

Investigation and Remediation

To Methanol Preserve or Not to Methanol Preserve? (That Is the Question)

by Blayne Hartman

Over the past few years, several states (e.g., Wisconsin, Massachusetts, Maine, New Mexico) have adopted regulations or policies requiring that soil samples slated for volatile organic compound (VOC) analysis be preserved in methanol immediately upon collection. Other states are considering similar measures. Why is this?

We have known since the early 1990s that volatile compounds can be lost quite readily from soil samples, even when the soils are kept chilled. A number of articles written by independent researchers have demonstrated that VOC losses from soils can reach 50 percent within 2 hours of collection and can exceed 90 percent within 24 hours. However, when preserved in an organic solvent, such losses were prevented. Fearing that regulatory decisions were being made based on data that woefully misrepresented true concentrations, the Wisconsin Department of Natural Resources adopted a methanol preservation requirement in 1994. Other state agencies began to follow Wisconsin's lead. But, alas, questions linger.

Preservation Protocol

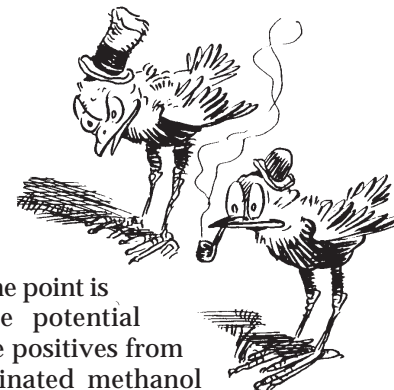
At first glance, the preservation protocol appears simple enough: Upon collecting an aliquot of the soil sample (typically 5 to 10 grams), immediately immerse it in vials containing methanol (typically 5 to 10 mL). Seal the vials and transfer them to the laboratory for subsequent analysis. Collectors may use vials containing premeasured amounts of methanol obtained from the laboratory prior to the sampling effort, or alternatively, they may purchase the methanol directly and add it to the vials themselves. The result? Immediately preserved soil samples that bear values more indicative of the true soil concentrations.

So What's the Worry?

Methanol has an extremely high affinity for many organic compounds. In fact, laboratories sometimes receive freshly purchased methanol with contaminant levels exceeding method detection limits. Once opened, a bottle (or vial) of methanol will adsorb organic compounds rapidly; the "shelf life" is very short if any organic compounds are immediately present. Because prices for laboratory-grade methanol can exceed \$30 per liter, it is difficult to "toss away" a partially used bottle of methanol once opened.

So now let's travel to the job site. Our on-site environmental geologist is busy directing and supervising the sampling subcontractor (e.g., driller, excavator), logging samples, screening samples with a hand-held PID, washing sampling sleeves, and communicating with the front office. Where does this flurry of activity normally take place? Typically on a tail gate of a pick-up truck (or some equivalent workbench), in close proximity to the sampling truck.

Now let's add methanol preservation to the other tasks. If everything is going fine, the methanol preservation step should be relatively painless. However, what happens when things don't go so fine? The driller has problems. The wind shifts and the "work area" is now downwind of the diesel exhaust. The job's running late and everyone is in a hurry. It starts to rain. The office calls. Now what happens to the vials or bottle of methanol? Was it left uncapped for a while? Do we use it the next day if the job shuts down for some reason? Two days later? Three days? How does one know if the methanol is still okay? What happens if the methanol-preserved samples are put in the same cooler as the highly contaminated soils themselves? Will the samples cross-contaminate the methanol extracts?



The point is that the potential for false positives from contaminated methanol increases with methanol preservation. If it occurs, the false positives will most likely not be discovered until after the job is demobilized. In this situation, who pays for the job to be redone? The tank fund? The consultant? The lab? Or does the job not get redone and the data "corrected" before submission?

Are There Alternatives?

Yes. The best alternative is on-site analysis. On-site analysis mitigates the volatile loss problem and also mitigates the potential for false positives because the real-time analysis will reveal the existence of the contaminated methanol before it is too late to correct the problem. Costs for on-site analysis have dropped over the past few years, and many reimbursement funds now allow it.

If the budget or logistics do not allow for the use of methanol, you have the alternative of using water as the preservation liquid. While this may initially sound strange, it turns out that MTBE, most aromatic compounds (BTEX), and many chlorinated compounds prefer to be in water over air by ratios exceeding 4 to 1. Thus, in a vial filled with 5 grams of soil, 5 mL of water, and 5 cc of air, 80 percent of the analyte will partition into the water. If the water to air ratio in the vial is 2 to 1 (say, 10 mL to 5 cc), about 90 percent of the analyte will partition in the water.

Why water over methanol? Because inexpensive, uncontaminated water is readily obtainable at every convenience store and its shelf life is much longer than that of methanol. If the job gets delayed for a day or two or three, a fresh, unopened bottle of drinking water can be purchased for \$1.

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Thus...

If you choose to use methanol VOC preservation, be sure to take appropriate steps (e.g., additional trip blanks) to ensure that the methanol doesn't become contaminated. While methanol preservation certainly is a proven way to maximize VOC concentrations from soil, the realities of life in the field introduce potential complications that may favor other alternatives. On-site analysis is by far the best alternative. Water preservation, although not as quantitatively accurate as methanol, does provide certain advantages depending on the compounds of interest. If water preservation is performed, the preserved samples should be kept chilled (4°C) and, preferably, poisoned with a bactericide to eliminate biodegradation prior to analysis. ■

