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Determining leaching of bisphenol A from plastic containers by solid-phase microextraction and gas chromatography–mass spectrometry☆

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Abstract

This study evaluates solid-phase microextraction (SPME) coupled with gas chromatography–mass spectrometry (GC–MS) to determine trace levels of bisphenol A in water and leached from plastic containers. The extraction using headspace post-derivatization with bis(trimethylsilyl) trifluoroacetamide (BSTFA), containing 1% trimethylchlorosilane (TMCS) vapor, following SPME was compared with extraction without derivatization. The SPME experimental procedures to extract bisphenol A in water were optimized with a relatively polar polyacrylate (PA)-coated fiber, an extraction time of 50 min and desorption at 300 °C for 2 min. Headspace derivatization following SPME was performed using 7 μL of BSTFA with 1% TMCS at 65 °C for 30 s. The precision was 5.2% without derivatization and 9.0% headspace derivatization. The detection limit was determined to be at the ng/L level. When SPME was used following headspace derivatization, the detection limit was one order of magnitude better than that achieved without derivatization. The results of this study reveal the adequacy of SPME–GC–MS method for analyzing bisphenol A leached from plastic containers. The concentrations of bisphenol A leached from plastic containers into water ranged from 0.7 to 78.5 μg/L.

Keywords: Bisphenol A; Solid-phase microextraction; Plastic containers; GC–MS

1. Introduction

Bisphenol A, 4,4′-(1-methylethylidene) bisphenol or 2,2-(4,4-dihydroxydiphenyl) propane is used as stabilizing material or antioxidant for numerous types of plastics including polyvinyl chloride [1]. It is also used by manufacturers as an intermediate in producing epoxy resins, polycarbonate, flame retardants and other specialty products [2,3]. The final products include protective coating, powder paints, automotive lenses, protective window glassing, building materials, adhesives, compact disks, optical lenses, paper coating and products for encapsulating electrical and electronic parts. The amount of bisphenol A used increases with the production of plastics. It has been discharged directly or indirectly into the environment, contaminating the atmosphere, water and soil. It has also been shown that bisphenol A leached from lacquer-coated cans [4] and baby feeding bottles [5] due to the hydrolysis of the polymer during thermal treatment. Bisphenol A is slightly to moderately toxic and has a low potential for bioaccumulation in aquatic organisms. Bisphenol A, which is leached from polycarbonate flasks during autoclaving, has been demonstrated to exhibit estrogenic activity [6–8]. Most countries have classified it as an endocrine disrupter. Yasuhara et al. [9] examined the concentration of bisphenol A in the most polluted leachate, and found that it was lower than the reported toxic concentrations for invertebrates or fish. The leaching of bisphenol A is likely to become an important problem because much of it is produced and this compound is widely used. Therefore, a rapid, accurate and sensitive analytical method is acquired to identify and determine the amount of

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bisphenol A in water or the amount leached from various plastics.

Numerous methods have been developed to identify trace bisphenol A in various matrices, although they are based primarily on chromatographic methods, including gas chromatography (GC) and liquid chromatography (LC) [10–15]. Many species of plastic additives, such as phthalates, with the potential to interfere in the detection of bisphenol A may leach from the plastics to the water. A gas chromatography–mass spectrometry (GC–MS) method is typically applied because it has high selectivity and sensitivity, preventing such interference. However, the validity of an analytical sample for trace bisphenol A analysis depends on suitable sampling and preconcentration. Earlier investigations have set forth various means of extracting bisphenol A from water, including liquid–liquid extraction [16,17] and solid-phase extraction [18–20] with reversed-phase materials. Conventional extraction methods, while efficient and precise, are relatively time-consuming, hazardous to human health since they use organic solvents, and extremely expensive because of the disposal of solvents. Hence, a relatively simple, rapid and solvent-free extraction method must be developed. Solid-phase microextraction (SPME) can solve many of the above problems. Zhang et al. detailed the underlying principles and merits of trace organic analysis and applying SPME to extract trace organic compounds from a complex matrix [21]. Some of the applications of SPME in environmental trace analysis have been evaluated in our laboratory [22–24].

Gas chromatographic analysis reveals that low-volatility polar compounds such as phenolic and acidic compounds exhibit low sensitivity and tailing. Derivatization methods have been extensively applied to improve various gas chromatographic parameters including accuracy, reproducibility, sensitivity and resolution, by suppressing tailing and enhancing thermal stability. The derivatization approaches such as methylation [25], acetylation [26–29] and silylation [20,30–34] have been used for analyzing trace bisphenol A. The goal of this work was to evaluate SPME coupled with GC–MS to determine trace levels of bisphenol A in water. In this study, bisphenol A adsorbed on the fiber coating of the SPME is derivatized after it is extracted from water with a mixture of bis(trimethylsilyl)trifluoroacetamide (BSTFA) and trimethylchlorosilane (TMCS) (99:1) vapor in a headspace device. The optimum conditions for extracting bisphenol A from water are also systematically studied. To confirm the proposed method's effectiveness, the optimized procedure combined with GC–MS to determine the amount of bisphenol A leached from plastic materials was performed.

2. Experimental

2.1. Reagents and materials

Bisphenol A (>99%) was purchased from Sigma–Aldrich Inc. (Milwaukee, WI, USA). Bis(trimethylsilyl)-trifluoroacetamide (BSTFA) that contained 1% trimethylchlorosilane (TMCS) were also obtained from Sigma–Aldrich Inc. Stock standard solution of bisphenol A was prepared at a concentration of 100 mg/L in acetone and diluted with water to yield the required concentration. The standard solutions were stored at 4 °C in a refrigerator. All chemicals and reagents used in this work were analytical or research grade without further purification. The purified water was obtained using an "Ultra Clear" purification system (SG Water, France). All glassware was silanized before it was used by soaking the glassware overnight in toluene solution with 10% dichlorodimethylsilane. The glassware was rinsed in toluene and methanol and then thoroughly dried for 4 h. The leached samples were collected from water at 100 °C in baby feeding bottles, and containers of polycarbonate and polyvinyl chloride.

2.2. Apparatus

Chromatographic analysis was undertaken on a Hewlett-Packard 5890 Series II gas chromatograph (Palo Alto, CA, USA) equipped with an MS Engine mass spectrometer and a split/splitless injection port. The column was a 30 m × 0.25 mm i.d. fused-silica capillary column DB-5MS and a stationary phase thickness of 0.5 μm (J&W Scientic, Folsom, CA, USA). Helium carrier gas was at a rate of 1 mL/min using an electronic pressure control. During fiber injection, the injector was used at 300 °C. The transfer line was held at 250 °C. The oven was initially set at 80 °C, for 2 min, a linear temperature gradient of 20 °C/min to 280 °C and held for 1 min.

Bisphenol A was quantified in the selected ion monitoring (SIM) mode, and its characteristic masses were selected from their full spectra. The ion, *m/z* 213 was selected for quantification, and that ion, *m/z* 228 was used as confirmed ion for bisphenol A analysis without derivatization. Following derivatization, the masses of the quantification and confirmed ions were changed to *m/z* 357 and *m/z* 372, respectively.

2.3. Sampling

SPME was performed using commercially available fibers and housed in the manual holder (Supelco, Bellefonte, PA, USA). The microextraction fibers tested herein were coated with poly(dimethylsiloxane) (PDMS) of 100 and 7 μm thickness; 85 μm thickness of polyacrylate (PA); 75 μm thickness of carboxen/poly(dimethylsiloxane) (CAR/PDMS); 65 μm thickness of polydimethylsiloxane/divinylbenzene (PDMS/DVB) and 65 μm thickness of carbowax/divinylbenzene (CW/DVB). All of them were purchased from Supelco. The fibers were conditioned before their first use according to the manufacturer's specifications. All analyses were undertaken using 40 mL sample vials that contained 30 mL of solution and closed using a PFTE-coated septum. During extraction, the aqueous samples were con-

tinuously agitated with a magnetic bar (0.8 cm × 2.0 cm) on a stir plate that resolved at about 1000 rpm.

After extraction equilibrium was reached, the fiber was transferred into the headspaced derivatization system. The derivatization system involves a 4.6 mL vial with a magnetic bar (0.95 cm × 0.48 cm) and a heating mantle. The vials were sealed with Teflon-backed silicone septum held by open screw caps. Briefly, 7 μL of BSTFA with 1% TMCS was placed in the vial and partially submerged in a water bath maintained at 65 °C with a heating mantle. The SPME needle pierced the septum and the fiber was exposed to the headspace, whereas the bisphenol A absorbed on the fiber was immediately derivatized with the BSTFA (1% TMCS) vapor arose from the bottom of the vial. After 30 s of derivatization, the SPME fiber was inserted into the GC injection port to perform thermal desorption.

The applicability of the method to real samples was tested by analyzing the leachate from the solution samples of the baby feeding bottle, PVC bottle and food platter. All the leachate samples were collected from the containers filled with 150 mL of 100 °C hot water. A 150 mL of boiling water (100 °C) was transferred into a commercially available bottle, which was tightly capped and kept in an oven at 95 °C for 30 min [35]. After it had been cooled to room temperature, a portion (30 mL) of the leachate was transferred into a 40-mL sample vial prior to extraction.

The recovery experiments were performed using spiked leachate samples from the baby feeding bottle, the PVC bottle and the food platter. The leachate samples were spiked with 30 μL of an aqueous solution of 10 μg/L bisphenol A. The samples were then mixed for 10 min, and made ready for sample extraction, as described above.

3. Results and discussion

3.1. GC–MS Analysis

A GC–MS technique with the highest possible sensitivity must be developed for monitor trace bisphenol A in water. The normal electron impact ionization (EI) mass spectrum of bisphenol A is characterized by molecular ion $[C_{15}H_{16}O_2]^{\bullet+}$ with *m/z* 228. The most abundant fragment ion has *m/z* 213, and is $[C_{14}H_{13}O_2]^+$, corresponding to the loss CH_3 from the molecular ion. Another major fragment ion at *m/z* 91 is present and may have come from $[C_7H_7]^+$ (Fig. 1a). The EI mass spectrum of the trimethylsilyl ether of bisphenol A with BSTFA contained 1% TMCS is very similar to that obtained without derivatization. Fig. 1b depicts the molecular ion, $[C_{21}H_{32}Si_2O_2]^+$, at *m/z* 372. The direct loss of CH_3 from the molecular ion (*m/z* 372) yields the most abundant ion with *m/z* 357, $[C_{20}H_{29}Si_2O_2]^+$. The relative abundances of other fragment ions are very small. In this study, ion $[M - CH_3]^+$ is always the most abundant fragment ion in the EI mass spectra of bisphenol A and bisphenol A–TMS derivative. The selected ion monitoring (SIM) mode of MS is normally chosen in quantitative trace analyses. The most abundant ion was generally monitored and quantified and the specific ion was used as the confirmed ion. Hence, the fragment ions $[M - CH_3]^+$ of bisphenol A (*m/z* 213) and TMS derivative (*m/z* 357) were adopted for quantification, and the molecular ions, $M^{\bullet+}$ of bisphenol A (*m/z* 228) and TMS derivative (*m/z* 372) were used as the confirming ions. The retention times of bisphenol A and TMS derivative were 10.31 and 10.44 min, respectively.

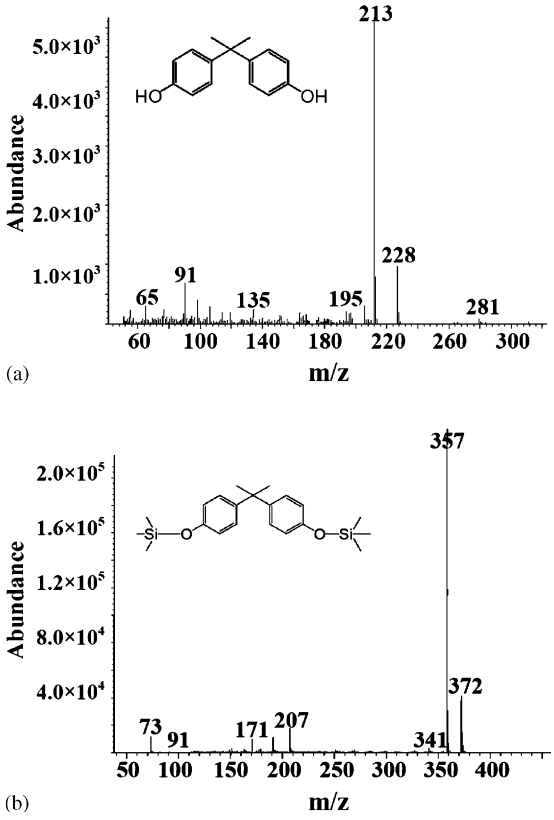

Fig. 1. Mass spectra of bisphenol A (a) and bisphenol A–TMS derivative (b) produced by EI.

3.2. Development of SPME

The extraction efficiency of the SPME experiment can widely vary due to matrix effects, the choice of absorbent, the absorption time, the desorption temperature and various other factors. Various coatings were tested under their optimum conditions. The results in Fig. 2 reveal that the 85 μm PA fiber was the most useful. This fact is related to the polarity of bisphenol A; PA has a moderate polarity between that of PDMS and that of CW-DVB; its polarity is similar to that of bisphenol A.

The amount of analytes extracted depends strongly on the mass transfer of analytes through the aqueous phase and the time of extraction. Extractions were performed from 10 to 60 min to determine the effect of extraction time. Fresh samples were used for each extraction time studied. The exposure time profiles were established by plotting the amount of

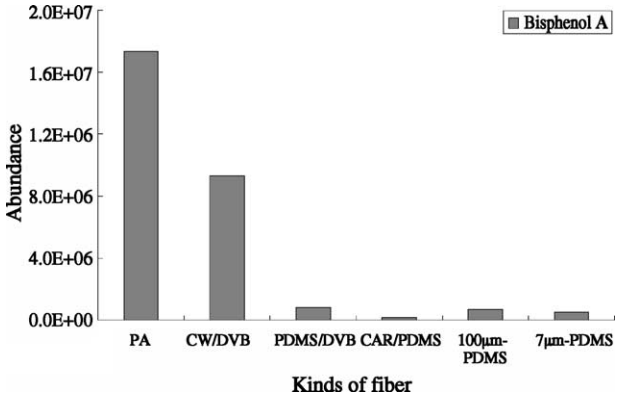

Fig. 2. Extraction efficiencies of 200 μg/L bisphenol A with various fiber coatings adsorption for 50 min.

eluted bisphenol A against the time for which the fiber was exposed to the samples. The bisphenol A reached equilibrium in over 50 min. Hence, bisphenol A was extracted from water samples using SPME at 50 min. The extraction temperature determines the mass transfer rate of bisphenol A from water into fiber. Extraction temperatures from 25 to 75 °C were investigated. The amount extracted increased with the extraction temperature, reaching a maximum at 55 °C, and then decreased as the temperature rose further. The extraction temperature was set at 55 °C in this test. Fig. 3 presents the effect of adding salt. Sodium chloride was added to the spiked water samples to yield final concentrations of the samples of 1.7, 2.9, 4.0, 5.1 and 6.3 M. A blank solution with no added sodium chloride was also tested. The amount extracted increased with the concentration of salt in water, which was related to the ionic strength of the solution and the equilibrium displacement of the fiber. The extraction was maximal at an added sodium chloride concentration of 4.0 M.

The pH effect was taken into account by altering the form of bisphenol A. The change in the pH from 3 to 11 was monitored to examine how pH influences the extraction of bisphenol A from water. The extraction did not change as the pH increased to pH 6, and then decreased as the solution became more basic. The maximum sorption was reached at

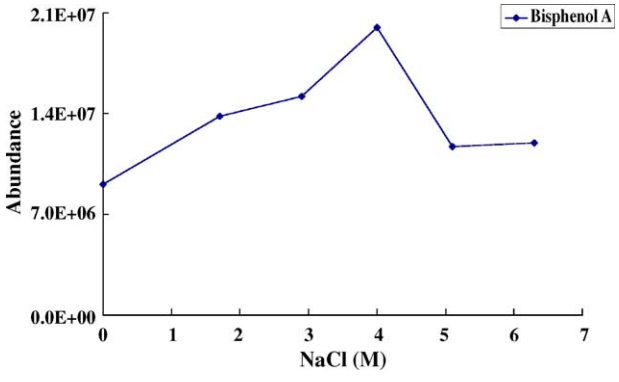

Fig. 3. Effect of addition of sodium chloride (M) on peak areas of 40 μg/L bisphenol A in water produced by using SPME–GC–MS.

almost neutral pH, so this nearly neutral pH supported the best bisphenol A analysis without the adjustment of any pH.

The desorption temperature, the desorption time and the depth of the fiber in the injector govern the quantity of bisphenol A desorbed from the fiber coating. The desorption temperature was monitored from 260 to 310 °C. The results indicate that the peak areas of bisphenol A increased with the temperature to a steady maximum at over 300 °C. In this case, the polyacrylate coating characteristics limited the temperature, which was fixed at 300 °C. The carryover or memory effect could detrimentally affect analytes with relatively high boiling points that are commonly encountered when the SPME method is used to analyze organic compounds. The fiber is again desorbed at 300 °C, after the initial desorption run was performed to determine whether bisphenol A remained on the fiber. No carryover was observed. Therefore, a desorption temperature of 300 °C was selected in the bisphenol A analysis. The amount of bisphenol A desorbed from the fiber depends not only on the desorption temperature but also on the desorption time and the depth of the fiber in the injector. The long desorption time will broaden the analyte peak and shorten the lifetime of the fiber. Desorption times in the range of 0.5–5 min were examined. The amount of bisphenol A desorbed increases with the desorption time to a maximum after 3 min. The studies also show that the amount of bisphenol A desorbed increased with the depth of the fiber in the injector port. Notably, in all subsequent experiments, the bisphenol A was desorbed at the maximum length (4.5 cm) of the syringe carriage in the injector for 3 mim. The extraction efficiency of the SPME procedure was investigated at a bisphenol A concentration of 40 μg/L. The extraction efficiency was determined by comparing the peak areas obtained of the extract from the spiked water sample with those obtained by directly injecting standard solutions. The extraction efficiency of bisphenol A was 13.8% when SPME–GC–MS was used. Low extraction efficiency was expected for bisphenol A because the analyte was partitioned between the small stationary phase of the SPME fiber and the sample water.

3.3. Post-derivatization of following SPME

Derivatization is a convenient means of improving chromatographic separation and increasing volatility and detector sensitivity, as well as selectivity. When bisphenol A was not derivatized, the tailing problem arose in the GC analysis (Fig. 4a). After the optimum conditions of SPME for bisphenol A in water had been studied, bisphenol A was derivatized as its trimethylsilyl (TMS) ether to increase its volatility and detector sensitivity. BSTFA with 1% TMCS was used to form the TMS ether. This study involved the post-derivatization of bisphenol A through the headspace on the fiber of SPME, following extraction using the vapor of the derivatization reagents. The results in Fig. 4b reveal that the peak shape and signal-to-noise ratio of bisphenol A is better than that obtained without derivatization. The sensitivity with post-derivatization is five times better than that

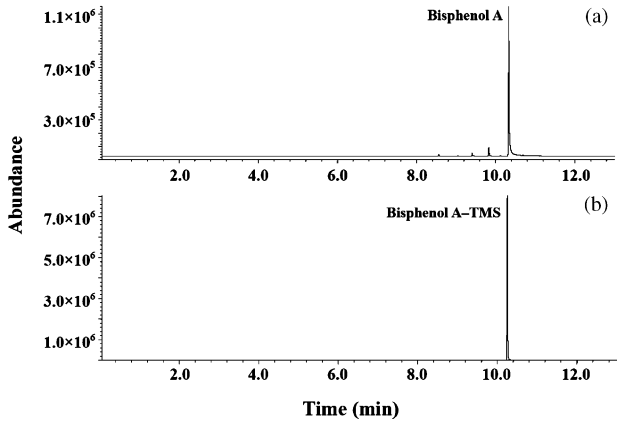

Fig. 4. (a) Mass ion chromatogram of 40 μg/L bisphenol A, (b) mass ion chromatogram of 40 μg/L bisphenol A–TMS derivative, produced by SPME–GC–MS.

without derivatization. The efficiency of derivatization depends on the derivatization time, the derivatization temperature and the amount of reagent used. The water samples were spiked with 40 μg/L bisphenol A standard solution to trace the derivatization efficiency.

In a water bath study at temperature from 45 °C to 85 °C, the derivatization was maximal at 65 °C. When the bath temperature exceeded 65 °C, the desorption of the adsorbed fiber reduced the overall extraction efficiency. The monitored derivatization time ranged from 15 to 80 s. The results indicated that the peak area of bisphenol A increased with the increasing time to a steady maximum after 30 s. Various volumes of derivatization reagent from 5 to 13 μL were used to explore the derivatization efficiency. The greatest derivatization was obtained with 7 μL of reagent. Herein, the post-derivatization of bisphenol A was performed following SPME by adding 7 μL bis(trimethylsilyl)trifluoroacetamide (BSTFA) that contained 1% trimethylchlorosilane (TMCS) at 65 °C for 30 s. After the study of the optimum desorption temperature had been completed, the temperature of the fiber in the GC injector was set to 300 °C for 3 min to prevent the carryover.

3.4. Precision and detection limits

The nine fibers consecutively extracted under optimum conditions were used to measure the precision of the SPME method. A 30 mL standard aqueous solution of 40 μg/L bisphenol A was used. The results in Table 1 show that the relative standard deviation (R.S.D.%) of bisphenol A and bisphenol A–TMS derivatives were below 5% (bisphenol A) and 9% (bisphenol A–TMS), respectively. Therefore, the precision of the SPME method was acceptable.

Table 1
Estimated limits of detection and precisions for SPME coupled with GC–MS for bisphenol A and trimethylsilyl (TMS) derivative

Compound	Relative coefficient	LOD (ng/L)	R.S.D. (%, $n = 9$)
Bisphenol A	0.9963	2	5.2
Bisphenol A–TMS	0.9981	0.4	9.0

The linear range experiments provide the necessary information to estimate the detection limits, based on the lowest detectable peak that has a signal-to-noise ratio of three. The peak areas were used for quantification through the calibration curves of bisphenol A and bisphenol A–TMS derivatives. The linearity was studied at bisphenol A concentrations from 0.01 μg/L to 200 μg/L for without derivatization. The correlation coefficient was 0.9963 (Table 1). In post-derivatization using BSTFA with 1% TMCS vapor following SPME, the linear ranges were monitored from 0.001 μg/L to 100 μg/L under optimum conditions. The linear correlation coefficient was 0.9981 (Table 1).

Table 1 compares the limits of detection (LOD) obtained for bisphenol A using post-derivatization with BSTFA contained 1% TMCS vapor following SPME, and that obtained without derivatization. The results obtained without derivatization reveal that the limit of detection can reach 2 ng/L, but the table indicates that the LOD obtained for bisphenol A in the derivatization is better than that achieved without derivatization. The LOD of this technique to determine bisphenol A in water by derivatization with BSFTA that contains 1% TMCS vapor following SPME can be reduced to 0.4 ng/L. The LOD of bisphenol A obtained in this study was better than that obtained using any of analytical methods reported elsewhere [28,29,31,33–35].

3.5. SPME–GC–MS of real-world samples

The applicability of the method to determine the trace amount of bisphenol A in real samples was tested by analyzing the leachate solution samples from the baby feeding bottle, the PVC bottle and the food platter. The food platter was made from melamine. All the leachate samples were collected from the containers that had been filled with 150 mL of 100 °C hot water. With and without post-derivatization by using BSTFA containing 1% TMCS vapor after SPME were operated at the optimum conditions studied herein. Triplicate analyses were undertaken. Fig. 5 displays the chromatograms of the leachate sample from a baby feeding bottle filled with 150 mL of hot water 100 °C. The results (Table 2) reveal that bisphenol A was present in all of the leachate samples.

The same results were obtained with and without derivatization following SPME; the concentrations of bisphenol A ranged from 1.4 to 78.0 μg/L and from 1.7 to 78.5 μg/L, respectively. The leachate samples spiked with 10 μg/L bisphenol A were used to investigate the recoveries obtained using this method to verify the precision and accuracy of the method. Recoveries in the range 100–110% were obtained for all samples. The results demonstrate the effectiveness of the SPME–GC–MS method for analyzing trace bisphenol A in fresh water and leachate supplies from plastic containers.

Table 2
Levels of bisphenol A leached from plastic materials

Real sample[a]	Bisphenol A (μg/L)	10 μg/L spiked	Recovery (%)	Bisphenol A-TMS (μg/L)	10 μg/L spiked	Recovery (%)
S_1	1.4	12.6	110.5	1.7	12.9	110.3
S_2	0.6	11.1	104.7	0.7	11.8	110.3
S_3	3.8	15.4	111.6	4.1	15.4	109.2
S_4	1.2	12.0	107.1	1.0	12.1	110.0
S_5	78.0	91.2	103.7	78.5	90.8	102.6

[a] S_1–S_3: polycarbonate, baby feeding bottle. S_4: polycarbonate, dish. S_5: polyvinyl chloride, container.

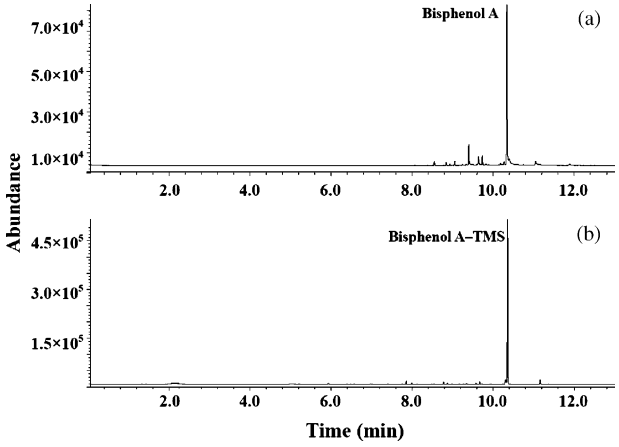

Fig. 5. Mass ion chromatogram of leachate of 150 mL of water at 100 °C in a baby feeding bottle without derivatization (a) and with derivatization (b).

4. Conclusion

This study shows that SPME combined with GC–MS is a precise method for reproducibly analyzing trace bisphenol A from aqueous samples. Better chromatographic shape and sensitivity were obtained by derivatizating bisphenol A using BSTFA that contained 1% TMCS following SPME. The post-derivatization following SPME was one order of magnitude better than that obtained without derivatization. The limits of detection were 2 ng/L and 0.4 ng/L for without and with derivatization, respectively. The feasibility of using the SPME–GC–MS system to measure the amount of bisphenol A in leachate from plastic containers and tableware was tested. Bisphenol A was detected in the range 0.7–78.5 μg/L.

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References

[1] M. Ash, I. Ash, Handbook of Plastic and Rubber Additives, Gower, Hampshire, UK, 1995.
[2] R.E. Morrissey, J.D. George, C.J. Price, R.W. Tyl, M.C. Marr, C.A. Kimmel, Fundam. Appl. Toxicol. 8 (1987) 581.
[3] C.A. Staples, P.B. Dorn, G.M. Klecka, S.T. O'Block, L.R. Harris, Chemosphere 36 (1998) 2149.
[4] J.A. Brotons, M.F. Olea-Serrano, M. Villalobos, V. Pedraza, N. Oles, Environ. Health Perspect. 103 (1995) 608.
[5] J.E. Biles, T.P. McNeal, T.H. Begley, H.C. Hollifield, J. Agric. Food Chem. 45 (1997) 3541.
[6] P. Perez, R. Pulgar, F. Olea-Serrano, M. Villalobos, A. Rivas, M. Metzler, V. Pedraza, N. Olea, Environ. Health Perspect. 106 (1998) 167.
[7] C. Nagel, S. vom Saal, A. Thayer, G. Dhar, M. Boechler, V. Welshons, Environ. Health Perspect. 105 (1997) 70.
[8] J.A. Brotons, M.F. Olea-Serrano, M. Villalobos, V. Pedraza, N. Olea, Environ. Health Perspect. 103 (1995) 608.
[9] A. Yasuhara, H. Shiraishi, M. Nishikawa, T. Yamamoto, T. Uehiro, O. Nakasugi, T. Okumura, K. Kenmotsu, H. Fukui, M. Nagase, Y. Ono, Y. Kawagoshi, K. Baba, Y. Noma, J. Chromatogr. A 774 (1997) 321.
[10] J. Simal, P. Paseiro, S. Paz, J. Simal, J. Chromatogr. Sci. 31 (1993) 450.
[11] J.E. Biles, T.P. McNeal, T.H. Begley, J. Agric. Food Chem. 45 (1997) 4697.
[12] J. Sajiki, J. Chromatogr. B 755 (2001) 9.
[13] J.E. Biles, T.P. McNeal, T.H. Begley, H.C. Hollifield, J. Agric. Food Chem. 45 (1997) 3541.
[14] H. Yoshida, H. Harada, H. Nohta, M. Yamaguchi, Anal. Chim. Acta 488 (2003) 211.
[15] R. Braunrath, M. Cichna, J. Chromatogr. A 1062 (2005) 189.
[16] M. Del-Olmo, A. Gonzalez-Casado, N.A. Navas, J.L. Vilchez, Anal. Chim. Acta 346 (1997) 87.
[17] E. Stephanou, W. Giger, Environ. Sci. Technol. 16 (1982) 800.
[18] W. Korner, U. Bolz, W. Sussmuth, G. Hiller, W. Schuller, V. Hanf, H. Hagenmaier, Chemosphere 40 (2000) 1131.
[19] U. Bolz, W. Korner, H. Hagenmaier, Chemosphere 40 (2000) 929.
[20] H.W. Kuo, W.H. Ding, J. Chromatogr. A 1027 (2004) 67.
[21] Z. Zhang, M.J. Yang, J. Pawliszyn, Anal. Chem. 66 (1994) 844A.
[22] M.R. Lee, R.-J. Lee, Y.-W. Lin, C.-M. Chen, B.H. Hwang, Anal. Chem. 70 (1998) 1963.
[23] M.R. Lee, Y.-C. Yeh, W.-S. Hsiang, B.H. Hwang, J. Chromatogr. A 806 (1998) 317.
[24] M.R. Lee, B.H. Hwang, J. Chromatogr. A 898 (2000) 245.
[25] J.A. Field, R.L. Reed, Environ. Sci. Technol. 30 (1996) 3544.
[26] T.R. Croley, B.C. Lynn Jr., Rapid Commun. Mass Spectrom. 12 (1998) 171.
[27] M.L. Bao, F. Pantani, K. Barbieri, D. Burrini, O. Griffini, Chemosphere 42 (1996) 227.
[28] M. Kawaguchi, K. Inoue, M. Yoshimura, N. Sakui, N. Okanouchi, R. Ito, Y. Yoshimura, H. Nakazawa, J. Chromatogr. A 1041 (2004) 19.
[29] S. Nakamura, S. Daishima, J. Chromatogr. A 1038 (2004) 291.
[30] J.L. Vílchez, A. Zafra, A. González Casado, E. Hontorio, M. Del Olmo, Anal. Chim. Acta 431 (2001) 31.

[31] R. Jeannot, H. Sabik, E. Sauvard, T. Dagnac, K. Dohrendorf, J. Chromatogr. A 974 (2002) 143.
[32] H. Fukazawa, K. Hoshino, T. Shiozawa, H. Matsushita, Y. Terao, Chemosphere 44 (2001) 973.
[33] R. Liu, J.L. Zhou, A. Wilding, J. Chromatogr. A 1022 (2004) 179.
[34] D. Li, J.R. Oh, J. Park, J. Chromatogr. A 1012 (2003) 207.
[35] Y. Sun, M. Wada, O. Al-Dirbashi, N. Kuroda, H. Nakazawa, K. Nakashima, J. Chromatogr. B 749 (2000) 49.