

Solid Phase Microextraction/Capillary GC: Rapid, Sensitive Detection of Gasoline in Fire Debris

Headspace sampling by SPME eliminated sample transfer/sample handling losses and offered, on average, a 1.0-, 3.8, and 11.2-fold increase in response, relative to passive sampling, for three measured components of gasoline samples. SPME/GC produced usable chromatograms from as little as 0.04 μ L of gasoline, a significantly smaller volume than the normal limit for passive sampling, 0.1 μ L.

Key Words:

- forensics analyses • fire debris • flammables • arson
- solid phase microextraction

Solid phase microextraction – SPME* – is a simple, solventless extraction procedure in which a phase-coated fused silica fiber is immersed in a liquid sample or exposed to the headspace above a liquid or solid sample. Analytes adsorb to the phase, and then are thermally desorbed in the injection port of a gas chromatograph and transferred to a capillary column. Selectivity can be altered by changing the phase type or thickness according to the characteristics of the analytes. For example, the small distribution constants and low polarity of chlorinated and aromatic volatile organic compounds in environmental samples dictate the use of a thick, nonpolar phase for efficient extraction. Analyte recovery can be improved, or selectivity altered in favor of more volatile or less volatile compounds, by agitating the sample, adding salt, changing the pH or temperature, or sampling the headspace rather than the sample (or vice versa).

Investigators in the Crime Laboratory Bureau of the Metro-Dade Police Department (Miami, Florida, USA) and the Department of Chemistry at Florida International University (Miami) developed what they described as a simple, inexpensive, rapid, and sensitive method for analyzing gasoline in fire debris, using SPME for headspace sampling (1). According to the investigators, current methods for sampling flammable or combustible liquid residues from fire debris include static headspace sampling (capable of detecting ~10 μ L of petroleum product residue) and concentration methods including solvent extraction, dynamic headspace concentration, and passive headspace concentration (capable of detecting ~0.1 μ L of petroleum product residue). All of the concentration methods are cumbersome and time-consuming, and require the analyst to use carbon disulfide, a toxic and highly flammable solvent. In a direct comparison of headspace SPME and passive headspace concentration on activated charcoal strips, SPME was faster, simpler, and more economical, and offered greater sensitivity. SPME also eliminated the need to expose the technician to carbon disulfide.

Figure A. Headspace Sampling of 0.1 μ L Gasoline

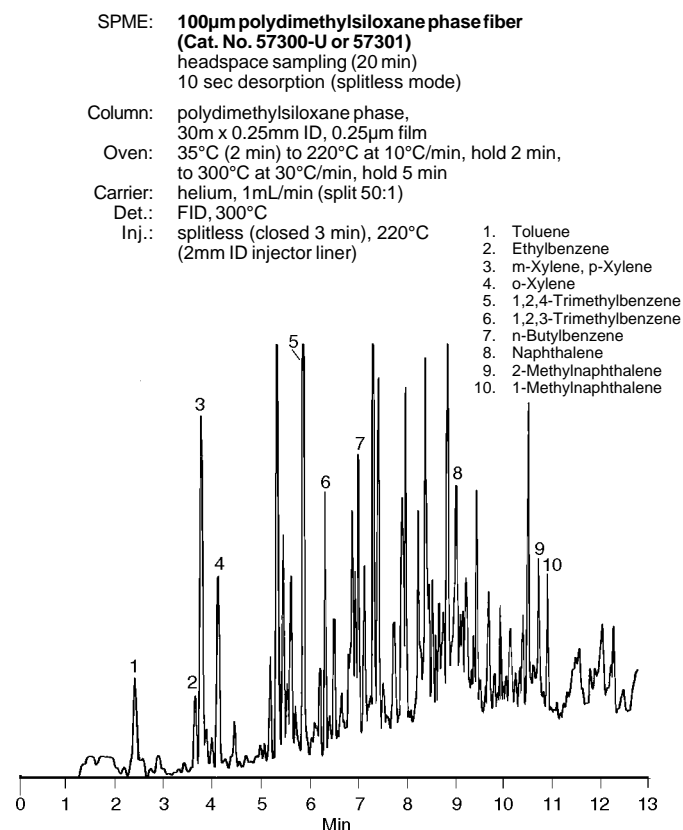


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Table 1. Detector Responses for Selected Hydrocarbons in Gasoline

Analyte	Gasoline Quantity (μ L)	FID Response (volts)		Response Ratio SPME/Passive
		SPME	Passive	
Ethylbenzene	5	0.07	0.12	0.6
	1	0.015	0.010	1.5
n-Butylbenzene	0.1	0.0057	0.0060	1.0 \bar{x} = 1.0
	5	0.26	0.078	3.3
2-Methylnaphthalene	1	0.042	0.0065	6.5
	0.1	0.0090	0.0062	1.5 \bar{x} = 3.8
1-Methylnaphthalene	5	0.28	0.02	14
	1	0.042	0.0023	18.3
	0.1	0.0076	0.0055	1.4 \bar{x} = 11.2

Data from reference 1.

After heating various fixed volumes of gasoline at 40°C for 30 minutes, the investigators exposed a 100µm polydimethylsiloxane-coated SPME fiber to the headspace above the sample for 20 minutes, then desorbed and analyzed the analytes under conditions listed with Figure A. They used a Hamilton® heated syringe cleaner (120VAC; Supelco Cat. No. 20770-U) to clean the fiber assembly between samples. Although relatively small amounts of analytes were recovered under these conditions, the SPME technique eliminated sample transfer/sample handling losses (the entire extract was introduced onto the GC column) and yielded high sensitivity. The investigators calculated that headspace SPME offered, on average, a 1.0-, 3.8-, and 11.2-fold increase in response, relative to passive concentration, for three measured components of the gasoline samples (Table 1). SPME produced acceptable, identifiable chromatograms from as little as 0.04µL gasoline, a significantly smaller volume than the normal limit for passive headspace sampling, 0.1µL. The forensics experts also were impressed with the savings in time and cost per sample offered by SPME (20 minutes or less, versus 16 hours; less than half the cost of passive sampling). These analysts now are applying their headspace SPME technique to analyses of other samples, including alcohols and diesel fuel.

Because liquid (immersion) and headspace sampling methods differ in kinetics, the two approaches can be considered complementary. For a given sampling time, other analysts found immersion SPME was more sensitive than headspace SPME for analytes predominantly present in the liquid (2). The reverse was true for analytes that were primarily in the headspace. These generalizations can be used to advantage to selectively adsorb more volatile or less volatile flavor compounds, as a situation warrants. For higher sensitivity from headspace SPME, the sample headspace should be as small as is practical. A detailed theoretical discussion of headspace SPME is presented in reference 3.

The results summarized here indicate that SPME is fast, easy, and economical, and eliminates the costs and hazards associated with using organic solvents. Under consistent sampling conditions, analytes can be extracted with good precision over wide ranges of concentrations. SPME can be used for screening samples prior to a detailed analysis. Good precision also makes SPME effective in quantitative analyses. If you are interested in reducing the time and expense of sample concentration in your analyses, SPME might be the ideal answer to your needs.

References

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Acknowledgments

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* US patent pending. European patent # 0523092. Technology licensed exclusively to Supelco.

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