

Investigation and Remediation

A Layman's Guide to the New EPA Methods for VOC Analysis

by Blayne Hartman and Rob Hitzig

Since the promulgation of Update III of EPA's SW-846, *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods*, the document's new methods for volatile organic compound (VOC) analysis have created apparent confusion throughout much of the environmental community. In response to this confusion, EPA released a memo on August 7 to clarify some of the issues. In this article, we'll address some of the key issues of concern and conclude with recommendations to help you to decide which protocols to follow or enact.

To understand the pros and cons of the new VOC methods, let's review the most salient changes in the new update.

Changes in Analytical Methods

In Update III, several obsolete packed-column gas chromatographic (GC) methods have been deleted and replaced with capillary GC methods. Specifically, analytical methods 8010 (halogenated hydrocarbons by GC), 8020 (aromatic hydrocarbons by GC), and 8240 (VOCs by GC/Mass Spectrometry (MS)) have been deleted. They have been replaced by methods 8021 (halogenated and aromatic hydrocarbons by GC) and 8260 (VOCs by GC/MS). The elimination of these analytical methods does not create significant changes in the quality or type of data received from laboratories, because most laboratories have been using the capillary methods for several years.

There are, however, two significant factors that you should be aware of in the new analytical methods:

- Soil values are reported on a dry-weight basis.
- Calibrations must be performed for every 10 samples rather than for every 20 samples.

The first factor should not be overlooked by regulators, because, in

some states, soil values are customarily reported on a wet-weight basis. Depending on the water content of a sample, use of dry versus wet weight could change reported values by a factor of 2. As a result, we recommended that you ask your laboratory to state clearly in its reporting whether the results represent dry-weight or wet-weight values.

Changes in Sample Preparation Methods

Prior to Update III, there were essentially three methods for preparing solid samples for volatile analysis:

- Solvent extraction and direct injection (typically done as a microextraction of soils or concentrated wastes in a VOA vial with methanol) for high-concentration samples;
- Direct purge-and-trap preparation (EPA method 5030) for soils with low concentrations; and
- Methanol extraction, dilution into water, and purge-and-trap (also by EPA method 5030) for medium- to high-concentration samples.

The purge-and-trap preparation methods offered much lower detection levels than the direct-injection method and were more commonly used for VOC analysis that required low (<50 µg/kg) detection limits. For soils, samples were either mixed with water and added directly to the purge-and-trap device (direct soil sparging for low-concentration samples), or, for higher-concentration samples, they were extracted with methanol, and an aliquot of the methanol (typically 10 µL to 100 µL) was added to the purge-and-trap device.

Update III includes seven sample preparation procedures:

1. Solvent extraction and direct injection
2. Headspace analysis (method 5021)

3. Purge-and-trap preparation (EPA method 5030B) for soil extracts
4. Closed-system purge-and-trap for soils (method 5035)
5. Vacuum distillation
6. Azeotropic distillation
7. Hexadecane dilution-direct injection for VOCs in waste oil

It is important to realize that VOC results can vary, depending on the preparatory method used (e.g., high-concentration methods may not work for low-concentration samples, and vice versa). Because there are now seven different preparatory methods, it is much more important that the end users of the VOC data understand which method was used to prepare individual samples and which method applies to which type of sample and analyte.

An Overview of the Sample Preparation Methods

Let's briefly review these sampling methods. Because methods 5, 6, and 7 are not commonly used, we will not discuss them in this overview.

1. **Solvent extraction and direct injection.** This method is extremely reliable and allows the reanalysis of the extract as many times as possible. For fuel-related aromatic compounds (e.g., BTEX, naphthalene, trimethylbenzenes) and MTBE, detection levels of 25 µg/kg to 50 µg/kg can be obtained. This method is the best to use for higher-concentration samples (greater than 200 µg/kg), because there is little potential for carryover between samples.
2. **Headspace analysis by method 5021.** Prior to Update III, EPA considered this method to be useful for screening purposes only, primarily because of the limitations of available equipment. However, because it is a relatively easy and fast method, many laboratories, particularly mobile laboratories, have used it for many years. These days, reliable data are readily achievable with automated instruments, especially for compounds with relatively high Henry's law constants, pro-

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vided the headspace conditions are kept constant (e.g., amount of sample, time of heating, temperature of heating). This is particularly true for fuel-related sites—data for aromatic hydrocarbons generated by this method should be fine. However, this method is not suitable for MTBE or ethylene dibromide (EDB) because both have low Henry's law constants. It is necessary to collect more than one sample for reanalysis in the event that VOC concentrations exceed the instrument's calibration range.

3. **Purge-and-trap by method 5030B.** This method is the same one used in earlier versions of SW-846, except for one key difference: It no longer allows the soil itself to be added directly to the purge-and-trap device (direct-soil sparging). To analyze soils by this method, the soil must be methanol-extracted; an aliquot of the extract is then added to the purge-and-trap device. This approach allows for detection levels in the low microgram/kilogram range (<10 µg/kg) for most fuel-related hydrocarbons and slightly higher levels (25 µg/kg to 50 µg/kg) for some halogenated compounds.
4. **Closed system purge-and-trap by method 5035.** This method is designed to minimize the loss of VOCs from soil. Soil samples are sealed in a gas-tight vial in the field and then analyzed without ever opening the vial. This method has an advantage over methanol preservation in that it allows for extremely low detection limits (<1 µg/kg) for all VOCs (including halogenated solvents); however, VOC concentrations exceeding 100 µg/kg to 200 µg/kg exceed the instrument's working range, depending on the compound. Since VOC concentrations this low are difficult to estimate prior to analysis, and the sample can be analyzed only once, it is necessary to collect more than one sample for reanalysis in the event that concentrations are high.

Changes in Soil Sample Collection, Preservation, and Storage

The most significant change in the new update is the addition of protocols that describe field preservation and storage of soil samples for VOC analysis. The purpose of these protocols is to provide for minimal loss of volatiles from samples caused by both volatilization and biodegradation from the time of collection to the time of analysis. The most effective way to do this is to preserve or analyze samples shortly after they have been collected.

The sample preservation protocols have introduced considerable confusion, because they differ for each preparation method and, in some instances, are contradictory within the same method. For example, method 5021 (headspace) describes on-site sample preservation using phosphoric acid; however, the method also allows for off-site preservation in the laboratory—which, in effect, defeats the purpose of the new protocols.

As another example, method 5035 (closed-system purge-and-trap) offers four on-site handling options from which the field sampler can choose. One of these options calls for the use of bisulfate solution as a preservative, a second option involves on-site methanol extraction, a third option is to collect the sample in a headspace-free, gas-tight sampler (e.g., EnCore), and a fourth option allows for off-site sample preparation.

Which method 5035 option you choose depends on a multitude of factors, including the concentration of VOCs in the soil (which you don't know at the time of field collection), the type of soil (e.g., percent carbonate), the method the lab uses, and whether you are shipping the samples.

What do all these options do for field sampling personnel? They create confusion and add an extra burden to their already demanding list of tasks. The consequence: an increased potential for errors in VOC data because of the variations in how samples are handled in the field.

What to Do?

The introduction to the new EPA

methods, which was restated in the August 7 memo, clearly states that the SW-846 methods are meant to be guidance only, not requirements. EPA encourages local agencies to adopt sampling methods that they feel are most applicable to their specific problems and needs. EPA encourages agencies to provide for performance-based flexibility and modifications that will meet the specific requirements of a project. So what protocols should you follow to ensure the most representative data?

First, let's begin with the presumption that most of the confusing issues and potential problems will be circumvented if samples are analyzed on-site. Because on-site analysis allows samples to be analyzed within hours rather than days, acid and methanol preservation should not be necessary. Mobile laboratories that are capable of conducting SW-846-quality analyses are available in most locations throughout the country.

EPA's Office of Underground Storage Tanks (OUST) has encouraged the use of field analytical methods for many years because of the advantages gained by having on-site data to make real-time decisions. (For more information on the use of field analysis in conducting site assessments, check out *Expedited Site Assessment Tools For Underground Storage Tank Sites*—EPA 510-B-97-001.)

As an alternative to on-site analysis, on-site methanol and/or on-site water preservation offer the most advantages, depending on the VOCs you are measuring.

• Methanol/Water Preservation for Fuel-Related VOCs

For fuel-related VOCs, on-site methanol preservation is much easier, more flexible, and more cost-effective than the other preservation options described in methods 5035 or 5021. Detection limits of 5 µg/kg are obtainable for the aromatic compounds and 20 µg/kg for MTBE.

A number of states (most notably Wisconsin) have been using this technique successfully for a number of years. In fact, Wisconsin has specifically stated in the spring 1998 edition of its *LabNotes* that EPA method 5035 will not be used in Wisconsin.

There are a few potential pitfalls with methanol preservation. First, because the shelf life of methanol is short, there is the possibility that the methanol could be contaminated. So, you need to be sure that your batches of methanol are fresh and analyzed for blanks just before the date of use. Second, detection levels using methanol extracts could be higher, depending on a lab's protocols, so there is the possibility that you may not achieve necessary quantitation limits. Third, there are potential shipping restrictions. Methanol is classified as a RCRA hazardous waste, regardless of whether the soil is contaminated.

An alternative to methanol preservation that is less confusing than method 5035 is to allow soils to be preserved on-site in water and analyzed by method 5030. Because the aromatic hydrocarbons and MTBE have low Henry's law constants (i.e., they prefer to remain in the water), they will not be lost by volatilization once in the water solution. However, to minimize possible biodegradation, the water-preserved sample should be capped, kept cold, and analyzed within a relatively short period of time (e.g., within 36 hours from the time of collection). If a TPH analysis for gasoline is required, then the preservation container should have no headspace, because of the high Henry's law constants of the alkanes in gasoline.

The water preservation alternative offers a few advantages over methanol in that detection limits are lower, the risk of contamination is less (pure, uncontaminated water is readily available at any convenience store, usually for less than \$1 per bottle), and the samples can be shipped as nonhazardous waste.

- **For Halogenated Compounds**

In this case, the optimum preservation choice depends on the required detection limits. For some VOCs, methods 8021 or 8260 will reach only 25 to 50 µg/kg detection limits using methanol extracts. If these detection limits are sufficient, then methanol

preservation is an easy and cost-effective option.

If lower detection limits are required, water preservation and analysis by method 5030 can reach 5 µg/kg detection limits while offering a less confusing alternative to method 5035. Because the halogenated VOCs are not readily biodegradable and have low Henry's law constants, they will not be lost by biodegradation or volatilization once in the water solution. To ensure minimal contamination during storage, the water-preserved sample should be capped, kept cold, and analyzed within a reasonable amount of time (e.g., within 72 hours from the time of collection).

Advantages

Methanol and water preservation with subsequent analysis using method 5030 offer the following advantages over methods 5021 and 5035:

- Potentially large errors resulting from the variety and multitude of field preservation steps are eliminated because the field personnel can use one or two simple on-site procedures that are not too burdensome.
- Laboratories can use existing methods (e.g., purge-and-trap by 5030) with existing equipment. Thus, they will not be forced to buy a lot of new equipment, and reported VOC data will be more consistent from lab to lab, because fewer analytical methods will be used.
- Increased costs of analysis (e.g., new analytical equipment, special gas-tight samplers, shipping of hazardous wastes) are eliminated.

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