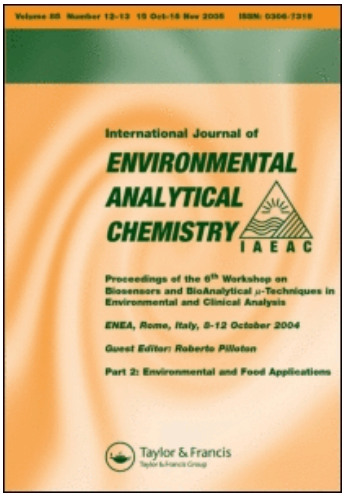

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Simultaneous determination of phenol, methylphenols, chlorophenols and bisphenol-A by headspace solid-phase microextraction-gas chromatography-mass spectrometry in water samples and industrial effluents

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A headspace solid-phase microextraction (HS-SPME) coupled with gas chromatography-mass spectrometry (GC-MS) automatic method for simultaneous determination of trace amounts of phenol, methylphenols (MPs), chlorophenols (CPs) and bisphenol-A (BPA) in water samples and industrial effluents has been developed. Prior to SPME extraction, a direct derivatisation step using acetic anhydride was performed. Four different SPME fibre coatings (75 μm CAR-PDMS, 65 μm PDMS-DVB, 100 μm PDMS and 85 μm PA) were tested. The parameters affecting the HS-SPME process and derivatisation step studied were: extraction time (5–60 min) and temperature (40–100°C), derivatisation time (5–10 min), sample agitation (0–500 rpm), addition of sodium chloride (0–40%). The GC-MS quantification was performed by internal standard calibration and the limits of detection (LODs) were in the low ng L^{-1}. The proposed analytical procedure provided a good linearity ($r^2 > 0.9931$) for standard solutions and a repeatability ranging from 4.8 to 15.2% ($n = 5$). The obtained results show that the developed method was rapid, simple and efficient for phenol, MPs, CPs and BPA analysis, and provides a good alternative to SPE and LLE. Finally, the proposed method has been applied successfully to analyse water samples, municipal solid waste landfill and industrial effluents.

Keywords: headspace solid-phase microextraction; gas chromatography-mass spectrometry; phenol; chlorophenols; bisphenol-A; derivatisation

1. Introduction

Bisphenol-A (BPA), 2,2-bis(4-hydroxyphenyl)propane, is a chemical substance widely used as the monomer for the production of polycarbonate plastic such as in baby bottles, and is a major component of epoxy resin used for lining food cans and dental sealants [1]. In 1993, BPA was found to have leached from a polycarbonate flask [2]. It was also found in saliva collected from patients who were treated with diglycidyl ether of BPA (DGEBA) based dental sealant [3]. Leaching of BPA was attributed to the migration of residual BPA not bonded to the polymer in polycarbonate plastic and in epoxy resin. Release of BPA

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can also occur from polycarbonate hydrolysis in extreme conditions. The safety of BPA has became a controversial issue because it not only possesses estrogenic endocrine disrupting properties [2,4,5], but may also be carcinogenic [6,7].

Other compounds which have attracted scientists' attention are phenol and substituted phenols such as methylphenols (MPs) and chlorophenols (CPs). These compounds are known to be widespread as components of industrial wastes, since they have been used in many industrial processes such as the manufacture of plastics, drugs and dyes [8]. In addition, they have been extensively utilised as preservative agents, pesticides, antiseptics and disinfectants. The USA Environmental Protection Agency (EPA) [9] and the Official Journal of the European Union (EU) [10] list some chlorophenols as priority pollutants owing to their carcinogenicity and considerable persistence.

Analytical methods for the environmental monitoring of these compounds in water samples are based on a preconcentration step followed by the selective determination of the target compounds. Most authors have used solid-phase extraction [11] and liquid-liquid extraction [12–14] for the preconcentration step, and liquid chromatography [15,16] or gas chromatography [17] with several kind of detectors for the detection step. Those methodologies are tedious, time consuming and solvent consuming.

SPME is a relatively new analytical technique (1990s) developed by Pawliszyn and co-workers [18] as an alternative solvent-free preconcentration technique. This technique has already been successfully used for the analysis of chlorophenols in aqueous samples by direct immersion [19] and headspace SPME [20]. Similarly, bisphenol-A has been analysed by direct immersion SPME [21] and in the headspace mode [22,23]. On the one hand, the polarity of low chlorinated CPs and BPA, on the other hand, the low volatility of BPA and high chlorinated CPs necessitate their derivatisation, to increase their volatility in order to improve the extraction efficiency, selectivity and detection. For instance, acetylation in the reaction mixture by acetic anhydride before SPME [24] or silylation after SPME with Bis(trimethylsilyl) trifluoroacetamide (BSTFA) and trimethylsilyl-imidazole (TMSI) [25,26] are usually used for aqueous samples. For BPA analysis only post derivatisation to improve chromatographic conditions has been used. In this work we propose to use a derivatisation with acetic anhydride prior to the headspace SPME extraction in order to increase BPA volatility and consequently the extraction recovery and the analytical sensitivity.

The aim of this study was to develop a simple, sensitive and automatic SPME method which enables the simultaneous determination of several, MPs, CPs, phenol and BPA at low level concentration in complex aqueous samples.

2. Experimental

2.1 *Chemicals*

The investigated phenol, MPs, CPs and BPA were purchased from Supelco (St Quentin Fallavier, France), and a working standard at $0.5\,\mu g\,mL^{-1}$ in Methanol was prepared containing the following compounds: phenol; *o*-cresol; *m*-cresol; *p*-cresol; 2-chlorophenol (2-CP); 2,4-dimethylphenol (2,4-DMP); 2,6-dichlorophenol (2,6-DCP); 4-chloro-3-methylphenol (4-C,3-MP); 2,4-dichlorophenol (2,4-DCP); 2,4,6-trichlorophenol (2,4,6-TCP); 2,3,6-trichlorophenol (2,3,6-TCP); 2,3,5-trichlorophenol (2,3,5-TCP); 2,4,5-trichlorophenol (2,4,5-TCP); 2,3,4-trichlorophenol (2,3,4-TCP); 3,4,5-trichlorophenol (3,4,5-TCP); 2,3,5,6-tetrachlorophenol (2,3,5,6-TeCP); 2,3,4,6-tetrachlorophenol (2,3,4,6-TeCP);

2,3,4,5-tetrachlorophenol (2,3,4,5-TeCP); pentachlorophenol (PCP); and bisphenol-A (BPA). Internal Standards were purchased: phenol-d_5 from Supelco; 2,4,6-trichlorophenol-$^{13}C_6$ (2,4,6-TCP-$^{13}C_6$) and pentachlorophenol-$^{13}C_6$ (PCP-$^{13}C_6$) from Cambridge Isotope Laboratory (Andover, USA) and bisphenol-A-d_4 (BPA-d_4) from CDN Isotopes (Pointe-Claire, Canada).

Methanol, acetone, acetic anhydride, potassium bicarbonate and NaCl, were obtained from Supelco. All the solvents and reagents were of analytical grade and ultra pure water from Milli-Q system (Eschborn, Germany) was used through the experiments.

2.2 *Instrumentation*

GC–MS was carried out with a Trace Ultra gas chromatograph coupled to a quadrupole mass spectrometer (Thermo Fisher, France). The system was equipped with a Combi PAL autosampler (CTC Analytics, Switzerland) allowing automatic SPME extraction. The GC split-splitless injector was operating in the Splitless mode and using a 60 m length, 0.25 mm I.D., 0.25 μm film thickness Zebron 5 MS column (5% phenyl-methyl polysiloxane, Phenomenex). Xcalibur Software from Thermo Fisher was used for online data acquisition and processing. The SPME fibres were purchased from Supelco. Four fibres were investigated, 100 μm polydimethylsiloxane (PDMS), 65 μm polydimethylsiloxane-divinylbenzene (PDMS-DVB), 75 μm carboxen-polydimethylsiloxane (CAR-PDMS) and 85 μm polyacrylate (PA). The fibres were conditioned in the hot gas chromatograph injector as recommended by the manufacturer.

2.3 *Chromatographic conditions*

Chromatographic separation was performed using the following temperature programme: 40°C for 5 min, increase in three steps, at 20°C min^{-1} to 120°C, then at 2°C min^{-1} to 164°C, and finally at 35°C min^{-1} to 280°C. At the end, oven temperature was held for 2 min at 280°C. The injector temperature was held at 250°C and the spiltless-time was 5 min. Helium was used as the carrier gas with a column flow rate of 1.2 mL min^{-1} in the constant flow mode. The transfer line and the ion source were kept at 280°C. MS was operated in the electron impact ionisation (EI) mode with a scan range of m/z 50–400 at 3.88 scans s^{-1}. The ions used for the quantification of each compound are summarised in Table 1. It is to be noted that for PCP-$^{13}C_6$ we selected ion $m/z = 274$ and not 272 (molecular ion) because of the presence of the ion $m/z = 272$ in the PCP mass spectrum.

2.4 *Optimisation of the HS-SPME procedure*

After filtration on 0.45 μm glass fibre filter (only for real environmental samples), a sample volume of 5 mL was added to a 20 mL vial. Then 200 mg of $KHCO_3$ and NaCl (from 0 to 40%) were introduced. An aliquot of 50 μL of a methanol solution containing 20 mg L^{-1} of BPA-d_4; 4 mg L^{-1} of phenol-d_5; 4 mg L^{-1} of 2,4,6-trichlorophenol–$^{13}C_6$ and 4 mg L^{-1} of pentachlorophenol-$^{13}C_6$ were added as internal standards. Finally, derivatisation was performed by adding 30 μL of acetic anhydride to standard sample and 200 μL of acetic anhydride for real water samples and industrial effluents. The vial was immediately sealed with a headspace aluminium cap with a PTFE-faced septum. In this study, several parameters were optimised: fibre coating, reaction time of derivatisation, extraction time

Table 1. Retention time, characteristic fragment (m/z) and quantification internal standards (IS).

n°	Compound		Retention time (min)	Quantification ions	Qualification ions	Quantification internal standards
1	Phenol-d_5	(IS1)	14.26	99	141	–
2	Phenol		14.44	94	136	IS1
3	*o*-cresol		16.02	108	107–150	IS1
4	*m*-cresol		16.62	108	107–150	IS1
5	*p*-cresol		16.89	108	107–150	IS1
6	2-chlorophenol		17.77	128	130–170	IS1
7	2,4-dimethylphenol		18.86	122	164	IS1
8	2,6-dichlorophenol		21.65	162	164–204	IS2
9	4-chloro 3-methylphenol		22.04	142	144–184	IS2
10	2.4-dichlorophenol		22.38	162	164–204	IS2
11	2,4,6-trichlorophenol-$^{13}C_6$	(IS2)	25.65	202	204–244	–
12	2,4,6-trichlorophenol		25.65	196	198–238	IS2
13	2,3,6-trichlorophenol		27.29	196	198–238	IS2
14	2,3,5-trichlorophenol		27.56	196	198–238	IS2
15	2,4,5-trichlorophenol		27.80	196	198–238	IS2
16	2,3,4-trichlorophenol		29.41	196	198–238	IS2
17	3,4,5-trichlorophenol		29.94	196	198–238	IS2
18	2,3,4,6-tetrachlorophenol		32.33	232	230–274	IS3
19	2,3,4,5-tetrachlorophenol		32.53	232	230–274	IS3
20	2,3,5,6-tetrachlorophenol		35.30	232	230–274	IS3
21	Pentachlorophenol-$^{13}C_6$	(IS3)	37.78	274	314	–
22	Pentachlorophenol		37.78	266	268–308	IS3
23	Bisphenol-A-d_4	(IS4)	43.67	217	232	–
24	Bisphenol-A		43.77	213	228	IS4

and temperature, derivatisation time, agitation and salt addition. Afterwards, validation was performed and method detection limits were determined.

2.4.1 *Reaction time of derivatisation*

Before extraction a reaction time of derivatisation is needed to achieve a complete derivatisation prior to the introduction of the SPME fibre. Two reaction times of derivatisation, 5 and 10 min, were tested with continuous agitation at 500 rpm and a derivatisation temperature set point of 80°C controlled by CTC PAL autosampler.

2.4.2 *Extraction temperature and time*

After derivatisation, the fibre was introduced in the vial and exposed to the headspace over the aqueous sample. To study the effect of temperature and time in the HS-SPME procedure, different extraction times, including 5, 15, 30 and 60 min, were performed to get the extraction time profile. Effects of four temperatures levels including 40, 60, 80 and 100°C were evaluated to obtain the highest efficiency for the extraction process. Finally, the fibre was inserted into the GC injector for thermal desorption. To insure that desorption was completed after 5 min desorption time, blank tests were performed after sample analyses and no carry-over was observed except for CAR-PDMS fibre. Recommended operating temperatures by the fibres manufacturer were chosen as

desorption temperatures: 250°C, 270°C, 280°C and 280°C for PDMS, PDMS-DVB, CAR-PDMS and PA, respectively.

2.4.3 *Salt addition*

The presence of salt in the vial has an influence on the extraction efficiency due to changes in ionic strength of the medium. In fact this addition can often improve recovery. NaCl is commonly used for this purpose [27]. This so called salting-out effect was examined through the addition of NaCl to the vial. The effect of 3 different salt amounts was tested: 0, 20 and 40% (weight/volume).

2.4.4 *Calibration, repeatability and method detection limits*

The range of the calibration curves was chosen to cover the possible concentration found in aqueous samples (0.5 to 100 $\mu g\,L^{-1}$ for BPA and 0.1 to 20 $\mu g\,L^{-1}$ for the remainder compounds). Repeatability was assessed as the relative standard deviation (RSD) of a 5-fold analysis. The instrumental detection limits were defined as three times the signal-to-noise (S/N) ratio [28]. As mentioned in [29], the method detection limit (MDL) is based on the analysis of seven samples of 5 mL water spiked with target compounds. Then, the standard deviation (S_d) of the seven replicate measurements is calculated and the MDL is computed as: $MDL = t_{(N-1,\ 1-\alpha=0.99)} \times S_d$. Where $t_{(N-1,\ 1-\alpha=0.99)}$ is the Student's t-value at 99% confidence level.

3. Results and discussion

3.1 *Optimisation of the method*

Fibre damaging by immersion SPME may occur when analysing complex matrices such as landfill leachates and other industrial effluents. In order to avoid this problem and to extend fibres lifetime, Headspace-SPME mode was selected. Due to the low volatility of some compounds (especially BPA) and the polarity of CPs, a derivatisation step was required in order to increase the concentration of those compounds in the headspace. According to Stoichev *et al*. [30], the choice of the appropriate headspace SPME method for BPA deserves further investigation, for this purpose we have studied the effect of several parameters such as fibre type, reaction time of derivatisation, extraction time, extraction temperature and agitation.

3.1.1 *Fibre selection*

Among several studies on the analysis of CPs [20,24,31,32] and BPA [22] by HS-SPME, the most recommended fibres are CAR-PDMS, PDMS-DVB, PDMS and PA. The CAR-PDMS fibre was eliminated since we observed an important carryover effect. Increasing desorption time to 8 min and operating at a desorption temperature of 280°C did not remove this memory effect. Campillo *et al*. [24] have observed the same effect when analysing CPs with this fibre. Average response of three extractions of all the considered compounds obtained with the PDMS, PDMS-DVB and PA fibres are shown in Figure 1. Extractions were performed at 80°C during 30 min after a derivatisation step of 5 min. The PA fibre presents the lowest extraction recovery for most of the compounds. The bipolar sorbent coated PDMS-DVB shows the highest affinity for phenol, MPs and CPs except

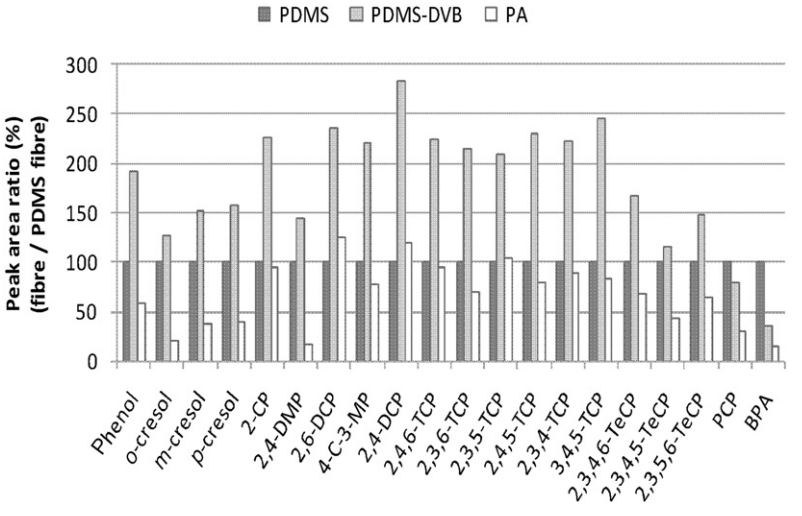

Figure 1. Comparison of the extraction performance of PDMS, PA and PDMS-DVB fibres for phenol, MPs, CPs and BPA, concentrations: BPA (10 μg L^{-1}), phenol, MPs and CPs (2 μg L^{-1}), (The responses of the PDMS-DVB and PA fibres are expressed in % compare to the PDMS response).

for PCP. For BPA the PDMS fibre exhibits much better extraction efficiency than the two other fibres tested. Consequently, we chose PDMS fibre in further optimisation experiments because BPA is of particular importance for landfill leachate study as it is suspected to be the principal compound responsible for the reprotoxicity of this type of effluent. If BPA is not a compound of interest our results show that the PDMS-DVB fibre should be used for phenol, MPs and CPs analysis.

3.1.2 *Reaction time of derivatisation*

The effect of the reaction time of derivatisation, which is necessary to obtain a complete derivatisation reaction prior to the extraction step, was investigated. Two reaction times of derivatisation, 5 and 10 min, were tested. For those experiments extractions were performed at 80°C, during 30 min with continuous agitation at 500 rpm. With the two different times tested no underivatised compound was observed showing that the derivatisation was complete. As a poor repeatability was observed with a 10 min reaction time of derivatisation (data not shown), a reaction time of derivatisation of 5 minutes was used for all the remaining experiments.

3.1.3 *Extraction temperature*

SPME efficiency is significantly influenced by temperature since it has two opposed effects. In fact, increasing temperature enhances the diffusion coefficient and Henry's constants of analytes; on the other hand, as the adsorption is an exothermic process, increasing temperature reduces the partition coefficients to the extraction phase [18]. In order to establish the optimal conditions, four extraction temperatures were investigated 40°C, 60°C, 80°C and 100°C (Figure 2). We remark that, for phenol, methylphenols, mono and di

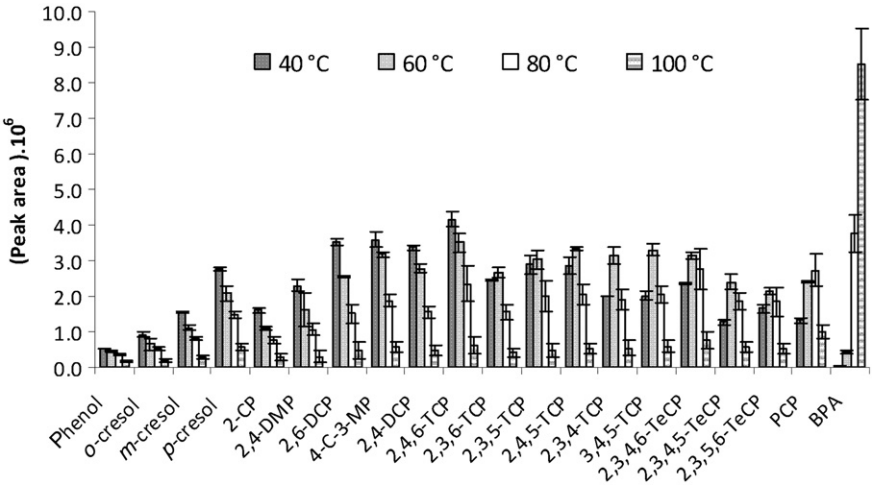

Figure 2. Temperature effect on HS-SPME (mean ± SD), 5 mL sample volume containing 40% of NaCl, 30 min extraction time and 500 rpm agitation, concentrations: BPA (10 μg L^{-1}), phenol, MPs and CPs (2 μg L^{-1}), ($n = 3$).

chlorophenols the best extraction temperature is 40°C. For tri and tetra chlorophenols 60°C is more suitable. Regarding PCP the greatest extraction efficiency was obtained at 80°C.

We noted that when increasing temperature from 80°C to 100°C only for BPA we have a recovery enhancement by about a factor of 2. For other compounds, recoveries decrease about 1.5- to 4-folds. Thus, 80°C is the better compromise for all compounds.

3.1.4 *Ionic strength*

The ionic strength effect was studied (Figure 3) by adding different amounts of NaCl to the sample, ranging from no addition to 40% (W/V). The extraction efficiency improved greatly with the amount of salt added for all compounds with the exception of BPA, where the maximum peak area was observed for 20% NaCl. As compromise, it was chosen to supersaturate the sample at 40% of NaCl prior to analysis.

3.1.5 *Agitation*

Another important parameter known to control the extraction process is the agitation (Figure 4). Some experiments were then performed without and with agitation (500 rpm). As the agitation allows one to increase extracted amounts especially for the heaviest compounds all the experiments were then performed with agitation.

3.1.6 *Extraction time*

In order to determine the optimal extraction time some experiments were performed in which only the extraction time varied and the rest of the experimental conditions (2 μg L^{-1} mixed phenol, MPs, CPs and 10 μg L^{-1} BPA in saturated NaCl) were kept constant. As illustrated in Figure 5 (a–d), except for BPA all the compounds reached the equilibrium after an exposure time of 5 min. A different behaviour was observed for BPA (Figure 5(d)),

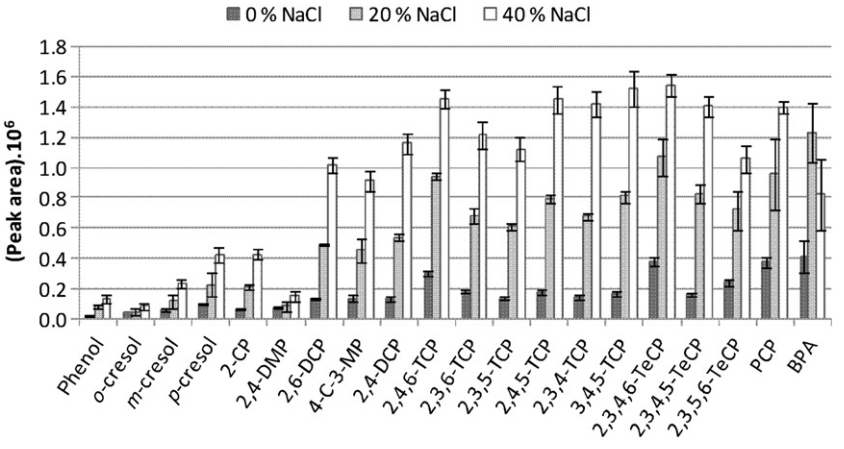

Figure 3. Ionic strength effect on HS-SPME at 80°C (mean ± SD), 5 mL sample volume, 30 min extraction time, and 500 rpm agitation, concentrations: BPA (5 μg L^{-1}), phenol, MPs and CPs (2 μg L^{-1}), ($n = 3$).

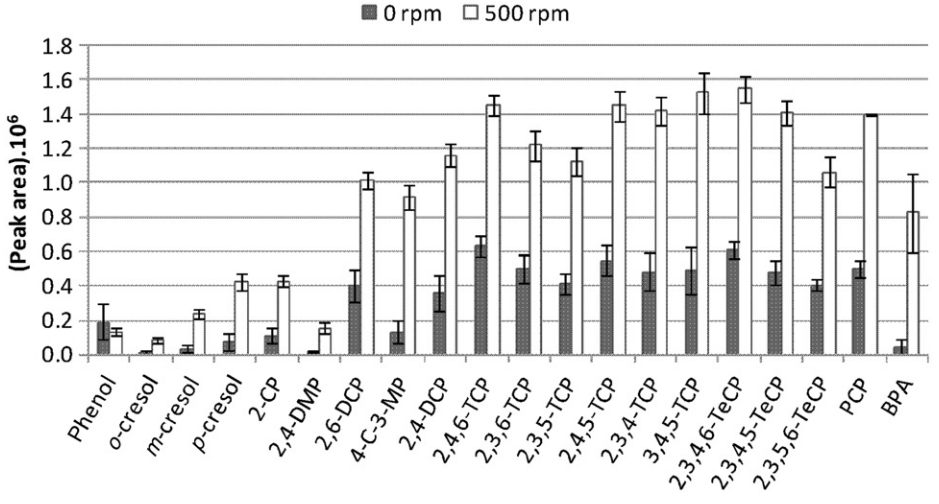

Figure 4. Agitation effect on HS-SPME at 80°C (mean ± SD), 5 mL sample volume containing 40% of NaCl, 30 min extraction time, concentrations: BPA (5 μg L^{-1}), phenol, MPs and CPs (2 μg L^{-1}), ($n = 3$).

which did not reach equilibrium even after 60 min. A decrease of the extraction efficiency was observed for some compounds even after 5 min (Figure 5(b)) and after 15 min (Figure 5(c, d)). As a compromise between increasing extracted amount of BPA, and assuring fast sample analysis, the extraction time was limited to 30 min.

3.2 *Optimised method*

First 5 mL of aqueous samples is introduced in a 20 mL PTFE-capped glass vial. Sodium chloride at 40% (W/V), 200 mg $KHCO_3$ and 30 μL of acetic anhydride are added. A reaction time of derivatisation of 5 min at 80°C is then necessary to obtain a complete

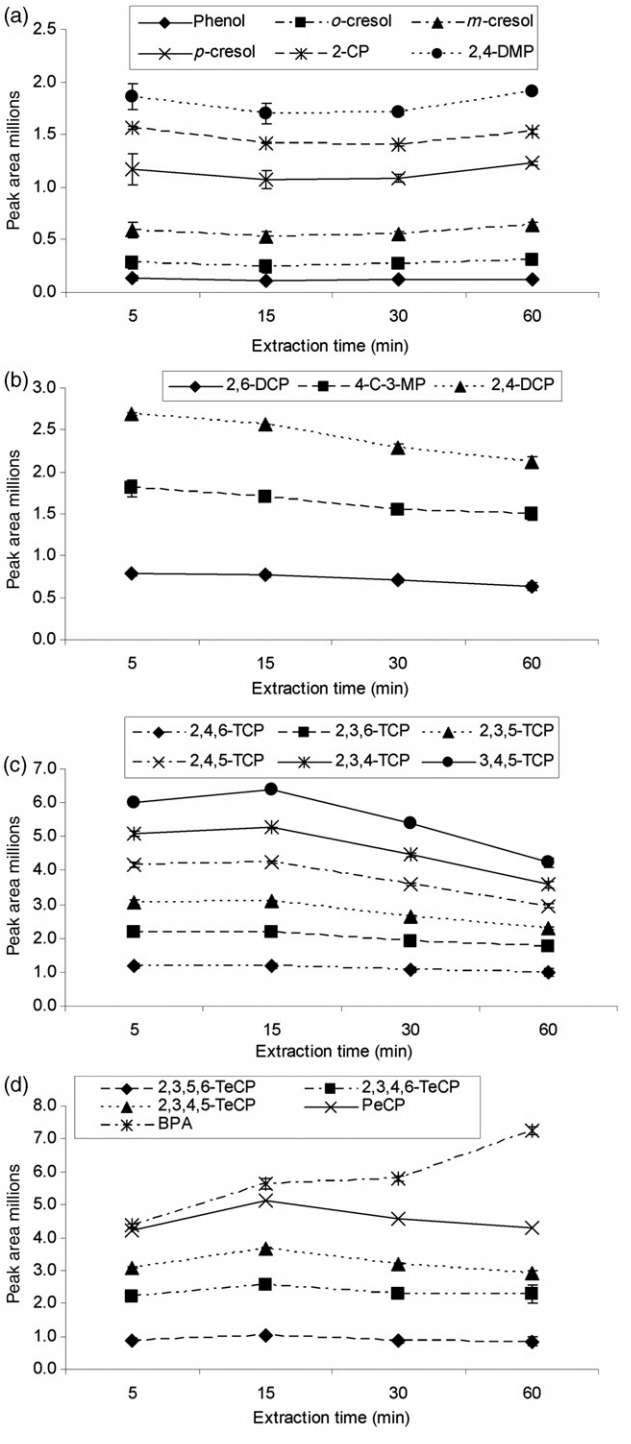

Figure 5. Extraction time profile (mean ± SD), for 2 μg L^{-1} (a) phenol, MPs and 2-CP, (b) 2,6-DCP, 2,4-DCP and 4-C-3-MP, (c) TCPs, (d) TeCPs, PCP and (10 μg L^{-1} BPA).

derivatisation reaction prior to the extraction step. The headspace extraction of target compounds is performed with a 100 µm PDMS SPME fibre at 80°C for 30 min with agitation (500 rpm). Afterwards, the SPME fibre is desorbed in the injector at 250°C for 5 min. GC/MS analysis is then performed as described in the experimental section.

If all the studied compounds in this paper are not of interest to the experimenter, a compound specific procedure can be optimised thanks to the results presented in this study. Indeed, for Phenol, methyl-phenols, mono-chlorophenols and di-chlorophenols the best fibre and temperature are PDMS-DVB and 40°C, respectively. For tri-chlorophenols and tetra-chlorophenols, the best extraction conditions are PDMS-DVB and 60°C. For pentachlorophenol, PDMS fibre and 80°C are the optimum conditions. Finally, better sensitivity for BPA was obtained with PDMS fibre at 100°C.

3.3 *Method validation*

Typical chromatogram for the standard solutions is illustrated in Figure 6. The linearity, the repeatability and the detection limits of the method were investigated (Table 2). The correlation coefficients indicated a good linearity (5 calibration points ranging from 0.5 to 100 µg L^{-1} for BPA and 0.1 to 20 µg L^{-1} for the remainder compounds performed 3-folds) for all compounds (above 0.99). In addition, the repeatability determined for replicate analysis (5) of a milli-Q water sample spiked with all the compounds

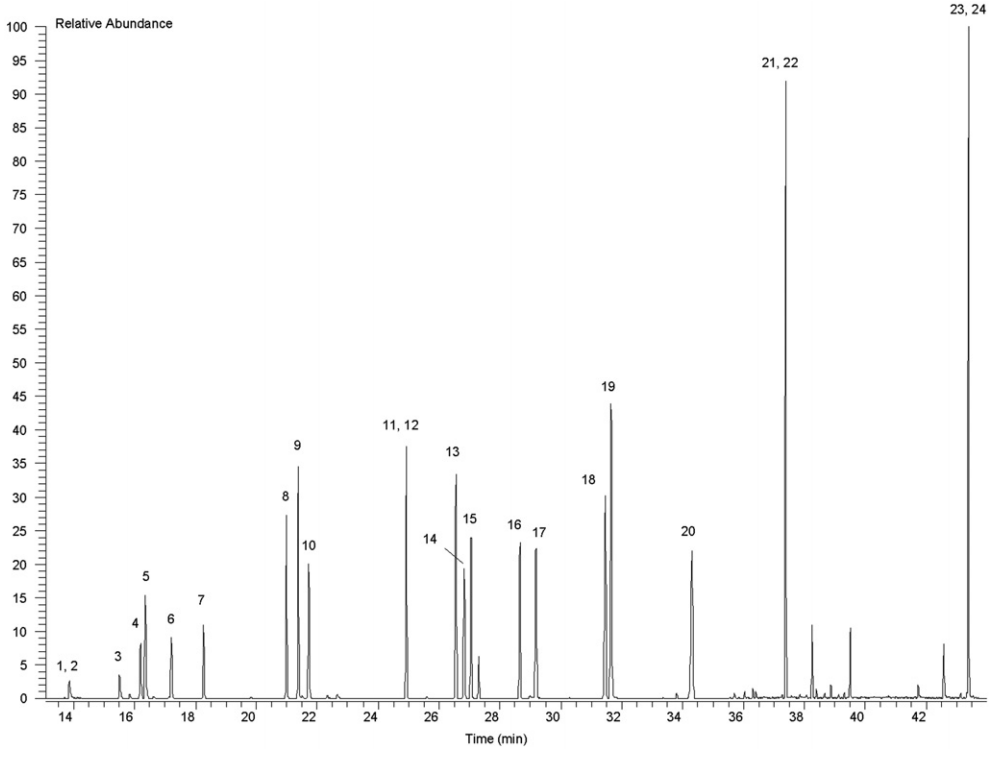

Figure 6. Chromatogram of a milli-Q water sample spiked with phenol, MPs, CPs and BPA at 2 µg L^{-1} (refer to Table 1 for compounds identification).

($2\,\mu g\,L^{-1}$) was acceptable (% RSD below 11.7% except 2,4-DMP 17.2% and BPA 15.2%). Instrumental detection limits were in the low $ng\,L^{-1}$ range except for phenol. Method detection limits were, generally, one order of magnitude higher than the instrumental detection limit.

It is to note that when performing blank analyses (milli-Q water analysed under identical SPME and GC conditions as effluent samples), we did not observe any chromatographic peaks at the retention times of target compounds. Nevertheless, we noted the presence of non-acetylated BPA eluted 2 min before the acetylated BPA retention time. This observation was in agreement with the work of other researchers [33] which attribute this peak to BPA present in the epoxy resin of SPME fibre. As the derivatisation step in our analytical procedure is done before the HS-SPME, the BPA contained in the fibre is not derivatised during extraction. Furthermore, BPA and acetylated BPA do not have the same retention time. Thus, BPA contained in the fibre is not taken into account for quantification. If the usual post-derivatisation method was applied, the problem could still remain. This is an important advantage of this method for BPA quantification by SPME. Another way to overcome this problem is to use a new kind of SPME fibre (metal alloy SPME fibre) free from BPA [29].

3.4 *Application*

The validated analytical method was used to investigate the occurrence of phenol, MPs, CPs and BPA in different environmental samples. To get a first impression on the occurrence of this class of contaminants, effluent samples from industrial area in the North

Table 2. Linearity, instrumental limit of detection, method limit of detection and repeatability (RSD%).

Compound	Linearity (R^2)	Instrumental limit of detection ($ng\,L^{-1}$)	Method limit of detection ($ng\,L^{-1}$)	RSD (%) spiked milli-Q water $2\,\mu g\,L^{-1}$
Phenol	0.9948	345.7	453.6	8.7
o-cresol	0.9931	43.8	83.3	11.7
m-cresol	0.9934	25.0	39.3	4.8
p-cresol	0.9958	14.5	25.6	10.4
2-CP	0.9938	16.5	25.2	9.5
2,4-DMP	0.9958	18.9	57.8	17.2
2,6-DCP	0.9952	11.2	26.8	7.9
4-C-3-MP	0.9935	4.8	16.6	5.4
2,4-DCP	0.9995	1.0	18.2	8.3
2,4,6-TCP	0.9958	1.1	11.3	7.3
2,3,6-TCP	0.9997	1.4	20.2	8.7
2,3,5-TCP	0.9997	2.4	25.4	10.7
2,4,5-TCP	0.9999	2.2	24.2	9.7
2,3,4-TCP	0.9993	2.4	26.3	11.6
3,4,5-TCP	0.9999	1.4	26.7	10.4
2,3,4,6-TeCP	0.9984	1.5	13.6	10.4
2,3,4,5-TeCP	0.9998	1.7	20.9	10.5
2,3,5,6-TeCP	0.9998	1.1	15.6	8.6
PCP	0.9998	1.1	10.6	11.6
BPA	0.9978	1.4	77.5	15.2

Table 3. Analysis results for detected compounds in different samples.

Compound	Concentration of the landfill leachate ($mg\,L^{-1}$)	%RSD ($n=3$)	Concentration of the raw industrial effluent A ($mg\,L^{-1}$)	% RSD ($n=3$)	Concentration of the raw industrial effluent B 1 ($mg\,L^{-1}$)	%RSD ($n=3$)	Concentration of the treated industrial effluent B2 ($mg\,L^{-1}$)	% R SD ($n=3$)
Phenol	0.101	1.0	39.009	2.8	0.779	5.7	n.d.	n.d.
o-cresol	0.254	24.0	3.681	9.5	0.574	17.6	n.d.	n.d.
m-cresol	0.517	4.7	2.222	5.4	0.330	8.2	n.d.	n.d.
p-cresol	0.129	2.3	8.124	5.7	0.046	6.3	n.d.	n.d.
2-CP	n.d.	n.d.	2.998	12.7	0.044	8.2	0.046	12.5
2,4-DMP	0.061	26.8	1.628	11.2	0.162	18.2	n.d.	n.d.
2,4-DCP	n.d.	n.d.	n.d.	n.d.	0.024	12.5	0.037	16.9
BPA	12.785	4.2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

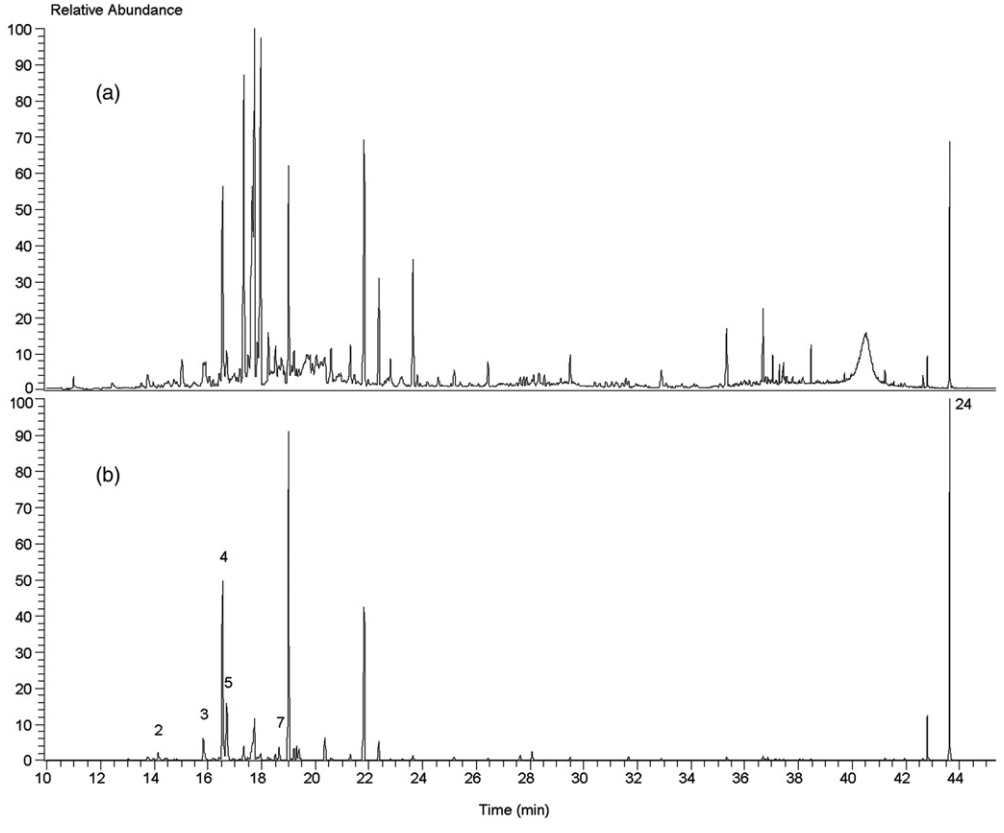

Figure 7. Municipal solid waste leachate chromatograms: The (a) chromatogram is in full scan mode, and the (b) chromatogram shows only the monitored ions for the compounds of interest (refer to Table 1 for compounds identification).

of Tunisia were analysed as well as a French municipal solid waste landfill leachate (Table 3).

The optimised method (see under 3.2 above) was applied. Analysis of the landfill leachate and the industrial effluents was performed in triplicate. Typical chromatograms for leachate in SIM and full scans modes are given in Figure 7.

In the landfill leachate, BPA, 2,4-DMP, *p*-cresol, *m*-cresol, *o*-cresol, and phenol were detected (Table 3). Phenol and MPs were found in concentrations ranging between 0.061 and 0.517 mg L^{-1} whereas BPA was present at 12.785 mg L^{-1}.

In the raw effluents of two industrial plants A and B1, all of the MPs, phenol and 2-CP were found in concentrations ranging between 1.628 and 39.009 mg L^{-1} for row effluent A, and 0.044 and 0.779 mg L^{-1}, for row effluent B1. In the treated effluent B2, none of the MPs and phenol could be detected in concentrations above the limits of determination indicating a high removal efficiency of the applied treatment process for these compounds. However, we noted the persistence of 2-CP and 2,4-DCP at concentrations of 0.046 and 0.037 mg L^{-1}, respectively.

It is interesting to note that, in all analysed samples, none of the tri, tetra and penta chlorophenols were detected in concentrations above the limits of determination.

4. Conclusions

The developed headspace SPME-GC-MS method allows the determination of phenol, methylphenols, chlorophenols and bisphenol-A with a good repeatability and sensitivity. It is the first time that direct derivatisation of bisphenol-A with acetic anhydride has been used prior to headspace SPME. This new procedure allows to increase the sensitivity for bisphenol-A and to overcome the quantification problem due to the presence of bisphenol-A in the epoxy resin of the fibre. If all the studied compounds are not of interest, a more sensitive compound specific procedure could be optimised, thanks to the results presented in this paper, as discussed under 'optimised method' (Section 3.2) above. This new developed method for phenol, MPs, CPs and BPA analysis was applied successfully to analyse landfill leachate, industrial effluents and water samples.

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