REMEDIATION AND REDEVELOPMENT DIVISION
STANDARD OPERATING PROCEDURE

Field Methanol Preservation of Solid Samples for Volatile Analysis
RRD SOP-35

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Distribution: ALL RRD Employees

PURPOSE

The Michigan Department of Environment, Great Lakes, and Energy (EGLE) has designated analytical methods capable of achieving the target detection limits (TDL) in accordance with MCL 324.20101(1)(bbb). In designating the analytical method, the appropriate preparation techniques included within the method are also designated. The designated analytical method for volatile organic compounds in the EGLE published list of TDLs for solid samples include preservation of the samples using the United States Environmental Protection Agency SW-846 Method 5035A, commonly referenced as methanol preservation. This document contains the technical specifications for methanol preservation in the field.

DEFINITIONS

EGLE – Michigan Department of Environment, Great Lakes, and Energy
mL - milliliter
RRD - Remediation and Redevelopment Division
SDS - Safety Data Sheet
TDL - Target Detection Limit.
VOC - Volatile Organic Compounds.

STANDARD OPERATING PROCEDURE

It is RRD's policy to collect solid samples for VOC analysis using the methanol preservation method. Methanol preservation kits are available from the EGLE laboratory for analysis at the EGLE laboratory. Methanol kits from other laboratories will vary. Some laboratories may provide methanol in the sampling vial.

Health and Safety

Safety Data Sheets (SDS) provide health and safety data and emergency procedures. The SDS should accompany staff in the field. Methanol ampoules, tubes, and vials must be provided to field staff inside protective containers to hold any spillage. Methanol is a toxic and flammable liquid. Handle with proper safety precautions. Wear safety glasses and protective gloves. Nitrile, rubber, or Viton gloves are recommended. Avoid inhalation. Store and handle in a ventilated area away from sources of ignition and extreme heat. Store the methanol in a cool place, preferably in sample coolers on ice. This is especially important for methanol in tubes where pressure buildup due to extreme heat may result in rupture. In the event of eye contact, immediately flush with large amounts of water for at least 15 minutes, occasionally lifting upper and lower lids. Seek medical attention immediately.

Shipping
The shipping of methanol may be regulated by the United States Department of Transportation, Title 49 of the Code of Federal Regulations.

Apparatus and Materials Needed for Sample Collection
- Calibration Weight: Near or equal to the target sample weight (i.e.,10 grams).
- Field Balance: Capable of holding sampling vial, syringe and the wide mouth jar used to prevent balance contamination and measurement within + 0.2 grams. A reliable spring scale is acceptable as an alternative to the field balance for weighing the sample.
- SDS: Should accompany sample collection personnel in the field.
- EGLE Sampling Kit.
  - Certified Methanol: Methanol certified for purge-and-trap gas chromatography is analytically verified prior to sampling (by lot). Methanol is provided in the kit in sealed Teflon tubes.
  - Sub-Coring Device: A syringe-type device with cap whose material has been tested and found free of contaminants. This device is used to sub-sample the targeted amount of soil for transfer into methanol in the field.
  - VOC Vials: Vials with Teflon™ lined septa, pre-weighed, with labels.
- Protective Wear: Nitrile, rubber, or Viton gloves. Splash proof safety goggles.
- Plastic Bags: Airtight seals to hold sample VOC vials and sub-coring device.
- Site protocol to be used for the collection of samples.
- Wide Mouth Jar (for preventing balance contamination): Of suitable size to allow temporary storage of the syringe-type sampler and VOC sample vial on the field balance.

EGLE Laboratory Specifications for Sample Collection
The following specifications apply to the methanol preservation sample collection kit provided by the EGLE laboratory.

Target Soil Weight = 10 grams
Allowed Weight = 9 to 11 grams
Size of VOC Sampling Vials = 40 mL
Plastic bag for sample containers
Methanol Volume (provided in Teflon tubes) = 10 mL
Soil Coring Device and Cap = 10 mL

Sample Containers, Preservation, and Holding Times
- Containers: Sample containers are VOC vials with Teflon™ lined septa of suitable size to hold the soil plus methanol, supplied with pre-weighed labels.
- Preservation: Samples are preserved in the field approximately with a one-to-one ratio of soil weight to methanol volume using pre-weighed vials and a field balance. The exact sample weights and ratios are determined at the laboratory. When soil weights are less than the specified minimum or more than the specified amounts of methanol are added, the reporting limits are increased. Samples must be stored and transferred at less than or equal to 6° C.
- Holding Times: The maximum allowable holding time is 14 days from the sample collection to analysis.

Methanol
Only purge-and-trap grade methanol verified to be suitable for methanol preservation should be used. Field staff should maintain documentation of the methanol lot numbers for all associated samples. If consistently high levels of compounds are measured in methanol field blanks associated with a specific lot number, request the laboratory to verify the quality of the methanol lot used to preserve the samples.

Contamination
Contamination by airborne VOCs is possible by diffusion through the vial septum during shipment, storage, collection, and analysis. To control such contamination:

- Use appropriate VOC sample vials.
- Avoid sources that generate VOCs such as petroleum products, especially auto exhaust fumes.
- Keep sample containers in coolers as much as possible.
- Collect samples quickly.
- Use methanol provided in sealed ampoules, tubes, or VOC vials.
- Collect samples as quickly as possible and cap the vial as soon as possible.

Attempt to isolate the source of contamination and incorporate the appropriate procedures to avoid similar circumstances.

Field Balance Calibration Check
The field balance calibration should be checked each day of use. Record this check in the field logbook.

Field Sampling Procedures
1. Make arrangements with the laboratory to obtain the appropriate Methanol Preservation Sampling Kits.
2. Record the tracking or lot number(s) for the methanol in the field logbook. If more than one lot is used, each lot must be associated with the samples for which it was used.
3. Prior to any sample collection, check the calibration of the balance. Also estimate the amount of the soil to be collected using the steps in this SOP. The soil used for the estimations must be discarded.
4. Prior to sample collection, prepare a sufficient quantity of methanol field blanks, i.e., at least one per cooler and one per methanol lot as follows:
   a. Select an area free of VOC sources.
   b. Remove a methanol tube.
   c. Use scissors to cut off the top and place the methanol into one of the pre-weighed sample vials.
   d. Place the cap on the vial and tighten it. Avoid over-tightening.
   e. Identify it as a methanol field blank.
5. Place the wide mouth glass jar used to prevent balance contamination on the balance.
6. Record the location, date, and time of sampling in the field logbook. **Do not place any labels, stickers, tape, etc., on the pre-weighed sample vials**.
7. For methanol field blanks, remove the cap from a methanol field blank which was prepared in Step 4 above, place the opened vial in the collection area for the approximate time it takes to collect a sample, then cap the methanol field blank for storage, and transport to the laboratory.
8. Place a pre-weighed VOC vial and syringe in the wide mouth jar on the balance.
9. Record the weight in the field logbook. If the balance features re-zeroing, zero the balance.
10. Remove the syringe. If a cap is provided, remove the cap, and place it in the jar.
11. Insert the open end of the syringe into a fresh face of undisturbed soil. Fill it as appropriate according to the amount of soil needed.
12. If necessary, use your gloved finger (decontaminate before next sample) or other appropriate instrument and push the soil deeper into the syringe sampler.
13. If a cap was provided, immediately cap the end of the syringe.
14. Place the syringe in the jar on the balance. Read the weight, and if necessary, subtract the weight of the syringe, vial, and jar as appropriate to determine the weight of the soil.
15. If the weight of the sample is determined to be more than the maximum amount allowed, extrude enough soil to obtain the target amount within the specified tolerance and re-weigh.
16. If the weight of the sample is less than the minimum amount allowed, re-sample.

17. Record the soil weight in the field logbook. **Do not record the weight on the sample vial label**.
18. Remove the cap from the sample vial and place it in the jar on the balance with the septum upwards.
19. Insert the open end of the syringe sampler into the mouth of the vial and carefully extrude the soil, taking care to avoid spillage.
20. If the required amount of methanol is not included in the pre-weighed vial, immediately add methanol from the Teflon tube by cutting off one end and pouring into the sample vial, taking care to avoid spillage. Loss of several drops will not make a significant difference in the results. If a significant amount is spilled, a new sample must be collected or the sample must be appropriately flagged to indicate estimated results. If methanol does not cover soil, add another tube, and note on chain of custody.
21. Using a clean brush, paper towel, or other suitable material, thoroughly wipe excess soil particles from the threads and vial body. Particles left on the threads will prevent a good seal.
22. Place the VOC cap on the sample vial. The cap must be tight; however, over-tightening should be avoided. Complete the label. **Do not add any labels, stickers, or tape to the vial**.
23. Gently swirl the sample and methanol for about ten seconds to break up the soil. **DO NOT SHAKE**.
24. Place the sample in a plastic bag on ice in a cooler.
25. If a jar was requested for another analysis, a syringe for dry weight does not need to be submitted, skip to step 29.
26. Using the syringe sampler, take another sample from the soil.
27. Cap and label the syringe with the sample identification.
28. Place the syringe with the sample vial in the plastic bag. This syringe sample is for dry weight determination.
29. Decontaminate the jar/balance using decontamination procedures appropriate for the type and level of contamination.
30. Unused methanol must be returned to the laboratory for disposal.

LINKS TO ADDITIONAL INFORMATION

Methanol Safety Data Sheet: https://www.avantorsciences.com/stibo/search/sds000001196_us_en.pdf

EGLE Laboratory Documents: https://www.michigan.gov/egle/about/organization/remediation-and-redevelopment/laboratory

Section 324.20101:
http://www.legislature.mi.gov/(S(z30i3fx3lk53hjcl0xerugza))/mileg.aspx?page=GetObject&objectname=mcl-324-20101

Method 5035A – Closed-System Purge-and-Trap and Extraction for Volatile Organics in Soil and Waste Samples: https://www.epa.gov/sites/production/files/2015-07/documents/epa-5035a.pdf

Target Detection Limits and Designated Analytical Methods: https://www.michigan.gov/egle/-/media/Project/Websites/egle/Documents/Programs/RRD/Remediation/Resources/EGLE-Published-List-of-Target-Detection-Limits-Designated-Analytical-Methods.pdf?rev=8ed963b82c164b68b7313b831a8f7abb&hash=B8EB37A632C53DB82BCE15F281588525

APPROVING AUTHORITY

DIVISION DIRECTOR APPROVAL:

Mike Neller, Director
Remediation and Redevelopment Division

HISTORY

Policy No.	Action	Date	Title
RRD-35	Original	10/22/2004	Standard Operating Procedure for Methanol Preservation in the Field
RRD-35	Revision	03/10/2016	Standard Operating Procedure for Methanol Preservation in the Field
RRD SOP-35	Reviewed	05/19/2022	Field Methanol Preservation of Solid Samples for Volatile Analysis

CONTACT/UPDATE RESPONSIBILITY

Any questions or concerns regarding this standard operating procedure should be directed to EGLE-RRD@Michigan.gov.