DETERMINATION OF VOLATILE ORGANIC COMPOUNDS IN MATERIALS FROM POLYSTYRENE INTENDED FOR CONTACT WITH FOOD: COMPARISON OF HS-GC/MS AND SPME-GC/MS TECHNIQUES

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ABSTRACT

Background. Plastic materials intended for contact with food sometimes exhibit unfavorable organoleptic properties which is related to the presence of volatile organic compounds. These substances not only worsen organoleptic properties, but can be very harmful to humans health. For the sake of consumer safety, it is necessary to control such materials for the content of substances harmful to health, as well as the possibility of their migration to food. Therefore, there is a need to have an appropriate and verified analytical method that could be used in the routine analysis of volatile organic substances present in food contact materials.

Objective. In this study, the possibilities of the application of HS-GC/MS and SPME-GC/MS analytical techniques for analyses of volatile organic compounds present in polystyrene food contact materials, demonstrating disadvantageous organoleptic properties were evaluated.

Materials and methods. On the basis of sensory tests four types of food contact materials (plastic dishes) were selected for the study. The analytical measurement was performed by HS-GC/MS and SPME-GC/MS techniques parallel.

Results. In quality examinations of samples the aliphatic and aromatic, saturated and unsaturated hydrocarbons, as well as other compounds, e.g. ketones contamination was estimated. For all the samples a quantitative analysis of the content of styrene, ethylbenzene and cyclohexane was carried out. Additionally, the optimization of SPME analysis parameters was carried out. It was assumed that the optimal SPME extraction conditions for this purposes are: extraction time of 15 - 30 min, extraction temperature of 80°C, CAR/PDMS fibre.

Conclusions. The results of this study indicated that from two chosen analytical methods, definitely HS-GC/MS technique was more universal, as well as more comfortable and faster. Sometimes, however additional studies should be undertaken and then it is recommended to use the SPME-GC/MS technique optimized for our purposes.

Key words: *materials intended for contact with food, gas chromatography, mass spectrometry, SPME*

STRESZCZENIE

Wprowadzenie. Opakowania i materiały z tworzyw sztucznych przeznaczone do kontaktu z żywnością niekiedy wykazują niekorzystne właściwości organoleptyczne. Jest to związane z obecnością lotnych związków organicznych. Substancje te nie tylko pogarszają właściwości organoleptyczne, ale mogą być bardzo szkodliwe dla zdrowia człowieka. Ze względu na bezpieczeństwo zdrowotne konsumenta konieczna jest kontrola takich materiałów pod kątem zawartości substancji szkodliwych dla zdrowia, a także możliwości ich migracji z wyrobu do żywności. Istnieje zatem potrzeba dysponowania odpowiednią, sprawdzoną metodą analityczną, która mogłaby być zastosowana w rutynowej analizie lotnych substancji organicznych obecnych w materiałach do kontaktu z żywnością.

Cel badań. W niniejszej pracy podjęto się oceny możliwości zastosowania technik HS-GC/MS i SPME-GC/MS do badania lotnych związków organicznych zawartych w wyrobach przeznaczonych do kontaktu z żywnością wykonanych z polistyrenu, a wykazujących niekorzystne właściwości organoleptyczne.

Materiał i metody. Na podstawie analizy sensorycznej wytypowano do badań cztery rodzaje wyrobów (naczyń z tworzyw sztucznych) przeznaczonych do kontaktu z żywnością. Badania prowadzono równolegle przy zastosowaniu dwóch technik analitycznych, a mianowicie HS-GC/MS i SPME-GC/MS.

Wyniki. W badaniach jakościowych stwierdzono zanieczyszczenie próbek nasyconymi i nienasyconymi węglowodorami alifatycznymi, węglowodorami aromatycznymi, a także innymi jeszcze związkami organicznymi, takimi jak np. ketony. Dla wszystkich próbek wykonano analizę ilościową zawartości styrenu, etylobenzenu i cykloheksanu w oparciu o zmierzone

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krzywe kalibracyjne. Ponadto przeprowadzono optymalizację parametrów analizy techniką SPME i na tej podstawie stwierdzono, że ekstrakcję SPME należy prowadzić przez 15 do 30 min. w temperaturze 80°C stosując włókno CAR/PDMS.

Wnioski. Na podstawie przeprowadzonych badań wykazano, że z pośród dwóch wybranych metod analitycznych, zdecydowanie bardziej uniwersalna, a także wygodniejsza w użyciu i szybsza jest technika ze statyczną analizą fazy nadpowierzchniowej, HS-GC/MS. Niekiedy jednak może zajść konieczność przeprowadzenia dodatkowych badań i wtedy warto sięgnąć po zoptymalizowaną dla naszych celów technikę SPME-GC/MS.

Słowa kluczowe: *materiały do kontaktu z żywnością, chromatografia gazowa, spektrometria mas, SPME*

INTRODUCTION

Materials which are intended to be in contact with food are all materials and articles that come into contact with food products, namely packaging, containers, kitchen equipment, dishes and cutlery. For the sake of consumer safety, it is necessary to control such materials for the content of harmful and toxic substances, as well as the possibility of their migration from material to food. Most often the test is subjected to the packaging material itself, not the food or food simulants [12, 15]. Plastic materials intended to be in contact with food, in addition, sometimes exhibit unfavorable organoleptic properties. It is related to the presence of volatile organic compounds [13]. These substances not only worsen organoleptic properties, but can be very harmful to humans. Their source in the materials and articles can be printed ink, but they can also be a residue after the production process of packaging material (monomers, plasticizers and others) [10]. An example of residual monomer contaminating packaging is styrene [8], classified as harmful, irritating to eyes, respiratory system and skin, and can cause lung damage if ingested and posing a serious risk to human health as a result of prolonged exposure [9]. Therefore, prior to the material being released for use, its sensory control and the identification of volatile substances potentially posing a risk to the consumer are extremely important.

The determination of volatile substances present in food contact material is currently conducted primarily based on gas chromatography (GC) [12], using different detection techniques. Furthermore, various techniques at the stage of taking volatile compounds from the tested material can be used. The most frequently chosen detection techniques are mass spectrometry (MS) [10, 12, 13] and flame ionization detection (FID) [14]. At the stage of taking volatile organic substances contained in the material, techniques such as static headspace (HS) analysis [1, 7], direct injection of water sample (DAI) [18], inside needle capillary adsorption trap (INCAT) [19], microextraction to the solid phase (SPME) [11, 17], and particularly, microextraction to the solid phase from the headspace (HS-SPME) [2, 10, 13], including multiple HS-SPME [4, 5] are used. The HS-SPME technique (hereafter referred to as SPME) consists of adsorption on a quartz fiber (covered with a suitable sorption material) of volatile substances in the gas phase above the surface of the sample, which are then desorbed under the influence of high temperature directly into the gas chromatograph injector.

The aim of the study was to compare two analytical techniques, HS-GC/MS and SPME-GC/MS, in terms of their suitability for testing volatile organic compounds contained in polystyrene packaging, exhibiting unfavorable organoleptic properties. The results obtained were used to determine the optimal analytical conditions for volatile compounds found in packaging and packaging materials intended for contact with food.

MATERIAL AND METHODS

Samples for testing

Four types of packaging materials (plastic dishes) for contact with food, available on the domestic market, were selected for the study. The selection was made on the basis of sensory tests. All selected samples showed a distinct chemical odor. The test samples were finely chopped and then 2 g of the sample (with accuracy 0.1 mg) were placed into 20 ml vial and immediately sealed with the teflon-lined/silicone septum crimp cap. The samples thus prepared were directly subjected to HS-GC/MS measurements (the samples were thermostated in the headspace sampler oven for 1 hour at 80°C) or conditioned for 1 hour at 80°C in the heating block and then subjected to SPME extraction.

Calibration reagents and solutions

This work uses commercially available reagents of analytical purity. All standard solutions used to measure of the calibration curves were prepared in methanol.

Calibration curve of styrene and ethylbenzene for HS-GC/MS measurements

To prepare the calibration curves (Figure 1, above), standard solutions of styrene and ethylbenzene with concentrations of 304 and 336 mg/l respectively, were used. After mixing in appropriate proportions and dilution, intermediate solutions of: 20, 40, 79, 149, 249 mg/l of styrene and 4, 8, 16, 30, 50 mg/l of ethylbenzene were obtained. After injection of 150 μl into the sealed 20 ml vials, points of calibration curves were obtained with the amount of styrene and ethylbenzene in the vial: 3, 6, 12, 22.5, 37.5 μg and 0.6, 1.2, 2.4, 4.5, 7.5 μg.
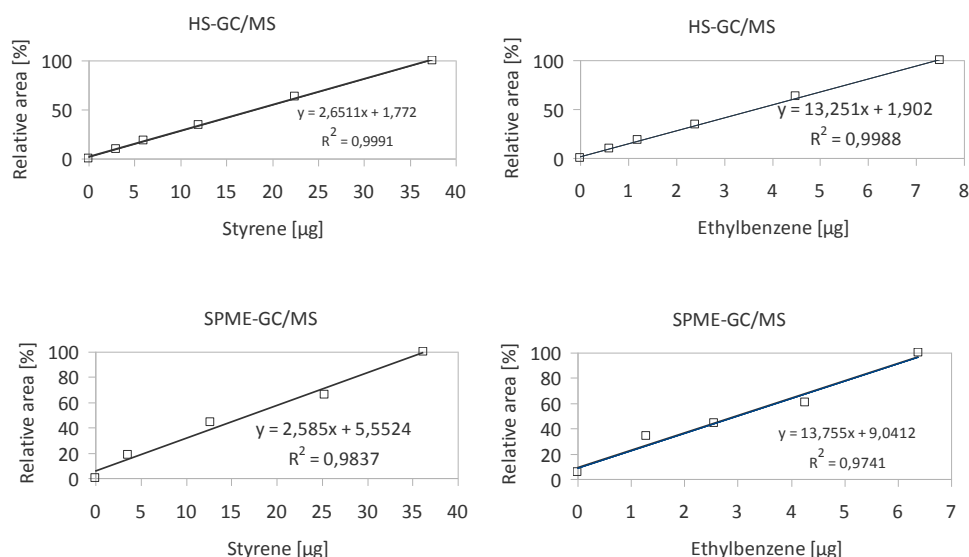
Figure 1. Calibration curves obtained for styrene and ethylbenzene in the HS-GC/MS (top) and SPME-GC/MS (bottom) measurements

Calibration curve of styrene and ethylbenzene for SPME-GC/MS measurements

For SPME measurements, more concentrated solutions were used for preparation of the calibration curves to avoid methanol displacement of reference substances from the microfilter fiber. Standard solutions of styrene and ethylbenzene at concentrations of 9050 and 4260 mg/l were used. After mixing in appropriate proportions and dilution, intermediate solutions with concentrations: 362, 1267, 2534, 3620 mg/l of styrene and 128, 256, 426, 639 mg/l of ethylbenzene were obtained. After injection of 10 μl into the sealed vials (20 ml capacity), the calibration solutions with the amount of styrene and ethylbenzene in the vial, respectively: 3.6, 12.7, 25.3, 36.2 μg and 1.3, 2.6, 4.3, 6.4 μg were finally prepared. In the case of styrene, a calibration curve was obtained with a regression coefficient of 0.9837 and for ethylbenzene of 0.9741 (Figure 1, bottom). These was satisfying result for as a rule, the SPME technique gives less repeatable results due to the additional variable, which is the process of fiber adsorption and fiber desorption in the apparatus.

SPME fibers

The SPME holder for manual sampling and fibers used were purchased from Supelco. Three different fibers were tested for our purpose: polydimethylsiloxane (PDMS; red fiber), polydimethylsiloxane/divinylbenzene (PDMS/DVB; blue fiber) and carbowax/divinylbenzene (CAR/PDMS; black fiber). All the fibers were preconditioned in the hot injector of the gas chromatograph according to supplier's manual.

Apparatus and measurement conditions

HS-GC/MS technique. Samples prepared in the test vials were placed directly into the Headspace and subjected to GC/MS analysis. Agilent Technologies 6890N gas chromatograph with MS 5973 detector and Headspace Sampler G1888 were used for analysis. Agilent Technologies HP-Plot/q capillary column (30 m, 0.32 mm, 20 μm) was used to separate the compounds. The conditions for chromatographic analysis are given in Table 1. Mass spectra were recorded in the mass range m/z = 30 - 300 Da. The measurement was carried out each time in SCAN mode. The identification of compounds was performed by comparing the recorded mass spectra with the standard mass spectral libraries - Wiley7n.1 or by comparison with the reference substance.

Table 1. Conditions of chromatographic analysis

	HS-GC/MS	SPME-GC/MS	
		Method I	Method II
headspace oven	80ºC, 1 hour	-	-
injector/detector temperature	240°C	240°C	240°C
carrier gas	helium	helium	helium
carrier gas flow	0.8 ml/min.	0.95 ml/min	0.95 ml/min
oven temperature	110-220°C (3°C/min), 220°C (17 min)	50°C (5 min), 50-250°C (8°C/min), 250°C (5 min)	50°C (5 min), 50-150°C (3°C/min), 150-250°C (8°C/min), 250°C (5 min)

SPME-GC/MS technique. The SPME-GC/MS analysis was carried out using a Hewlett Packard 5890 Series II gas chromatograph with an MS 5972 detector equipped with an HP-FFAP Agilent Technologies capillary column (30 m, 0.25 mm, 0.25 μm). The conditions of the chromatographic analysis are shown in Table 1. The mass spectra were recorded in the mass range m/z = 50 - 250 Da. The measurement was carried out each time in SCAN mode. Two similar measurement methods were used (Table 1). Method I was used for qualitative analysis and was longer (55 min) than method II (35 min) used in the quantitative analysis. The identification of compounds was performed by comparing the registered mass spectra with the standard mass spectrum library - Wiley 138.l or by comparison with the reference substance.

RESULTS

Studies using the HS-GC/MS technique

Qualitative analysis. In the first stage of the HS-GC/MS investigation a qualitative analysis of the available samples was performed. The obtained total ion current (TIC) chromatograms were analyzed based on the mass spectral basis. Figure 2a is an exemplary chromatogram obtained by the HS-GC/MS technique for a PS1 sample. Dominant peak with retention time 42.3 min comes from styrene - residual monomer. The next largest peaks are derived from ethylbenzene (retention time, RT = 40.2 min) and cyclohexane (RT = 24.2 min). In addition, PS1 samples were found to contain various aromatic hydrocarbons, such as toluene, dimethylbenzene isomers and (1-methylpropyl)benzene.
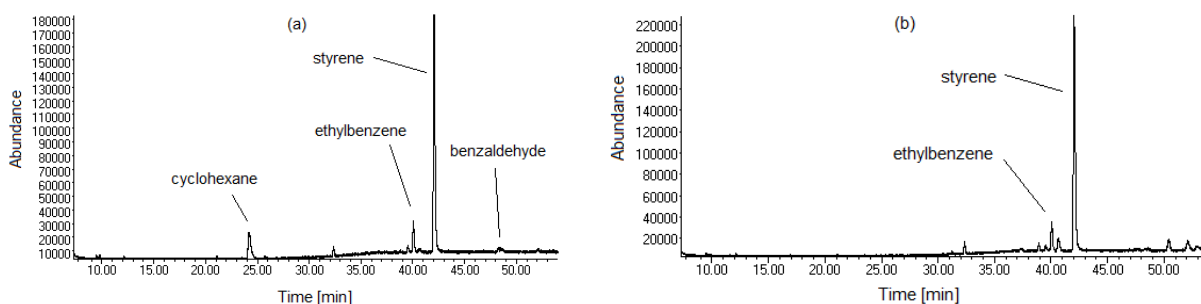

Figure 2. Total ion chromatograms (TIC) registered by HS-GC/MS: (a) PS1 sample, (b) PS4 sample.

A very similar result was obtained in the GC/MS measurement of the PS2 sample. The differences between the PS1 and PS2 dishes were rather quantitative than qualitative. The presence of styrene and ethylbenzene was also demonstrated for other packaging materials, namely PS3 and PS4. In PS2 - PS4 samples, as in the case of PS1 samples, other aromatic hydrocarbons such as toluene, dimethylbenzene isomers and (1-methylpropyl) benzene were found. Cyclohexane was found only in PS1 and PS2 samples. Figure 2b shows a chromatogram of the PS4 sample with clear peaks from ethylbenzene and styrene, but no cyclohexane signal.

The contamination of the packaging materials with residual styrene monomer, ethylbenzene, cyclohexane and benzaldehyde was confirmed in the measurement of standard substances (retention times: styrene, 42.28 min, ethylbenzene, 40.17, cyclohexane, 24.23, benzaldehyde, 47.02 min).

Quantitative analysis. Quantitative studies of volatile impurities of selected dishes included determination of styrene, ethylbenzene and cyclohexane content. It was found that the content of the styrene monomer was the highest in PS4 samples, slightly smaller in PS3 and PS1 samples (see Table 2). The content of ethylbenzene was the highest for PS3 samples, while cyclohexane was detected only in PS1 and PS2 samples in amount of only about 0.1 - 0.2 mg/kg (Table 2).

Table 2. List of the results of quantitative analysis of styrene, ethylbenzene and cyclohexane content in the tested dishes, expressed in mg of the substance determined per kg of the tested sample, obtained by the HS-GC/MS technique

	Sample (*)	PS1 (10)	PS2 (8)	PS3 (5)	PS4 (10)
		mg/kg			
styrene	mean	10.8	10.3	14.3	15.7
	RSD%	6	5	12	6
ethylbenzene	mean	1.2	3.1	5.9	1.8
	RSD%	5	8	14	11
cyclohexane	mean	0.2	0.1		
	RSD%	17	15		

* The number in parenthesis represents the total number of samples tested.

Studies using the SPME-GC/MS technique

Optimization of the solid-phase microextraction (SPME) process. The SPME method optimization parameters include type of fiber, extraction time and extraction temperature. The optimization of SPME analysis parameters was carried out for PS1 samples, and the selected extraction conditions were then applied in the analysis of all tested products.

First task was the fiber selection. For our research purposes, three fibers were chosen, each of which could potentially be used for extraction of volatile organic compounds, namely: PDMS, PDMS/DVB, and CAR/PDMS [16]. Based on our research, we have determined that the most efficient in the headspace analysis of polystyrene packaging is CAR/PDMS fiber, as illustrated in Figure 3, showing the intensity of the SPME-GC/MS peak obtained using different fibers.
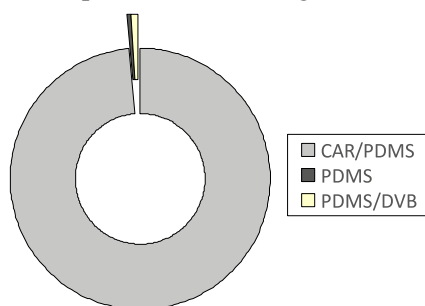

Figure 3. Results of SPME-GC/MS analysis of SP1 samples: dependence of the peak area of styrene on the type of fiber used. Extraction temperature and extraction time: 80°C, 15 min.

Due to the obtained results, further optimization of the SPME process was carried out by the use of the SPME fiber with CAR/PDMS coating. Using our previous work and literature data [3, 6, 9, 14] we selected two extraction temperatures: 60°C and 80°C. It is known that the increase in temperature causes an increase in the extraction rate due to the increase of the diffusion rate of molecules towards the fiber, at the same time worsening the partition coefficients, as the adsorption is a strongly exothermic process [3, 6]. Additionally, the increase in the temperature can lead to the decomposition of unstable substances. Finally, based on the measurements made (Figure 4), the extraction temperature of 80°C was selected for further testing.
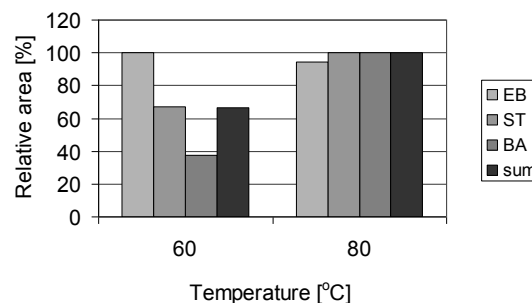

Figure 4. Results of SPME-GC/MS analysis of SP1 samples: dependence of the peak area of styrene (ST), ethylbenzene (EB) and benzaldehyde (BA) on the extraction temperature. Fiber and extraction time: CAR/PDMS, 15 min.

The final step in the process of SPME optimization was the selection of the appropriate time for extraction of volatile substances from the headspace of the samples. All measurements were performed using CAR/PDMS fiber and an extraction temperature of 80°C. Various publications on the applications of SPME technique addressing the optimization of the extraction time usually take into account time from 15 to 60 minutes, although it may also be encountered with the extraction lasting even above 2 hours [4, 10, 13]. In this work the extraction time from 5 to 120 minutes was used. The results of the measurements performed are shown in Figure 5. It was found that the maximum absorption in most cases is obtained already after 15 minutes and this extraction time was used in all quantitative determinations. In qualitative studies, the extraction time was extended to 30 minutes.
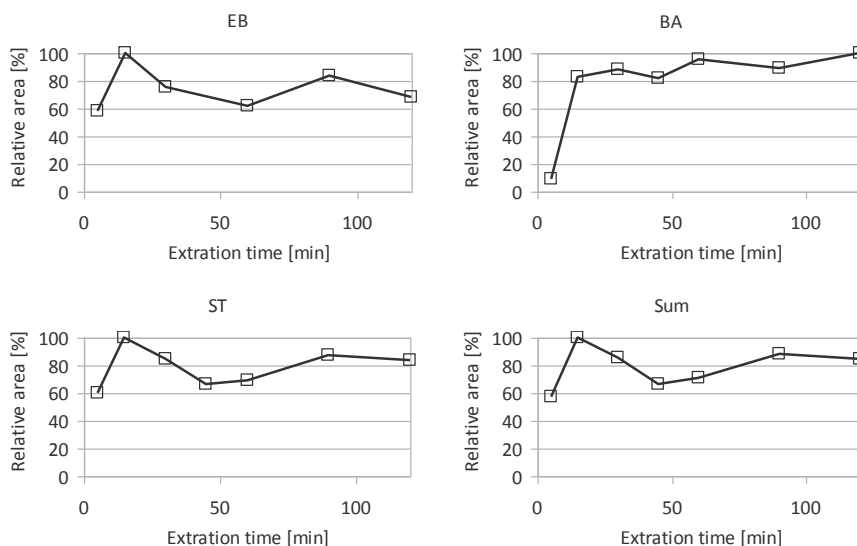

Figure 5. Results of SPME-GC/MS analysis of SP1 samples: dependence of the peak area of ethylbenzene (EB), benzaldehyde (BA) and styrene (ST) on the extraction time. Fiber and extraction temperature: CAR/PDMS, 80°C.

Qualitative analysis. All analyzed packaging materials were subjected to SPME extraction under optimized conditions, i.e. 30 minutes at 80°C. The measurements were made using method I (Table 1). The presence of residual styrene, ethylbenzene and benzaldehyde was found in the dishes (Figure 6), while in none of the samples tested was observed the presence of cyclohexane (RT = 2.88 min), which gave a clear peak when analyzed by the HS-GC/MS technique. The presence of benzaldehyde (RT = 21.95 min), styrene (RT = 11.04 min) and ethylbenzene (RT = 6.68 min) in the packaging materials was confirmed by chromatography of the standard samples. In addition, in PS1 - PS4 samples, we have detected less volatile aromatic hydrocarbons and their derivatives such as naphthalene, methylnaphthalene, acetophenone, and benzoic acid.
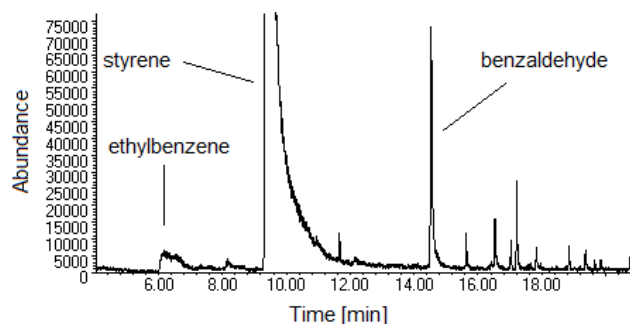

Figure 6. A fragment of the SPME-GC/MS total ion chromatogram (TIC) of a PS1 sample. Extraction temperature and extraction time: 80°C, 15 min.

Table 3. Comparison of the results of quantitative analysis of the styrene and ethylbenzene content in the tested dishes expressed in mg of the substance determined per kg of the tested sample, obtained by the SPME-GC/MS technique

	Sample (*)	PS1 (5)	PS2 (6)	PS3 (5)	PS4 (5)
		mg/kg			
styrene	mean	12.9	13.2	11.3	7.9
	RSD%	4	5	8	9
ethylbenzene	mean	0.6	1.2	5.1	
	RSD%	20	15	11	

* The number in parenthesis represents the total number of samples tested

Quantitative analysis. Based on the calibration curves obtained using the SPME-GC/MS technique, quantitative determinations of styrene and ethylbenzene content were carried out. Analysis showed a similar amount of styrene in PS1 - PS3 samples, with the observed styrene content in samples PS1 and PS2 being the same in the limit of measurement error (Table 3). Unlike HS-GC/MS measurements, this time a clearly smaller amount of residual monomer was determined in PS4 samples, however, this result is not entirely reliable, as the tailing part of the peak was not included in the quantitative analysis due to the overlap of other signals. The presence of ethylbenzene was found in three dishes: PS1 - PS3. In PS1 sample it was the smallest and in PS3 sample the largest (Table 3). In the PS4 samples, ethylbenzene, which was visible in the HS-GC/MS measurements, could not be determined. Presumably, a large amount of other volatiles competed with ethylbenzene at the fiber extraction stage and, as a result, ethylbenzene was not adsorbed.

DISCUSSION

This study compares the SPME-GC/MS and HS-GC/MS techniques with respect to their suitability for the analysis of volatile organic compounds in polystyrene packaging. The main difference between the analytical techniques chosen was the use of another method at the stage of collecting volatiles contained in the samples. Both in SPME-GC/MS and HS-GC/MS, substances were removed from the headspace of the sample, not using solvents for this purpose. In both cases, the sample was heated for 1 hour at 80°C, however, in the SPME technique, an additional step took place, which is the extraction on the capillary fiber.

This is obvious that the SPME extraction process can theoretically reduce or increase both the sensitivity and selectivity of the assay. For this reason, it is important to choose the SPME conditions, so that they are the most favorable for the assays of all compounds from the test group. In our case, the conditions of 30 min/80°C for the qualitative determinations were considered as optimal, whereas in the quantitative determinations of styrene and ethylbenzene, the extraction time of 15 minutes was sufficient. In the case of quality determinations, a slightly longer extraction time is indicated, since, as noted, for the determination of certain substances, such as benzaldehyde (Figure 5), it would be advisable to extend the extraction time even up to 1 hour.

When comparing the SPME-GC/MS and HS-GC/MS techniques, we also noticed, that the thresholds for individual analytes could be significantly different. The possibility of competition of certain substances at the fiber extraction stage, which may lead to erroneous

determinations, should be taken into account, as can be seen from the example of PS4 sample in which ethylbenzene was determined by the HS-GC/MS method only. Certain substances, due to the unfavorably selected SPME conditions, may not be observed at all, as was in the case of cyclohexane. On the other hand, however, less volatile substances are easier to determine using the SPME technique than the static headspace method. In PS1-PS4 dishes, less volatile aromatic hydrocarbons such as naphthalene and methylnaphthalene were detected by the SPME-GC/MS method and were not recorded in the HS-GC/MS measurements.

It remains to pay attention to the labor intensity of the SPME method with manual injection compared to the automated HS technique.

CONCLUSIONS

1. From the studies and the obtained results it could be concluded that two applied analytical methods, HS-GC/MS and SPME-GC/MS, are appropriate for the determination of volatile organic compounds present in polystyrene materials intended to come into contact with food. However, the HS-GC/MS technique is more convenient and faster in the quantitative routine analysis.

2. If the static headspace analysis will not give an explanation of unfavorable organoleptic properties, it is worth to use the alternative SPME-GC/MS technique. It was found out that the less volatile substances are easier to determine using the SPME-GC/MS method than the HS-GC/MS one.

3. Based on our research, CAR/PDMS fiber is the most efficient in the SPME analysis of polystyrene packaging. The extraction conditions of 30 min/80°C were considered as optimal but in some applications the extraction time can be reduced to 15 minutes.

Acknowledgements

Conflict of interest
The authors declare no conflict of interest.

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