Solid-Phase Microextraction Method for the Quantitative Analysis of Styrene in Water

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Abstract

A headspace solid-phase microextraction (HS-SPME) method is developed for the determination of styrene in drinking water. Gas chromatography (GC)–mass spectrometry is utilized for qualitative analysis. A manual SPME holder with 85-µm polyacrylate coating is used to extract the styrene from water, which is determined to have good linearity (correlation coefficient r = 0.9999 for 1.00–100.00 µg/L range), a relative standard deviation of 1.9%, and a detection limit of 0.30 µg/L. This method is compared with a classical headspace GC method.

Introduction

Styrene has been used in the manufacture of numerous types of plastic, glass fiber-reinforced resins, protective coatings, and ion-exchange resins, in addition to synthetic rubber. Styrene monomer can be in direct contact with food when polymers such as polystyrene and acrylenitrile–butadiene–styrene are used as packaging material. A wide range of food is either packaged in or otherwise comes in contact with various polymers and copolymers of styrene. The most important uses of these food-contact applications are in the fabrication of containers (e.g., drinking cups) for a wide range of foods.

Styrene is a volatile compound that enters the human body mainly through the lungs or skin. Several adverse effects on the health of humans have been detected. At lower atmospheric levels, styrene produces irritation of the mucous membranes. The substance is absorbed upon dermal contact and may cause dermatitis (1,2). Higher concentrations cause central nervous system depression, nausea, headache, and fatigue. Organ toxicity due to chronic exposure is rare, although the compound may potentially produce hepatotoxic cancer. Styrene levels of 100.0 µg/L change the organoleptic parameters of drinking water.

Several methods to assay residual styrene have been published, including headspace with gas chromatography–flame ionization detection (GC–FID) (3–5) or mass spectrometric detection (MS) (6–9), purge-and-trap with GC–FID (10), and high-performance liquid chromatography (HPLC) methods (11,12).

Although headspace has been widely used for the analysis of residual styrene, it suffers from low sensitivity and requires careful calibration.

Solid-phase microextraction (SPME) has some advantages over headspace extraction (13). In this paper, an efficient method is developed to determine residual styrene in water based on SPME and GC analysis with an FID.

Experimental

Reagents

Analytical-grade styrene was obtained from Aldrich Chemical (Milwaukee, WI). A stock solution (500.0 mg/L) was prepared in HPLC-grade methanol (Carlo Erba, Milan, Italy) and diluted in water from a Milli-Q (Millipore, Milford, MA) water purification system.

Equipment

The identification of the composition of water was performed by an HP 5890 series II GCS (Hewlett-Packard, Wilmington, DE) equipped with an HP 5972 MS. The electron impact ionization conditions were as follows: ion energy was 70 eV and the mass range scanned was under full-scan acquisition mode in the range of 50 to 150 u.

Quantitation of residual styrene in drinking water was performed on a HP 5890 series II GC (Hewlett-Packard) equipped with an FID.

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The chromatographic analyses in both systems were carried out on a Hewlett-Packard HP-5 capillary column (cross-linked 5% phenyl methysiloxane film, 25 m × 0.20-mm i.d. with a phase thickness of 0.33 µm).

The carrier gas was helium at a flow rate of 0.65 mL/min. The oven program for GC began at 50°C and was held at this temperature for 1 min. The oven was then raised to 100°C at 10°C/min and then to 150°C at 5°C/min. The temperature of 150°C was maintained for 25 min. A split/splitless injector in the splitless mode was used, and it was held isothermally at 220°C.

The detector was set at 280°C in the analysis using the GC–FID system.

SPME

The SPME device was purchased from Supelco (Supelco Co., Bellefonte, PA). The fiber selected to extract the styrene had 85-µm polyacrylate coating. A heater unit (Figure 1) was assembled according to Pataca (14) and placed into a hot plate.

The polyacrylate fiber was conditioned before initial application in the hot port injector of the GC by heating it at 280°C for 3 h.

For the SPME process, the solution (10.0 mL) was introduced into 22-mL Pyrex vials; the vials were immediately sealed with aluminum caps containing septa that had Teflon lining on the inside and rubber on the outside.

The fiber was exposed to the headspace of the sample for an optimized adsorption time of 10 min at 55°C and introduced into the GC injector, where the thermal desorption of the analytes at 220°C for 2 min was carried out. A SPME inlet liner (splitless, 0.75-mm i.d.) was used in the injection port.

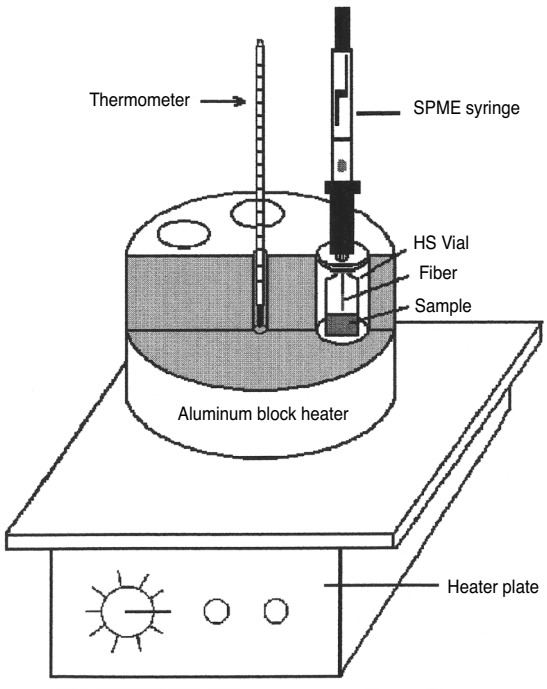

Figure 1. Heater system used in headspace microextraction.

Headspace

The styrene solution was prepared with aqueous samples containing 20% NaCl. For the headspace process, 250.0 µL of styrene solution was placed in 6-mL Pyrex vials, which were immediately sealed with Teflon-lined rubber septum aluminum caps. The vials were placed for 20 min at 80°C in a

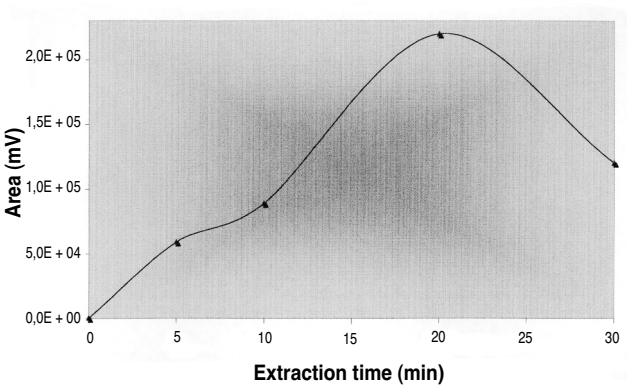

Figure 2. Effect of varying the extraction time for the styrene solution at 30.0 µg/L.

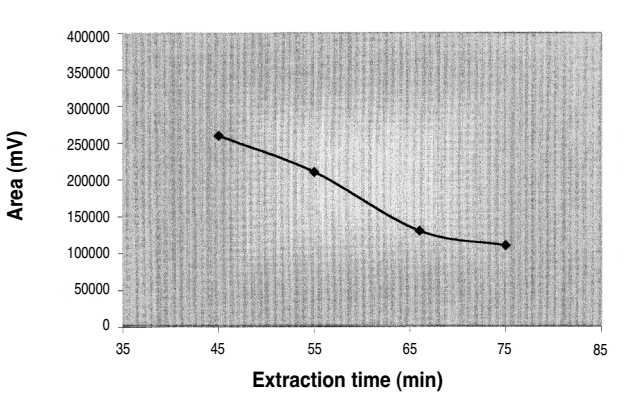

Figure 3. Adsorption temperature profile of styrene solution at 10-min extraction time.

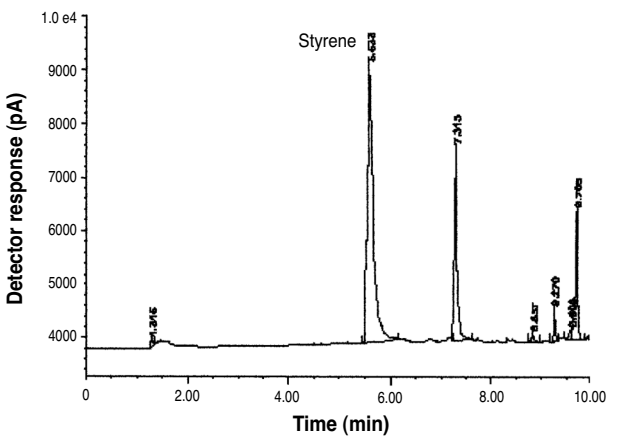

Figure 4. Chromatogram obtained by SPME–GC–FID of the styrene solution at 30.0 µg/L.

Multi-BloK heating device (Cole Parmer, Vernon Hills, IL) consisting of a standard heater base and a heating block of six 25-mm openings. The 250.0 µL of the headspace phase of the sealed vial was injected into the GC using a Gastight syringe (Supelco). After each injection, the syringe was flushed several times with air in order to remove any residual traces of styrene.

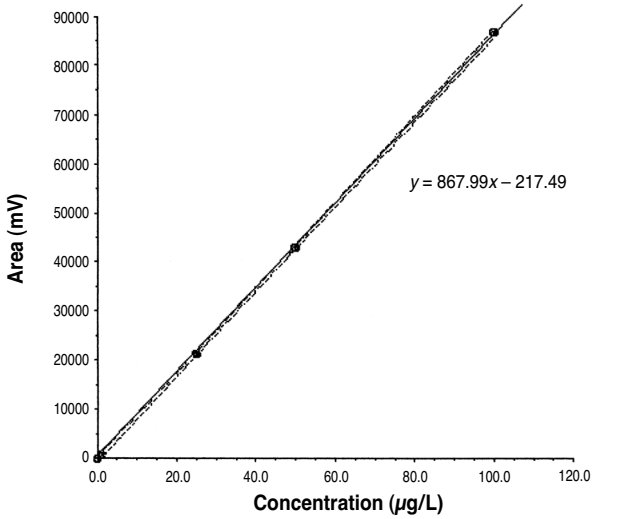

Figure 5. Calibration curve for styrene using the SPME method.

Results and Discussion

Optimization of SPME

In SPME, analytes are extracted for an adequate time by a solid stationary phase until an equilibrium is established in the headspace above the sample and polymer-coated fiber. The amount of analyte extracted under such conditions depends on the partition coefficient between the sample and the coating. Optimum extraction time is determined by the length of time required to obtain precise extractions for the analyte. The absorption time profile was studied by varying the time from 5 to 30 min.

The pH of the sample was not adjusted. Because the method gives very good sensitivity, salt was not added, thus preserving the SPME system because the fiber causes much waste when it is used in saline solutions. All the extractions were carried out at 65°C for standard solutions of styrene in a concentration of 30.0 µg/L.

Figure 2 shows that the extraction increases with time. An adsorption time of 10 min was selected because this is a reasonable compromise between good sensitivity and acceptable time of analyzation.

The effect of the adsorption temperature was examined in the range from 45 to 75°C. The optimum temperature was 55°C, allowing for the adsorption of a sufficient amount of styrene while maintaining good extraction conditions (Figures 3 and 4).

Table I. Analysis of Variance in the SPME Method*

Source	dF	Sum squares	Mean square	F-test
Regression	1	4.22×10^9	5.22×10^9	5.34×10^4
Residual	3	2.93×10^5	9.77×10^4	$p = 0.0001$
Total	4	5.22×10^9		

* Linearity parameters in Figure 4.

Table II. Linear Regression Analysis Parameters of Styrene Standards in the Headspace Method*

Concentration (mg/L)	tr (min)	Area (mV)	Repeatability
0	–	–	–
0.05	4.107	8548	$\bar{x}$ = 7497 ± 1025
0.05	4.099	7835	%RSD = 13
0.05	4.096	6107	
0.10	4.111	13777	$\bar{x}$ = 15176 ± 1236
0.10	4.107	16121	%RSD = 8
0.10	4.098	15629	
0.20	4.109	38734	$\bar{x}$ = 36771 ± 3685
0.20	4.105	32519	%RSD = 9
0.20	4.104	39059	
0.30	4.107	53322	$\bar{x}$ = 51725 ± 1458
0.30	4.098	51389	%RSD = 3
0.30	4.100	50465	

Source	dF	Sum squares	Mean square	F-test
Regression	1	1.83×10^9	1.83×10^9	616.48
Residual	3	8.92×10^6	2.97×10^6	$p = 0.0001$
Total	4	1.84×10^8		

* Headspace GC parameters in text.

Chromatographic methods

The linearity of the SPME method was determined over the range of 1.00 to 100.00 µg/L. Figure 5 shows that there is a linear relationship between the concentration and the area; with narrow confidence limits, the correlation coefficient r was 0.9999. The analysis of variance (Table I) shows that it was the best straight line through the calibration graph point, because the mean squares were smaller than the F-test. Repeatability was studied by making seven injections of a styrene solution of 50.0 µg/L. The relative standard deviation (RSD) was 1.9%.

The limit of detection (peak area three times higher than background level) was found to be 0.30 µg/L.

Headspace

The parameter time of heating (10, 20,

and 30 min), temperature of heating (60°C, 80°C, and 100°C), and effect of the ionic strength of the sample were studied. Under optimized conditions (heating at 80°C for 20 min in 20% NaCl solution), linearity and repeatability were obtained. The results are shown in Table II. The values indicate that in the range of 0.05 to 0.30 mg/L, this method is linear and gives good repeatability. The detection limit was 0.05 mg/L.

Analysis of real samples

The analytical method developed for real samples was validated by analyzing samples of drinking water out of plastic cups and samples of river water. Five series of measurements were performed: (*a*) commercial drinking water out of sealed cups; (*b*) ordinary drinking water after 30-, 60-, and 90-min storage periods; (*c*) drinking water at two different pH values (1.5 and 4) to simulate soft drink storage; (*d*) drinking water at 80°C stored for 5-, 15-, and 30-min periods to favor the migration of styrene into the liquid as a means of simulating the storage of hot drinks (e.g., coffee or tea); and (*e*) samples of water from rivers in the vicinity of industrial installations.

The results obtained in series *a*, *b*, and *c* show null styrene contents. This means that drinking water stored in plastic cups is not contaminated by styrene, even if the liquid shows pH values typical of those found in soft drinks. On the other hand, the samples of drinking water at 80°C presented styrene concentrations of 2.07 µg/L for 5-min, 6.13 µg/L for 15-min, and 9.03 µg/L for 30-min storage periods. This indicates that styrene may migrate into hot drinks stored in plastic cups. Finally, styrene was detected in only one of the eleven analyzed river-water samples. In this case, the styrene concentration was found to be 0.20 mg/L.

Conclusion

This paper describes an SPME method for the assay of styrene in water. The aim of this study was to compare classical headspace GC and the SPME–GC method. This comparison shows that the SPME method enables the following to be achieved: very low detection limits, better linearity, and better repeatability than the headspace method. Therefore, because of these advantages, the SPME method is the technique of choice for the quantitative analysis of styrene in water.

Acknowledgments

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