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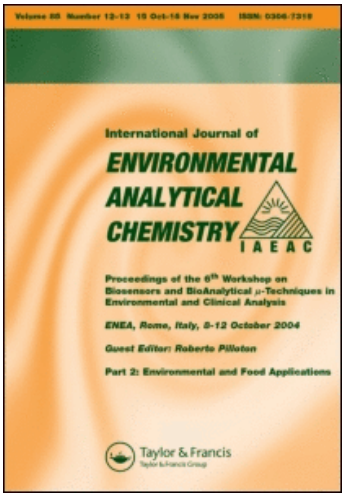

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SOLID PHASE MICROEXTRACTION (SPME) ANALYSIS OF WHOLE AIR SAMPLES

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Air samples can be collected by a number of means and whole air sample collection in canisters or bags is one of the most frequently used options. However, whole air samples normally require preconcentration before analysis to achieve sufficient method sensitivity for trace components and the procedures are usually time consuming. This application note demonstrates that such a preconcentration for whole air samples can be done quickly with the solid phase microextraction (SPME) technique, which is fast, simple to use, low in cost, solvent free, and combines the sample concentration and introduction procedures for whole air samples into one single step. In addition to the improved sensitivity, the SPME also provides a better precision than direct injection of an air sample with a syringe.

Keywords: Solid phase microextraction; whole air samples; preconcentration; VOCs; GC

INTRODUCTION

Air samples are normally collected and concentrated by adsorbent tubes and solvent extraction or thermal desorption is used to release the collected analytes from the adsorbent materials for gas chromatographic analysis of organic compounds. Solvent extraction requires use of expensive and sometimes toxic organic solvents, and results in sample dilution and thus reduced method sensitivities. Thermal desorption of analytes from adsorbent tubes, although no solvents are used and the method sensitivity is generally higher than the solvent extraction approach, requires separate desorption equipment and cryogenic re-focusing of analytes is sometimes necessary. This is not only expensive but also time consuming.

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Organic air pollutants can also be collected from sampling sites as whole air samples in gas sample bags and canisters. A whole air sample may either be concentrated at the laboratory with a cold or adsorbent trap followed by thermal desorption onto the GC, or be introduced directly into the GC by means of syringe or valve injection. Direct syringe injection of whole air samples onto the GC for analysis is no doubt the fastest and easiest way for sample introduction and is sometimes the only viable choice. This is especially true in process control and on-site environmental monitoring, where the sampling and analytical methods are determined to a large extent by the time available for sample collection and analysis and the field logistics. However, the sensitivity of this method is low compared to methods employing sample concentration steps. Also, the analytical precision is often affected by the skill of the analyst and the injection technique. A fast, simple and reproducible alternative for concentration and injection of whole air samples is desirable.

Solid phase microextraction (SPME) is a new, solvent-free sample preparation technique[1–7] and can be used for whole air sample concentration followed by *direct* introduction to a gas chromatograph (GC). It also has the potential to be used directly as an on-site sample collection technique. The SPME assembly looks like a syringe, but in place of the hollow needle is a sorbent-coated silica fiber inside a protective sheath.[4–6] The fiber is attached to the plunger and can be moved out of the sheath, thus exposing it to aqueous or gaseous samples. Organic analytes are extracted from the sample media onto the coated fiber. Then, the exposed fiber is directly transferred to the GC injector and the analytes are thermally desorbed directly onto the column. The usefulness of the SPME as a sample concentration and introduction technique for GC analysis of whole air samples is demonstrated in this application note.

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EXPERIMENTAL SECTION

Air samples were collected with, and gas standards were prepared in, 1-L, 3-L or 10-L Tedlar® Gas Sample Bags (SKC Inc., Eight-Four, PA). The air samples were collected, by means of a Teflon diaphragm pump, from a gas treatment facility used for removal of BTEX (benzene, toluene, ethylbenzene and xylene) from air or process gases. Gas standards containing these compounds at different concentration levels were prepared by injecting known amounts of chemicals into Tedlar bags filled with known volumes of air. The chemicals (purity ≥ 99%) were from Aldrich Chemical Company, Milwaukee, WI.

The SPME manual holder (Cat. # 5–7330) and three fiber assemblies (Cat. # 5–7300) with fibers coated with polydimethylsiloxane (100 μm thickness) used for

whole air sample concentration/injection were obtained from Supelco Canada, Oakville, ON. After exposure to air samples or gas standards for a known period (normally 10 minutes) at 23 °C, the fiber was retreated into the sheath and the sheath was inserted into the GC injector in a depth of 4 cm for thermal desorption, with the fiber moved out of the sheath. The typical desorption time was 2 minutes. The GC injector temperature, i.e. the desorption temperature was 200°C. Whole air sample injection (0.5 mL) was made by using a Hamilton (Reno, NE) 1002SN 2.5 mL gas-tight syringe.

An HP5890 Gas Chromatograph (Hewlett Packard Company, Avondale, PA) equipped with a flame ionization detector (FID) and a 15 m × 0.53 mm × 1.0 μm DB-Wax column (J&W Scientific, Folsom, CA) was used for sample analysis. The detector and the (split/splitless) injector temperatures were 200 °C. The column temperature program was: 40 °C for 2 minutes and ramped at a rate of 10°C/min to 150 °C. Other conditions were: column flow rate, 10 mL/min (helium); injector split flow rate, 35 mL/min; make-up gas flow rate, 20 mL/min (helium); air flow rate, 30 mL/min; hydrogen flow rate, 300 mL/min. GC signal integration was performed by a HP3396 Integrator. Ultra high purity helium, "zero gas" grade hydrogen and air used for the GC/FID operation and preparation of gas standards were supplied by Praxair, Bramption, ON.

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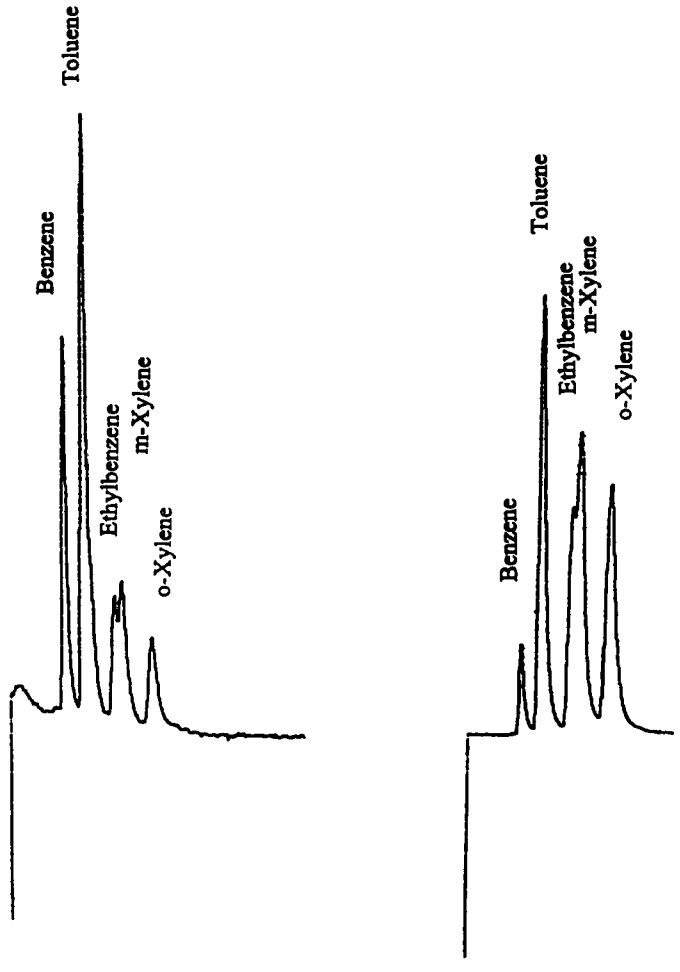
RESULTS AND DISCUSSION

In Table I are listed the GC/FID responses (area counts) to samples of a gas standard injected with a syringe (0.5-mL aliquot) and by means of the SPME technique. Since p-xylene and m-xylene were not resolved by this column under the test conditions, p-xylene was not included in the study. By using the SPME, the method sensitivities for these five test compounds were increased by factors ranging from 1.2 for benzene to 14.6 for o-xylene. Figure 1 shows the chromatograms obtained with the direct injection and SPME techniques. With a longer column, a programmable temperature injector and/or a retention gap, better GC resolution can be expected.

The relative standard deviations (RSD) of the SPME for the test compounds (1.5% to 4.7 %, n = 3) were also smaller than those (3.6% to 10.5%, n = 3) obtained with direct syringe injection. The SPME technique relies on the partitioning of analytes between the SPME coating and the sample medium (which is air in this case), and its sensitivity is thus greater for compounds with higher partition coefficients (i.e., xylenes) than those with lower partition coefficients (i.e., benzene and toluene). Also, once the sampling and desorption conditions are



A. Direct Injection, 0.5 mL

B. SPME, 10 min. (Attenuation 4 times greater than A)

FIGURE 1 Chromatograms of Direct Injection and SPME Analyses

consistent, the SPME injection is subjected to less variations (e.g., in the sample volume) possibly caused by the analyst and therefore better precision than man-

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ual injection with a syringe can be achieved. The variation between the three fiber assemblies used was less than 5% RSD.

The increase in method sensitivity for the less volatile compounds (e.g., xylenes) may be less than what are shown in Table I. This is due to the slower desorption of the less volatile compounds from the SPME coating and thus slightly broader peaks than those achieved by direct injection of an air sample. For example, while the peak area for o-xylene with the SPME is 14.6 times of that with direct injection of 0.5 mL air, the peak height ratio is only 10.8. It may also be argued that if the volume of direct injection is increased, the direct injection technique may outperform the SPME. This is true at least in the case of benzene if the sample volume is increased to 1 mL or greater. However, the sample volume which will not cause a severe reduction in GC resolution of a Megabore column (with limited splitting) without cryogenic re-focusing is probably 0.5 mL, which is what was used in this work. Peak broadening caused by a larger sample volume also offsets the effect on method sensitivity by the increase in sample volume. Therefore, the analytical sensitivity for BTEX in a whole air sample can be easily increased by factors from 1.2 to 10.8 by simply switching from the conventional syringe injection to the SPME technique.

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TABLE I Comparison of SPME and Direct Injection

	Direct injection (0.5 mL)		*SPME (10 minutes)*		*Response Ratio (SPME/Direct)*
	Average (Area Count)	*RSD (%)*	*Average (Area Count)*	*RSD (%)*	
Benzene	450357	7.4	557371	1.6	**1.24**
Toluene	906039	10.5	3127679	1.8	**3.45**
Ethylbenzene	163854	5.0	1178206	4.7	**7.19**
m-Xylene	277651	4.2	2905589	4.5	**10.5**
o-Xylene	191719	3.6	2801776	1.5	**14.6**
Average		6.1		2.8	

* Gas standard containing 175 mg/m^3 benzene, 350 mg/m^3 toluene, 87 mg/m^3 ethylbenzene, 131 mg/m^3 m-xylene and 87 mg/m^3 o-xylene.
** Triplicate measurements.

One question remained is how significant such increases in analytical sensitivity is to a real-world problem? The question can be answered by examining the data tabulated in Table II. In assessing the removal efficiency of a process for

BTEX in air, the inlet and outlet concentrations of BTEX in the gaseous flow were monitored with whole air sampling (with Tedlar bags) followed by direct injection (0.5 mL) and also SPME concentration/injection GC/FID analyses. Benzene was below the detection limit of 0.5 mg/m^3 in both inlet and outlet samples with both injection techniques, and is therefore not listed in Table II. With the direct injection technique, the removal efficiencies for toluene, ethylbenzene, p/m-xylene and o-xylene were determined as 99.2%, >96.2%, >98.7% and >96.6%, respectively. The efficiencies for ethylbenzene, p/m-xylene and o-xylene could actually be ≥ 99% as that for toluene, but was not confirmed since the outlet concentrations of these compounds were below the detection limit of 0.5 mg/m^3 using the direct injection technique. By means of the SPME technique, the detection limits for these three compounds were 5 fold lower. Although it was still not sufficient to detect these compounds in the outlet flow, it was possible to state with confidence that the removal efficiencies for toluene, ethylbenzene, p/m-xylene and o-xylene were all >99%.

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TABLE II BETX Removal Efficiencies Determined Based on Different Injection Techniques

Injection		*Toluene*	*Ethylbenzene*	*p/m-Xylene*	*o-Xylene*
Direct	Inlet, mg/m^3	185	13.2	37.7	14.6
(0.5 mL)	Outlet, mg/m^3	1.5	<0.5	<0.5	<0.5
	Removal, %	**99.2**	**>96.2**	**>98.7**	**>96.6**
SPME	Inlet, mg/m^3	189	13.0	40.1	14.1
(10 min)	Outlet, mg/m^3	1.6	<0.1	<0.1	<0.1
	Removal, %	**99.2**	**>99.2**	**>99.8**	**>99.3**

References

[1] M. Chai and J. Pawliszyn, *Environ. Sci. Technol.*, **29**, 693–701 (1995).

[2] D.W. Potter and J. Pawliszyn, *Environ. Sci. Technol.*, **28**, 298–305 (1994).

[3] Z. Zhang and J. Pawliszyn, *Anal. Chem.*, **65**, 1843–1852 (1993).

[4] M. Chai, C.L. Arthur, J. Pawliszyn, R.P. Belardi and K.F. Pratt, *Analyst*, **118**, 1501–1505 (1993).

[5] C.L. Arthur, M. Chai and J. Pawliszyn, *J. Microcol. Sep.*, **5**, 51–56 (1993).

[6] J.R. Berg, *Amer. Lab.*, November (1993).

[7] C.L. Arthur, L.M. Killam, K.D. Buchholz and J. Pawliszyn, *Anal. Chem.*, **64**, 1960–1966 (1992).