Application Note 56

Fast Analysis of Volatile Organic Compounds by Solid Phase Microextraction/Capillary GC

Solid phase microextraction is a fast, solventless alternative to conventional sample extraction techniques. Because no solvent is injected, and the analytes are rapidly desorbed onto the GC column, short, narrow bore capillary columns can be used. This greatly reduces analysis time and improves minimum detection limits, while maintaining resolution. SPME can be effective in analyses of volatile organic compounds, for sample screening or as an alternative extraction method in a formal analysis.

Key Words:
- volatile organic compounds • solid phase microextraction
- wastewater

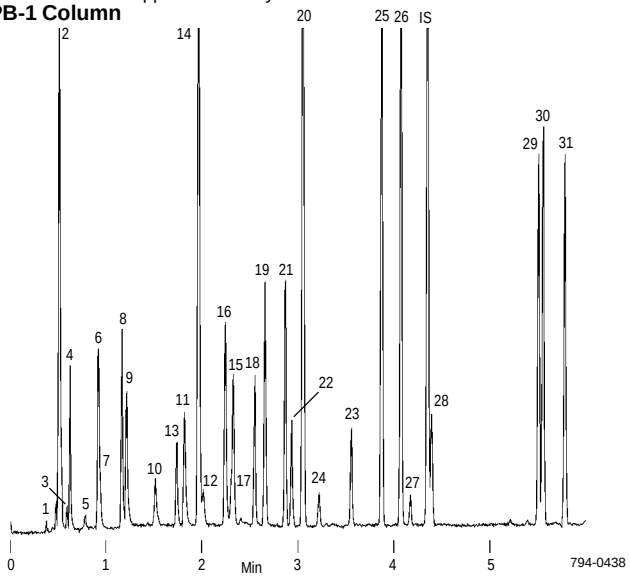
In analyses of volatile organic compounds (VOCs) in water, a purge and trap system typically is used to concentrate the analytes. This methodology has important limitations. To efficiently remove the analytes from the trap, carrier gas flow rates greater than 5mL/minute are required. Long (60-105m), large bore (320-750µm) capillary columns are most compatible with these high flow rates, but such columns yield long analysis times (30-50 minutes). Without a jet separator, high flow rates are not compatible with a mass spectrometer, but a jet separator raises minimum detection limits and increases instrument downtime. One can eliminate the jet separator and shorten the analysis by using a narrow bore column and splitting the effluent from the trap before it enters the column, or by using cryogenics. Splitting the sample can reduce the amount of analyte entering the column by 90-95%, so detection limits often are no better than with a jet separator, and a cryogenic system increases both cost and total cycle time.

A new approach to concentrating analytes is fully compatible with short, narrow bore capillary columns that yield sharper peaks and better minimum detection limits, and greatly reduce analysis time. Solid phase microextraction▪ (SPME), like purge and trap, is a solventless extraction procedure, but SPME does not require the complex instrumentation of purge and trap methodology. SPME simply involves immersing a phase-coated fused silica fiber into the liquid sample or the headspace above the sample, to adsorb the analytes of interest. The adsorbed analytes are thermally desorbed in the injection port of the GC and transferred to the capillary column.▲ Selectivity can be altered by changing the phase type or thickness. For example, the small distribution constants and low polarity of chlorinated and aromatic VOCs dictate the use of a thick, nonpolar phase for efficient extraction (see the conditions in Table 1). Agitation, addition of salt, pH adjustment, and immersion of the fiber in the liquid sample improve recovery of difficult-to-extract compounds.

Figure A. Rapidly Screen a Sample for VOCs, Using SPME/Dual Column GC

SPME:	**100µm PDMS phase fiber (Cat. No. 57300)** immersed in 1.8mL saturated salt water (5 min, rapid stirring)
Columns:	**10m x 0.20mm ID, 1.2µm film**
Cat. Nos.:	**24134-U (SPB-1), 24129-U (VOCOL)**
Oven Temp.:	40°C (0.75 min) to 160°C at 20°C/min
Carrier:	helium, 40cm/sec (set at 40°C)
Det.:	FID, 260°C
Inj.:	230°C, splitless (closed 3 min)
	50ppb each analyte in Table 1

SPB-1 Column



VOCOL Column

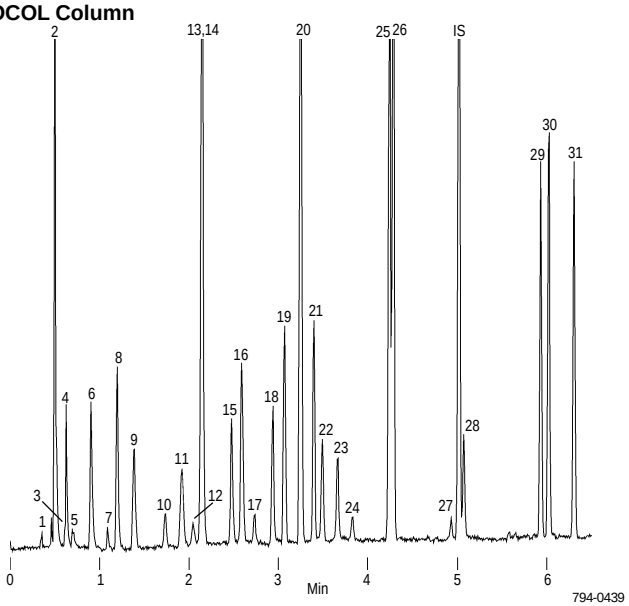


Table 1. Linearity of Response Factors for US EPA Method 624 Volatile Compounds

No.	Compound	Column▲	Response Factors Mean	% RSD
1.	Chloromethane	SPB-1	0.022	17.0
2.	Vinyl chloride	SPB-1	0.663	23.0
3.	Bromomethane	SPB-1	0.025	11.4
4.	Chloroethane	SPB-1	0.229	14.7
5.	Trichlorofluoromethane	SPB-1	0.022	8.3
6.	1,1-Dichloroethene	VOCOL	0.341	13.3
7.	Methylene chloride	VOCOL	0.040	14.7
8.	trans-1,2-Dichloroethene	VOCOL	0.354	15.3
9.	1,1-Dichloroethane	VOCOL	0.272	9.1
10.	Chloroform	VOCOL	0.106	12.1
11.	1,1,1-Trichloroethane	SPB-1	0.374	5.1
12.	Carbon tetrachloride	VOCOL	0.080	11.9
13.	1,2-Dichloroethane	SPB-1	0.183	7.8
14.	Benzene	SPB-1	1.951	5.1
15.	Trichloroethene	VOCOL	0.336	3.9
16.	1,2-Dichloropropane	VOCOL	0.529	3.4
17.	Bromodichloromethane	VOCOL	0.072	9.9
18.	2-Chloroethylvinyl ether	VOCOL	0.324	6.0
19.	cis-1,3-Dichloropropene	VOCOL	0.551	3.6
20.	Toluene	VOCOL	2.091	5.2
21.	trans-1,3-Dichloropropene	VOCOL	0.501	4.3
22.	1,1,2-Trichloroethane	VOCOL	0.247	3.4
23.	Tetrachloroethene	VOCOL	0.251	13.0
24.	Dibromochloromethane	VOCOL	0.060	6.1
25.	Chlorobenzene	SPB-1	1.543	6.5
26.	Ethylbenzene	SPB-1	1.892	14.0
27.	Bromoform	SPB-1	0.086	6.4
IS	1,4-Dichlorobutane (int. std.)			
28.	1,1,2,2-Tetrachloroethane	VOCOL	0.274	4.9
29.	1,3-Dichlorobenzene	VOCOL	1.021	16.9
30.	1,4-Dichlorobenzene	VOCOL	1.078	16.3
31.	1,2-Dichlorobenzene	VOCOL	1.032	17.4

▲Column used to quantify the analyte

Sample: US EPA 624 VOCs in 1.8mL saturated salt water (2mL vial) 25ppb-1ppm, 7 concentration points
Fiber Type: 100µm polydimethylsiloxane (PDMS)
Extraction: direct immersion of fiber in sample (5 min, rapid stirring)

For screening VOCs with nonspecific detectors, such as FIDs and TCDs, a dual column analysis on, for example, a nonpolar column and an intermediate polarity column provides better identification and quantification of the analytes. A 10m x 0.2mm x 1.2µm SPB™-1 column and a 10m x 0.2mm x 1.2µm VOCOL™ column each provided good resolution of US EPA Method 624 analytes without long analysis times. Figure A shows the dual column analysis of the Method 624 analytes at 50ppb, following extraction by SPME. All analytes were identified and quantified in only 6 minutes. The cool down time – about 4 minutes – was greatly shortened by starting the analysis at 40°C instead of at 35°C. The 10-minute cycle time for the analysis is compatible with the sample preparation time by SPME – 5 minutes for extraction and 3 minutes for desorption. SPME is equally compatible with the conditions required by a GC/MS system.

Because wastewater samples can contain analytes at concentrations ranging from trace ppb to ppm levels, a sample screening technique must be suitable for quantifying analytes over a wide range of concentrations. In a purge and trap instrument, analytes at concentrations greater than 200ppb can saturate the trap and contaminate the valves and lines, requiring downtime to clean the system. SPME is effective over a wide range of analyte concentrations, and thus is well suited for screening samples on site or prior to purge and trap/GC/MS analysis. Samples found to be highly concentrated can be diluted prior to the formal analysis.

We determined average response factors for 31 volatile analytes in US EPA Method 624 at a concentration range of 25ppb-1ppm, using SPME to extract the analytes. Data are summarized in Table 1. The low percent relative standard deviations (% RSD) for most analytes indicate good linearity for the response factors for this range of concentrations. The % RSD for vinyl chloride is unusually high because vinyl chloride coelutes with methanol, the solvent used with the standard. Responses for vinyl chloride are more linear with specific detectors, such as a mass spectrometer or ELCD.

These results show that SPME is fast, easy, and compatible with short, narrow bore columns that provide fast analysis times. Volatile organic compounds can be extracted with good accuracy over a wide concentration range. Because the apparatus is portable and easy to use, SPME can be employed in the field for quick turnaround methods, or for screening a sample prior to GC/MS analysis. Precision and accuracy also make SPME effective in quantitative analyses. If your analyses involve these or similar analytes, SPME might be the ideal answer to your sample preparation needs.

Ordering Information:

Description	Cat. No.
SPME Holder	
Initially you must order both holder and fiber assembly. Holder is reusable indefinitely.	
For manual sampling	**57330-U**
For Varian 8100/8200 AutoSampler (requires Varian SPME upgrade kit)	**57331**
SPME Fiber Assembly (pk. of 3)	
100µm polydimethylsiloxane coating	
For manual sampling	**57300-U**
For Varian 8100/8200 AutoSampler	**57301**
Capillary GC Columns	
10m x 0.20mm ID, 1.2µm film	
SPB-1	**24134-U**
VOCOL	**24129-U**

▪ Solid phase microextraction technology is licensed exclusively to Supelco (US patent pending; European patent #0523092).

Fused silica columns manufactured under HP US Pat. No. 4,293,415.

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▲Gaseous VOCs must be rapidly desorbed and introduced into the column if they are to be resolved without cryogenics. The injection port is a major source of band broadening that can be reduced by reducing the inlet volume. When we replaced the 2mm ID splitless liner in the standard splitless/split injection port in our GC/MS system with a 0.75mm ID liner, peak shape and height for the gaseous VOCs were greatly improved.

Notes SG

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