RATIONALE FOR PRESERVATION OF SOIL AND SEDIMENT SAMPLES FOR DETERMINATION OF VOLATILE ORGANIC COMPOUNDS

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INTRODUCTION

Soil and sediment samples are routinely collected and analyzed for volatile organic compounds (VOCs) to determine whether contamination has occurred that is detrimental to the public health and environment. In the last decade, there have been several studies to determine what effect sample handling and preservation have on the concentration of volatile organic compounds in such samples. This paper attempts to summarize the results from these studies and to recommend a reasonable approach to insuring that the concentrations determined in the laboratory accurately reflect what is present at the point of sampling.

BACKGROUND

Since the early 1980s, environmental laboratories have routinely used the dynamic headspace, or purge and trap, procedure as a means of concentrating and introducing the volatile organic compounds in a sample into a gas chromatograph for analysis. Soil and sediment samples (hereafter referred to as soil samples) were typically collected in the field, placed in glass jars sealed with Teflon® liners and solid caps, and sent to the laboratory for analysis. This is referred to as the "dirt in a jar" procedure. Once in the laboratory, samples would be held at 4º C until analysis. The standard holding time for VOCs in soil samples is 14 days from collection, meaning that the samples must be analyzed in this time-frame or the results are considered invalid due to losses of the volatiles in the sample.

On the day of analysis, samples would typically be brought to room temperature. A sub-sample would be weighed out in a fume hood into a sparging flask or test tube, which would then be attached to the purge and trap instrument. Water, surrogates, and internal standards would be added, and the sample would be purged to transfer the volatiles onto the trap. The trap would then be ballistically heated, and the volatiles determined using either a gas chromatograph (GC) or a gas chromatograph/mass spectrometer (GC/MS). The focus of this paper is on the steps that occur prior to the purging of the sample.

Based on informal surveys with Connecticut-based laboratories, approximately 50% of the soil samples currently submitted for VOC determination are "dirt in a jar"-type samples, with no preservation other than cooling at 4º C.

As the environmental testing industry acquired more experience and expertise, a phenomenon was noted that samples classified as "hot" in the field, either due to field screening or odor, would come back from the laboratory with only low levels (<200 ppb) of VOCs present. People began to suspect that the current sampling and sample storage procedures were not adequate.

In May 1993, EPA published a report entitled, *Behavior and Determination of Volatile Organic Compounds in Soil: A Literature Review* (1). This report noted that substantial losses of volatile organics occur when samples are stored at 4º C in only a few days. Furthermore, laboratory handling of the sample can also create substantial losses in VOC concentrations, averaging 60%. Studies have shown that VOCs are also subject to microbial degradation even when stored at

4º C (2). The combination of losses due to poor sample seals, headspace, and microbial action will lead to rapid loss of VOCs in general, but even if the sample containers are completely sealed, significant losses of certain analytes, notably the aromatics such as benzene, toluene, etc., will occur due to microbial degradation (2). Thus, in order to store samples for any appreciable length of time, it was determined that the samples should be sealed from the atmosphere and steps taken to limit any biological activity.

Sample collection and field handling were also determined to be critical issues. In 1996, Alan Hewitt and Nicole Lukash of the U.S. Army Corps of Engineers Cold Regions Research and Engineering Laboratory (CRREL) conducted a study (3) in which various types of sample collection devices and techniques were evaluated. The results of this study are significant. Some key findings were as follows:

1. When sampling soils for VOCs it is important to keep the sub-sample soil structure intact (i.e. the sample should remain as a plug, and not be broken apart).

2. Soil samples exposed to air for two minutes in a sealed plastic bag showed a 90% loss in certain analytes (e.g. trichloroethene or TCE). This indicates that any handling of a soil sample with spoons, trowels, or any type of field compositing will result in significant losses of volatile analytes.

3. Samples collected using some type of coring device (e.g. a plastic syringe with the tip cut off), allowed for an undisturbed plug of sample to be collected and easily added to a 40-milliliter (ml) volatile organic analysis (VOA) vial.

4. Samples collected in core liners and uncapped showed significant losses in less than 40 minutes (e.g. >90% loss of TCE). Samples collected in core liners and capped with either Teflon® or aluminum foil had significant losses in 5 days.

5. Samples collected with cut-off syringes and added to VOA vials containing 5 mls water, with a Teflon®-lined, butyl rubber septum showed only slight losses (5-15%) when stored at 4º C after 28 days.

After the results of this study were published, the first commercial sampling device (the En Core® sampler) was introduced. This device uses Viton® o-rings to provide a hermetic seal that will prevent losses of volatiles due to evaporation. However, due to potential microbial degradation, samples must be transferred to a medium that will inhibit degradation (such as sodium bisulfate or methanol) or frozen at -12º C within 48 hours of collection.

As a result of these and other studies, EPA developed and published Method 5035. This method calls for collection of samples using a coring device and either immediately transferring the sample to a pre-weighed VOA vial (a vial that uses a Teflon®-lined, rubber or silicone septum as a seal) containing either water, a sodium bisulfate solution, or methanol. Samples collected in water must either be analyzed within 48 hours of collection or frozen to prevent microbial degradation. The bisulfate solution has a low pH, which effectively stops any microbial degradation. The methanol has two functions. It stops the microbial degradation, and the volatile

organic compounds are soluble in it. Thus, samples collected in methanol can be opened for short periods of time (e.g. less than 1 to 2 minutes) in the laboratory without fear of analyte loss. Samples collected in bisulfate or water should not be opened, as analyte loss will rapidly occur. The typical holding time for soils preserved with either methanol or sodium bisulfate is 14 days from collection.

Another option is collecting the sample using a coring device such as the En Core® sampler, and shipping the device to the laboratory. At the laboratory the sample can be transferred to the VOA vial (containing bisulfate, water, or methanol). Regardless of whether the sample is collected in methanol, bisulfate, or kept in the En Core®-type device, the sample may be frozen to extend the holding time.

Sample Collection Considerations

The first step in obtaining meaningful volatile organic compound concentrations is to obtain a sample that is representative of in-situ conditions. It is obvious that the major problem with collecting samples for this class of analyte is that they are volatile, and easily lost from a sample. Therefore, the following steps should be taken to limit any losses of analytes:

1. The sample should not be exposed to air. Exposure of a minute or two will result in significant losses. VOCs will be lost even in a sealed container if there is headspace present and the container is opened. In general, compositing of soil samples for volatile organics is not recommended.

2. A coring device should be used so that the structure of the sample is maintained. Coring devices can be syringes, En Core®-type devices, etc. The device should be able to extrude the sample in a plug, thus preserving the soil structure.

3. Samples should be collected as soon as possible after the soil is exposed. Any delay in collecting the sample will result in losses of VOCs. Prior to sampling, the technician should scrape away several inches of soil to obtain a fresh sample. The coring device should be inserted directly into the soil.

4. If samples are to be chemically preserved, the preservation should occur immediately after collection. The container must already contain the preservative, and then sealed immediately after the sample is added. The chilling process must then be begun immediately. Samples should not be collected from one area of the site, brought to a central staging area, and then added to the storage container.

5. The contact surfaces of the sample container must be cleaned of all soil particles to insure a hermetic seal. Any sample received at the laboratory without a good seal should be rejected.

In October 1998, the U.S. Army Corps of Engineers (USACE) published a paper describing sample collection and preparation strategies (4). This paper goes into much detail and rationale for collecting soil samples for volatiles and is strongly recommended reading.

An Appraisal of Preservation Options

It has been shown that collection of soil samples using the "dirt in a jar" method will lead to significant losses of volatile organic analytes. This section describes the various preservation options currently available and their strengths and weaknesses.

Preservation with Sodium Bisulfate

Sodium bisulfate is an acidic salt, which in aqueous solution lowers the pH to inhibit any microbial degradation of the VOCs. Many chemical suppliers offer VOA vials with a sodium bisulfate solution and a small magnetic stir bar already present. Samples collected in the field can be added directly to pre-weighed vials with little difficulty. The vial is then either weighed in the field or back at the laboratory to obtain the exact sample weight. A separate container must be submitted for percent solids determination. The concentration range, assuming a 5-gram sample, is 1 to 200 µg/kg (ppb). Once the sample is placed in the vial, and the vial sealed, it is not opened until after the analysis is completed. Assuming the vial is sealed correctly and stored at 4º C, there will be either minimal or no loss of analytes.

There have been some identified weaknesses with this procedure. Regardless of the type of sample container used, the contact area (e.g. the threads and top of VOA vials or the o-rings and contact surfaces of En Core®-type devices) must be free of soil particles. An airtight seal is critical. Being acidic, the sodium bisulfate solution will corrode the laboratory purge and trap unit over time. This is not a significant issue, but may require addressing by the laboratory every 3 to 5 years. Since the sample can only be analyzed once per vial, samples are usually collected in duplicate in case of breakage or other problems.

Perhaps the most significant issue is that certain naturally occurring compounds (humic acids, etc.) will decompose when exposed to the bisulfate solution and form ketones, notably acetone. The amount of acetone formed is extremely matrix dependent, but may be produced in significant concentrations. When using sodium bisulfate as a preservative, the data user must keep this in mind when evaluating the data. Also, it has been found that acidification with sodium bisulfate causes the loss of styrene (5). Therefore, if styrene is a compound of concern, sodium bisulfate should not be used.

Another significant issue with sodium bisulfate is for samples which react with the acid and effervesce. The effervescing will result in significant losses of volatile organics, and in such cases the sodium bisulfate cannot be used.

Preservation with Methanol

Methanol, or methyl alcohol, is commonly used for preservation of soil samples. Equal amounts of soil mass and methanol volume are commonly used (e.g. 10 grams soil added to 10 mls methanol). Again, a pre-weighed VOA vial containing methanol would be sent to the field. A sample would be extruded into the vial, the vial sealed, and reweighed either in the field or back at the laboratory. A separate container must be submitted for percent solids determination. Aliquots of the methanol extract are analyzed using the same procedure as for aqueous samples. (e.g. a 100-µL aliquot of the methanol is added to 5 mls of reagent water and analyzed the same way as a water sample). The concentration range, assuming a 10-gram sample and 10 mls methanol, is approximately 250 to 10,000 µg/kg (ppb). Since the methanol extract can be diluted, the upper range can be extended further.

The most serious limitation with this procedure is the relatively high detection limit. To counteract this, most projects call for collection of both sodium bisulfate-preserved and methanol-preserved samples from the same sampling point. If the sample has high concentrations, the methanol-preserved vials are analyzed. If the sample is low, then the bisulfate-preserved vial is analyzed.

The sample matrix itself can affect the solubility of the volatile organics in methanol. It might take several hours for concentrations to stabilize (5). Some procedures call for sonicating the vial containing the methanol/soil mixture for 30 minutes prior to analysis. Samples immersed in methanol should be sonicated at 40º C for 30 minutes as a precaution.

In a discussion of its sample collection strategies, the USACE mentioned that methanol could react with certain aluminum silicates to form acetone (4). However, this has not been as extensively noted as with the sodium bisulfate reaction, and does not seem to be an issue.

Use of En Core® -Type Samplers

En Core®-type samplers are very popular with sampling technicians. The devices function as both a sample coring device and sample storage unit (6). The device is inserted into the soil, removed, the contact surfaces wiped clean, the device sealed, placed in a resealable pouch, placed in a cooler, and shipped to the laboratory. The laboratory has 48 hours from collection to extrude the sample into a VOA vial containing either water, sodium bisulfate solution, or methanol. Samples in bisulfate or methanol can be held for 14 days at 4º C until analysis. Samples extruded into water must either be analyzed within 48 hours of collection or frozen. Samples frozen can be held up to 14 days from collection. Once a frozen sample is thawed, it must be analyzed within 48 hours (subtracting the time elapsed from sampling to initial freezing). Samples collected in En Core®-type devices may also be frozen and kept for up to 14 days. Again, once a frozen sample is thawed, it must be analyzed within 48 hours (subtracting the time elapsed from sampling to initial freezing).

The 14-day holding time for frozen samples is under study. There is conjecture that samples kept frozen may be stored for significantly longer than 14 days from collection with no significant

loss of VOCs. To date, the QA/QC Work Group is unaware of any published studies that verify this, and therefore recommend that the holding time of 14 days from collection be used for all preserved samples.

Use of Either Empty VOA Vials or Vials Containing Water

Studies (4,6) have shown the either empty VOA vials or VOA vials containing water are effective storage containers for up to 48 hours. This holding time may also be extended by freezing. A 5-gram sample is collected in a coring device and extruded into either a preweighed VOA vial containing 5 mls of water plus a stir bar or one that only contains a stir bar. The vial is sealed, and either reweighed in the field or back at the laboratory. For the vial that was originally empty, upon receipt in the laboratory, the laboratory has three options: 1) samples can be frozen, as is, until analysis; 2) sample can be preserved with methanol by adding via syringe through the septum; 3) samples can be analyzed within 48 hours of collection.

Water or bisulfate cannot be added prior to storage at 4º C, as this would involve either adding through the septum via syringe and storing with a pierced septum or removing the cap. Studies have shown that either of these options will lead to loss of analytes. If methanol is added, the septum should be replaced after the methanol has completely mixed with and wetted the soil. This technique may be used because the partial pressure of the volatile organic compounds over the methanol is very low, and thus losses by volatilization are greatly reduced during repeated opening and closing of the sample container. However, studies have shown that over time volatile analytes will be lost through a pierced septum even in methanol (6).

For the vial containing only water, the sample must either be analyzed within 48 hours of collection or frozen upon receipt in the laboratory. As noted previously, the threads and top of the vial must be free of soil particles, which could prevent an airtight seal. As discussed in the sodium bisulfate section, acetone can be produced when using sodium bisulfate. Using only water eliminates this problem. A serious drawback to using water alone was that the samples had to be analyzed within 48 hours of collection. With the advent of freezing samples to extend the holding time, this is no longer an issue and has become the method recommended by EPA as most desirable.

RECOMMENDATIONS

General

Regardless of the type of preservation method selected, all soil samples should be collected using a coring device. Cut-off syringes, En Core®-type devices, etc. are examples. Samples should be placed in the appropriate containers as soon as possible (e.g. less than one minute). If chemical preservation is to be used, the containers should already contain the preservative. The contact surfaces of the sample container must be cleaned of all soil particles to insure a hermetic seal. Any sample received at the laboratory without a good seal should be rejected.

Preferred Preservation Method

Supplies:

1 small plastic container for percent solids determination
Electronic field balance accurate to 0.01 grams
2 VOA vials (40 ml), pre-weighed and containing 5 mls of water and a magnetic stir bar
1 VOA vial (40 ml), pre-weighed and containing 10 mls of methanol
Coring device, such as a 10-ml plastic syringe with the tip removed or three 5-gram En Core®-type devices

Procedure For Using VOA Vials:

1. Select the area to be sampled as soon as possible after the soil is exposed.
2. Label the vials as appropriate. Do not add excessive labels (e.g. more weight) to the pre-weighed vials.
3. Using the coring device and field balance, determine approximately how much volume of soil to add that will yield 5 grams and 10 grams of soil. Note that the sample weight should be within 1 gram of the nominal weight, e.g. 5± 1 gram and 10± 1 gram.
4. Scrape away 1 to 2 inches of material from the area to be sampled.
5. Rapidly insert the syringe into the soil to obtain the first 5-gram sample. Quickly extrude the sample into one of the two vials containing the water. Wipe off the threads and cap, seal vial.
6. Repeat step 5 for the second vial containing water.
7. Rapidly insert the syringe into the soil to obtain a 10-gram sample. Quickly extrude the sample into the vial containing methanol. Wipe off the threads and cap, seal vial.
8. Add approximately 10 to 20 grams of the soil to the plastic bottle. Close and label.
9. Using the field balance, weigh and record the weight of each vial. A copy should be submitted with the samples to the laboratory.
10. Place all samples in cooler with ice. Proceed to next sampling point.

Procedure For Using En Core®-type Devices:

1. Select the area to be sampled as soon as possible after the soil is exposed.
2. Label the devices as appropriate.
3. Scrape away 1 to 2 inches of material from the area to be sampled.
4. Rapidly insert the first device into the soil to obtain the sample. Quickly wipe the contact areas to remove any soil particles, and close and seal the device.
5. Repeat step 4 with the remaining two devices.
6. Place devices in resealable pouch, place in cooler on ice. Proceed to next sampling point.

Other Recommended Sampling Procedures

Sodium Bisulfate Option

Note: This procedure is identical to the preferred sampling method, except sodium bisulfate preserved VOA vials are substituted for the VOA vials containing water.

Supplies:

1 small plastic container for percent solids determination
Electronic field balance accurate to 0.01 grams
2 VOA vials (40 ml), pre-weighed and containing 5 mls of sodium bisulfate solution and a magnetic stir bar.
1 VOA vial (40 ml), pre-weighed and containing 10 mls of methanol
Coring device such as a 10 ml plastic syringe with the tip removed

Procedure:

1. Select the area to be sampled as soon as possible after the soil is exposed.
2. Label the vials as appropriate. Do not add excessive labels (e.g. more weight) to the pre weighed vials.
3. Using the coring device and field balance, determine approximately how much volume of soil to add that will yield 5 grams and 10 grams of soil. Note that the sample weight should be within 1 gram of the nominal weight, e.g. 5± 1 gram and 10± 1 gram.
4. Scrape away 1 to 2 inches of material from the area to be sampled.
5. Rapidly insert the syringe into the soil to obtain the first 5-gram sample. Quickly extrude the sample into one of the two vials containing the sodium bisulfate solution. Wipe off the threads and cap, seal vial.
6. Repeat step 5 for the second vial containing the sodium bisulfate solution.
7. Rapidly insert the syringe into the soil to obtain a 10-gram sample. Quickly extrude the sample into the vial containing methanol. Wipe off the threads and cap, seal vial.
8. Add approximately 10 to 20 grams of the soil to the plastic bottle. Close and label.
9. Using the field balance, weigh and record the weight of each vial. A copy should be submitted with the samples to the laboratory.
10. Place all samples in cooler with ice. Proceed to next sampling point.

Collecting Samples in VOA Vials with No Additives

Supplies:

1 small plastic container for percent solids determination
Electronic field balance accurate to 0.01 grams
3 VOA vials (40 ml), pre-weighed and containing a magnetic stir bar.
Coring device such as a 10 ml plastic syringe with the tip removed

Procedure:

1. Select the area to be sampled as soon as possible after the soil is exposed.
2. Label the vials as appropriate. Do not add excessive labels (e.g. more weight) to the pre weighed vials.
3. Using the coring device and field balance, determine approximately how much volume of soil to add that will yield 5 grams and 10 grams of soil. Note that the sample weight should be within 1 gram of the nominal weight, e.g. 5± 1 gram and 10± 1 gram.
4. Scrape away 1 to 2 inches of material from the area to be sampled.
5. Rapidly insert the syringe into the soil to obtain the first 5-gram sample. Quickly extrude the sample into one of the two vials. Wipe off the threads and cap, seal vial.
6. Repeat step 5 for a second vial.
7. Rapidly insert the syringe into the soil to obtain a 10-gram sample. Quickly extrude the sample into the third vial. Wipe off the threads and cap, seal vial.
8. Add approximately 10 to 20 grams of the soil to the plastic bottle. Close and label.
9. Using the field balance, weigh and record the weight of each vial. A copy should be submitted with the samples to the laboratory.
10. Place all samples in cooler with ice. Proceed to next sampling point.

Upon receipt in the laboratory, the laboratory has three options: 1) samples can be frozen, as is, until analysis; 2) sample can be preserved with methanol by adding via syringe through the septum; or 3) samples can be analyzed within 48 hours of collection.

Water or bisulfate cannot be added prior to storage at 4º C, as this would involve either adding the liquid through the septum via syringe and storing with a pierced septum or removing the cap. Studies have shown that either of these options will lead to loss of analytes. If methanol is added, the septum should be replaced after the methanol has been in contact with the soil and the soil has been completely wetted by the methanol. Studies have shown that volatile analytes will be lost over time if samples, immersed in methanol, are stored in a vial with a pierced septum (6). However, the cap may be removed for short periods of time (e.g. <1 minute) allowing the septum to be replaced without fear of significant loss of analytes.

Collection of Soil Samples for TCLP or SPLP Volatile Organic Analysis

Soil samples intended for analysis for VOCs following extraction using either the Toxicity Characteristic Leaching Procedure (TCLP) or Synthetic Precipitation Leaching Procedure (SPLP) present some additional problems. Both methods call for leaching of the sample in a zero headspace extractor (ZHE). In this procedure, the sample is weighed into a ZHE, which is then immediately sealed. Any excess water is separated by pressure filtration, and stored at 4º C in a vessel with no headspace. The ZHE is then charged with the appropriate fluid. TCLP extraction uses a sodium acetate/acetic acid buffer at pH 4.93. The SPLP extraction for VOCs specifies the use of laboratory reagent water (e.g. deionized/distilled water). The ZHE device is then subjected to mixing using a rotating end-over-end apparatus. After rotating for 18 ± 2 hours, the extraction fluid is again removed by pressure filtration, and the resulting leachate is then mixed with any liquid removed in the initial filtration step. The leachate is then ready for analysis. Throughout the entire process, from sample collection to final filtration and storage, the sample and resulting leachate must be protected from loss of volatile analytes.

ZHEs are designed to hold 25 grams of sample. En Novative Technologies, the manufacturer of the En Core® sampler, also makes an En Core® sampler designed to hold 25 grams of soil. A device such as this must be used to collect soil samples for TCLP/SPLP extraction prior to analysis for VOCs. After collection, the sampling device must be appropriately sealed and frozen as soon as possible, but in any case within 48 hours of collection. Current EPA guidance states that there is a 14-day holding time for the preparation of the TCLP/SPLP leachate. Once the leachate is prepared, it can be preserved with 1:1 hydrochloric acid and held an additional 14 days prior to analysis, provided the sample is stored at 4º C with no headspace.

It is critical that the soil sample collected for TCLP/SPLP extraction with subsequent analysis for volatile organic compounds be subjected to a minimum of handling by the laboratory. If the laboratory is required to weigh out a sub-sample, there will be significant losses of volatile analytes (1). The use of a sample coring and storage device such as the En Core® sampler allows the laboratory to extrude the entire sample into the ZHE with a minimum of handling. The ZHE is immediately sealed, and there should be only minimal losses of analytes. Failure to take these precautions will lead to significant losses of volatile analytes and erroneous results.

Additional Recommendations:

1. The practice of collecting soil in containers without closures that provide a hermetic seal should be disallowed.

2. The practice of collecting soil samples in containers from which the laboratory has to parse out a sub-sample should be disallowed.

3. Trip blanks should be created using the same matrix (i.e. water, sodium bisulfate, methanol) as that used for the samples.

Comments

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