

DETERMINATION OF RESIDUAL VOLATILE ORGANIC COMPOUNDS MIGRATED FROM POLYSTYRENE FOOD PACKAGING INTO FOOD SIMULANT BY HEADSPACE SOLID PHASE MICROEXTRACTION-GAS CHROMATOGRAPHY

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Abstract

The residual styrene and other volatile organic compounds (VOCs) present in the polystyrene food packaging are of concern as these compounds have the potential to migrate into the food in contact. This work describes a method for quantitative determination of VOCs, namely styrene, toluene, ethylbenzene, iso-propylbenzene and n-propylbenzene that have migrated from polystyrene food packaging into food simulant by gas chromatography-flame ionization detection (GC-FID). Headspace solid phase microextraction (HS-SPME) technique was applied for migration test using water as food simulant. The effects of extraction variables including sample volume, elutropic strength, extraction temperature, extraction time, desorption time, sample agitation, and salt addition on the amounts of the extracted analytes were studied to obtain the optimal HS-SPME conditions. The optimized method was applied to test the VOCs migrated from polystyrene bowls and cups at storage temperatures ranging from 24°C to 80°C for 30 min. Styrene and ethylbenzene were found to migrate from the samples into the food simulant. The migration of analyte was found to be strongly dependent upon the storage temperature. The HS-SPME is useful as an alternative method to determine the migration of VOCs from food packaging material into food simulant.

Keywords: Styrene, Volatile organic compounds, Food packaging, Headspace solid phase microextraction, Gas chromatography.

Introduction

In this modern society, food packaging plays an important role to promote safe transportation, delivery and storage of food. It becomes an indispensable element in the food sector. Among the major polymers used in food packaging, polystyrene has made up a large volume of the consumption of plastic containers. Polystyrene is widely used as food servicing packaging because it is strong, lightweight, and it provides excellent insulation properties.

In Malaysia, polystyrene is most commonly used for take-away foods in some fast-food joints, hawkers and food court outlets due to the changing of food consumption patterns and increasing preferences for convenience and fast food by the people.

The usage conditions of polystyrene food packaging range from low temperatures for periods of days or weeks, for example packaged dairy and meat products, to high temperatures approaching the boiling point of water for short periods of time, for example vending cups and instant noodle bowls. The low molecular weight constituents present in the polystyrene plastic have the potential to migrate into the foodstuff in contact with the plastic especially during extended periods of time, or at the elevated temperatures. Substances migrating to foodstuffs are of concern if they present a possible health hazard to the consumer, or cause unacceptable changes to the organoleptic properties of the food or beverages. Numerous studies have shown that styrene and other volatile compounds present in polystyrene food packaging have the potential to migrate out into the contacting food [1-8]. Therefore, it is necessary to develop a reliable and efficient method for testing of chemicals in food packaging materials in order to provide assurance to consumers about the safety of the products.

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This work aims to study the viability of SPME methodology with gas chromatography to determine the migration of five volatile organic compounds (VOCs), namely styrene, toluene, ethylbenzene, iso-propylbenzene and *n*-propylbenzene simultaneously from polystyrene food packaging into a selected food simulant i.e. water.

Experimental

Reagent and chemicals

The following chemicals were used to prepare the standard solutions: styrene (99.9%), toluene (99.9%), ethylbenzene (99.8%), iso-propylbenzene (99.9%) from Sigma-Aldrich (Germany) and *n*-propylbenzene (99.9%) from Kanto Chemical (Japan). 1,4-dichloromethane (99.9%) was used as internal standard and obtained from Sigma-Aldrich. Other chemicals included Methanol (99.99%, J.T. Baker, USA) and postassium chloride (KCl) (99.7%, Scharlau Chemie, Spain)

Samples

Three types of commercially available polystyrene samples consisted of disposable cup and bowl were chosen for the study. The capacity of each sample was determined and the test specimen was filled with food simulant up to the measured capacity and kept at two different conditions.

Food Simulant and migration condition

Water was chosen as food simulant to represent food group with pH of 4.5 and above. The food simulant was prepared by heating the purified deionized water to the temperature required for the migration study, i.e. 24°C (room temperature), 60°C and 80°C. Migration test was performed both at room temperature for 30 min and at the temperature of the food simulant used and held for 30 min.

HS-SPME sampling conditions

SPME parameters (sample volume, elutropic strength, extraction temperature and time, stirring rate, salting out effect and desorption time) were studied using the standard mixture in order to get the optimum conditions that would have the best extraction efficiency.

For calibration standard and samples, the working conditions for HS-SPME were as follows: The analytes were extracted with HS-SPME technique using a 100 µm PDMS fiber and 22 mL head space vials. The new fiber was conditioned at the injection port at 250°C for 30 min. An aliquot of 10 mL of test solution obtained from section 2.2 was placed in a 22 mL vial and 10 µL of 5 µg/mL ISTD was added to the vial. After placing a 0.8 cm long stir bar in the vial, it was sealed with a headspace cap with a PTFE-faced septum. The vial was shaking vigorously for few seconds and left at room temperature for 5 min. After 5 min pre-incubation, the fiber was inserted into the centre of the vial and placed about 2 mm above the water sample. The extraction time was 15 min with constant stirring at 800 rpm to speed up equilibrium process. Once extraction time was completed, the fiber was immediately retracted into the protective sheath, removed from the vial, and transferred into the injector of the gas chromatograph for thermal desorption.

Instrumentation

A Shimadzu (Kyoto, Japan) GC-17A gas chromatography equipped with flame-ionization detector and a Shimadzu AOC-20i autosampler was used. The chromatographic data were analyzed and processed using a Shimadzu Class-VP 4.3 acquisition program.

Gas chromatographic separations were carried on a DB-WAX fused-silica capillary column (30 m × 0.25 mm I.D., 0.25 µm film thickness, J & W) with helium as carrier gas. Other conditions were as follows: injection volume 1 µL, split ratio 1:10 (after 5 min); inlet temperature, 220°C; oven temperature, 40°C hold 3 min, rate 10°C/min to 120°C, 40°C/min to final temperature 260°C and hold 2 min; FID temperature, 260°C.

Method validation

The method performance was evaluated for limit of detection (LOD), limit of quantification (LOQ), linearity, accuracy and precision. Statistical evaluation of each performance parameter was performed by using built-in statistical functions of Microsoft office excel 2003.

Results and Discussion

Optimization of SPME Parameters

The parameters for SPME extraction were evaluated to determine the best conditions to use for the extraction of VOCs from the aqueous solution. In the experiments, the studied variable was varied according to the specified range; other parameters were fixed.

Sample Volume Studies

Fig. 1 shows the variation of response (peak area) with sample volume, it was observed that peak area response improved as the sample volume increased from 5 mL to 10 mL. Beyond that, further increase in sample volume to 15 mL only slightly increased the overall response. The sample volume determines the volume of the headspace, so it affects the response of SPME. The mass transfer from the liquid phase to the gas phase increases as the volume of the liquid phase is increased. However, the mass transfer from the liquid phase to the gas phase slows down when approaching equilibrium stage.

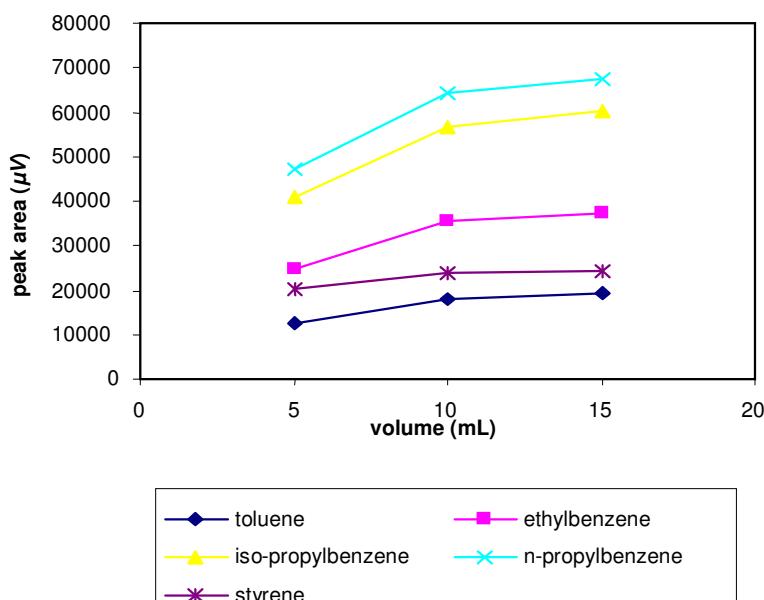


Fig. 1: Effect of sample volume on extraction efficiency of analytes

This study also indicated that the RSD increased as the sample volume increased. The RSD values ranged from 0.22% to 2.76% at 5 mL of sample volume, 0.35% - 4.56% at 10 mL of sample volume and 4.46% to 9.71% at 15 mL of sample volume. This may be due to the errors during volume dispensing by using different types of pipettes. Therefore, sample volume of 10 mL was selected for further experimental testing.

Elutropic Strength Studies

As the increase of the analyte concentration also increase the volume of methanol required as spiking solvent, the possible competitive displacement effect of methanol in the analyte adsorption by the fiber was studied. The small amounts of added methanol were expected to dissolve completely in the water and not significantly alter the properties of that phase. The variations of peak area with the amount of methanol are shown in Fig. 2. As methanol concentration increased, less analyte was absorbed.

The decrease in absorption of the analytes in 0.5% methanol was in the range of 6% to 14%. This is because an increased proportion of methanol in the aqueous solution decreases the polarity of the aqueous sample so that the distribution constant decreases. The presence of organic solvent in the sample suppresses the adsorption of analyte onto the fiber. To overcome the non-linearity attributed to competitive displacement of the analyte by

the spiking solvent, preparation of calibration standard solution and sample spiking solution was limited to 0.1% methanol.

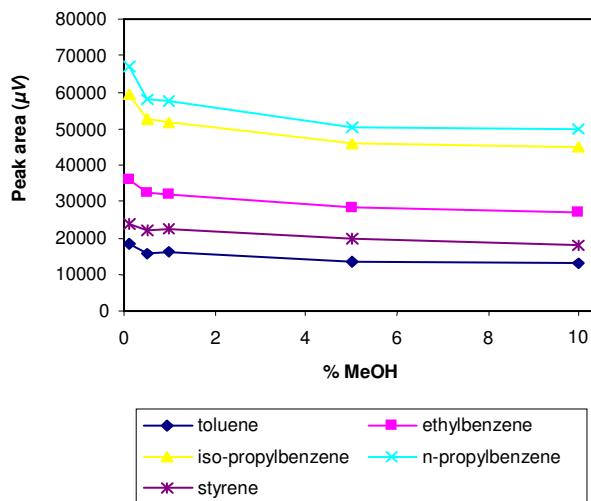


Fig. 2: Studies of elutropic strength effect on the targeted analytes

Extraction Temperature Studies

In HS-SPME, an increase in extraction temperature leads to an increase of analyte concentration in the headspace, and helps to facilitate faster extraction. However, at high temperature, coating headspace partition decreases and the fiber coating begins to lose its ability to adsorb analytes. Thus the temperature effect between 24°C – 80°C was studied.

From the experiment, a decrease in peak area was observed when the extraction temperature increased from laboratory room temperature (24°C) to 80°C (Fig. 3). This can be explained by the exothermic adsorption process by which the VOCs are partitioned between the headspace and the PDMS coating. A higher temperature increases the concentration of VOCs in the headspace by decreasing the partition coefficient between the PDMS coating and the headspace. As a result, the total amount of VOCs adsorbed into the fiber decreases as extraction temperature decreases. The optimum extraction efficiency for all the analytes was at laboratory room temperature (24°C). Thus, a temperature of 24°C was selected for further experiments since this temperature provides a maximum for VOCs and working under these conditions enables the obtainment of good chromatographic signals

Extraction Time Studies

The influence of extraction time was studied from 1 min to 45 min. The results are shown in Fig. 4.

An increasing efficiency was observed for the five analytes when the longer extraction time was used (0 – 30 min). However, the increase was not that significant from 5 min to 30 min especially for styrene and toluene. The extraction efficiency reached a maximum at 30 min for toluene, ethylbenzene, iso-propylbenzene and *n*-propylbenzene, however, for styrene a maximum peak area at 35 min was observed. The decrease in peak area after further increase of extraction time (45 min) was due to the desorption of the analytes from the fiber that were supposed to compete with the absorption process for excessively long extraction time.

In order to extract the maximum amount of analyte, the equilibrium time has to be reached, but this is too long and impractical for routine analysis. A short extraction time is preferred in rapid detection, and so the extraction time of 5 min was considered to be adequate for the subsequent experiments as a compromise between response and analysis time.

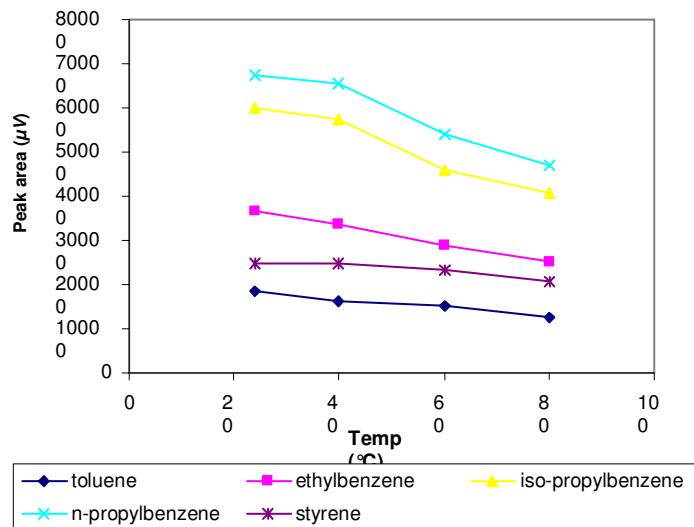


Fig. 3: Effect of extraction temperature on analyte extraction efficiency

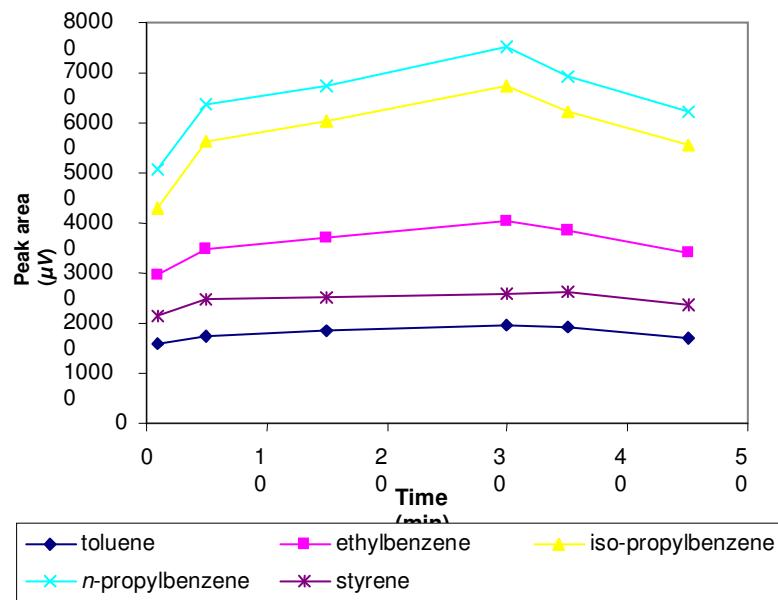


Fig. 4: Extraction time profile for the five analytes

Desorption Time Studies

Various desorption times (1, 3, 5 and 10 min) were evaluated (Fig. 5). By decreasing the time of desorption, chromatographic resolution was improved, while avoiding overlapping of some of the peaks that occurred at longer periods of desorption. On increasing desorption time from 1 to 3 min, the uptake of most of the compounds was slightly increased. However, further increased to 5 min and above gave no significant differences in peak areas for most compounds. On this basis, the time of desorption yielding the best

chromatographic resolution without relevant decreases in the peak areas of most of the compounds was taken as 3 min.

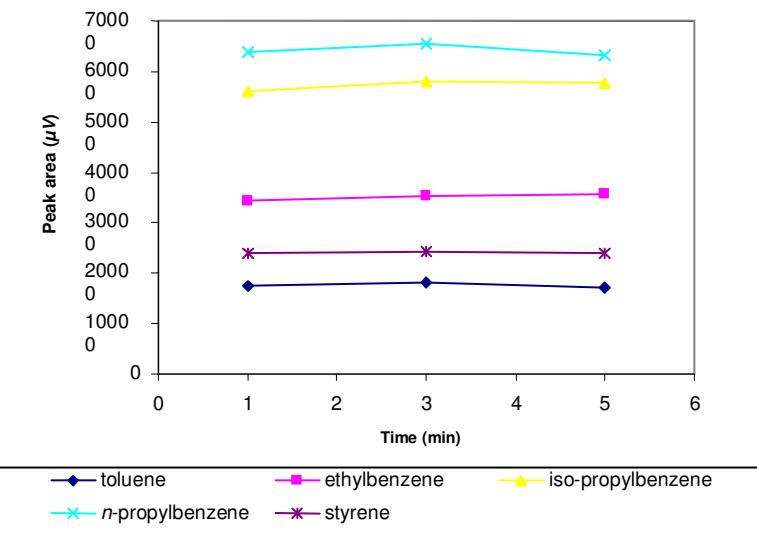


Fig. 5: Desorption time profile for the five analytes

In order to determine whether the desorption was completed, the SPME fiber was again desorbed after each analysis. No carryover was observed, demonstrating that 5 min were enough for complete desorption of the compounds from the stationary phase.

Sample Agitation

The extraction efficiency was enhanced when stirring rate was increased from 0 rpm to 800 rpm except for styrene (Fig.6). For toluene, the increase of extraction efficiency was not observed after the stirring rate reached 800 rpm, and the extraction efficiencies for ethylbenzene, iso-propylbenzene and *n*-propylbenzene also increased slowly at the same time. The extraction efficiency for styrene was slightly reduced with stirring, this may be due to the stirring speed causing the transfer of styrene from water to headspace faster than that of the mass transfer from headspace to fiber coating, and thus a stirring speed increase does not improve the HS-SPME kinetics for the analyte. Competition among the different analytes for fiber absorption during stirring may also cause the decrease in extraction efficiency for styrene. Based on these results, the stirring speed of 800 rpm was selected for further experiments.

Addition of Salt

The influence of salt addition in HS-SPME procedure was investigated by comparing the extraction efficiency of samples with addition of 30% KCl and without addition of KCl. The addition of 30% KCl yielded a saturated solution and this resulted in increased in the peak area of the analytes, from 6% (iso-Propylbenzene) to 41% (styrene) enhancement (Fig.7). The reason was considered to be the increase of ionic strength in aqueous samples by adding salt, and the decrease in solubility of analytes and therefore, more analyte was released into the headspace. Thus, saturation with salt additives was shown to be an effective method to lower the LOQ, and it could also normalize the influence of a random salt concentration in sample matrix to improve reproducibility.

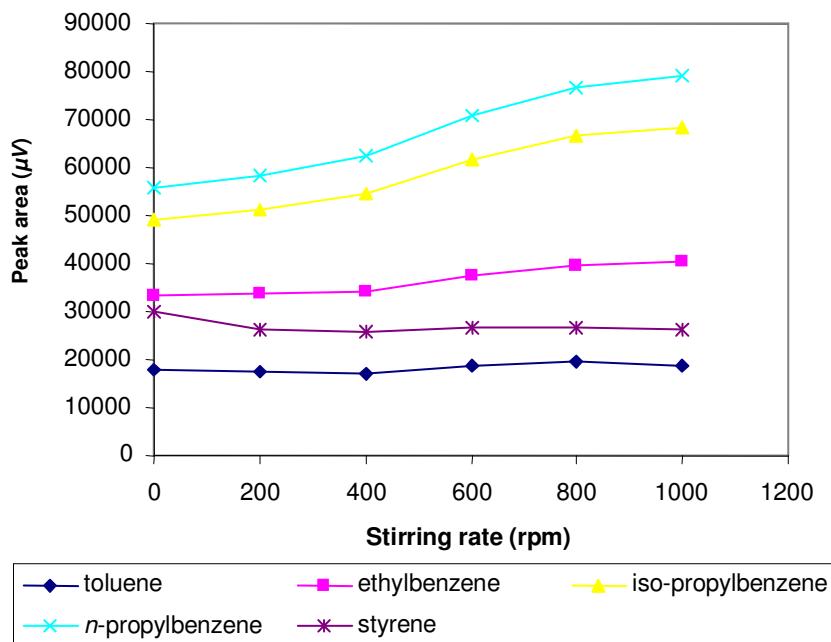


Fig. 6: Effect of sample agitation rate on the extraction efficiency of analyte.

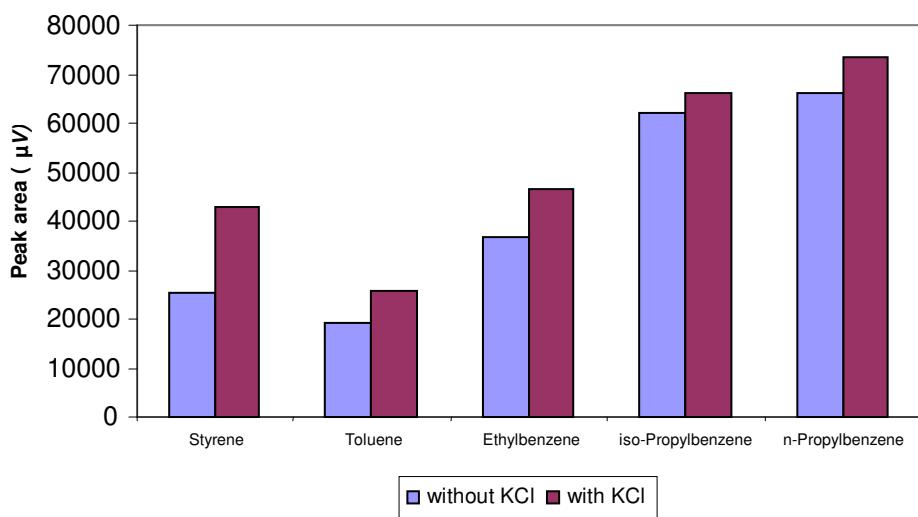


Fig. 7: Salting out effect on the five analytes

Performance of The Method

The method was validated in terms of LOD, LOQ, linearity, precision and accuracy by using the experimental setting providing the optimized conditions. A blank sample was prepared using purified deionized water. Calibration curve was prepared by spiking blank sample with different level of standard mixtures. Using the chosen HS-SPME conditions for water sample spiked with standard mixture at different levels, the performance characteristics of the method were evaluated for each analyte using the developed method and the results are summarized in Table 1.

Table 1: Summary of method validation results

Performance parameters	Method	Performance characteristic				
		Styrene	Toluene	Ethylbenzene	IPB	NPB
LOD (ng/mL)	N/S =3	0.58	2.66	0.78	0.40	0.28
LOQ (ng/mL)	N/S = 5	0.97	4.43	1.63	0.67	0.47
Linearity range (ng/mL)		1 - 20	4.5 – 90	1.5 - 30	0.5 - 10	0.5 – 10
Precision (%RSD)	Intraday repeatability	1.72 -2.98	0.77 – 4.51	3.53 – 7.65	0.55 – 6.09	0.23 – 4.83
	Interday repeatability	3.55 – 16.98	3.83 – 10.30	4.48 – 10.25	3.97 – 13.13	3.04 – 8.01
% Recovery	Spiked sample	1ppb – 74 5 ppb – 115 15 ppb - 100	4.5ppb -78 22.5 ppb – 116 67.5 ppb – 102	1.5ppb – 61 15 ppb – 101 30 ppb - 89	0.5ppb – 62 5 ppb – 105 10 ppb - 84	0.5ppb – 71 2.5 ppb – 107 7.5 ppb - 100

Application of The Method

The applicability of the validated method for the determination of VOCs in PS food packaging samples was demonstrated (Fig. 8 & 9). The analyte peaks were sharp, well resolved and the analysis was about 12 min.

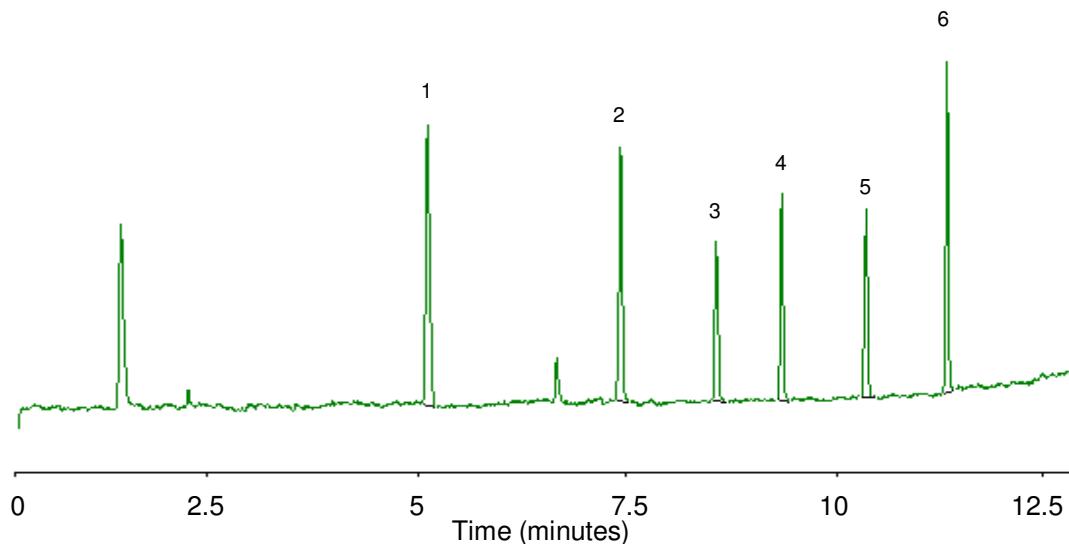


Fig. 8: GC chromatogram of analyte mixture using HS-SPME method. Peak: 1 = Toluene (45 ppb); 2 = ethylbenzene (15 ppb); 3 = iso-propylbenzene (5 ppb); 4 = *n*-propylbenzene (5 ppb); 5 = styrene (10 ppb); and 6 = 1,4-diethylbezene (ISTD, 5 ppb)

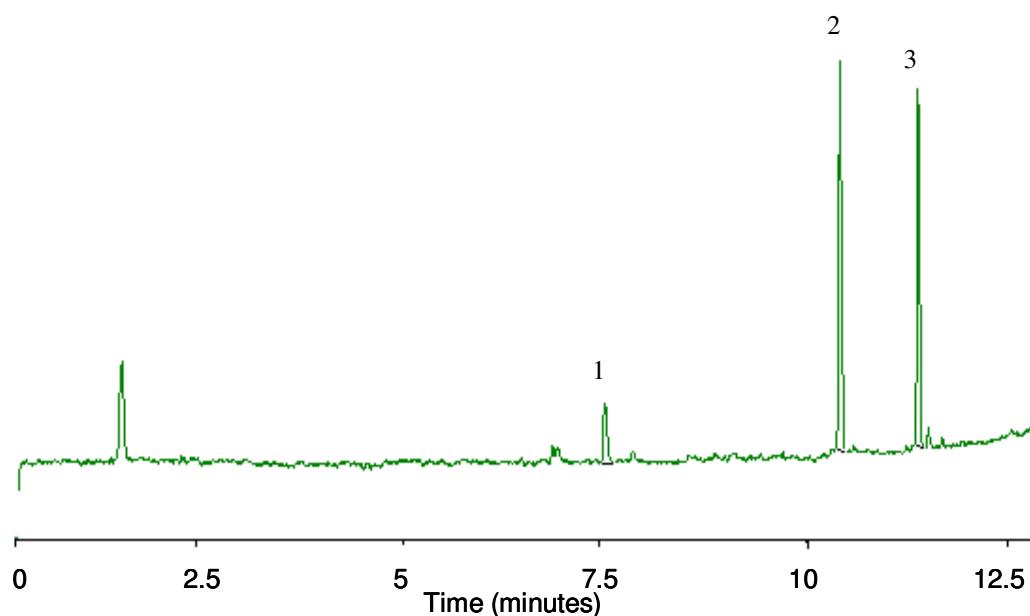


Fig. 9: GC chromatogram showing the analytes migrated from a polystyrene cup. Peaks: 1 = ethylbenzene; 2 = styrene; and 3 = 1,4-diethylbenzene (ISTD)

Three types of commercial available disposable polystyrene cup and bowl were purchased for analysis and data obtained are reported in Table 2. Prior to performing the migration test, the levels of residual VOCs in packaging materials were determined using the material test method developed. The concentrations were calculated by interpolation of the total area values obtained for the samples in the linear graphs obtained for standards in aqueous solution. Toluene, iso-propylbenzene and *n*-propylbenzene were not detected in the selected samples under the studied conditions.

Table 2: Mean concentration of analytes migrated from samples into water solution.

Sample type/capacity (material test results, mg/kg)	Leaching solution	Leaching condition	Mean analyte conc. (ng/mL)	
			Styrene	Ethylbenzene
PS bowl /500mL (Styrene: 657, Ethylbenzene: 134)	Water (80°C)	80°C/30 min	86	ND
		24°C/30 min	50	ND
	Water (60°C)	60°C/30 min	<LOQ	ND
		24°C/30 min	ND	ND
	Water (24°C)	24°C/30 min	ND	ND
PS bowl /400 mL (Styrene: 250, Ethylbenzene: 32)	Water (80°C)	80°C/30 min	97	<LOQ
		24°C/30 min	45	ND
	Water (60°C)	60°C/30 min	<LOQ	ND
		24°C/30 min	ND	ND
	Water (24°C)	24°C/30 min	ND	ND
PS cup /200 mL (Styrene :593, Ethylbenzene: 243)	Water (80°C)	80°C/30 min	293	64
		24°C/30 min	224	50
	Water (60°C)	60°C/30 min	126	<LOQ
		24°C/30 min	48	ND
	Water (24°C)	24°C/30 min	<LOQ	ND

ND – not detected

As shown in Table 2, styrene and ethylbenzene were detected and quantitated at different concentration levels depending on the types of samples and leaching conditions. Styrene and ethylbenzene were below LOQ levels by using leaching solution of room temperature (24°C). When the samples were in contact with water of higher temperature (60°C), styrene (126 ng/mL and 48 ng/mL) was detected in the leaching solution of polystyrene cup samples, and all the samples detected with styrene in leaching solution of highest temperature (80°C). Ethylbenzene was below LOQ levels for samples that were exposed to leaching solution of 60°C and 80°C, except for polystyrene cup in which ethylbenzene at the levels of 64 ng/mL and 50 ng/mL was detected at the two different leaching conditions. This shows that migration of analytes increased when leaching solution of higher temperature was used. The results also showed that the amount of analytes migrated were increased when the temperature of the leaching solution was kept constant in comparison with the leaching condition of room temperature for 30 min. This could be due to the migration of analytes was slow down as the leaching solution began to cool down at room temperature condition.

Even though the number of samples considered does not make possible a definitive conclusion, this behavior could be ascribed to the temperature effect of the migration. Under higher temperature, the analyte, being extremely volatile can be more easily released from the matrix. Based on the results obtained for the samples of different capacities, higher levels of styrene were generally found for container of small size (polystyrene cup, capacity of 200 mL), this is in good agreement with the findings reported by MAFF, 1999, in which higher levels of styrene were found in food products packed in small containers.

Conclusions

Haedspace-solid phase microextraction (HS-SPME) is very effective as a sample preparation technique for studying the migration of VOCs from polystyrene packaging material. SPME provides simple, rapid and solvent-free technique, and offers a dramatic sensitivity enhancement as compared to the conventional sample preparation techniques. The optimized HS-SPME procedure can be proposed as a fast monitoring method for the analysis of migration of VOCs from polystyrene and other food packaging material.

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