APPLICATION NOTE

Gas Chromatography/
Mass Spectrometry

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Volatile Organic Compound Screening in Soil Using SPME-GC/MS

Introduction

The ability to screen soil samples in the field by identifying volatile organic compounds (VOCs) is a valuable tool where sampling decisions are required in near real-time. Results of the screening procedure may be used to guide sample collection activities, and can help identify which sampling and/or extraction methods are most effective.

U.S. Environmental Protection Agency (EPA) Screening Method 3815 provides limited VOC concentration information by only reporting an estimate of the total VOC concentration in a sample. This method uses a photoionization detector (PID) without any separation technique, thus individual VOCs and their relative concentrations are not identified and reported.[1] Sampling using the Custodion® SPME syringe, with separation and analysis using the Torion® T-9 portable GC/MS, was used to positively identify 37 VOCs and their relative concentrations in the field in under three minutes.

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Volatile organic compounds (VOCs) were extracted and concentrated from soil using water, a salting-out technique, and a Custodion solid phase microextraction (SPME) syringe. The Torion T-9 portable Gas Chromatograph/Mass Spectrometer (GC/MS) was used to separate and identify 37 VOCs in less than three minutes. The SPME GC/MS technique is fast, reliable, and eliminates the need for special laboratory equipment or solvents for VOC screening from complex matrices in the field.

Experimental

The Custodion SPME syringe consists of a 1 cm SPME fiber coated with 50-100 µm of liquid polymer film, solid sorbent or a combination. The SPME polymer phase traps target analytes from air, headspace, liquids, or dissolved solid samples.[2] The SPME fiber is housed inside the Custodion syringe in a manner similar to a retractable ballpoint pen. A push-button trigger on top allows the SPME fiber to be extended and retracted into and out of a protective sheath using a single hand. In this application, a Custodion SPME syringe with a 65 µm Polydimethylsiloxane/Divinylbenzene (PDMS/DVB) phase was used to extract volatile compounds from a soil sample.

Only water was required as the extraction solvent, which eliminates organic solvent interferences during GC analysis and reduces overall sampling and analysis costs.

Method Parameters

The GC/MS method parameters are shown in Table 1.

Solvents, Standards and Samples

Table 1. GC/MS Method Parameters.

Sampling:	Solid phase microextraction (SPME)
SPME Phase:	Divinylbenzene/Polydimethylsiloxane (DVB/PDMS, 65 µm)
GC Inj. Temp:	250 °C
GC Column:	MXT-5, 5 m x 0.1 mm, 0.4 µm d_f
GC Carrier Gas:	Helium, 0.2ml/min., constant pressure
GC Column Temp:	40-280 °C at 2 °C/s
Transfer Line:	250 °C
Injector Split Ratio:	20:1
Mass Analyzer:	Toroidal ion trap (TMS)
TMS Mass Range:	41-500 Da
Ionization Mode:	In-trap electron impact
Detector:	Electron multiplier
Vacuum:	Roughing and turbo molecular pumps
Resolution:	Less than unit mass to 230 amu, nominal unit mass to 500 amu

A standard reference soil sample prepared by the supplier with a VOC mixture of 42, compounds at concentrations ranging from ~15,000 µg/kg (15 ppm, w/w) to ~2400 µg/kg (2.4 ppm, w/w), was obtained and analyzed (NSI Solutions, Raliegh, NC). 5 mL of water with 25% NaCl (w/v) was added to five grams of the spiked soil sample. The sample vial was shaken vigorously by hand for 10 seconds after which the Custodion SPME fiber was exposed to the sample head-space for 50 seconds. The shaking/exposure technique was repeated five times for a total sampling time of ~five minutes. Following extraction, the Custodion SPME syringe was inserted into the Torion T-9 GC/MS injection port (250 °C) where the VOCs were desorbed and transferred to a low thermal mass capillary GC column (MXT-5, 5 m x 0.1 mm, 0.4 µm d_f). Ultra-high purity helium was used as the GC carrier gas under constant flow conditions. The GC temperature program conditions were 40 ° to 280 °C at 2 °C/s, for total run times under 2.5 minutes. The GC is directly interfaced to the MS detector, which has a mass range of 41-500 Da and an average scan rate of ~10 Hz. A user-defined deconvolution target compound library positively identified the VOCs.

Results and Discussion

Figure 1 shows the GC/MS separation of VOCs extracted from a spiked soil sample. 37 of the 42 VOCs were identified in less than two minutes. In some cases, analytes co-eluted (e.g., 1,3-Dichloro-1-propene (E), Toluene, and 1,1,2-Trichloroethane compounds 15-17) but were positively identified by the target compound library using the automated on-board deconvolution algorithm. The five analytes not detected included 2-Hexanone, Acetone, Bromomethane, Chloroethane, and Chloromethane. These compounds are all very volatile and may have either been lost from the sample during extraction, lost prior to analysis through handling , or these particular compounds may have suffered selective discrimination during the SPME sampling process.

1. Trichlorofluoromethane
2. 1,1-Dichloroethylene
3. Dichloromethane
4. MTBE
5. 1,2-Dichloroethylene (Z)
6. Chloroform
7. 1,1-Trichloroethane
8. 1,2-Dichloroethane
9. Carbon Tetrachloride
10. Benzene
11. 2-Butanone
12. Trichloroethylene
13. Bromodichloromethane
14. 1,3-Dichloro-1-propene (Z)
15. 1,3-Dichloro-1-propene (E)
16. Toluene
17. 1,1,2-Trichloroethane
18. 4-Methyl-2-pentanone
19. Tetrachloroethylene
20. Chlorobenzene
21. 1,1,1,2-Tetrachloroethane
22. Ethylbenzene
23. Xylene
24. Bromoform
25. Styrene
26. 1,1,2,2-Tetrachloroethane
27. Isopropylbenzene
28. Bromobenzene
29. 1,2,3-Trichloropropane
30. 1,3,5-Trimethylbenzene
31. 1,2,4-Trimethylbenzene
32. 1,3-Dichlorobenzene
33. 1,4-Dichlorobenzene
34. 1,2-Dichlorobenzene
35. 1,2-Dibromo-3-chloropropane
36. 1,2,4-Trichlorobenzene
37. Naphthalene

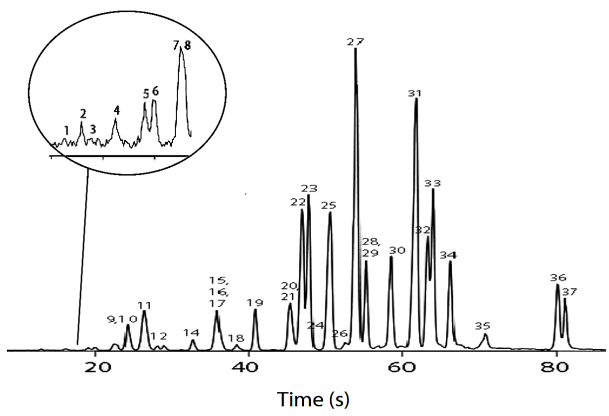

Figure 1. Chromatogram of 37 volatiles extracted from soil.

Conclusion

The Custodion SPME and Torion T-9 GC/MS are uniquely suited for near real-time field analysis screening of VOCs and other organic compounds to support rapid decision making in the field. If additional sample analyses are required, results can be obtained in minutes. This SPME-GC/MS sample screening method allows the user to determine the presence of individual VOCs and their relative concentrations. Following initial screening, highly concentrated samples can be diluted before causing cross-over contamination during analysis on laboratory-based instruments. This reduces sample re-analysis costs and instrument down time from carryover and contamination that may occur following analysis of highly concentrated samples on GC-MS systems.

References

1. EPA SW-846 Method 3815 Screening Solid Samples for Volatile Organics, Revision 0, February 2007, http://www.epa.gov/epawaste/hazard/test methods/sw846/pdfs/3815.pdf.
2. Zhang, Zhouyao; Pawliszyn, Janusz. Analysis for organic compounds in environmental samples by headspace solid phase microextraction. Journal of High Resolution Chromatography (1993), 16(12), 689-92.

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