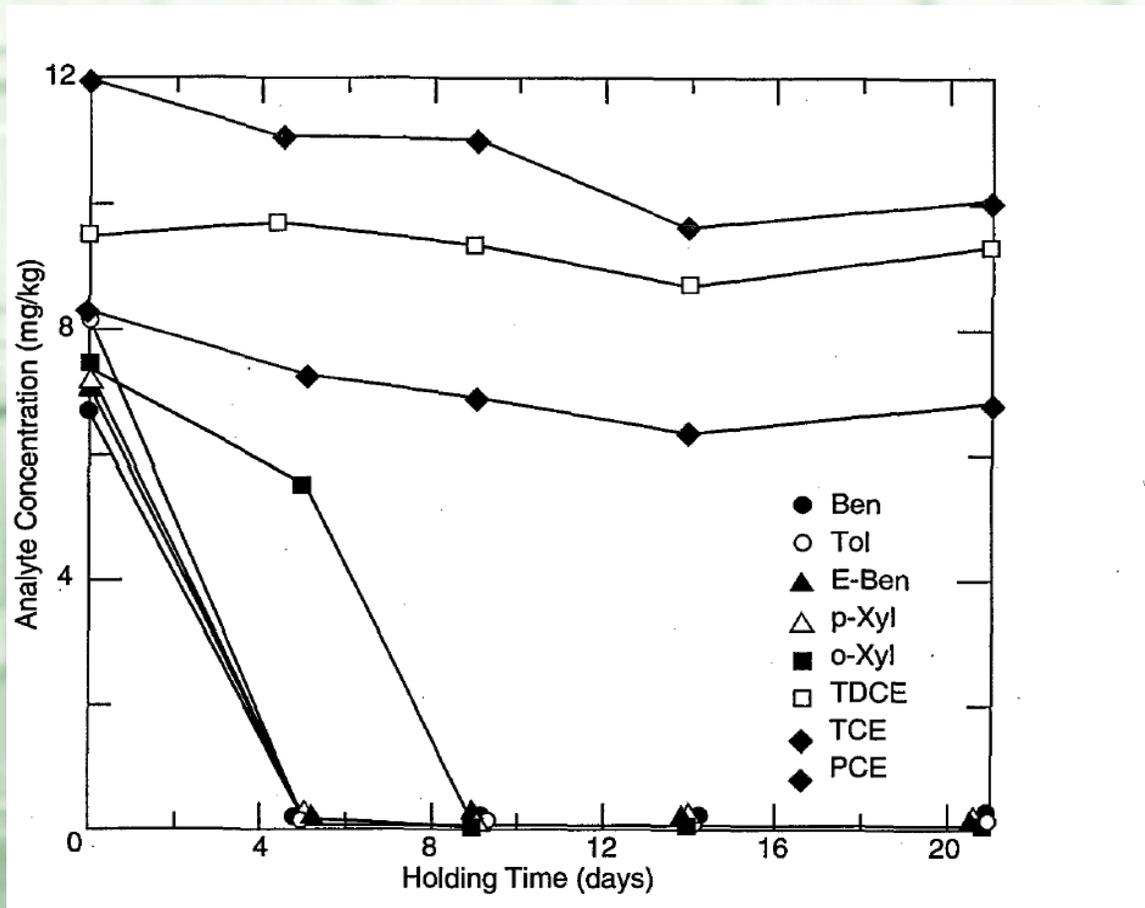
- Even when stored and transported at <6 C, microbial degradation can impact VOC concentrations in soils and solid waste material
- Slower loss rate than from volatilization
- Loss rate is compound selective



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Effects of Aerobic Microbial Degradation on Select Volatile Organic Analytes



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Effects of Aerobic Microbial Degradation on VOC Concentrations

- Aromatic compounds selectively lost over halogenated analytes
- Loss of > 98% of Benzene originally present in the sample occurred within 5 days of collection
- Historical holding time for VOCs collected in bulk was 14 days to analysis only



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History and Justification of Method 5035

- To address these potential issues, the EPA published method 5035 On 13 June 1997
 - Collection of VOCs into a sealed vial in the field to prevent loss to evaporation
 - Require preservation technique be employed within 48 hours to prevent microbial activity



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Application of Method 5035 Requirements

- Collect samples into a tared VOA vial containing either water or methanol and a Teflon coated stirring bar
- Preserve immediately in the field by acidification with NaH_2SO_4 or methanol or freeze ($< -7\text{ C}$) within 48 hours of collection.



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TCEQ Remediation Guidance Document

Collect soils via a closed-system using an open-bore syringe and 40-milliliter (mL) volatile organic analysis (VOA) vials without preservatives.

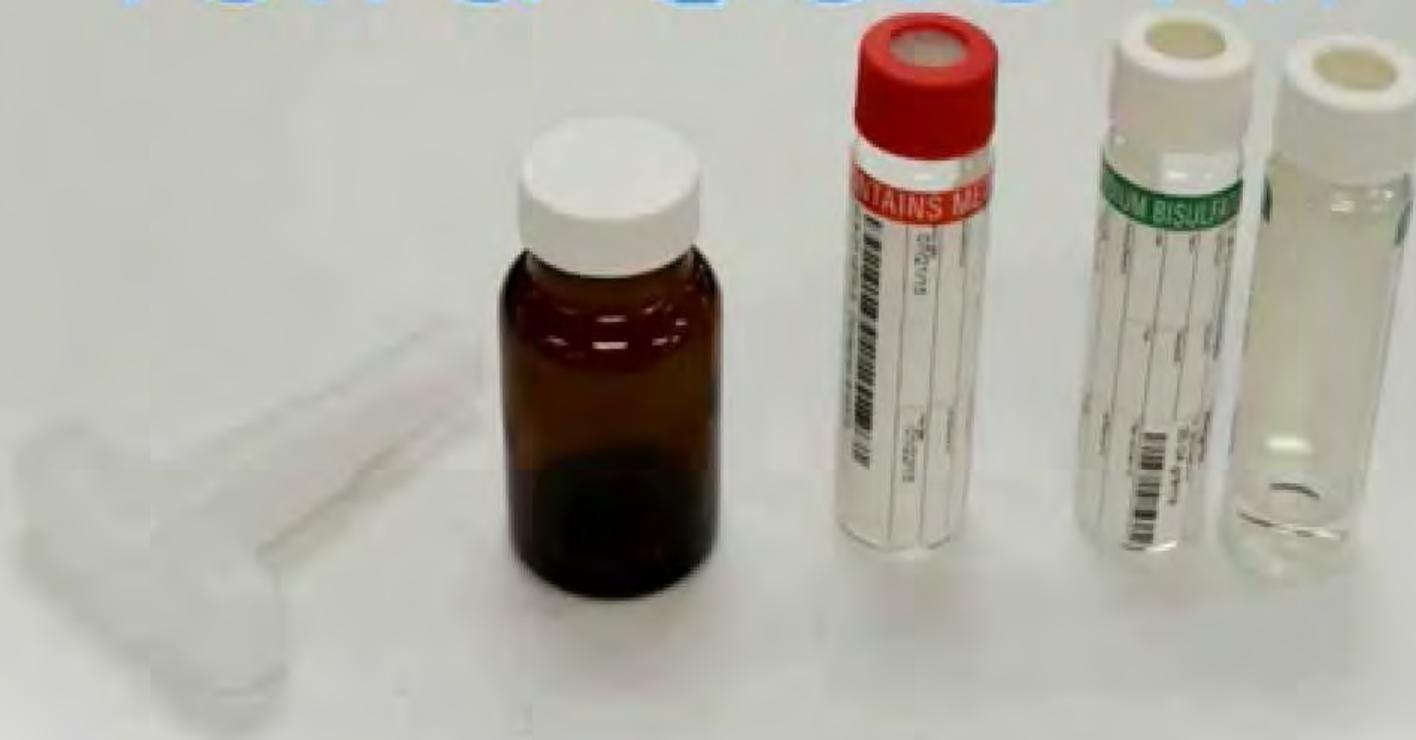
NOTE: Samples collected in VOA vials can only be analyzed one time. Therefore, collect at least three separate vials at each sample location



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Terra Core Kit



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TCEQ Remediation Guidance Document

- 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.



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TCEQ Remediation Guidance Document

- Wipe the threads of the vial clean prior to sealing the vial, then quickly seal and chilling the vial and hold and ship the vials at $<6^{\circ}\text{C}$ to the laboratory.



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TCEQ Remediation Guidance Document

- **Section 3.0:** 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



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Laboratory Practices

- Samples properly submitted to the laboratory are analyzed within 48 hours or properly preserved by freezing to extend the holding time to 14 days
- Sample vials collected in DI Water are never opened in the laboratory prior to analysis
- Dilutions can only be performed by analyzing an aliquot not to exceed 200 μ l / 5 ml of the methanol solution collected in the field (apparent 25 fold dilution)



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Frequently Asked Questions

- **What happens if the sample needs a 5 fold dilution for analysis?**
 - The only available dilutions for soil samples are undiluted or 25 fold or greater.



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Frequently Asked Questions

- **How does the laboratory manage an MS/MSD on low level samples for VOC analysis**
 - An MS/MSD can only be performed for VOC analysis when a sample is designated for this purpose and collected in triplicate in the field. If no samples in the analytical batch are submitted in triplicate, MS/MSD results can not be provided for the batch. LCS/LCSD data is used to provide precision and accuracy representations.



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Frequently Asked Questions

- **Since the triplicate collected vials are not truly split samples, how does that affect the MS/MSD analysis**
 - While not a true split sample, the aliquot historically used for soil VOC MS/MSD was also not a true split sample. Only a 1-5 gram aliquot of the submitted samples was used for analysis. Considering the non-homogeneity of soil samples, this was in effect the same process as defined in Method 5035



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Frequently Asked Questions

- **Does adherence to Method 5035 requirements affect the cost of the analysis?**
 - Laboratories typically pass on the additional cost of supplying sampling devices to the client. This is accomplished by the addition of a separate device charge or by increasing the cost of the VOC analysis in soil.



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Frequently Asked Questions

- **When collecting samples for VOCs, why do we need both VOAs preserved with methanol and unpreserved VOAs?**
 - The purpose of the methanol preserved VOA vial is to provide a means of dilution for the analysis when analyte concentrations exceed the upper limit of the calibration curve, typically 200 ug/Kg wet weight.



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Frequently Asked Questions

- **What are the stir bars for in the NaH₂SO₄ Or DI Water VOC VOAs?**
 - The purpose of the magnetic stirring bars is to provide agitation of the soil during the purge phase of the analysis, primarily to allow sufficient movement of helium through the matrix to continually evolve the target compounds into the headspace



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Frequently Asked Questions

- **What is percent moisture used for?**
 - The moisture content of the soil is used for two determinations. First, it allows all samples to be normalized to only the concentration present in the solid sample (dried sample) and second allows for the correction of the water miscible solvent volumes when analyzing dilutions from the methanol preserved container



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Frequently Asked Questions

- **How do we manage field screening of cores before deciding which samples to prepare for analysis?**
 - **Collect all samples and preserve or seal in VOA Vials with the proper preservatives. Additionally collect a bulk sample for moisture determination that can be used for screening in the field to determine which samples to submit to the laboratory.**



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Additional Questions or Comments?

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