U.S.EPA REGION 9 LABORATORY

RICHMOND, CALIFORNIA

FIELD SAMPLING GUIDANCE DOCUMENT #1210

SOIL SAMPLING FOR VOLATILE COMPOUNDS

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1.0 Scope and Application

This Standard Operating Procedure (SOP) describes recently modified procedures for field collection, handling, and preparation of soil samples for analyses of volatile organic compounds (VOCs) in solid material (e.g., soils, sediments and solid waste). This SOP includes recent guidance published by EPA Office of Solid Waste (1998) and complements EPA Laboratory Methods 5035 (purge and trap) and 8015, 8021, 8260 (gas chromatography). The primary focus of this SOP is to explain four possible sampling techniques, yet it also describes some procedures to be completed in the laboratory prior to sample collection in the field. Field personnel must coordinate with the receiving laboratory to ensure the selected sampling methodology matches the analytical procedures used in the lab. Specialized equipment and containers are designed to maintain sample integrity for soil or solid materials which may contain contaminants with boiling points less than 200°C (e.g., BTEX).

Revision of these SW-846 field and laboratory procedures was a result of research conducted by both the private and public sector which showed that traditional sample collection techniques results in substantial losses of volatiles. These losses (an order of magnitude or more) are the culmination of volatilization and biodegradation losses that occur during the sampling, storage, and subsequent sub-sampling in the laboratory.

Under ideal circumstances, field instruments are available to prescreen samples for initial concentrations and subsequently utilize optimal sample collection, preservation and laboratory analyses. In lieu of prescreening samples on site, field personnel may need to collect samples with both low (<200 ug/kg) and medium (>200 ug/kg) level VOC concentrations. Two different field preservation and one laboratory preservation options are described here in order to address sampling for soils with various concentrations. It must be noted that field preservation options are inherently more difficult and increase chances of sample contamination as compared to using pre-preserved sample vials.

To address significant problems with soil VOC analyses, the method was dramatically revised in Update III of SW-846 (finalized in the June 13, 1997 Federal Register). In particular, Method 5030A was deleted for low-level soil analysis and was replaced with Method 5035. A revised medium-level method was also presented in Method 5035. Samples must be handled differently from the onset of sample collection, depending upon the action levels for the project and the anticipated concentrations of VOCs at the site.

2.0 Method Summary

Samples to be analyzed for VOC compounds are collected from freshly exposed soil. Approximately 5 grams of sample is obtained by one of several methods described in Table 1. Either a hand-held coring device or a modified plastic syringe is used to gather the soil plugs or solid material sample. (The modified syringe has had the front end sliced off and uses a plunger without lubricant.) If the plastic syringe is used, then field personnel extrude these soil plugs into vials containing preservatives (sodium bisulfate solution or methanol**).** Vials may be preweighed and pre-preserved in the laboratory or vials can be weighed and filled with preservatives in the field. Samples in vials are re-weighed after the sample aliquots are added to obtain the net sample weights. All weights must be recorded to within 0.2 g.

In addition to the samples collected for analysis, one co-located sample must be collected for a moisture content determination in order to report the VOC results on a dry-weight basis. Samples for moisture content determinations should not be chemically preserved and may be collected in conventional vials.

Table 1: Field Collection and Sample Preparation Options

Coring Device used in field, Laboratory Preservation (Protocol # 1)

- no field chemicals required
- limited to consolidated soils which can be collected in a coring device
- samples can be preserved in the laboratory using chemical preservatives or by freezing
- if samples are frozen until analysis, low level analyses can be performed in water
- limited suppliers of validated devices (e.g., Encore™ sampling equipment)

Low Level (<200 ug/kg) Sample Field Preserved with acidic solution (Protocol # 2)

- sodium bisulfate ($NaHSO_4$) solution added to vial in laboratory prior to sample collection in field
- limited to consolidated soils which can be collected in a coring device
- cannot be used on carbonaceous soils
- weighed in the field
- sample container (glass vial) also serves as the purge vessel
- bias may exist for some soil types (high clay or organic carbon)
- limited on the high end by instrument calibration which typically is 200 ug/Kg
- detection limits are based on the analyte, method, and laboratory capability, but typically range from 0.5 to 5 ug/kg
- VOA vial used as sparge vessel, samples cannot be diluted and VOA vials cannot be reanalyzed.
- additional samples required for QC and contingencies
- must comply with special DOT shipping requirements

Medium Level (>200 ug/Kg) Sample field preserved with Methanol preservation (Protocol # 3)

- methanol added to sample vial in laboratory prior to sample collection in field
- often referred to as preservation/extraction procedure
- aggregate and cemented materials can be collected by increasing sample size and volume of methanol
- negligible bias due to matrix effects
- method is not limited on the high end by instrument calibration since samples can be diluted and re-analyzed
- detection limits are based on the analyte, method, and laboratory capability
- analyzed by purge and trap
- must comply with special DOT shipping requirements

No Preservation (Protocol # 4)

- methodology selected as a last resort
- must be "clearly documented" in a sampling and analysis plan that is reviewed and approved by Region 9
- limited to unusual matrices
- data will be flagged as estimated

2.1 Selection of Sample Methodology

Part of the planning stages of the project is the selection of methodology. Potential contaminants of concern, often referred to as target analytes, must be carefully identified and defined relevant to data quality objectives. When the nature of the contamination is not well known, method-specified target analyte lists are typically selected by default. However, in many situations a target analyte list can be reduced based upon historic activities at the site. If there is no reason to suspect the presence of a contaminant it may be appropriate to omit it from the method analyte list. Since low-level analyses are usually more resource-intensive than medium-level analyses, it recommended that rationale for the testing of the more toxic contaminants be carefully evaluated prior to analytical testing (since these contaminants will possess the lowest action levels).

Action levels should be established once the contaminants of concern have been identified (e.g., using regulatory and risk-based criteria). Table 2 lists Region 9 Preliminary Remediation Goals (PRGs) for both residential and industrial soils for selected compounds. As shown in this table, for many analytes, the medium level method can provide acceptable quantitation levels.

Once action levels are established during the planning stages of the project, in order to select methodology with adequate sensitivity (i.e., to determine whether the high-level or low-level VOC analyses are more appropriate), **the action levels must be compared to the quantitation limits of the laboratory that will be performing the actual analyses**. (*It is important to note that laboratories frequently fail to report scientifically valid quantitation limits*.) Ideally, the action level for each target analyte should be at least two times greater than the laboratory's corresponding quantitation limits.

Table 2: Comparison of Region 9 PRGs to Laboratory Quantitation Limits

	Laboratory Quantitation Limit		Region 9 PRG	
Compound	Low Level	Medium Level	Industrial	Residential
Benzene	0.005	0.05	1.4	0.63
Bromodichloromethane	0.005	0.05	1.4	0.63
Carbon tetrachloride	0.005	0.05	0.5	0.23
Chloroform	0.005	0.05	0.53	0.25
1,2-Dibromo-3-chloropropane	0.005	0.05	1.4	0.32
1,2-Dibromoethane	0.005	0.05	0.02	**0.0049**
cis-1,4-Dichloro-2-butene	0.025	0.10	0.017	**0.0075**
1,2-Dichloroethane	0.005	0.05	0.55	0.25
1,1-Dichloroethene	0.005	0.05	0.08	**0.037**
1,2-Dichloropropane	0.005	0.05	0.68	0.31
cis-1,3-Dichloropropene	0.005	0.05	0.55	0.25
1,1,2,2-Tetrachloroethane	0.005	0.05	1.1	0.45
1,1,2-Trichloroethane	0.005	0.05	1.6	0.65
Vinyl chloride	0.005	0.05	0.035	**0.016**

Notes: Only compounds with PRGs > 1 ppm are shown. All values are in mg/kg. Values which exceed medium-level quantitation limit are shown in bold.

3.0 Sample Preservation, Containers, Storage and Handling

3.1 Preservation

Note: Method 5035 suggests several other options (e.g. freezing in water, freezing in the VOA vial, polyethylene glycol, etc.) None of these other preservation options have been validated and are not recommended by Region 9 unless validated prior to use.

3.2 Containers

Specific sample containers required will depend on the sampling methodology and corresponding laboratory analytical method. The most common soil VOC container is a 40 mL glass vial with a special frit and equipped with two TFE-faced silicon septa. These are large enough to contain at least 5 g of soil or solid material and at least 10 mL of liquid. 60 mL vials of equivalent materials and construction may also be used.

Another container is the plastic coring device which holds about 5 g of soil and can be tightly fitted with a cap equipped with a seal of inert rubber. These are commercially available (En Core); however, the receiving laboratory must have special tools to open this core.

3.3 Handling

3.3.1 Encore™ Samples (Protocol #1)

Ideally, the samples should be transferred to a VOA vial with a chemical preservative on the day of sample receipt. If this is done, a 14 day holding time will apply. If this action cannot be performed, either due to carbonaceous soils scheduled for low level analysis, or due to laboratory logistical issues, the samples should be stored in a freezer (-12°C) until the day of analysis. Such samples can be held for up to 7 days after sample collection.

3.4 Shipping & Storage

Once samples are collected, it is imperative that they be stored in conditions which maintain the integrity. All samples should be placed in shipping containers or other suitable containers with ice to reduce the temperature as soon as possible. Ideally, samples should be shipped the day of collection for overnight delivery to the laboratory. If overnight transit is not feasible due to site logistics, samples should be held at 4°C until shipping. Samples collected in the Encore™ sampler should be received at the laboratory within 4 days of sampling. *Note: DOT regulations associated with the use of preservatives in the field may be avoided by using Encore™ samplers.*

Chemically preserved samples should be stored at 4°C until analysis. A 14 day holding time is applicable.

Depending on the quantity and method of packaging, sodium bisulfate and methanol may be DOT Hazardous Materials and may be subject to the DOT and International Air Transportation Association (IATA) hazardous materials regulations.
Section 12 of this SOP provides a complete description of DOT regulatory considerations

4.0 Interferences and Potential Problems

Contamination of preservatives could result in a high bias of data. Personnel should optimize handling preservatives and sample vials in laboratory with controlled conditions. When samples are preserved in the field, it is especially critical to avoid the introduction of contamination from external sources. Consequently, personnel should work upwind of any possible source of VOCs (emissions from engines and backhoes, tobacco smoke, etc.) while adding preservatives to soil samples.

It is important to recognize that organic-free methanol can solubilize contaminants in ambient air. Forethought while sampling or handling vials is crucial to avoid possible contamination while using Protocol #3. The acidic solution used in Protocol #2 also has the potential for absorbing contaminants from ambient air. Do not leave vials open and exposed to ambient air.

Equipment blanks and field blanks are expected to be included in the sampling plan. For example, when samples are preserved with methanol in the field, a methanol blank should be exposed to field conditions during the sample collection process. Another example, if soil sample plugs are to be collected using the modified plastic syringe then "clean" soil should be extracted into the modified syringe then pushed into a

clean vial.

4.1 Instrumentation

The low level method requires a new autosampler which has two key features: 1. the ability to analyze low level samples without opening the vial and 2. a mechanical device for stirring the samples during analysis.

4.2 Operational Details

Screening at the laboratory is recommended regardless of whether samples were screened in the field (although laboratory screening is more important when field screening is not performed). When both medium-level and low-level samples are submitted to the laboratory, the laboratory must screen the samples prior to analysis or perform both medium-level and low-level analyses on a trial-and-error basis. For example, if the laboratory does not perform screening, then a sample is analyzed using the medium-level method, *but* VOCs are not detected or are detected below the quantitation limits, then the laboratory would be required to analyze the corresponding co-located low-level sample. Conversely, if the low-level sample is initially analyzed and exceeds the calibration range of the instrument, then the laboratory would be required to analyze the corresponding sample using the medium-level method.

5.0 EQUIPMENT/APPARATUS

- maps/site sample plan
- safety equipment
- GPS data logger and receiver
- plastic syringes, disposable, with barrel smaller than neck of sample vial, syringe end is cut off prior to sampling, one syringe per sample aliquot to be collected
- glass vials, 40 mL, screw cap, TFE lined, septum sealed
- magnetic stir bars, TFE or glass-coated
- portable top-loading balance ±0.01g (for protocol# 3); balance weights for reference and calibration once per day
- zip-type plastic bags
- logbook
- sample labels
- chain of custody forms
- custody seals
- field data sheets
- cooler(s)
- ice
- stainless steel, plastic, or other appropriate composition bucket
- decontamination supplies/equipment
- spade or shovel
- scoop
- bucket auger
- hand auger and extension rods

6.0 REAGENTS

Sodium bisulfate, reagent grade, and organic-free water are required for the low level method. High-purity methanol is required for the medium level method.
Decontamination solutions are specified in SOP #109, Sampling Equipment Decontamination.

7.0 Sampling Procedures

Whether sampling from the surface or from depth using such devices as a split spoon, collection of the sample will be the same. Samples should be collected as quickly as possible (< 10-15 seconds). *Temporary storage of soil in split spoons, jars, or ziplock bags is not permitted*. Field screening may still be used to decide which samples will be submitted for analysis but all potential samples must be immediately chemically preserved or placed in a coring device. All protocols have been written assuming that both medium and low level sample will need to be collected.

In order to help maintain the physical structure of samples, for cohesive granular material, a hand-operated coring device must be used to collect samples of appropriate size for laboratory analysis (e.g., cylindrical soil plugs are extruded into vials using disposable plastic syringes with the tapered front ends removed). Field personnel transfer samples into preweighed vials containing liquid preservatives(e.g., sodium bisulfate solution or methanol). The vials are weighed in the field before use and are subsequently reweighed after the sample aliquots are added to obtain the net sample weights.

7.1 Preparation of sample vials

Sample vials should be prepared in a fixed laboratory or other controlled environment, sealed and shipped to the field location. Gloves should be worn during the preparation steps.

Low level samples field-preserved with sodium bisulfate solution

- Add a clean magnetic stirring bar to each clean vial. If the purge and trap device employs a means of stirring the sample other than a magnetic stirrer (e.g., sonication or other mechanical means), then the stir bar is omitted.

- Add preservative to each vial. The preservative is added to each vial prior to shipping the vial to the field. Add approximately 1 g of sodium bisulfate to each vial. If sample volume is markedly smaller or larger than 5 g, adjust the amount of preservative at a ratio of 0.2 g preservative for each 1 g of sample. Enough sodium bisulfate should be present to ensure a sample pH of <2.

- Add 5 mL of organic-free reagent water to each vial. The water and the preservative will form an acid solution that will reduce or eliminate the majority of the biological activity in the sample, thereby preventing biodegradation of the volatile target analytes.

- Seal the vial with the screw-cap and septum seal. If the double-ended, fritted vials are used, seal both ends as recommended by the manufacturer.

- Affix a label to each vial. This eliminates the need to label the vials in the field and assures the tare weight of the vial includes the label. (The weight of any added markings is negligible.)

- Weigh the prepared vial ± 0.01 g, record the tare weight, and write it on the label.

- Because VOCs will partition into the headspace of the vial from the aqueous solution and will be lost when the vial is opened, surrogates, matrix spikes, and internal standards (if applicable) should only be added to the vials after the sample has been added to the vial. These standards must be introduced in the laboratory, either manually by puncturing the septum with a small-gauge needle or automatically by the sample introduction system, just prior to analysis.

Medium level samples field preserved/extracted with Methanol

♦ Add 10 mL of methanol to each vial.

♦ Seal the vial with the screw-cap and septum seal.

♦ Affix a label to each vial. This eliminates the need to label the vials in the field and assures the tare weight of the vial includes the label. (The weight of any added markings is negligible.)

♦ Weigh the prepared vial ± 0.01 g, record the tare weight, and write it on the label.

NOTE: Vials containing methanol should be weighed a second time the day they are used. Vials found to have lost methanol (reduced weight by >0.02g) should not be used for sample collection.

♦ Surrogates, internal standards and matrix spikes (if applicable) must be added to the samplein the laboratory and prior to analysis.

7.2 Sample Collection

7.2.1 Protocol #1: Field collection with coring type samplers followed by laboratory preservation

Expose a fresh surface using a clean spatula or other suitable tool. Collect a sample using a coring device (e.g., the hand-held Encore™) and immediately cap following manufacturer's directions. Collect two five gram cores for the low level (if needed) and one five gram core for the medium level. Label cores and transfer to laboratory on ice as soon as possible, but within four days.

7.2.1.1 Unconsolidated Materials

Certain soil types may not be sufficiently consolidated to collect a core sample. Two examples would be dry sand or sludges/sediments with a very high moisture content. In such cases, the plunger of the Encore™ should be pulled back and locked. The Encore™ should be held with the opening facing upward and the sample transferred by spatula or pouring until the Encore™ is filled. The Encore™ is then capped and handled as previously outlined. *Note: Samples which are unconsolidated should be labeled as such on the chain of custody so that the laboratory can handle these samples with additional caution.*

7.2.1.2 Aggregate or Cemented Material

The Encore™ sampler should not be used for these materials. It can only be used for soil types that can be collected using a small diameter coring device. For other materials, the only collection technique which will maintain the integrity of the sample is field collection with methanol–protocol #3.

7.2.2 Protocol #2: Low level soil samples field preserved with Sodium Bisulfate

The sample vials for the low-level method are designed to be placed directly in the laboratory's instrument so that they remain hermetically sealed until the VOCs are withdrawn during analysis. The entire content of each vial is processed during analysis. Hence, when low-level VOC analyses are required, it is necessary to collect at least two co-located samples. This gives the laboratory an opportunity to perform an additional analysis should the first analysis be unacceptable. Since the vials remain sealed, dilutions cannot be performed. When low-level VOC analyses are required, an extra co-located sample for the medium-level method must be collected with each set of low-level samples. Also aqueous acidic solutions are used to preserve samples for the low-level analyses; therefore, low-level samples must be initially tested for carbonate interferences in the field before samples are collected.

7.2.2.1 Laboratory Preparation

Add 1 gram sodium bisulfate, clean magnetic stir bar, and 5 mL of deionized water to a 40 mL VOA vial. Label vial and record weight ± 0.01 grams.

Note: VOA vials with special low bleed septa must be used to prevent false positives due to siloxane peaks from standard septa. Teflon coated stir bars absorb VOCs. This is a potential loss of VOCs. Disposable stir bars should be used or if stir bars are to be re-used, the stir bars should be cleaned and the cleanliness verified.

7.2.2.2 Field sampling

Whenever possible, samples should always be collected using a coring device (modified plastic syringe) as a transfer tool. A simple coring device can be made by cutting off the front part (with tip) of a disposable non-lubricated syringe, removing the rubber plunger tip and (with repeated experimentation) marking the length of core (2--3 cm) that corresponds to 5.0 ± 0.5 g. *Note: Use disposable syringes are NOT lubricated since so as to avoid contaminating the VOC sample.*

If the test sample passes the initial test for both effervescence and pH (section below), use the plastic syringe to collect approximately 5 g of sample as soon as possible after the surface of the soil or other solid material has been exposed to the atmosphere: generally within a few minutes at most.

Transfer the 5 g soil sample ("or plug") into the prepared and pre-labeled sample vial by placing the syringe tip inside the vial and squeezing the syringe plunger. Cap immediately and carefully wipe the exterior of the sample collection device with a clean cloth towel.

For each sampling point, use a new plastic syringe to collect soil. Quickly brush any soil off the vial threads and immediately seal the vial with the septum and screw-cap.

An initial test sample should be collected to evaluate effervescence and chemical preservation (pH $\leq$ 2). A five gram core should be placed in a VOA vial which contains the acid solution. If effervescence occurs, the sample should be collected in a VOA vial with no sodium bisulfate. (*Note: if effervescence does occur, immediately unscrew the cap to release built up pressure*.) The unpreserved sample should be analyzed within 48 hours, the holding time. Results from the analysis may be biased low and should be flagged as estimated.

The test sample must also have the pH evaluated either by a pH meter or test strip to ensure that the pH has been reduced to <2 to limit biodegradation. If the sample has not been properly acidified, there are two options:

- Vials can be used which contain a higher amount of sodium bisulfate. This additional sodium bisulfate should be added in the lab when the vial is prepared since addition in the field would affect tare weight. The exact amount of sodium bisulfate will be determined by the buffering capacity of the soil which makes prescreening of the site prior to the actual sampling event a necessity. Sodium bisulfate can be added in the field if the field personnel record the weights of the additional preservative and sample.

- Analyze the sample within the 48 hour holding time and flag the data as estimated.

Hints:
When practical, use a portable balance to weigh the sealed vial containing the sample to ensure that 5.0 g ± 0.5 g of sample were added. The balance should be calibrated in the field using an appropriate weight for the sample containers employed. Record the weight of the sealed vial containing the sample to the nearest 0.01 g.

Alternatively, collect several trial samples with plastic syringes. Weigh each trial sample and note the length of soil in the syringe that corresponds to 5.0 + 0.5 g. Discard each trial sample.

As with the collection of aqueous samples for volatiles, collect at least two replicate samples. This will allow the laboratory an additional sample for reanalysis. The second sample should be taken from the same soil stratum or the same section of the solid waste being sampled, and within close proximity to the location from which the original sample was collected.

In addition, since the soil vial cannot be opened without compromising the integrity of the sample, at least one additional aliquot of sample must be collected for screening, dry weight determination, and medium concentration analysis (if necessary). This third vial may be collected in a 60 ml vial or another 40 ml soil sample vial. However, this third vial must not contain the sample preservation solution, as an aliquot will be used to determine dry weight. If medium concentration samples are collected in vials containing methanol, then two additional vials should be collected, one for medium concentration analysis collected in a vial containing methanol, and another for the dry weight determination in a vial without either methanol or the low concentration aqueous preservative solution.

If samples are know or expected to contain target analytes over a wide range of concentrations, thereby requiring the analyses of multiple sample aliquots, it may be advisable and practical to take an additional sample aliquot in a low concentration soil vial containing the preservative, but collecting only 1- 2 g instead of 5 g as described in section 7.2.3.

NOTE: When the low level samples are strongly alkaline or highly calcareous in nature, the sodium bisulfate solution may not be strong enough to reduce the pH of the soil/water solution to below 2. Additional steps may be required to preserve the samples. Such steps include: addition of larger amount of the sodium bisulfate preservative to non-calcareous samples, storage of low level sample as -12°C, or significantly reduce the maximum holding time for low concentration soil samples. Whichever steps are employed, they should be clearly described in the sampling and QA project plans and distributed to both the field and laboratory personnel.

Record weight and transfer to ice.

A duplicate low level sample should be collected for the laboratory since low level samples cannot be reanalyzed. Ship to the laboratory per DOT regulations. (Corrosive.) *Note: Additional samples need to be collected for matrix spikes or other QC objectives.*

7.2.2.3 Aggregate or Cemented Material

Protocol #2 should not be used for these materials. For other materials, the only collection technique which will maintain the integrity of the sample is field collection with methanol–protocol #3.

7.2.3 Protocol # 3: Medium level samples field preserved with Methanol

This particular sampling protocol has been suggested by some as a combined preservation and extraction procedure. Carbonates are not problematic for methanol preservation and methanol sample extracts may be diluted in the laboratory when concentrations exceed the calibration range of the instrument. In addition, when samples are preserved with methanol, field personnel are not limited to single grab samples (as in the low-level method) but may composite subsamples from several locations.

7.2.3.1 Laboratory Preparation

Add 5 mL of methanol to a 40 mL VOA vial. Label vial and record weight ± 0.01 grams.

7.2.3.2 Field Sampling

Vials containing methanol must be reweighed (in the field) on the day of use to ensure that there has been no significant loss of methanol. Vials which exhibit a difference of greater than 0.2 grams should not be used. Quickly collect a 5 gram sample using a coring device as in 7.2.1 above and transfer soil plug into VOA vial containing methanol. Take care to ensure that no soil particles exist on vial threads.

Weigh to 0.2 grams and complete label. Ship to lab per DOT regulations. (Flammable liquid, Poison.) Samples which have been preserved but are not submitted to the laboratory must be treated as hazardous waste. *Note: Other sample sizes may be used. The 1:1 soil to methanol ratio by weight should be maintained and a larger bottle may be required.*

Using the appropriate sample collection device, collect approximately 5 g of sample immediately (15 mins.) after the surface of the soil or other solid material has been exposed to the atmosphere. Carefully wipe the exterior of the sample collection device with a clean cloth or towel.

Using the collection device, add about 5 g (2--3 cm) of soil to the vial containing 10 mL of methanol. Brush any soil off the vial threads and seal the vial with the septum and screw-cap. Total sampling time not to exceed 10 minutes. Store samples on ice at 4°C.

When practical, use a portable balance to weigh the sealed vial containing the sample to ensure that 5.0 g ± 0.5 g of sample were added. The balance should be calibrated in the field using an appropriate weight for the sample containers employed. Record the weight of the sealed vial containing the sample to the nearest 0.01 g.

Alternatively, collect several trial samples with plastic syringes. Weigh each trial sample and note the length of the soil column in the syringe. Use these data to determine the length of soil in the syringe that corresponds to 5.0 g ± 0.5 g. Discard each trial sample.

Other sample weights and volumes of methanol may be employed, provided that the analyst can demonstrate the sensitivity of the overall analytical procedure is appropriate for the intended application.

The collection of at least one additional sample aliquot is required for the determination of the dry weight, as described in sec. 7.3. Samples collected in methanol should be shipped as described in Sec. 12 and must be clearly labeled as containing methanol, so the that the samples are not analyzed using the closed-system purge and trap equipment described in this procedure.

NOTE: Collection of medium concentration soil samples that are NOT preserved in the field generally follow similar procedures as for the other types of samples described in section 7.2.4, with the obvious exception that the sample vials contain neither the aqueous preservative solution nor methanol. However, when field preservation is not employed, it is better to collect a larger volume sample, filling the sample container as full as practical in order to minimize the headspace. Such collection procedures generally do not require the collection of a separate aliquot for dry weight determination, but it may be advisable to collect a second sample aliquot for screening purposes, in order to minimize the loss of volatiles in either aliquot.

7.2.3.3 Large Aggregate and Cemented Materials

Sample will need to be placed in a larger, wide mouth, 4 0z. glass jar and preserved with a proportionately larger volume of methanol (to maintain the 1:1 ratio). In this event, the weight or volume of methanol must be recorded.

7.2.4 Protocol # 4: No preservation

Under limited circumstances, Region 9 will permit the collection of unpreserved samples, such as hard or cementitious materials, debris, or large aggregates which cannot be easily collected using the options above. Field methanol preservation is the preferred approach for these types of materials. Losses of VOCs are likely and all results should be considered as estimated values.

7.3 Moisture Content Sample

In addition to the samples collected as described above, a separate container must be collected to determine moisture content. This sample can be any conveniently sized container, of glass or plastic. Ordinary soil sampling procedure are used to collect samples to measure moisture content. If samples are being collected for other analytes (e.g. metals, semivolatiles) that sample container can serve as the container for moisture content.

8.0 Calculations

For low level analyses, the laboratory should correct surrogate concentrations for the percent moisture in the samples. Otherwise this section is not applicable to this field sampling SOP.

9.0 Quality Assurance/Quality Control

There are no specific quality assurance activities which apply to the implementation of these procedures. However, the following QA/QC procedures apply:

1. All data must be documented on field data sheets and in site logbooks.

2. All instrumentation must be operated in accordance with operating instructions as supplied by the manufacturer, unless otherwise specified in the work plan. Equipment checkout and calibrations activities must occur prior to sampling/operation, and they must be documented.

10.0 Data Validation

This section is not applicable to this field sampling SOP.

11.0 Health and Safety

Methanol is a toxic and flammable liquid. Therefore, methanol must be handled with all safety precautions related to toxic and flammable liquids. Inhalation of methanol vapors must be avoided. Vials would be opened quickly during the sample preservation procedure. Methanol must be handled in a ventilated area. Protective gloves should be worn when vials containing methanol are handled. Methanol should be stored away from open flames, areas of extreme heat, and other ignition sources. Vials containing methanol should be refrigerated (e.g., stored in coolers with ice).

Aqueous sodium bisulfate is a strong mineral acid. Therefore, solutions must be handled with all safety precautions related to mineral acids. Protective clothing (gloves, safety glasses, etc.) should be worn when vials containing sodium bisulfate are handled.

12. Regulatory Considerations for Sample Shipping

Field personnel involved in the shipment of samples prepared in the field for laboratory analysis by Method 5035, should be aware of the pertinent EPA, Department of Transportation (DOT) and International Air Transportation Association (IATA) regulations so that regulatory compliance can be maintained. Three levels of regulations apply depending on type and quantity of preservative and method of packaging. These regulations are summarized as follows:

1. small quantity exception--($\leq$ 30 mL inner containers), *not subject* to Hazardous Material Regulations (HMR) *provided* package is in accordance with 49 CFR 173.4.

2. limited quantity DOT hazardous material--must meet regulatory requirements minus UN specification containers (49 CFR 172.700 training applies)

3. fully regulated DOT hazardous material--Ltd Qty exception not taken, package must be in *full* compliance with HMRs (49 CFR 172.700 training applies)

Note: DOT regulations associated with the use of preservatives in the field may be avoided by using Encore™ samplers.

12.1 Shipment as a Small Quantity Exception (49 CFR 173.4)

The DOT small quantity exception described in 49 CFR 173.4(a)(1)(i) states that the maximum quantity of material per inner container is limited to thirty (30) mL for authorized liquids, other than Division 6.1, Packing Group I materials (i.e., poisons). As applied to the preservatives of Method 5035, *if there is less than or equal to 30 mL of methanol or aqueous sodium bisulfate solution per inner container (VOC vial), this material is not subject to any other requirements of the hazardous materials regulations except those presented in 49 CFR 173.4.* However, aside from the 30 mL receptacle limit, there are additional

restrictions:

- Each inner receptacle with a removable closure, has its closure held securely in place with wire, tape or other positive means.
- Unless equivalent cushioning and absorbent material surrounds the inside packaging, each inner receptacle is securely packed in an inside packaging with cushioning and absorbent material that (i) will not chemically react with other material and (ii) is capable of absorbing the entire contents (if liquid) of the receptacle.
- The inside packaging is securely packed in a strong outside packaging.
- The completed package, as demonstrated by prototype testing, is capable of sustaining each of the following free drops made from a height of 1.8 m (5.9 feet) directly onto a solid unyielding surface without breakage or leakage from any inner receptacle and without a substantial reduction in the effectiveness of the package:
  - One drop flat on bottom
  - One drop flat on top
  - One drop flat on the long side
  - One drop flat on the short side
  - One drop on a corner at the junction of three intersecting edges
  - A compressive load as specified in 49 CFR 178.606(c)

The gross mass of the completed package must not exceed 29 kg (64 pounds). The package must not be opened or otherwise altered until it is no longer in commerce. The shipper must certify conformance with this section by marking the outside of the package with the statement: *This package conforms to 49 CFR 173.4,"* or, until 1 October 2001, with the statement: *This package conforms to the conditions and limitations specified in 49 CFR 173.4.* Furthermore, the shipper must indicate on the air waybill under nature and quantity of goods: *Dangerous Goods in Excepted Quantities.*

IATA also requires the application of an *excepted quantities label.* This label contains the certification language identified above. Label entries include shipper signature, title, date, address and indication of the hazard class and associated UN number.

One final restriction needs to be noted. While 49 CFR 173.4 does not have a total net quantity limitation, IATA Dangerous Goods Regulations (DGR Section 2.7.4.2) *does.* For packing group II materials (e.g., methanol and sodium bisulfate), the total net quantity limit is 500 mL. This equates to 60 inner containers (VOC vials) containing approximately 8 mL of material (sample plus preservative) per outer package (i.e., sample cooler).

When discussing the shipment of DOT hazardous materials in the air mode, shippers have additional restrictions that are identified in Columns 9A/9B of the 49 CFR 172.101 hazardous materials table. Net quantity limits for methanol for passenger and cargo aircraft are one (1) liter and sixty (60) liters, respectively. The net quantity limits for sodium bisulfate solutions are one (1) liter and thirty (30) liters, respectively. Shippers should note that these quantities exceed the IATA small quantity exception. **Therefore, if preservative volume (methanol or sodium bisulfate solution) is less than 30 mL per**

VOC vial (inner container) and the total net quantity per cooler (outer package) is limited to 500 mL, DOT HMRs or IATA DGR's quantity limits are never an issue provided packaging conforms with 49 CFR 173.4.

If more than 30 mL of methanol is used per VOC vial, shippers must address regulations for DOT-regulated hazardous material.

12.2 DOT Regulated Hazardous Materials Shipments, Limit Quantity

Personnel offering chemically preserved environmental samples for shipment in commerce in inner packaging (containers) containing more than 30 mL of methanol *are Hazmat employees* and are subject to the DOT training requirements in 49 CFR 172.700. If these individuals do not possess DOT training and do not have an employer certification, it is a violation of DOT regulations to offer these materials for transportation in commerce! Also, some generally used air shipping couriers *may not* ship hazardous materials or limited quantity hazardous materials. It is recommended that the proposed carrier be consulted in advance to determine if there are any company-specific requirements or limitations.

Methanol-preserved samples in greater than 49 CFR 173.4 inner-container quantities will void the 49 CFR 173.4 small quantity exception. These materials meet the definition of a DOT flammable liquid. On the shipping paper, these samples must be described using any of the following text:

- Methanol solution, 3, UN1230, PGII
- Methanol solution, 3, UN1230, PGII Limited Quantity
- Methanol solution, 3, UN1230, PGII Ltd Qty.

(Note that methyl alcohol may be substituted for "methanol.)

It is emphasized that DOT allows for a limited quantity exception. Under the limited quantity exceptions, packages need not be UN specification. Labels are not required *unless* the shipment is by air. Additionally, limited quantity shipments are not subject to placarding requirements. There are restrictions on the type of combination packaging that is acceptable for use. Since methanol is a PGII flammable liquid, 49 CFR 173.150 states the inner packaging limitation is one (1.0) liter. The outer packaging is described in the regulations as a strong outer package (i.e., a box, can, or cooler). Marking requirements must be met. An outline of the limited quantity exceptions and requirements for methanol is as follows:

Packaging:
Inner packaging: Plastic or glass < 1.0 liters
Outer Packaging: Strong outer package
Gross Weight: 66 lb (30 kg)

Labeling: Not required unless shipped by air
Primary Hazard: Flammable Liquid
Secondary Hazard: Poison

Marking: The outer package must be marked with the following items:

1. Proper shipping name: Methanol Solution
2. UN Number: Not required for Ltd Qty shipment/Otherwise required
3. DOT specification orientation arrows (See 49 CFR 172.312 for exception)
4. Shipper or receiving facility name and address
5. Cargo Aircraft only may be required depending on quantity shipped.

Shipping Paper:
1. Complete DOT shipping description
2. Number of containers (i.e., complete package)
3. Weight
4. Emergency Response information (ERG #)
5. Emergency Contact information

12.3 DOT Regulated Hazardous Materials Shipments, Fully Regulated

If shippers *do not* take a limited quantity exception and their materials are regulated in commerce, they must have DOT specification packages and would probably have to consider the cooler a DOT overpack (49 CFR 173.25). All inner packaging must be marked and labeled. Also, since the inner markings and labels will not be visible, the overpack must be marked and labeled on the outside *and* be marked with the following statement:

Inside (inner) packages comply with prescribed specifications

This means that the inner receptacles (glass jars or vials) must be in an authorized (UN specification) outer package. These combination packages would then be placed in the cooler (DOT overpack). For this case, all DOT shipping paper, labeling, marking (including UN numbers), and placarding requirements in 49 CFR 171 - 177 apply.

12.4 RCRA Regulations

The RCRA hazardous waste regulations are also be applicable to shipping of chemically preserved samples. 40 CFR 261.4 discusses the RCRA exemption for shipping samples. These regulations provide an exemption from the hazardous waste regulations for “samples” but not for materials which are not analyzed. Materials preserved with aqueous sodium bisulfate or methanol, which are not considered “samples,” would be classified as hazardous wastes due to characteristics (corrosivity and ignitability) and would need to meet the RCRA manifesting and shipping requirements in 40 CFR 262.