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Sensitive determination of bisphenol A and bisphenol F in canned food using a solid-phase microextraction fibre coated with single-walled carbon nanotubes before GC/MS

N. Rastkari[a]*, R. Ahmadkhaniha[b], M. Yunesian[ac], L.J. Baleh[b] and A. Mesdaghinia[ac]

[a]*Center for Environmental Research, Tehran University of Medical Sciences, Tehran, Iran;* [b]*Department of Medicinal Chemistry, Faculty of Pharmacy and Pharmaceutical Sciences Research Center, Tehran University of Medical Sciences, Tehran 14174, Iran;* [c]*School of Public Health, Tehran University of Medical Sciences, Tehran, Iran*

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A reliable and sensitive method for simultaneous determination of bisphenol A (BPA) and bisphenol F (BPF) in canned food by gas chromatography-mass spectrometry (GC/MS) is described after extraction and pre-concentration by a new solid-phase microextraction (SPME) adsorbent. The potential of single-walled carbon nanotubes (SWCNTs) as SPME adsorbent for the pre-concentration of environmental contaminants has been investigated in recent years. This work was carried out to investigate the feasibility of SWCNTs as a headspace SPME adsorbent for the determination of bisphenol derivatives in canned food. Potential factors affecting the extraction efficiency, including extraction time, extraction temperature, desorption time, desorption temperature, and salinity were optimized. Calibration curves were linear ($r^2 \geq 0.994$) over the concentration range from 0.30 to 60 $\mu g\,kg^{-1}$. For both target analytes, the limit of detection (LOD) at signal-to-noise (S/N) ratio of 3 was 0.10 $\mu g\,kg^{-1}$. In addition, a comparative study between the SWCNT and a commercial polydimethylsiloxane (PDMS) SPME fibre for the determination of bisphenol derivatives in canned food was conducted. SWCNT fibre showed higher extraction capacity, better thermal stability (over 350°C) and longer life span (over 150 times) than the commercial PDMS fibre. The method was successfully applied to determine BPA in canned food samples which were purchased from local markets. BPA was found in some of the samples within the concentration range from 0.5 to 5.2 $\mu g\,kg^{-1}$.

Keywords: gas chromatography-mass spectrometry (GC/MS); headspace; solid-phase microextraction (SPME); bisphenol A; cans; environmental contaminants; alkyl phenols; food-contact materials; canned foods

Introduction

Bisphenol A (2,2-*bis*(4-hydroxyphenyl)propane), known as BPA and bisphenol F (*bis*(4-hydroxyphenyl)methane) known as BPF, are chemical substances widely used in industry as monomers in the production of epoxy resins and polycarbonates, and as antioxidants in polyvinylchloride (PVC) plastics. Epoxy resins are used as inner surface coating of food and beverage cans. Polycarbonates are used in the manufacture of plastic food containers, such as infant feeding bottles and tableware, frequently replacing glass. PVC is used in a variety of products that includes materials intended to come into contact with food, such as cling film used for food packaging (Nordic Council of Ministers 1998; Scientific Committee on Food (SCF) 2002). The migration of bisphenol derivatives (BPA and BPF) from epoxy-coated can surfaces (Yoshida et al. 2001; Kang and Kondo 2002; Goodson et al. 2002, 2004; Thomson and Grounds 2005), polycarbonate plastics (Nerín et al. 2003; Ehlert et al. 2008), and PVC products (López-Cervantes et al. 2003; López-Cervantes and Paseiro-Losada 2003) into food simulants and food has been reported. The potential adverse effects of BPA on human health through beverage and food consumption have generated a great concern during the last years (European Commission 2004). Therefore, many works were conducted to evaluate the bisphenols contamination of canned foods. BPA contamination was identified in canned vegetables (Brotons et al. 1995; Yoshida et al. 2001), in infant formula (Biles et al. 1997), in canned beverages (Horie et al. 1999), and in canned fish (Munguía-López et al. 2005). The food matrices are very complex; therefore, to determine the BPA contamination, extensive sample clean-up is usually necessary before the instrumental analysis of food samples. Liquid–liquid extraction (LLE) and solid-phase extraction (SPE) were mostly used for the separation of bisphenol derivatives (Biles et al. 1997; Yoshida et al. 2001). However, the extensive use of organic solvents is no longer desirable as these are expensive and harmful to the environment and human health. In recent years,

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*Corresponding author. Email: nr_rastkari@yahoo.com

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solid-phase microextraction (SPME) has been proposed as a promising alternative to the LLE and SPE due to its simplicity of use, high pre-concentration power, and ability to extract target compound selectively (Arthur and Pawliszyn 1990; Pawliszyn 1997). Despite the attractive sensitivity obtained using direct SPME, a dramatic matrix effect can occur when complex matrices such as food materials are analysed (Aguerre et al. 2000; Slack et al. 2003). Headspace solid-phase microextraction (HS-SPME) could be a solution in these cases. In HS-SPME, the extraction time is usually shorter and the selectivity is higher than the direct SPME. The use of HS-SPME has been reported for the determination of BPA in canned food (Ballesteros-Gómez et al. 2009). Since the volatility of bisphenol derivatives is not sufficient, these compounds are usually derivatized to semi-volatile compounds by an *in-situ* reaction with acetic acid anhydride before HS-SPME procedure (Kawaguchi et al. 2004, 2005, 2006). Based on the literature review, commercial SPME fibres such as polydimethylsiloxane (PDMS)-coated fibres are the most employed SPME fibres for acylated phenols (Llompart et al. 2000; Kawaguchi et al. 2004, 2005). Although commercial SPME fibres have been widely used, they still have some drawbacks such as lower thermal and chemical stability, higher cost, lower stability to non-polar organic solvents, and less reusability (usually less than 100 times) which restrict the application of SPME technique (Sun et al. 2005; Li et al. 2009). Therefore, it is of interest to develop a new low-cost SPME fibre with improved analytical characteristics, which can be easily prepared.

Carbon nanotubes (CNTs) are allotropes of carbon that were first discovered in 1991 by Iijima (Iijima and Ichihashi 1993). They are classified into single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs) depending upon the number of layers of graphene sheets that are rolled up for their formation (Sae-Khow and Mitra 2009). Due to the unique mechanical, electrical, thermal and magnetic properties of CNTs, they have been used in many areas (Valcárcel et al. 2007, 2008). Carbon-based materials have excellent adsorption and sieving properties for a wide range of organic and inorganic species (Pyrynska 2007). There is no doubt that the sorption capabilities of these materials are also responsible for the high selectivity of filtration processes. To this end, nanomembranes, especially those without polymer barrier between CNTs, could be used in analytical chemistry for sample pre-concentration or clean-up. In this way, recently, poly(vinyl alcohol)/CNT hybrid membranes were used in pervaporation to separate benzene from cyclohexane (Peng et al. 2007). Also, porous polypropylene membrane modified with MWCNTs has been used to pre-concentrate organophosphorus pesticides from wastewater (Basheer et al. 2006). Previous studies have indicated that CNTs may have great analytical potential as an effective SPE phase for a wide range of compounds. Cai et al. (2003a, 2003b) have used this material as a SPE sorbent for extracting organic compounds. Their studies showed that CNTs are similar to, or more effective than, silica-based sorbents. It is therefore conceivable that CNTs may have great analytical potential as an effective SPME adsorbent for target compounds. The promising application of CNTs as material coatings in SPME was shown by recent works (Fang et al. 2006; Wang et al. 2006; Wei et al. 2007; Rastkari et al. 2009, 2010). The superior analytical features of CNT coatings, such as good extraction capacity, more resistance to extreme temperatures and organic solvents were indicated by these studies. In the present paper, the feasibility of SWCNTs used as adsorbent for solid-phase microextraction of bisphenols in food samples was investigated. By using the SWCNT fibre developed in the previous studies (Rastkari et al. 2009, 2010) many of the analytical problems were solved and considerable improvement was obtained. SWCNTs were attached onto a stainless steel wire through organic binder. Potential factors affecting the extraction efficiency were optimized, and the analytical performance of the developed SWCNT-coated fibre was compared with that of PDMS. The application of the developed method in food analysis was shown by the determination of trace amounts of bisphenol A and bisphenol F in canned food samples.

Materials and methods

Reagents and chemicals

The SWCNTs synthesized by chemical vapour deposition process used as the material coating are 1–2 nm in diameter and 1–10 μm in length (SWCNT-1, Nanoshel, Panchkula, India). The specific surface area and thermal conductivity of the SWCNTs are $350–450\,\mathrm{m^2\,g^{-1}}$ and $3000 \pm 450\,\mathrm{W m^{-1} k^{-1}}$, respectively. Bisphenol A (99%) and bisphenol F (98%) and BPA-d_{16} were obtained from Aldrich (St. Louis, MO, USA). BPA-d_{16} was converted to BPA-d_{14} by dissolving in aqueous sodium hydroxide and re-precipitation by acidifying with dilute sulfuric acid as described by Goodson et al. (2002). This BPA-d_{14} was used as internal standard. Stock solutions were prepared for all the standard substances at $100\,\mu\mathrm{g\,ml^{-1}}$ in acetonitrile. For the preparation of the calibration curves and development of the assay, different amounts of the phenol standards were added to 10 g of each food material before canning (blank matrix) to make the final concentration range from 0.30 to $60\,\mu\mathrm{g\,kg^{-1}}$. The method was optimized by using blank food samples spiked with the BPA and BPF at $10\,\mu\mathrm{g\,kg^{-1}}$ concentration as quality control samples (QCs). Acetic anhydride, acetone, sodium chloride, and potassium bicarbonate were purchased from Merck (Darmstadt, Germany).

Samples

Canned food (tomato paste and corn) samples ($n = 12$) were obtained from four local markets in March 2009 in Tehran. All samples were stored at room temperature before analysis and subjected to chemical analysis less than 1 year after production date.

Instrumentation

SWCNT-coated fibres were prepared according to our previous studies (Rastkari et al. 2009, 2010). Commercial 100 µm PDMS fibres for comparative purpose and a SPME holder were purchased from Supelco (Bellefonte, PA, USA). A magnetic stirrer (Heidolph, Germany) was used to stir the sample. A thermostat oven (Heraeus, Germany) was used to control the extraction temperature. The instrument used for GC-MS analysis was an Agilent gas chromatograph 6890 plus (Agilent Technologies, Palo Alto, CA, USA) equipped with a 5973 quadrupole mass spectrometer. The gas chromatograph was fitted with an HP-5 capillary column (30 m, 0.25 mm i.d., 0.25 µm film thickness). The instrumental temperatures were as follows: injector temperature, 270°C; initial oven temperature, 100°C (held for 1 min), increased to 210°C at a rate of 10°C min^{-1}, then increased to 250°C at a rate of 5°C min^{-1} and to the final temperature 280°C at 30°C min^{-1}, where it was held for 1 min. The total time required for one GC-MS run was 22 min. The inlet was operated in splitless mode. The temperature of the transfer line was maintained at 290°C. Helium (99.999%) was used as carrier gas at 1 ml min^{-1} (constant flow). The source and quadrupole temperatures were kept at 230 and 150°C, respectively. The electronic beam energy of the mass spectrometer was set at 70 eV. The mass selective detector was operated in electron impact (EI) mode using selected ion monitoring (SIM). The dwell time of each ion was set at 100 ms. The GC conditions were selected to minimize the time of analysis while allowing all the analytes to elute in acquisition groups containing suitable number of ions for monitoring (Table 1).

Table 1. Selected ions used for the detection of target analytes by GC-MS in SIM mode.

Ion group	Analyte	Molecular ion (*m*/*z*)	Selected ion (*m*/*z*)	Confirmed ions (*m*/*z*)
1	BPF-diacetyl	284	200	242, 283
2	BPA-diacetyl	312	213	228, 270
2	(BPA-d_{14})-diacetyl	326	224	242, 284

Headspace solid-phase microextraction

For the HS-SPME, a manual SPME holder and different fibres were used. The fibres were conditioned at 20°C higher than desorption temperature (270°C). Two blank injections were performed before the actual analysis. Between uses, fibres were kept sealed from ambient air by piercing the tip of the SPME needle into a small piece of septum to prevent accidental contamination. The HS-SPME parameters were determined by experiments in which all the parameters kept constant except one, and the remaining one was modified to find optimum condition. Before analysis the entire contents of each can was mixed with a homogenizer. To 10 g of each homogenized sample, 10 µl of internal standard solution (BPA-d_{14}, 10 µg ml^{-1}) were added. Then 15 ml of acetonitrile–water (90:10) solution were added to each sample and the mixture was intensively stirred by a stirring paddle with constant velocity for 24 h at 25°C. The obtained mixture was placed in a 20 ml headspace vial. After the addition of potassium bicarbonate (0.2 g), acetic anhydride (0.2 ml) and sodium chloride (0.1 g), each vial was sealed with a headspace aluminium cap and a Teflon-faced septum. Then the vials were immersed in a water bath. Samples were let to equilibrate for 10 min before HS-SPME. Upon insertion of the SPME fibre into the vial, the fibre was exposed to the headspace over the sample for 20–70 min depending on the experiment and allowing *in-situ* derivatization and extraction to the fibre. During this step, the mixture was intensively stirred with a glassy magnetic stirring bar with constant velocity. After the extraction, the fibre was inserted into the GC injection port for thermal desorption. The SPME holder was adjusted so that the exposed fibre tip was positioned about halfway (3.8 cm) into the GC injection port when extended from the protective needle. Injection was accomplished by extending the fibre in the heated inlet for 5 min, and the splitter was opened after 3 min. The additional 2 min of exposure time in the injection port allowed the fibre to be cleaned of any compound that was not desorbed in the initial 3 min. Preliminary studies indicated that the above procedure allowed for reproducible, quantitative transfer of BPA and BPF into the GC system. Blank samples containing internal standard were analysed at the beginning and at the end of the sample queue. Each sample was extracted in triplicate and the average response was considered for quantification.

Quantification

Quantification of BPA and BPF in each sample was performed by constructing the calibration lines, using BPA-d_{14} as internal standard. Tomato paste and corn samples before canning were selected as blank matrices. The suitability of these blank matrices was confirmed by preliminary studies. The calibration samples were prepared by spiking the blank matrices with the analytes standards over the concentration range 0.30–60 μg kg^{-1} (six levels, three replicates at each). The samples were then analysed as described above.

Results and discussion

Characterization of SWCNT fibre

The surface characteristics of the SWCNT and PDMS fibres were investigated by scanning electron micrograph (SEM) technique. The surface of commercial fibre is smoother, without considerable porosity, which could negatively affect the extractive capacity of these kinds of SPME fibres. The coating of SWCNT-coated fibre possesses a rough surface with considerable porosity, which results in larger surface area and higher extractive capacity than conventional polymeric phases (Rastkari et al. 2009, 2010).

Optimization of HS-SPME procedure for SWCNTs coating

Extraction time profile

The extraction time profile for phenols was established by plotting the detector response versus the extraction time. The equilibrium is reached when a further increase of the extraction time does not result in a significant increase in the detector response. The effect of extraction time on the HS-SPME of BPA and BPF was investigated at 20, 30, 40, 50, 60 and 70 min by exposing the SWCNT fibre to the headspace of the sample. The extraction amounts of target compounds increased with increasing exposure time, up to 40 min, but it is also noticeable that extraction efficiencies decreased after 50 min. The probable cause could be that the SWCNT fibre has stronger adsorption to some unknown compounds in the sample than to the bisphenol derivatives; therefore competitive adsorption took place between those compounds and the bisphenol derivatives with further increase in extraction time. Considering these results, 40 min is adopted as extraction time in the following experiments.

Effect of extraction temperature

Acylated bisphenol derivatives are semi-volatile compounds. Thus, in order to extract them in headspace, it is important to increase their vapour pressure by heating the mixture. The effect of extraction temperature on the HS-SPME of BPA and BPF was investigated at 60, 70, 80, 90, and 100°C. The peak area count of the phenols increased as extraction temperature increased, up to 95°C; Therefore the extraction temperature of 95°C was considered as the optimum condition.

Salting out effect of NaCl

Salting out effect has been well established in other experiments through adding NaCl to the sample. Most authors agree on the positive effect of NaCl addition to the sample for improving the extraction efficiency in HS-SPME (Arthur and Pawliszyn 1990; Pawliszyn 1997). In this study to investigate the effect of NaCl addition on the extraction efficiency, a series of experiments was designed and performed by adding different amounts of NaCl (from 0 to 0.5 g) into the quality control samples. According to the results, the highest extraction efficiency was obtained by adding 0.3 g of NaCl into the sample. Therefore, 0.3 g of NaCl per 10 g of sample were selected as the optimum condition in the following experiments.

Effects of desorption time and temperature

For the desorption process, two parameters, including desorption time and temperature need to be optimized. Experiments with different desorption times from 0.5 to 6 min were carried out, and the results showed that desorption was completed in 3 min. The temperature monitored for desorption ranged from 200 to 290°C. According to the results, the peak areas of the analytes increased slightly with increasing the desorption temperature. Since the best responses were obtained at 270°C, this temperature was selected as the desorption temperature. Experiments showed that no carry-over effect took place at 270°C. Therefore, a 3-min desorption time and 270°C desorption temperature were used as optimum condition in all experiments.

Optimization of HS-SPME procedure for PDMS fibre

The same methodology as the one described above was used to find the optimum HS-SPME condition for PDMS fibre and the optimum condition was determined as follows: extraction time, 20 min; extraction temperature, 100°C; desorption time, 3 min; desorption temperature, 270°C; and concentration of NaCl, 0.3 g per 10 g of sample.

Comparing SWCNT fibre with PDMS fibre

In HS-SPME the affinity of the analyte for the three phases involved in the extraction process (fibre coating, headspace and sample matrix) determines the extraction yield. Therefore, the choice of an appropriate fibre coating is extremely important. Commercial PDMS fibre, which has frequently been used to determine the bisphenol derivatives in different matrices (Llompart et al. 2000; Kawaguchi et al. 2004, 2005), is chosen to compare with SWCNT fibre used in the present study. The affinity of the commercial fibres depends on the properties and thickness of fibre coating and the properties of compounds extracted (Sun et al. 2005). For example, non-polar polydimethylsiloxane (PDMS) fibre is preferred for the extraction of non-polar and volatile analytes, and polar polyacrylate (PA) fibre is suited for the extraction of more-polar analytes. However, SWCNTs coating adsorbs compounds depending on its surface pores and it can adsorb polar and non-polar compounds simultaneously. Results of the previous studies indicated that SWCNTs coating has higher surface area and pore volume than commercial porous fibres which makes SWCNT has excellent adsorption and desorption abilities (Sun et al. 2005). Moreover, due to the presence of oxygenated groups on SWCNTs and the π–π interaction between SWCNTs and aromatic compounds, the SWCNT fibre is superior to commercial PDMS fibre in extracting the studied phenols from samples (Li et al. 2009). Comparison of the extraction yields of commercial PDMS and SWCNT fibres for bisphenol derivatives was carried out under the optimal HS-SPME condition of each fibre. The results are shown in Figure 1. These results indicate the higher extraction efficiency of SWCNT coating which could be due to the higher adsorption ability of SWCNT. In HS-SPME, thermal stability and life span are important properties of fibre coating. Most of the commercial fibres show poor thermal stability due to the absence of proper chemical bondings between the stationary phase coating and the silica surface. As a result, relative low operating temperature is generally recommended (Gonçalves and Alpendurada 2002). Generally, for commercial PDMS fibre, thermal stability is lower than 280°C and the range of lifetime is from 50 to 100 times. SWCNTs are made of graphite, therefore high chemical and thermal stability of the prepared SWCNT fibre could be expected. The thermal stability of the developed SWCNT fibre was studied and it was found that the extraction ability of SWCNT fibre is not significantly affected after conditioning for 1 h at 250, 300 and 350°C. These results show the considerable thermal stability of SWCNT fibre. The extraction efficiency of SWCNT fibre for extracting bisphenol derivatives from sample mixture after being used for more than 100 times was also studied. The results indicated that the extraction efficiency of SWCNT-coated fibre has no obvious decline after being used for 150 times. On the other hand most of commercial fibres are breakable due to the use of fused silica as substrate for coating. The developed SWCNT fibre was unbreakable since stainless steel wire was used as the substrate (Rastkari et al. 2009, 2010). These advantages of SWCNT fibre expand the HS-SPME-GC application range toward higher-boiling compounds and prolong the fibre lifetime.

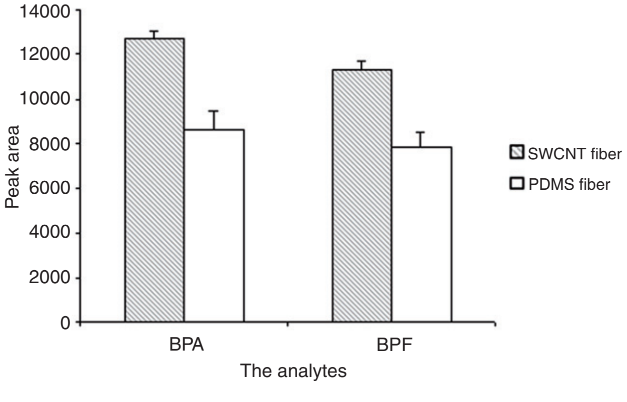

Figure 1. Comparison of the extraction efficiency between SWCNT and PDMS fibres. Concentrations of bisphenol derivatives: 10 μg kg^{-1}. Experimental conditions for SWCNT fibre: extraction time, 40 min; extraction temperature, 95°C; desorption time, 3 min; desorption temperature, 270°C; and amount of NaCl, 0.3 g; and for PDMS fibre: extraction time, 20 min; extraction temperature, 100°C; desorption time, 3 min; desorption temperature, 270°C; and amount of NaCl, 0.3 g.

Quantitative analysis

The calibration curves parameters listed in Table 2 were obtained under the optimized condition. Linearity of the calibration curves was determined in the range of 0.30–60 μg kg^{-1} for BPA and BPF. Coefficient of estimation ranged from 0.994 to 0.998. Limit of detection (LOD) was calculated as three times the baseline noise ($S/N = 3$) after five successive HS-SPME extractions of blank samples. According to the ICH (International Conference on Harmonization of Technical Requirements for Analytical Methods) criteria for analytical method validation, limit of quantification (LOQ) for each analyte was determined as the lowest concentration on the calibration curve with a precision of less than 20% coefficient of variation (CV, %) and an accuracy of 80–120% (Garofolo 2004). For both target analytes, LOD and LOQ were determined as 0.10 and 0.30 μg kg^{-1} respectively, which indicates sensitivity of the method. The precision of the method was evaluated in terms of repeatability (or interday precision) through calculating the analyte concentrations in quality control samples, prepared at three levels (each six replicates) on three consecutive days. Interday precision values for the analytes were always less than 12%. Fibre reproducibility was evaluated with QC samples (10 μg kg^{-1}) through headspace extraction. Batch produced five fibres were used for the evaluation of the reproducibility between fibres. As shown in Table 3, the reproducibility between the SWCNT fibres for headspace extraction

Table 2. Calibration line parameters of the developed SWCNT-HS-SPME method for determination of the bisphenol derivatives in canned food samples.

Canned food	Target compound	Linear range (μg kg^{-1})	Limit of detection (LOD) (μg kg^{-1})	Calibration line equation	Coefficient of estimation
Tomato paste	BPA	0.30–60	0.10	$y = 0.339x - 0.147$	0.998
	BPF	0.30–60	0.10	$y = 0.381x - 0.439$	0.994
Corn	BPA	0.30–60	0.10	$y = 0.318x + 0.184$	0.997
	BPF	0.30–60	0.10	$y = 0.341x + 0.196$	0.997

Table 3. Estimated recoveries and method precision for target bisphenol derivatives at different concentrations ($n = 6$) in QC samples.

Canned food	Target compound	Sample	Nominal concentration (μg kg^{-1})	Mean of calculated concentration (μg kg^{-1})	CV (%) of calculated concentration	RE (%) of calculated concentration[a]	Estimated recoveries (%)	CV (%) of calculated recovery	RSD between fibres (%)	
									SWCNT	PDMS
Tomato paste	BPA	QC$_1$	1	0.91	10.2	9.0	79	14.1	11.8	7.2
		QC$_2$	10	9.21	8.1	7.9	81	11.8		
		QC$_3$	50	47.38	7.2	5.2	82	11.5		
	BPF	QC$_1$	1	0.89	11.3	11.0	80	13.6	11.3	7.5
		QC$_2$	10	9.05	9.1	9.5	82	13.4		
		QC$_3$	50	47.11	7.6	5.8	84	12.6		
Corn	BPA	QC$_1$	1	0.90	10.8	10.0	81	14.3	12.2	7.4
		QC$_2$	10	9.11	8.5	8.9	83	12.5		
		QC$_3$	50	46.87	6.9	6.3	86	11.7		
	BPF	QC$_1$	1	0.89	11.1	11.0	79	13.8	12.8	6.9
		QC$_2$	10	9.27	8.6	7.3	83	12.4		
		QC$_3$	50	47.01	7.7	6.0	84	10.2		

Note: [a]Relative error = [(calculated concentration/nominal concentration) – 1] × 100.

of BPA was acceptable (RSD < 15%). The results proved the feasibility of the fibre preparation method proposed in this work. Expression of the intraday precision is based on the CVs of determined responses of six replicates of quality control (QC) samples, which were prepared at three levels and reported in Table 3. The estimated recoveries at three different concentration levels are also shown in Table 3. To determine the recovery, mean peak area of each analyte at each concentration level was determined for a blank food sample spiked with the analyte and compared with that of standard solution (in acetonitrile–water) at the same concentration. All these results indicate the feasibility and reliability of the developed method for determining bisphenol derivatives in canned food. To carry out a preliminary study on the status of canned food contamination by BPA and BPF, 24 canned food samples were collected from local markets and analysed by the developed method in this study. The results are shown in Table 4. Quantitative analysis was carried out based on spiked calibration samples and analyses were performed for each sample in triplicate. The results (Table 4) show that BPA was present in analysed samples ranged from 0.51 to 5.16 μg kg^{-1}. Bisphenol F was not detected in any of the samples. A representative chromatogram of the canned tomato paste sample is shown in Figure 2.

Table 4. Levels of bisphenol A in canned food samples from local markets quantified by the calibration curves ($n = 12$).

Number	Tomato paste (μg kg^{-1})	Corn (μg kg^{-1})
1	0.99	1.90
2	n.d.	n.d.
3	2.52	5.16
4	5.12	0.51
5	1.58	n.d.
6	n.d.	n.d.
7	n.d.	2.14
8	1.19	0.65
9	0.89	1.70
10	n.d.	n.d.
11	2.09	1.81
12	2.74	0.96

Note: n.d., not detected.

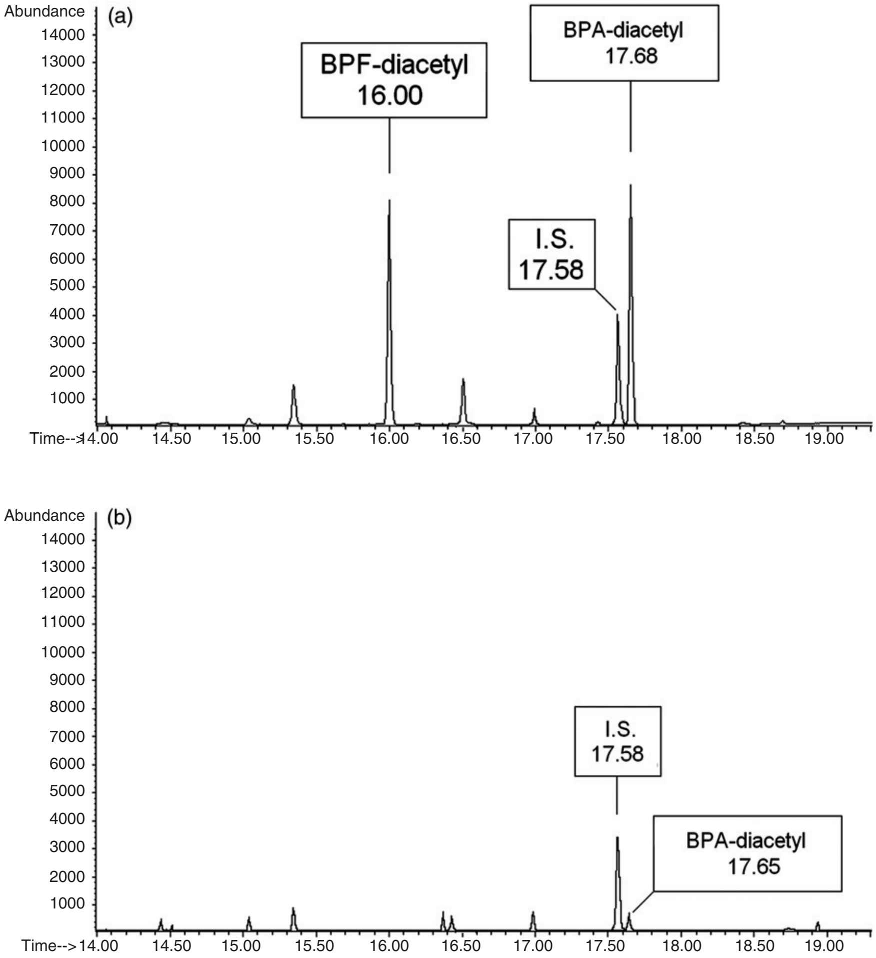

Figure 2. Representative HS-SPME-GC-MS chromatogram in SIM mode of (a) a quality control sample, tomato paste (before canning) spiked with BPA at $20\,\mu g\,kg^{-1}$, BPA-d_{14} at $10\,\mu g\,kg^{-1}$, BPF at $20\,\mu g\,kg^{-1}$; and (b) one of the studied tomato paste sample. Quantitation results: BPA $= 0.9\,\mu g\,kg^{-1}$.

Conclusions

The performance of the SWCNT-coated fibre for determination of BPA and BPF in different kinds of canned foods was evaluated and based on the results, the SWCNT fibre showed a higher sensitivity and longer life span (over 150 times) than the commercial PDMS fibre, as well as good precision and high thermal stability. The other advantages of the developed SPME fibre in comparison with the commercial fibres are the ease of preparation, physical resistance to damage, and low cost. The HS-SPME method is a precise means of analysing trace bisphenol derivatives in food matrices, which contain a high degree of interferences. The range of mean concentration of BPA was determined from 0.5 to $5.2\,\mu g\,kg^{-1}$ in the analysed samples. The results indicated the fact that SWCNT fibre was superior to PDMS fibre in extracting the studied bisphenols from canned food samples.

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