Application Note 11

Solid Phase Microextraction of Volatile Compounds

Solid phase microextraction eliminates most of the drawbacks to purge and trap sample preparation techniques. The volatile compounds listed in US EPA Method 524.2 (a drinking water analysis) were analyzed by using SPME-capillary GC-MS.

Key Words:
- volatile organic compounds
- solid phase microextraction
- water analysis

In analyses of organic compounds in water samples, purge and trap or headspace methods for concentrating volatiles, and liquid-liquid or solid phase extraction methods for semivolatiles/nonvolatiles have various drawbacks, including cost and excessive preparation time. Solid phase microextraction (SPME)* requires no solvents or complicated apparatus, can be used to concentrate volatile or nonvolatile compounds in either liquid or gaseous samples, provides linear results over a wide range of analyte concentrations (down to parts per trillion for some compounds), and can be used with any gas chromatograph or gas chromatograph-mass spectrometer system (1-4). The technique has the potential for meeting detection limits specified by US Environmental Protection Agency methods and the Ontario Municipal/Industrial Strategy for Abatement program.

We analyzed the volatile compounds listed in US EPA Method 524.2 (a drinking water analysis), using SPME to introduce the analytes onto the column. The analytes in Figure A were extracted from the sample by immersing a 100µm polydimethylsiloxane (PDMS) SPME fiber in the sample for 5 minutes. Without cryogenic focusing, even the early eluting VOCs were resolved and exhibited fairly sharp peaks (inset, Figure A). When we cooled the column to 10°C, peaks for these early eluting components were sharpened, affording lower detection limits.

To investigate potentials for improving volatiles collection, we compared the advantages of sampling the headspace to immersing the fiber in the water sample, using selected volatile compounds (Table 1). High positive numbers for the % difference for the means indicate a favorable extraction in the headspace; high negative numbers indicate better recovery by direct immersion. Differences might be attributed to differences in analyte density or solubility in water.

SPME shows potential for screening samples prior to GC-MS analysis, particularly for EPA Method 624 (wastewater) analytes. A sample could be extracted in 1-3 minutes and injected onto a short column with the effluent split to two detectors (e.g., FID and ECD). Samples containing high concentrations of contaminants (100-2000ppb) could be identified and properly diluted for GC-MS. This could reduce downtime required to clean the MS source and eliminate the need to re-analyze samples, allowing more samples to be analyzed per day.

As with purge and trap techniques, detection limits for SPME differ from compound to compound. In SPME, detection limits depend on the distribution constants and polarity of the analytes. With a 100µm PDMS fiber, nonpolar compounds with high distribution

Table 1. Relative Responses for Volatile Compounds Extracted by SPME

Compound	Headspace Sampling Mean	Std. Dev.	%RSD	Immersion Sampling Mean	Std. Dev.	%RSD	% Diff. for Means
1,1-Dichloroethene	0.18	0.01	6.7	0.18	0.01	7.3	0
2,2-Dichloropropane	0.29	0.02	6.3	0.54	0.06	10.4	-82 ❐
Chloroform	0.19	0.01	5.7	0.18	0.03	16.3	4
Bromodichloromethane	0.06	0.01	11.2	0.04	0.00	8.8	21 ■
1,1,1-Trichloroethane	0.40	0.03	8.6	0.72	0.06	7.8	-80 ❐
Carbon tetrachloride	0.42	0.05	12.0	0.89	0.15	17.2	-112 ❐
Benzene	0.81	0.02	2.8	0.83	0.01	1.4	-2
Fluorobenzene	1.00	0.00	0.0	1.00	0.00	0.0	0
Toluene	2.35	0.08	3.3	2.38	0.20	8.6	-1
Tetrachloroethene	1.15	0.08	6.9	1.16	0.17	14.3	-1
Ethylbenzene	6.49	0.25	3.8	5.27	0.50	9.5	19 ■
Styrene	3.43	0.18	5.2	2.47	0.18	7.4	28 ■
Bromoform	0.20	0.02	8.8	0.12	0.01	9.1	40 ■
Bromobenzene	1.47	0.11	7.6	0.99	0.01	0.6	33 ■
1,2,4-Trimethylbenzene	14.98	0.87	5.8	6.69	0.15	2.3	55 ■
n-Butylbenzene	32.58	2.60	8.0	11.30	1.56	13.8	65 ■
1,2,4-Trichlorobenzene	11.64	0.69	6.0	3.28	0.29	8.9	72 ■
Naphthalene	15.75	0.95	6.1	8.16	0.38	4.6	48 ■

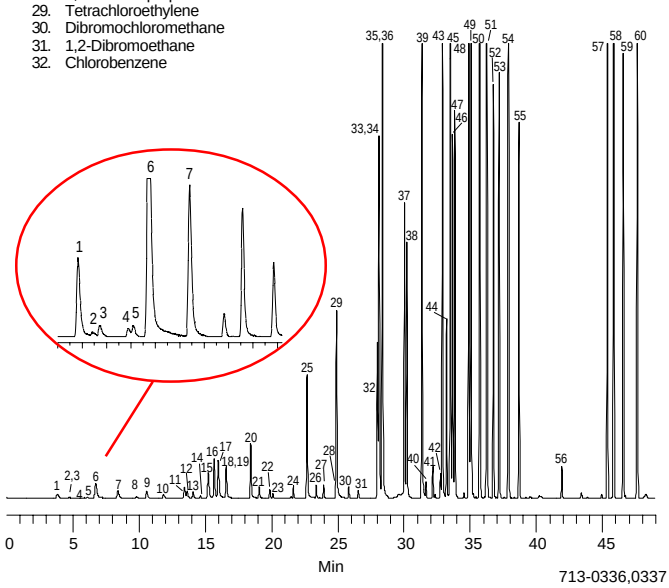
Data for 3 SPME fibers, two samplings per fiber.

❐ Immersion sampling preferred. ■ Headspace sampling preferred.

Figure A. US EPA Method 524.2 Volatile Analytes

Sample:	50ppb each analyte in 20mL water
SPME Fiber:	**polydimethylsiloxane, 100µm film**
Cat. No.:	**57300-U**
Sampling:	5 min
Desorption:	6 min, 220°C, split/splitless (splitter vent closed 6 min, then vented at 100mL/min)
Column:	**VOCOL, 60m x 0.25mm ID, 1.5µm film**
Cat. No.:	**24154**
Col. Temp.:	35°C (4 min) to 200°C at 4°C/min
Carrier:	helium, 2mL/min
Det.:	MS (m/z = 35-260 at 0.6 sec/scan)

1. Dichlorodifluoromethane
2. Chloromethane
3. Vinyl chloride
4. Bromomethane
5. Chloroethane
6. Trichlorofluoromethane
7. 1,1-Dichloroethylene
8. Methylene chloride
9. trans-1,2-Dichloroethylene
10. 1,1,-Dichloroethane
11. 2,2-Dichloropropane
12. cis-1,2-Dichloroethylene
13. Chloroform
14. Bromochloromethane
15. 1,1,1-Trichloroethane
16. 1,1-Dichloropropene
17. Carbon tetrachloride
18. 1,2-Dichloroethane
19. Benzene
20. Trichloroethylene
21. 1,2-Dichloropropane
22. Bromodichloromethane
23. Dibromomethane
24. cis-1,3-Dichloropropene
25. Toluene
26. trans-1,3-Dichloropropene
27. 1,1,2-Trichloroethane
28. 1,3-Dichloropropane
29. Tetrachloroethylene
30. Dibromochloromethane
31. 1,2-Dibromoethane
32. Chlorobenzene
33. 1,1,1,2-Tetrachloroethane
34. Ethylbenzene
35. m-Xylene
36. p-Xylene
37. o-Xylene
38. Styrene
39. Isopropylbenzene
40. Bromoform
41. 1,1,2,2-Tetrachloroethane
42. 1,2,3-Trichloropropane
43. n-Propylbenzene
44. Bromobenzene
45. 1,3,5-Trimethylbenzene
46. 2-Chlorotoluene
47. 4-Chlorotoluene
48. tert-Butylbenzene
49. 1,2,4-Trimethylbenzene
50. sec-Butylbenzene
51. p-Isopropyltoluene
52. 1,3-Dichlorobenzene
53. 1,4-Dichlorobenzene
54. n-Butylbenzene
55. 1,2-Dichlorobenzene
56. 1,2-Dibromo-3-chloropropane
57. 1,2,4-Trichlorobenzene
58. Hexachlorobutadiene
59. Naphthalene
60. 1,2,3-Trichlorobenzene



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constants have lower minimum detection limits than more polar analytes with lower distribution constants. Branched aromatic compounds and chlorinated alkenes exhibit the lowest detection limits. The more polar Method 524.2 compounds with extremely low distribution constants (bromomethane and chloromethane) have much higher minimum detection limits. The extremely volatile compounds can begin to leave the fiber before the sample is injected. Therefore, when analyzing volatile compounds, it is best to minimize the time between extraction and desorption and to maintain consistent timing for each step.

Several factors affect the precision of the method: positioning of the fiber in the injector (it must be in the hottest part during desorption), a consistently low cryofocusing temperature, and the time lapse between analyte extraction and desorption (short lapses minimize evaporation of volatile analytes from the fiber). Precision can be increased by dividing a sample into multiple small aliquots and extracting each aliquot. A 2mL vial containing analytes with high distribution constants can be depleted after one extraction, and can be exhaustively extracted if required (1).

To begin SPME extractions, you will need both an SPME fiber assembly and a fiber holder. The fiber assembly is reusable – we recommend replacing it after 50-100 extractions. SPME can be automated in a Varian 8100 or 8200 AutoSampler, with an SPME upgrade kit to control plunger movement and timing.

Ordering Information:

Description	Cat. No.
SPME Fiber Assembly	
100µm polydimethylsiloxane coating, pk. of 3	
For manual sampling	**57300-U**
For Varian 8100/8200 AutoSampler	**57301**
Fiber Assortment Kit	
100µm and 7µm PDMS, 85µm polyacrylate	
For manual sampling	**57306**
For Varian 8100/8200 AutoSampler	**57307**
SPME Fiber Holder	
For manual sampling	**57330-U**
For Varian 8100/8200 AutoSampler	**57331**
VOCOL™ Fused Silica Capillary Column	
60m x 0.25mm ID, 1.5µm film	**24154**

*Solid phase microextraction technology is licensed exclusively to Supelco (US patent no. 5,691,206; European patent #0523092).

Fiber assemblies with other phase coatings are available. Refer to the current Supelco catalog.

References

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