Method Based on Solid Phase Extraction, LC and GC for Analysis of Bisphenol A in Drinking Water*

I. RYKOWSKA**, A. SZYMAŃSKI, and W. WASIAK

Faculty of Chemistry, A. Mickiewicz University, PL-60 780 Poznań
e-mail: obstiwo@amu.edu.pl, arekszym@amu.edu.pl, wasiakw@amu.edu.pl

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Dedicated to the 80th birthday of Professor Elemír Kossaczký

A new procedure is described to determine the bisphenol A (BPA) in drinking water that was in contact with polycarbonate (PC) plastic. To evaluate the amount of BPA migrating from the plastic into the water high-performance liquid chromatography (HPLC) and gas chromatography (GC) were used. HPLC and GC enable detection of the BPA concentration as low as 0.2 μg dm^{-3} and 0.5 μg dm^{-3}, respectively. Recovery of dissolved bisphenol A and other endocrine disruptors from water was also performed, locating recovery yield in the range of 82.1—93.3 % as determined by HPLC and 82.3—92.6 % by GC.

The results confirmed that BPA is migrating from the PC package to the drinking water contained in it. BPA concentration in two samples of bottled drinking water of 0.49 μg dm^{-3} and 0.54 μg dm^{-3} was determined by HPLC, and 0.55 μg dm^{-3} and 0.61 μg dm^{-3} by GC analysis.

Bisphenol A (BPA) is used for polycarbonate resins (PC) production [1], which in turn finds application in fabrication of plastic bottles for food industry, water distribution, baby feeders, medical equipment accessories, *etc.* PCs are also employed during the production of epoxy resins, which are used for surface coverage, and development of further plastic materials. According to the published data [2—5], BPA may be liberated from plastic goods made of such resins. Since 1996, a lot of papers dealing with the noxious influence of BPA on human health was published, noting that BPA was extracted from the plastic containers made of polycarbonates (PC).

Earlier research found that BPA may act like estrogens, *i.e.* female hormones, and thus it is included into the group of Endocrine Disrupting Compounds (EDC) [3, 5, 6] accumulated in the human fat tissue. Since 1996, the European Commission has classified the BPA as "external-derivative chemical influencing human health and offspring". BPA noxious properties were re-evaluated recently by the Scientific Committee on Food (SCF) and a provisional tolerable daily intake (TDI) value for BPA was set at 0.01 mg day^{-1} per 1 kg body mass [7].

Main aim of this work was to provide a simple and sensitive analytical method for determination of bisphenol A in drinking water.

EXPERIMENTAL

All analyzed chemicals were purchased from Sigma—Aldrich; their purity was higher than 98 %. Structure of some analyzed components is shown in Table 1. Methanol (HPLC grade) was purchased from P.O.Ch. (Poland). Water was purified making use of a Milli-Q apparatus (Millipore S.A. 67120 Molsheim, France).

All standard stock solutions were prepared by diluting the sample in methanol. Water samples, in which PC content was measured, were obtained from bottled drinking water purchased in the city market.

Preconcentration of the analyte from the water samples was performed using small columns with C18 sorbent. The columns were conditioned prior to the samples introduction. First, 5 cm^3 of methyl chloride—methanol (φ_r = 1 : 1) mixture passed through the column, followed by 5 cm^3 of pure methanol. Then, the precolumn was washed by 15 cm^3 of deionized water.

During preconcentration 500 cm^3 of analyzed water passed through the column. Then, the sorbent was

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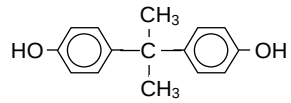
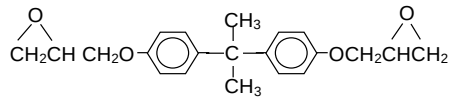
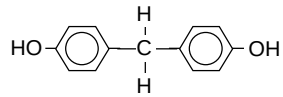
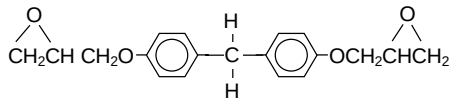
**The author to whom the correspondence should be addressed.

Table 1. Structure of the Analyzed Compounds

Compound	Structure
BPA 2,2-Bis(4-hydroxyphenyl)propane	
BADGE 2,2-Bis(4-hydroxyphenyl)propane bis(2,3-epoxypropyl) ether	
BPF Bis(4-hydroxyphenyl)methane	
BFDGE Bis(4-hydroxyphenyl)methane bis(2,3-epoxypropyl) ether	

dried for 10 min under vacuum, and the adsorbed components washed out with 3 cm^3 of methanol. The extract was dried up and dissolved again in 0.5 cm^3 of methanol.

Quantitative BPA determination in water was performed by the use of the addition standard method. Two preconcentrated samples were prepared in parallel using two identical columns. In the first column 500 cm^3 of mineral water was preconcentrated, meanwhile, in the second one 500 cm^3 of mineral water doped with known amount of BPA was employed. These samples were analyzed using both HPLC and GC systems.

Liquid chromatography separation of analyzed components was performed using a Hewlett—Packard HPLC chromatograph equipped with quaternary pump, variable-wavelength UV detector operated at 277 nm, and an injector Rheodyne 7125 with a 20 mm^3 sample loop. Column (250 mm × 4 mm i.d., supplied by Merck) was packed with 5 μm LiChrospher 100 RP-18 particles. During experiments, the gradient elution method was employed starting with a 4 min isocratic elution with methanol—water ($\varphi_r = 1 : 1$) mixture containing 0.5 vol. % of acetic acid. During the following 10 min the content of methanol in the mobile phase was linearly increased so that at the end eluent contained pure methanol. Finally, 2 min isocratic elution with pure methanol followed by 1 min linear gradient to methanol—water ($\varphi_r = 1 : 1$) mixture containing 0.5 vol. % acetic acid was carried out. The mobile phase flow rate was kept constant at the value 1 cm^3 min^{-1}.

For GC analysis of BPA a Varian CP-3380 gas chromatograph equipped with flame ionization detector (FID) and a CP-SIL 5 CB (10 m × 0.53 mm; DF = 2.0) capillary column was used. The analysis was performed at the temperature of 250 °C with He as the carrier gas. During the whole experimental run a constant flow of 3.5 cm^3 min^{-1} was maintained.

RESULTS AND DISCUSSION

Variation of the peak area with the component concentration based on the result of chromatographic analysis (HPLC and GC) of water samples containing known amounts of 2,2-bis(4-hydroxyphenyl)propane (BPA), bis(4-hydroxyphenyl)methane (BPF), 2,2-bis-(4-hydroxyphenyl)propane bis(2,3-epoxypropyl) ether (BADGE), or bis(4-hydroxyphenyl)methane bis(2,3-epoxypropyl) ether (BFDGE) was used to prepare calibration graphs. For this purpose, solutions containing 1 to 100 μg cm^{-3} of BPA, and 2.5 to 100 μg cm^{-3} of BADGE and BFDGE were employed. For each pollutant concentration the corresponding peak area was calculated as an average of three experiments. A set of concentration-peak area data was used to evaluate the calibration curve parameters. Usually, linear model was used to fit the experimental data

$$y = ax + b \qquad (1)$$

y being the peak area, x concentration (μg cm^{-3}) of analyzed pollutant, and a and b the model parameters. Regression coefficient, r^2, was always higher than 0.9984.

The detection limits were defined as the amount of component producing a peak three times higher than the noise level recorded for a matrix free of the determined component.

Recovery tests were performed for deionized water with known amount of pollutant added (0.5 μg and 5 μg into 500 cm^3). The preconcentrated samples

Table 2. Parameters of Calibration Curves, Recovery Rate, and Detection Limits (LOD) for Analyzed Compounds

Parameters	HPLC				GC		
	BPA	BPF	BADGE	BFDGE	BPA	BADGE	BFDGE
a	24.52	20.38	10.74	6.92	29.05	12.23	3.96
b	−37.59	12.32	13.19	13.76	−60.45	−10.36	0.86
r	0.9986	0.9984	0.9988	0.9969	0.9995	0.9997	0.9989
Recovery/%	93.3	91.6	85.4	82.1	92.6	84.8	82.3
LOD/(μg dm^{-3})	0.20	0.20	0.50	0.50	0.50	1.0	1.0

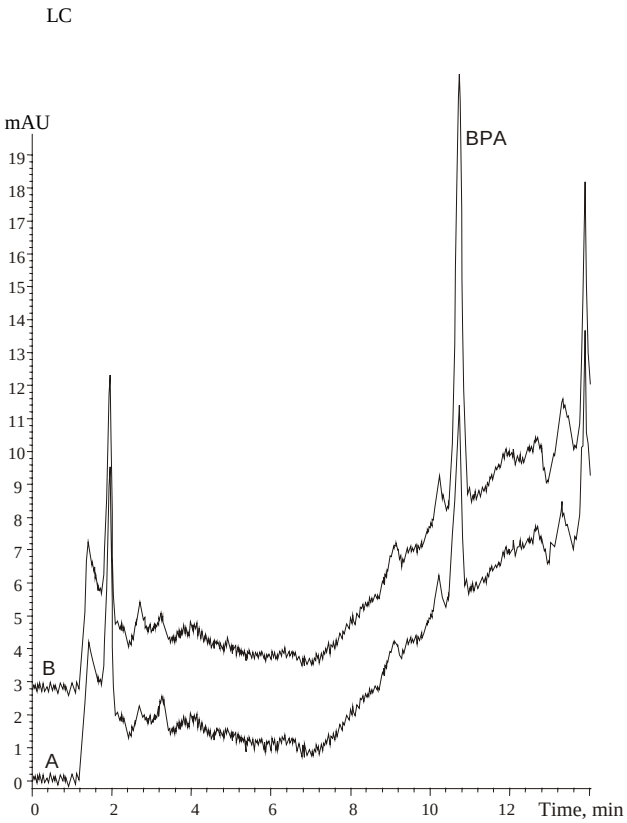


Fig. 1. LC chromatogram of analyzed compounds with (A) and without (B) BPA addition.

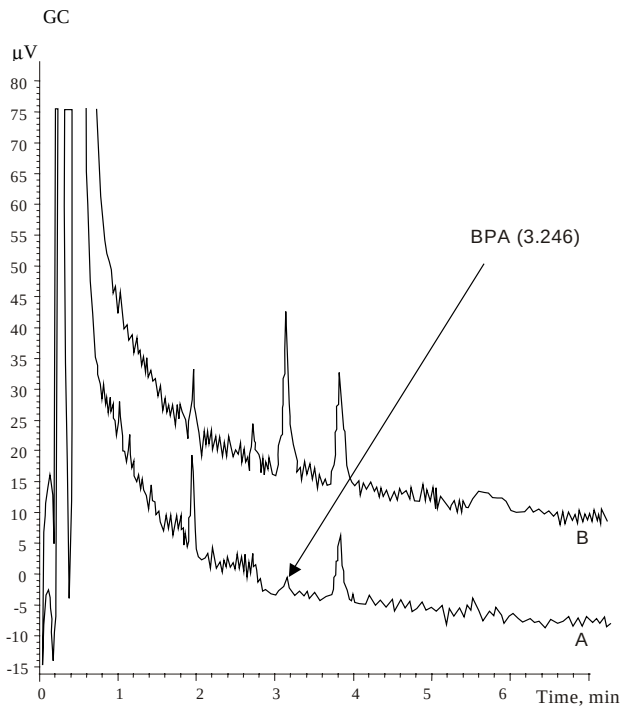


Fig. 2. GC chromatogram of analyzed compounds with (A) and without (B) BPA addition.

Table 3. Average BPA Concentrations in Bottled Mineral Water "Dar Natury" (Sample A) and "Ekol" (Sample B)

Sample	Concentration/(μg dm^{-3})	
	HPLC	GC
A	0.49 ± 0.06	0.55 ± 0.05
B	0.54 ± 0.04	0.61 ± 0.07

were prepared in parallel using two identical columns. In the first column 500 cm^3 of deionized water was preconcentrated. In the meanwhile, in the second one 500 cm^3 of mineral water doped with known amount of BPA was employed. These samples were analyzed using both HPLC and GC systems.

Table 2 summarizes the obtained parameters of calibration curves, recovery rates, and detection limits for the analyzed compounds. Based on these results, it could be concluded that the method is characterized by good recovery rates, as well as low detection limits.

For the analysis of BPA content in drinking water the samples from a 19-litre PC recipient were taken. Such cans are widely used by several companies for distributing large amount of drinking water for staff. The analysis was performed by the use of the addition standard method. Sample chromatograms obtained as a result of the analysis performed are presented in Figs. 1 and 2 for HPLC and GC, respectively. Six parallel determinations of BPA concentration were performed for two water samples. The results are presented in Table 3 as arithmetical-average results for the 95 % confidence interval.

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