Application Note 141

Air Sampling of VOCs by SPME for Analysis by Capillary GC

The disposable SPME portable field sampler and the Carboxen/ PDMS fiber are an ideal combination for monitoring VOCs in air samples. The ability to collect air samples in the lab or field with the sampler for analysis at a later time is convenient, simple, and reliable for compounds at trace levels.

Key Words

- SPME • portable field sampler
- volatile organic compounds • air analysis

Solid phase microextraction (SPME) can be used efficiently in the field to extract volatile organic compounds (VOCs) from air samples and to store the samples for testing in the lab at a later time. Our SPME portable field sampler, which includes an SPME fiber coated with 75µm of Carboxen™/polydimethylsiloxane (PDMS) material, has a unique sealing mechanism that eliminates the need to ship bag samples or liter containers from the field to the lab.

With the SPME portable field sampler, volatile and semivolatile compounds extracted from air or water remain on the SPME fiber until they are thermally desorbed. The highly retentive Carboxen/ PDMS coating ensures that the compounds remain on the fiber for up to 3 days after sampling, at -4°C. After sampling, the fiber is retracted into the protective outer needle, the outer needle is drawn within a replaceable sealing septum in the nosepiece, and the unit is transported for analysis. The lightweight disposable holder can be used for the life of the fiber.

We extracted US EPA Method 624 VOCs from a water sample, stored the analytes for 3 days under various conditions, and then analyzed the samples. We compared the response values with those obtained in an extraction in which we performed *immediate* desorption (Table 1). With the Carboxen/PDMS fiber, stored at -4°C, no loss of sample was observed. The slight differences were within expected deviations between two extractions. Results of fibers stored at ambient temperature were nearly identical to the fiber stored at -4°C. Even when the fiber was left unsealed for 3 days at ambient temperature, the average loss was less than 15%. The Carboxen/PDMS fiber proved to be much more suitable for storing VOCs than the 100µm PDMS fiber, which typically has been used for VOC extractions.

Table 1. Percent Change in Analyte Response After 3 Days Storage

Method 624 Analytes and Naphthalene at 20ppb

	75µm Carboxen/PDMS		**100µm PDMS**
Analyte	**-4°C, sealed with septa**	**Ambient, not sealed**	**-4°C,sealed with septa**
Chloromethane	2.9	-22.7	-100.0
Vinyl chloride	-13.9	22.6	-100.0
Bromomethane	0.0	-44.8	-100.0
Chloroethane	-4.7	-10.8	-100.0
Trichlorofluoromethane	1.8	-29.0	-100.0
1,1-Dichloroethene	-1.8	-12.4	-100.0
Methylene chloride	5.1	-17.8	-100.0
trans-1,2-Dichloroethene	5.3	-7.7	-100.0
1,1-Dichloroethane	6.6	-4.8	-100.0
Chloroform	0.0	-2.9	-100.0
1,1,1-Trichloroethane	-0.8	-23.7	-100.0
Carbon tetrachloride	1.9	-18.5	-100.0
Benzene	1.5	-14.1	-99.6
1,2-Dichloroethane	3.3	-9.7	-99.7
Trichloroethene	-0.6	-3.7	-98.7
1,2-Dichloropropane	2.2	-17.1	-94.6
Bromodichloromethane	6.5	-7.7	-97.7
cis-1,3-Dichloropropene	7.0	-28.8	-99.2
Toluene	-2.0	-5.0	-95.8
trans-1,3-Dichloropropene	-1.0	-40.9	-94.8
1,1,2-Trichloroethane	1.8	-33.5	-96.3
Tetrachloroethene	-2.4	-18.5	-92.1
Dibromochloromethane	-4.1	-17.3	-95.2
Chlorobenzene	-0.1	-41.3	-88.1
Ethylbenzene	-1.7	-16.7	-82.7
Bromoform	-1.6	20.5	-83.7
1,1,2,2-Tetrachloroethane	0.0	-16.9	-69.6
1,3-Dichlorobenzne	-0.4	-1.3	-51.1
1,4-Dichlorobenzene	-0.2	-14.5	-49.9
1,2-Dichlorobenzene	0.1	-1.4	-37.6
Naphthalene	-4.8	-0.2	-14.2
Mean Change	**0.2**	**-14.2**	**-88.4**

Using a mixture of 9 VOCs, we attempted to determine the capacity of the Carboxen/PDMS fiber, and to determine whether analytes with low distribution constants would be displaced by analytes with higher distribution constants. The analytes were obtained from a 1ppm gas stream and spiked into a 125mL bulb with a final concentration ranging from 400ppt to 400ppb. Using an SPME portable field sampler containing a Carboxen/PDMS fiber, the analytes were extracted for 10 minutes at ambient conditions. Figure A shows the analytes at 10ppb.

Figure B shows the concentration plots for three analytes. Excellent linearity is indicated by the correlation coefficients of 0.98 or higher. Of the 9 VOCs, only 1,2-dichloroethane yielded a value less than 0.98 (Table 2). Vinyl chloride and 1,3-butadiene had the lowest distribution constants, while tetrachloroethene and trichloroethene had the highest.

Classical adsorption mechanism theory suggests that, due to limited adsorption sites, the lighter analytes will be displaced by the heavier analytes as concentration increases. At concentrations

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Figure A. VOCs in Air at 10ppb

Sample: VOCs in air at 10ppb, 125mL bulb
SPME Fiber: **Carboxen/PDMS, 75µm film**
Cat. No.: **57318**
Extraction: headspace, 10 min
Desorption: 5 min, 300°C
Column: **SPB™-1 SULFUR, 30m x 0.32mm ID, 4.0µm film**
Cat. No.: **24158**
Oven: 40°C (2 min) to 150°C at 8°C/min
Carrier: helium, 35cm/sec
Inj.: splitless (closed 2 min), 0.75mm ID liner
Det.: GC/MS ion trap, m/z = 45 - 260

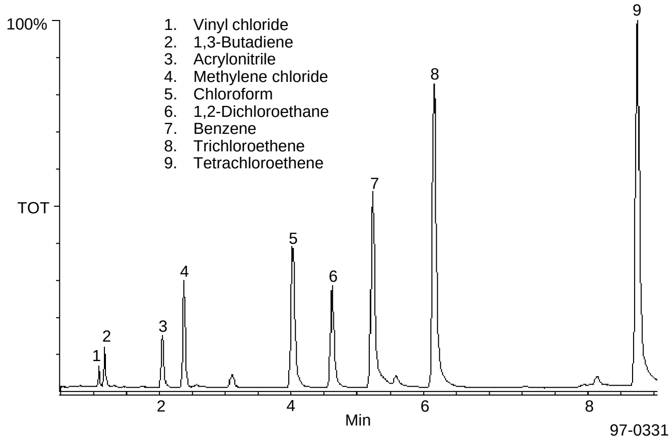

Figure B. Linear Analyte Response Using Carboxen/PDMS Fiber

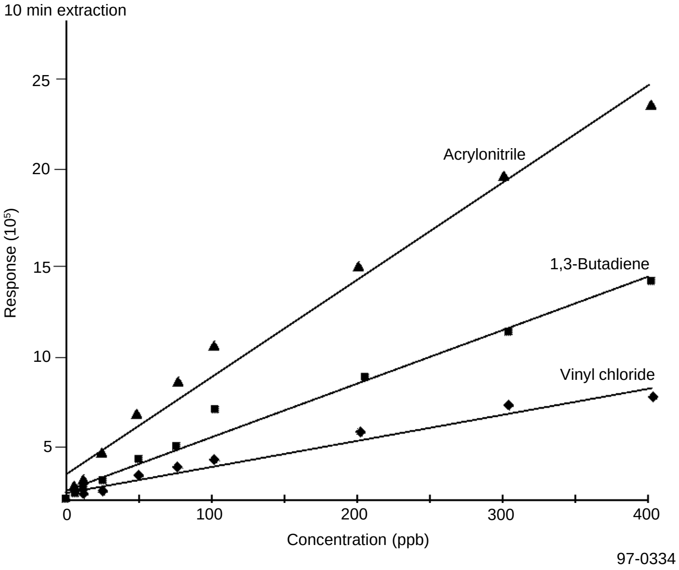

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Table 2. Correlation Coefficients for VOCs

Analyte	R^2
Vinyl chloride	0.980
1,3-Butadiene	0.990
Acrylonitrile	0.980
Methylene chloride	0.986
Chloroform	0.984
1,2-Dichloroethane	0.953
Benzene	0.995
Trichloroethene	0.982
Tetrachloroethene	0.990

above 400ppt, the amount of analyte extracted would level off. However, the unique pore structure of Carboxen-1006 enables extraction of all analytes without displacement of the lighter analytes.

The portable field sampler and the Carboxen/PDMS fiber are an ideal combination for monitoring air samples. The ability to collect both air and water samples in the lab or field with the sampler and analyze at a later time is convenient, simple, and reliable for trace level analyses.

Ordering Information:

Description	Cat. No.
SPME Portable Field Sampler, pk. of 2 Permanent 75µm Carboxen/PDMS fiber**	**504831**
SPME Fiber Assembly, pk. of 3 75µm Carboxen/PDMS	**57318**
SPME Holder for Manual Sampling Order fiber assemblies separately.	**57330-U**
Thermogreen™ LB-2 Septa, 5mm pk. of 100	**20638**
SPME Septum Tool	**504858**
SPB-1 SULFUR Capillary GC Column 30m x 0.32mm ID, 4.0µm film	**24158**

*Solid phase microextraction technology licensed exclusively to Supelco. US patent 5,691,206; European patent #0523092.

**Note: Our original SPME unit and replaceable Carboxen/PDMS fibers can be used for this application if the analytes are analyzed immediately after the extraction.

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