

A Brief Discourse on the Implications of 5035A

The Washington State Department of Ecology has specified the use of method 5035A for soil samples to be analyzed for volatile organic compounds. This is a change from the previous method, 5030, and like every method change is open to some interpretation by the analytical laboratory doing the analysis. CCI Analytical would like to take this opportunity to present our feelings on the various possible sampling and preservation methods represented by this change. Hopefully this discourse will serve to help our clients decide on the sampling protocol that best fits their unique needs.

A more technical discussion on the work done by Alan D. Hewitt¹ should be forthcoming as his work is one of the primary sources for the changes to 5035 that resulted in 5035A. This is not to discount the work done by the countless other individuals who contributed to 5035A and the expansion of the field of analytical environmental chemistry, but Hewitt's work was used repeatedly as a source for CCI's interpretation of the nuances of 5035A. Additionally, an article by Sorini, Schabron, and Rovani² was referenced as well.

In the most basic terms, preservation changes for VOC solid matrix samples can be broken down into three different preservation methods. First, there is the extraction preservation method whereby the solid matrix is extracted by a suitable solvent (methanol) and an aliquot of the extract is then run much like a water sample. Secondly there is the chemical preservation method where the sample is immersed in a sodium bisulfate solution to acid-preserve the target compounds by eliminating any biological activity in the sample matrix. Finally, there is the temperature preservation method where the sample is frozen to preserve the integrity of the target compounds. In each of these approaches 5035A specifies that preservation or analysis of unpreserved samples must be done within 48 hours of sampling.

Chemical preservation will be addressed first. A sample vial is prepared by pre-weighing a 40mL VOA vial containing approximately 10mL of sodium bisulfate solution. A 10 gram sample core is then added to the vial in the field and the sample is analyzed within 14 days of sampling. This method presents several problems. Sample weight may be invalidated if preservation solution is lost in the field. If the sample matrix contains carbonate materials the sample may effervesce and cause loss of target analytes, requiring the use of a different preservation method. Additionally, certain reactive compounds (vinyl chloride or 2-chloroethyl vinyl ether, for example) may break down in a low pH solution. As this preservation method requires the same level of pre-prep and sampling issues as a methanol extraction method preservation sample and cannot be used for all sample matrixes and for all target analytes CCI has determined that it will be used only if specifically requested by the client.

¹ A list of his work and contact information can be found at:
<http://www.crrel.usace.army.mil/es/personnel/pubs/hewitt.html>

² Evaluation of VOC Loss from Soil Samples: Extrusion into Empty VOA Vials, Refrigerated Storage, and Methanol Injection in Preparation for Volatile Organic Analysis

Extraction preservation is an excellent method for maintaining the integrity of VOC's in solid matrixes. A sample vial is prepared by pre-weighing a vial prepped with 10mL of methanol. A 10 gram sample core is then added to the vial in the field and the sample is analyzed within 14 days of sampling. Data collected by Sorini, Schabron, and Rovani shows excellent recovery of VOC's, from a low of 66% for vinyl chloride to 87% for ethyl benzene. Unfortunately analysis using this preservation method is compromised by the raised reporting limits necessitated by the use of an extraction solvent (limits are 100 times higher for most compounds analyzed by this method). Therefore CCI recommends the use of methanol preservation for all VOC samples, but also recommends that additional samples be prepared for direct sparge, low level analysis. Unless requested by the client methanol preserved samples will be analyzed only if an initial low level analysis detects high levels of target analytes.

While low temperatures are used along with the previous methods to preserve samples (each of the previous methods requires that the sample be kept below 4C until analysis), a distinction is made when the sample is kept frozen at -7C. A sample vial is prepared by pre-weighing a vial prepped with a stir bar. A 10 gram sample core is then added to the vial in the field, the sample is frozen within 48 hours of sampling, and the sample is analyzed within 14 days of sampling. By this method the vial is opened to add the sample and then not opened again until after the sample has been analyzed (during the disposal process). This ensures that analytes outgassed into the headspace are not lost. In the field the samplers should find it easier to handle a dry vial with a stir bar than a vial filled with pre-weighed preservative. It is recommended that clients concerned with BTEX compounds on a site with biologically active soils notify the samplers so that the samples may be frozen as quickly as possible. Unfortunately analysis using this preservation method can only be done once on a single vial, and in the event of high levels of target analytes the sample cannot be used to give reliable data. Unless the client has excellent historical data suggesting the presence of only low levels (please contact CCI for exact numbers) of target analytes a methanol preserved sample should be collected at the same time as the freezer-preserved sample.

In conclusion, CCI Analytical feels that the following sampling system is best suited for the analysis of VOC's in a solid matrix:

- Two ~10g samples will be collected in 40mL VOA vials and frozen for low level analysis.
- One ~10g sample will be collected in a 40mL VOA vial and methanol extracted for high level analysis.
- One wide-mouth four ounce jar will be collected for determining percent solids.

If you have any questions or comments please feel free to contact CCI Analytical.

Inconvenient

