

Volatile Organic Compound Identification in Water using SPME-GC-TMS

Volatile organic compounds (VOCs) were rapidly sampled and concentrated from water in 5 seconds using a CUSTODION™ solid phase microextraction (SPME) syringe. Compounds were analyzed on-site using the TRIDION™-9 portable gas chromatograph-toroidal ion trap mass spectrometer (GC-TMS). The SPME-GC-TMS technique can be used to effectively extract, concentrate, separate and identify complex mixtures of VOCs quickly and reliably in under 3 minutes.

Introduction

Groundwater and drinking water are routinely tested for VOCs of environmental concern. On-site prescreening analysis is rapid and reliable using a CUSTODION SPME syringe and the TRIDION-9 portable GC-TMS. SPME extraction¹ at the sample source allows for analysis of volatile target analytes which may be lost during sample storage and transport for off-site analysis. Compounds such as Benzene, Toluene and Ethylbenzene are susceptible to biological degradation under environmental conditions where refrigeration alone may not be adequate to preserve these compounds in wastewaters for more than seven days². The ability to perform on-site, near real-time chemical analysis is important for accurate and positive detection of analytes subject to degradation. SPME sampling with GC-TMS analysis is a useful method for screening samples prior to analysis on laboratory-based GC-MS instruments. Pre-screened samples known to contain environmental contaminants at high concentrations can be diluted to prevent sample to sample carryover and contamination of laboratory GC-MS instruments. This can minimize re-analysis of samples and reduce down time due to GC-MS system overloading and/or contamination.

Sampling Equipment

The CUSTODION-12 SPME sampling syringe consists of a 1cm fiber coated with a liquid polymer film, solid sorbent or a combination. The SPME fiber is housed in a durable syringe that can be operated with a single hand.

Much like a retractable ball point pen, the push button trigger on top of the CUSTODION syringe allows the SPME fiber to be extended and retracted into and out of a protective metal sheath. The SPME fiber can be used to trap target analytes from air, headspace, liquids or dissolved solid sample matrices.

For this application, a 65 μm coating of Divinylbenzene/Polydimethylsiloxane (DVB/PDMS) SPME phase was used to extract VOCs from a drinking water sample spiked with 25 environmental contaminants listed in U.S. EPA Method 624.

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|--------------------------------|--------------------------------|
| 1. 1,1-Dichloroethylene | 14. 1,3-Dichloro-1-propene (E) |
| 2. Dichloromethane | 15. Toluene |
| 3. 1,2-Dichloroethylene (E) | 16. 1,1,2-Trichloroethane |
| 4. 1,1-Dichloroethane | 17. Dibromochloromethane |
| 5. Chloroform | 18. Tetrachloroethylene |
| 6. 1,1,1-Trichloroethane | 19. Chlorobenzene |
| 7. 1,2-Dichloroethane | 20. Ethylbenzene |
| 8. Carbon Tetrachloride | 21. Bromoform |
| 9. Benzene | 22. 1,1,2,2-Tetrachloroethane |
| 10. Trichloroethylene | 23. 1,3-Dichlorobenzene |
| 11. 1,2-Dichloropropane | 24. 1,4-Dichlorobenzene |
| 12. Bromodichloromethane | 25. 1,2-Dichlorobenzene |
| 13. 1,3-Dichloro-1-propene (Z) | |

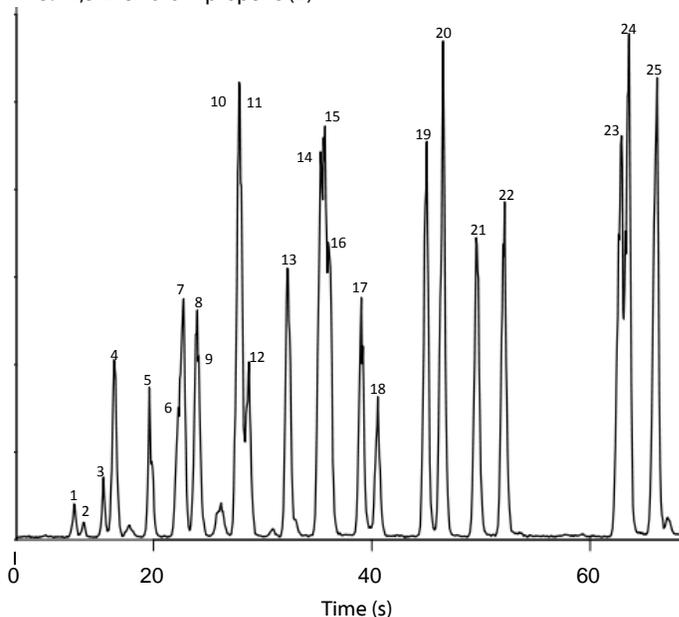


Figure 1. Chromatogram of 25 volatiles extracted from a water sample.

Sample Preparation and Analysis

A culinary water sample was spiked with a mixture of 25 target VOCs in methanol (Restek, Bellefonte, PA) with each compound at a concentration of ~0.04 µg/µL in the final sample solution. The CUSTODION SPME fiber was immersed in the water sample for 5 sec, which was adequate for VOC adsorption onto the SPME fiber.

Immediately following sample collection, the CUSTODION SPME fiber was introduced into the heated injection port (270°C) of the hand-portable TRIDION-9 GC-TMS system where the VOCs desorbed quickly from the SPME fiber into the GC inlet. The low thermal mass GC was temperature programmed at 2°C/s from 40° to 270°C to provide rapid separation of the VOC analytes. The TMS has a mass range from 45 to 500 Da, which is suitable for detection of most compounds of environmental concern. A VOC target compound library based on retention time and key mass ions was pre-loaded into the GC-TMS target compound library and used to positively identify all 25 volatiles in the sample. Identification of VOCs on the TRIDION-9 was accomplished using an on-board automatic deconvolution algorithm (Ion Signature Technology, North Smithfield, RI) together with the mentioned VOC target compound library. The sample analysis and identification method is rapid, requiring <3 min for sample analysis and compound identification.

Experimental Conditions

Sampling:	Solid phase microextraction (SPME)
SPME Phase:	Divinylbenzene/Polydimethylsiloxane (DVB/PDMS, 65 µm)
GC Inj. Temp:	270°C
GC Column:	MXT-5, 5 m x 0.1 mm, 0.4 µm dr
GC Carrier Gas:	Helium, 0.2ml/min, constant pressure
GC Column Temp:	40-270°C, 2°C/s
Transfer Line:	270°C
Injection Split Ratio:	20:1
Mass Analyzer:	Toroidal ion trap (TMS)
TMS Mass Range:	45-500 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

Results and Discussion

Figure 1 shows the GC-TMS separation of 25 VOCs spiked into a drinking water matrix. Using a rapid GC temperature gradient, the separation was achieved in ~70 s, with a total cycle time, including automated library identification of the VOCs, of less than 3.5 minutes. Using an embedded deconvolution algorithm, the co-eluting compounds Trichloroethylene and 1,2-Dichloropropane (Figure 1, compounds 10 and 11) were positively identified.

On-site pre-screening of VOCs in environmental samples can be reliably achieved using SPME-GC-TMS. This methodology is uniquely suited for near real-time field analysis screening of VOCs and other organic compounds in air, headspace, water, or dissolved solids to support rapid decision making and appropriate sample selecting in the field. If additional samples are required, SPME-GC-TMS results can be achieved in less than 5 minutes.

References

1. 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.
2. 40 CFR Chapter 1(7-1-07 edition), Appendix A to Part 136, *Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater*, Method 624-Purgeables.

Acknowledgements

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