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Solid-phase microextraction of phthalates from water

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Abstract

Solid-phase microextraction (SPME) with six different non-polar and polar fibres was used to extract seven phthalate esters from water samples for analysis by gas chromatography–mass spectrometry. With regard to extraction efficiency and repeatability of the extractions, the 70-μm Carbowax–divinylbenzene fibre was especially suitable for the selected phthalates with water solubilities between 4200 mg l^{-1} (dimethyl phthalate) and 0.0003 mg l^{-1} (di-*n*-octyl phthalate). Linearity was controlled in the range between 0.02 and 10 μg l^{-1}. In analysed drinking water samples from Leipzig (Germany) and Katowice (Poland) four of the investigated phthalates [diethyl phthalate, di-*n*-butyl phthalate, butylbenzyl phthalate and di(2-ethylhexyl) phthalate] were found to be present in concentrations between 0.02 and 0.6 μg l^{-1}.

Keywords: Solid-phase microextraction; Water analysis; Phthalates

1. Introduction

Phthalic acid diesters, commonly known as phthalates, are produced all over the world in large quantities, and they are a group of organic chemicals with a variety of industrial uses. These compounds are stable, liquid in ambient temperature, while the ones of higher molar mass have low volatility and are slightly soluble in water (see Table 1). Phthalates are used primarily as plasticizers in plastics. The release of phthalates to the environment may occur during the production and distribution of these compounds, during incineration and migration of plasticizers from the materials containing them [1–3]. Because of that, these compounds constitute are amongst the most common organic pollutants, and their presence in environmental samples should be monitored. In the 1980s the US Environmental Protection Agency (EPA) and several other countries classified the commonly occurring phthalates as priority pollutants [4,5] and recommended maximum admissible concentration in water of 6 μg l^{-1} for the di(2-ethylhexyl) phthalate [6]. As phthalates are widespread in the environment, a proof was furnished of oestrogenic properties exhibited by some phthalates [7–9] in recent years.

During the determination of these compounds by the analytical procedure, the separation of phthalates from the sample matrix is a very important stage.

In recent years solid-phase microextraction (SPME) has become a popular method of sample preparation. The main elements of this technique are fused-silica fibres coated by stationary phase; by means of the fibres the analytes are extracted out

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Table 1
List of phthalate esters determined in the study and their selected physico–chemical properties [3]

Name	Abbreviation	Alkyl chain	Molar mass	Solubility in water (mg l^{-1})
Dimethyl phthalate	DMP	1	194.2	4200
Diethyl phthalate	DEP	2	222.2	1100
Di-*n*-butyl phthalate	DBP	4	278.4	11.2
Butylbenzyl phthalate	BBP	4.6[a]	312.4	2.7
Di-(2-ethylhexyl) phthalate	DEHP	8	390.6	0.003
Di-*n*-octyl phthalate	DOP	8	390.6	0.0005
Di-*n*-nonyl phthalate	DNP	9	418.6	0.0003[b]

[a] Aromatic ring.
[b] Ref. [28].

from various gas media or water. The method combines isolation and enrichment of investigated substances in one stage. The advantages of the method are: simplicity, no use of solvents, sensitivity, portability; it is also relatively independent of the design of the instrument that is used in subsequent analysis.

Until now, sampling by SPME has been used only in some cases for the determination of phthalates. Recently, this method has been applied to phthalate extraction from water samples [10–12], sediments and sludge [13]. Kelly and Larroque [10] chose diethyl phthalate as the first compound to be determined in water samples, and used a SPME–HPLC–UV (226 nm) method with a 50-μm Carbowax–templated resin (CW–TPR) and a 65-μm polydimethylsiloxane (PDMS)–divilnylbenzene (DVB) fibre. Peñalver et al. [11] determined six phthalates and an adipate ester by a SPME–GC–MS method using 85 μm polyacrylate (PA) fibres. Dibutyl phthalate (DBP) and di-(2-ethylhexyl) phthalate (DEHP) were determined in water soluble form from sludge and sediments by SPME coupled with HPLC–electrospray ionization (ESI)–MS method with Carbowax (CW)–DVB) fibres [13].

At present, the Supelco company has made available a number of SPME fibre coatings for the extraction of non-polar and more polar compounds from liquid or gaseous samples.

Considering the SPME type of extraction method, the commercially available SPME fibres can be divided into absorbent- and adsorbent-type fibres [14]. Absorbent-type fibres extract by partitioning of analytes into a 'liquid-like' phase. Adsorbent type fibres extract the analytes by physical interacting with the analytes [14]. Both types of fibres have been chosen for our study.

Some fibres were tested for the analysis of phthalates in water samples. The following fibres coated by phases were selected: 100 μm PDMS, 7 μm PDMS, 85 μm PA, 65 μm PDMS–DVB, 30–50 μm DVB–Carboxen–PDMS and 70 μm CW–DVB. The coatings used for the investigations are examples for fibre types introduced by Supelco. SPME was coupled with phthalate determination by GC–MS in the single ion monitoring (SIM) mode. The determined phthalates are listed in Table 1. The recent investigations used one or two fibre coatings only for the extraction of the phthalates. The aim of our investigations was to study six non-polar and more polar fibres to find fibres of optimum extraction efficiency for the phthalates which have a broad spectrum of polarity.

The fibres were compared in respect of the extraction yield (ratio of the extracted sample mass to the total content of a given compound in the water sample) [15] of direct SPME of phthalates from water samples. This parameter enables one to estimate the affinity of the analytes for the fibre coating and makes it possible to select the best fibre for the extraction of a given analyte.

2. Experimental

2.1. Chemicals and materials

Table 1 presents phthalates selected for investigation. All standards (purity range 95–99%) were purchased from Dr. Ehrenstorfer (Augsburg, Ger-

many). The solvents (hexane and methanol) were of Suprasolv quality (for organic trace analysis).

Stock solutions of the standards of concentration 5 mg ml^{-1} were prepared in methanol. From these solutions a working mixture in methanol was prepared containing all standards of concentration 50 μg ml^{-1} each. Also, standard mixtures in hexane were prepared for direct injection calibration containing all esters in the range of 0.1–50 μg ml^{-1}. The solutions were stored at 4°C. The six SPME fibres selected (see Table 2) were supplied by Supelco (Deisenhofen, Germany). Most of the fibres had StableFlex quality. This implies greater flexibility of the fibre, which should minimise breakage and these fibres were used in connection with a Merlin microseal high-pressure septum (Agilent Technologies). Before the extraction, all fibres were conditioned in the hot injector of a GC device using a helium stream according to the manufacturer's recommendations. The purity of the fibre was controlled by three blank runs to verify the absence of impurities and phthalate peaks.

The laboratory glassware and glass vials used were washed prior to analysis several times with acetonitrile and finally with Suprasolv-quality hexane.

2.2. Preparation of water samples

To test the fibres, water standards with phthalate standard addition was used. The stock solutions were prepared in methanol with a concentration of 5 mg ml^{-1}. Aqueous standards were prepared by diluting suitable aliquots of the stock solution with 1 l of bidistilled water. The 1-l water standard containing 10 μg l^{-1} of each phthalate was used for comparison of the extraction efficiency for all investigated fibres. Spiked water standards were prepared at phthalate concentrations of 0.02–10 μg l^{-1} to obtain SPME–GC–MS calibration curves for CW–DVB fibres. Before spiked water standard preparation, the bidistilled water was checked for phthalate presence by GC–MS analysis (in three-time blank runs). Blank runs were considered in calibration curves made for quantitative analysis for CW–DVB fibres.

2.3. SPME procedure

Spiked water samples (5 ml) were placed in vials (Klimax, USA), and the fibres were immersed in the liquid phase. The extraction was performed at constant temperature of 22°C by intensive agitating the liquid (ca. 1000 rpm) using a magnetic stirrer (Heildoph M 3000) with glass-coated mini-impeller. To optimize the extraction conditions we did not apply the salt addition as it reduces the lifetime of some fibre types [16].

Previous investigations on phthalate determination with different fibres [10,11] showed the time of phthalate extraction from water to be from 15 min to 15 h. A 40-min extraction by fibres is a compromise between sufficiently high quantities of analytes and an acceptable extraction time (of the same order of magnitude as the time of the analysis). Equilibrium is not reached during this time for the most investigated phthalates. When the extraction was completed, the fibres were placed in the chromatograph injector, where, during 5 min at a temperature of 270°C, desorption followed by the analysis took place.

2.4. Chromatographic process

An Agilent Technologies gas chromatograph HP 6890 (Palo Alto, CA, USA) coupled with a HP 5973 mass-selective detector was used. This device was equipped with a HP-5MS column (5% phenyl-

Table 2
SPME fibers used in the study

Name	Fibre type	Phase polarity
7 μm PDMS	Absorbent	Non-polar
100 μm PDMS	Absorbent	Non-polar
85 μm PA	Absorbent	Polar
65 μm PDMS–DVB (StableFlex)	Adsorbent	Bipolar
50–30 μm DVB–Carboxen–PDMS (StableFlex)	Adsorbent	Bipolar
70 μm CW–DVB (StableFlex)	Adsorbent	Polar

methylsiloxane) size 30 m×0.20 mm, 0.25 μm film thickness, a split/splitless injector with Merlin microseal high-pressure septum and insert liner of 0.75 mm I.D. (Agilent Technologies).

The main parameters of the apparatus were the following: injector temperature 270°C, transfer line temperature 280°C, initial GC oven temperature 60°C (5 min), increased at 15°C min^{-1} to 280°C (10 min). Helium flow through the column was set at 40 cm s^{-1}. Splitless time was experimentally determined to be 4 min, and desorption time from the fibres was found to be 5 min (during the 5 min the substances were trapped on the GC column). Electron ionization energy was set at 70 eV and the mass range at m/z 45–450. The SIM mode was used as a sensitive tool for quantitative measurements [17,18]. Based on the literature [19,20], the esters were monitored at quantities according to following target ions — m/z DMP: 163, 194, DEP: 149, 177, DBP: 149, 223, BBP: 149, 206, 91, DEHP: 167, 149, 279, DOP: 149, 279, DNP: 149, 167. Before quantification in the SIM mode, the compounds were identified on the basis of mass spectra and GC retention times received from full scan acquisition mode.

2.5. GC–MS calibration curve — solvent injections

A direct injection calibration curve was generated based on the standard injections in the solvent solution. Detector signals, measured in arbitrary units (peak areas), were plotted versus the amount of analyte injected, expressed in mass units (μg). Hexane solutions (1 μl) of phthalates with concentrations of 0.1, 0.5, 1.5, 10, 20, 25, 35 and 50 μg ml^{-1} were injected with the autosampler of the gas chromatographic device and 2 min splitless time. The calibration curve was used for calculating the quantities of analytes extracted by the fibres.

2.6. Extraction efficiency of the SPME fibres

The extraction efficiencies were calculated as the ratio of the SPME extracted compound mass to the total content of the compound in the 5-ml water sample. The extracted compound mass was determined from the direct injection calibration curve and this volume was divided by the initial mass of the analyte in the water sample.

3. Results

3.1. Calibration

A chromatogram of all tested phthalate esters is given in Fig. 1. With the chromatographic conditions selected, all analysed phthalates were separated. For the considered range of phthalate concentrations (0.1–50 μg ml^{-1}) the response of the mass-selective detector was linear. Correlation coefficients (r^2) were from over 0.98 to over 0.99. Limits of detection (LODs), calculated according to Winefordner and Long's criterion [21], were 0.015–0.06 μg ml^{-1}. The GC–MS method precision, expressed as relative standard deviation (RSD) ($n=3$), was found to be in the range 5.6–7%, and reproducibility was below 8.5%. These values are comparable with those obtained from phthalate GC–MS analysis in full scan mode by Peñalver et al. [11].

3.2. Characteristics of tested fibres and SPME extraction efficiency

The set of the six fibres used for these investigations is given in Table 2. CW–DVB, DVB–Carboxen–PDMS, PDMS–DVB are fibres of the adsorption type, while 100 μm (7 μm) PDMS and PA fibres are of the absorption type. The absorption type fibres (PA, 100 μm PDMS) have a similar phase thickness, but are of different polarity. A PDMS coating is a liquid film which is cross-linked to the silica rod. A PA coating is a solid-phase [22]. In the extraction process using such fibres, the analytes migrate into and out of the coating phase without competition between them. The ability of the coating phase to retain and release the analyte basically depends on the coating thickness and analyte size. The coating thickness and its polarity determine what analyte is retained [14].

Table 3 compares the extraction efficiencies of the selected fibres for the test substances. The comparison of the efficiency of the 7- and the 100-μm PDMS fibres shows that the thicker phase extracts essentially more DBP and BBP than the thin 7-μm

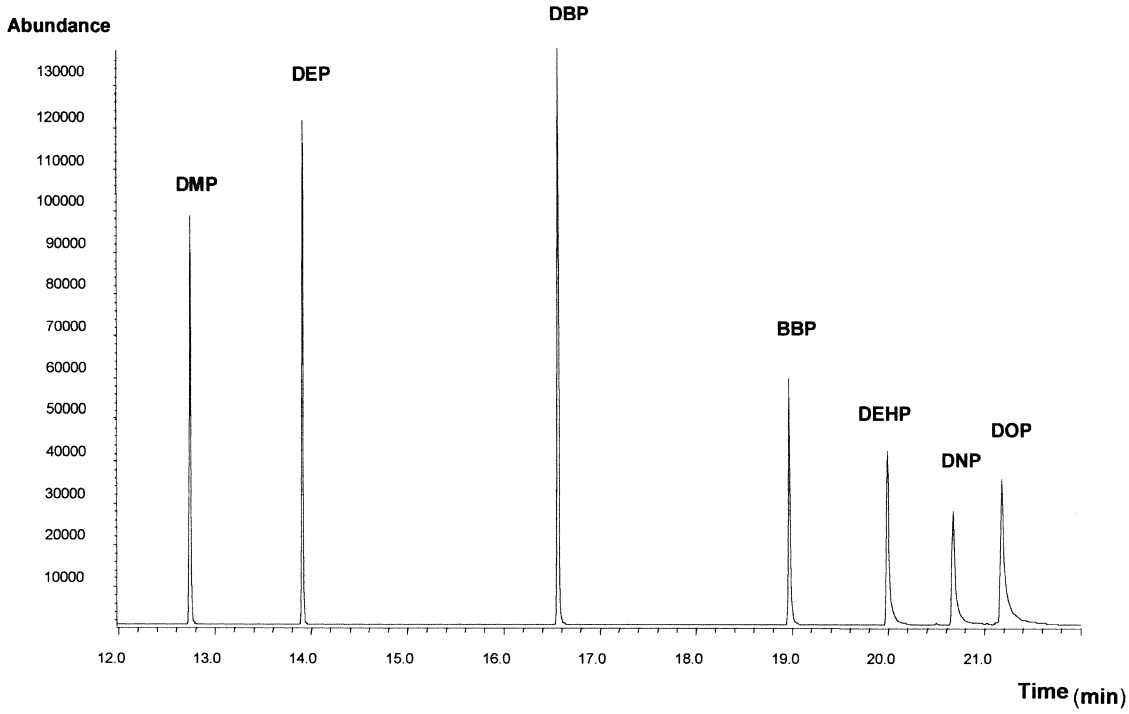

Fig. 1. GC–MS chromatogram of phthalate standards obtained by direct injection. Chromatographic conditions are given in the text.

coating. Because of the lower phase ratio (volume of the water sample divided by the volume of the coating) this should be also the case for the extraction of DMP and DEP but the volatility of these compounds causes losses of the extracted analytes during the time between extraction and desorption in the hot injector. Small differences in the extraction efficiencies of the hydrophobic and non-volatile compounds DOP and DNP can be explained by the fact that after the extraction time of 40 min the equilibrium is not reached. In the case of the 7-μm fibre, the equilibrium times are shorter (60 min) than for 100-μm PDMS fibre (80 min) and thus, a relatively larger quantity of the analytes is extracted.

In fact, adsorption-type fibres contain solid bodies as phases, which have pores or developed surfaces

Table 3
Comparison of phthalate extraction yields obtained by different fibre coatings[a]

Compound	Extraction yields (%)					
	7 μm PDMS	100 μm PDMS	PDMS–DVB	DVB–Carboxen–PDMS	PA	CW–DVB
DMP	0.2	0.26	0.48	3.94	0.42	2.97
DEP	0.04	0.89	1.4	12.5	1.42	5.52
DBP	2.99	29.15	18.7	34.46	28.66	27.5
BBP	3.48	49.11	43.55	41.66	45.75	59.31
DEHP	6.38	4.31	1.48	3.71	2.93	3.53
DOP	2.14	1.55	1.77	1.26	1.42	3.65
DNP	2.16	1.96	2.32	1.9	1.2	1.5

[a] Extraction conditions: concentration of phthalates in 5 ml water samples, 10 μg l^{-1}; extraction time, 40 min; sampling temperature, 25°C; stirring rate, 1000 rpm; desorption temperature, 270°C; desorption time, 5 min.

[14]. Micro- and meso-pores can perfectly capture small and medium analytes. Macro-pores, which are mainly on the surface of the material, are very helpful in trapping the analytes due to Van der Waals effect and hydrogen bonds [14].

In such a porous material, where there are a limited number of sites, the analytes can complete and it can influence the fibre efficiency. Out of this group of fibres, we selected coatings of mixed composition: PDMS–DVB and CW–DVB, and of different polarity (Table 2). Both of these fibres have DVB, which became suspended in PDMS (one fibre) and in CW — the other fibre. The next coating selected was a three-component fibre with DVB and Carboxen suspended in PDMS. The liquid phase polarity used for adsorbent suspension in the fibres results in greater selectivity of the fibres [14]. We used three different adsorptive fibre coatings: CW–DVB, PDMS–DVB, DVB–Carboxen–PDMS (see Table 2).

The comparison of all investigated coatings shows that the maximum values of the efficiency for particular analytes were in the range between 2.5 and 60% (Table 3). The highest values, close to 60%, were achieved for BBP. Also, the efficiency of the DBP and DEP extractions was good (about 40 and 14%, respectively).

Phthalates of low molar mass (see Table 1) and a hydrocarbon side chain length of one to four carbons atoms, i.e. DMP, DEP and DBP, were best extracted by DVB–Carboxen–PDMS fibres (Table 3). This might be due to the porous nature of Carboxen and DVB phases, i.e. due to micro- and meso-pores which trapped smaller phthalate molecules. CW–DVB fibres are also convenient for the extraction of DMP and DEP from aqueous solutions and the absorption type fibres (i.e. 100 μm PDMS and 85 μm PA) extract DBP also very effectively. BBP — phthalate with a molar mass greater than that of the previously mentioned compounds — was extracted by CW–DVB fibres, porous solid coatings, which were primarily determined by properties of the DVB surface [13], but all fibres investigated (except 7 μm PDMS) are favourable for the extraction of BBP. The fibres with DVB surface could be also good for extraction of DOP, a phthalate with eight carbons atoms in its side chains. For di-nonyl phthalate, DVB–PDMS fibres appeared to be the best. The fibres with PDMS phase would be the most suitable for DEHP, and under the given conditions (non-equilibrium) 7 μm PDMS extracted it best (more than 6%).

So if we assume the highest efficiency of SPME as a selection criterion, phthalates in the tested mixture can be determined with different fibres, and these are the fibres containing a DVB phase.

Extraction efficiency is an important parameter in a fibre coating selection. Repeatability of measurements for fibres is another important factor. Table 4 presents repeatability of the measurements for the tested fibres. Considering all phthalates, the lowest RSD values in comparison with other fibres were obtained for CW–DVB fibres and were between 4.4% (DBP) and 28.3% (DEHP). And these are the

Table 4
Relative standard deviation (RSD) of SPME–GC–MS measurements (repeatability) obtained by using different fibres[a]

SPME phase	RSD (%, n=5–7)						
	DOP	DMP	DEP	DBP	BBP	DEHP	DNP
PDMS 100 μm	43.3	17.4	15.3	4.3	13.2	40.5	35.7
PDMS 7 μm	22.2	16.2	78.8	27.1	25.2	16.9	14.1
PA	40.5	18.8	20.4	7.5	16.5	39.7	34.8
PDMS–DVB	33.1	11.3	17.0	21.0	21.6	43.9	31.7
DVB–Carboxen–PDMS	26.9	25.7	24.7	15.8	19.2	28.3	36.4
CW–DVB	15.1	15.4	12.0	4.4	7.4	28.3	15.6

[a] Extraction conditions: concentration of phthalates in 5 ml water samples, 10 μg l^{-1}; extraction time, 40 min; sampling temperature, 25°C; stirring rate, 1000 rpm; desorption temperature, 270°C; desorption time, 5 min.

fibres which can be recommended for SPME of phthalates. Over 80 analyses can be carried out with these fibres.

3.3. Optimization process of SPME extraction for CW–DVB fibres

An Optimization procedure was performed for SPME–GC–MS quantitative determination of phthalates in environmental samples — drinking waters. This process was carried out at 25°C with the use of aqueous test solution of concentration 40 μg l^{-1} of each standard. Other extraction conditions were not changed (see Experimental).

Extraction time optimization showed that after 140 min of extraction the state of equilibrium was not achieved for most phthalates. To shorten the analysis time the shorter microextraction time was chosen, i.e. 60 min. This is acceptable because previous work [10,11,16,23–27] has shown that it is possible to carry out SPME extraction under non-equilibrium conditions for quantitative determination if the extraction time and other conditions are strictly controlled during each subsequent extraction.

In the case of CW–DVB fibres ionic salts were not added to the extracted water samples due to salting in the GC–MS apparatus injector and due to possibility of CW–DVB fibres degradation, which was found out by some investigations of that type carried out before [16]. Moreover, the salting-out effect on SPME efficiency has been widely discussed, but some contradictory results have been reported [16]. We believe that salt may be added only when the sensitivity of the procedure is very poor.

Based on the data, the calibration curves for CW–DVB fibres were made in the following conditions: 5 ml water samples, extraction time 60 min, sampling temperature 25°C, stirring rate 1000 rpm, desorption temperature 270°C, desorption time 5 min.

3.4. Analysis of environmental samples

The most important parameters of SPME–GC–MS quantitation of phthalates in water samples are given in Table 5. The linear range for phthalates concentrations in water from 10 to 0.02 μg l^{-1} is characterised by a very good linear correlation coefficient r^2, which is over 0.99 (for $n=4$), except for DEHP ($r^2=0.8438$). Repeatability and reproducibility of the SPME–GC–MS method calculated at spiking level (1 μg l^{-1}) were 15–21%, $n=4$, and 8–51% $n=7$ days, respectively, while the LODs for the identified phthalates were between 0.02 and 0.005 μg l^{-1}. In the analysed water samples four phthalates, i.e. DEP, DBP, BBP, DEHP, were found. The concentrations of these compounds were low in drinking water coming from the water pipes in two cities: Leipzig, Germany and Katowice, Poland, and they were from 0.6 to 0.02 μg l^{-1}.

Table 5
The linear range of SPME–GC–MS calibrations of CW–DVB fibres, detection limits and contents of identified phthalates in drinking waters[a]

Compound	Linear range (μg l^{-1})	r^2	LOD (μg l^{-1})	Real sample (μg l^{-1})	
				1[b]	2[b]
DEP	10–0.02	0.9999	0.02	0.16	0.2
DBP	10–0.02	0.9811	0.005	0.64	0.38
BBP	10–0.02	0.9991	0.005	0.05	0.02
DEHP	10–0.05	0.8438	0.04	0.06	0.05

[a] Extraction conditions: extraction from 5 ml water samples; extraction time, 60 min; sampling temperature: 25°C; stirring rate, 1000 rpm; desorption temperature, 270°C; desorption time, 5 min.
[b] 1, drinking water from Katowice, Poland; 2, drinking water from Leipzig, Germany.

The chromatogram obtained by the SPME–GC–MS (SIM) analysis of drinking water collected in Leipzig is shown in Fig. 2.

4. Conclusions

In our investigations we used extraction efficiency as a parameter for estimation of SPME fibre usability for phthalate microextraction from water samples. This parameter was a basis for selection of SPME fibres that could be the best for phthalates.

All fibres investigated (except 7 μm PDMS) are favourable for the extraction of BBP. Phthalates of low molar mass (DMP, DEP and DBP) were best extracted by DVB–Carboxen–PDMS. Also CW–DVB adsorption type fibres extract DBP very effec-

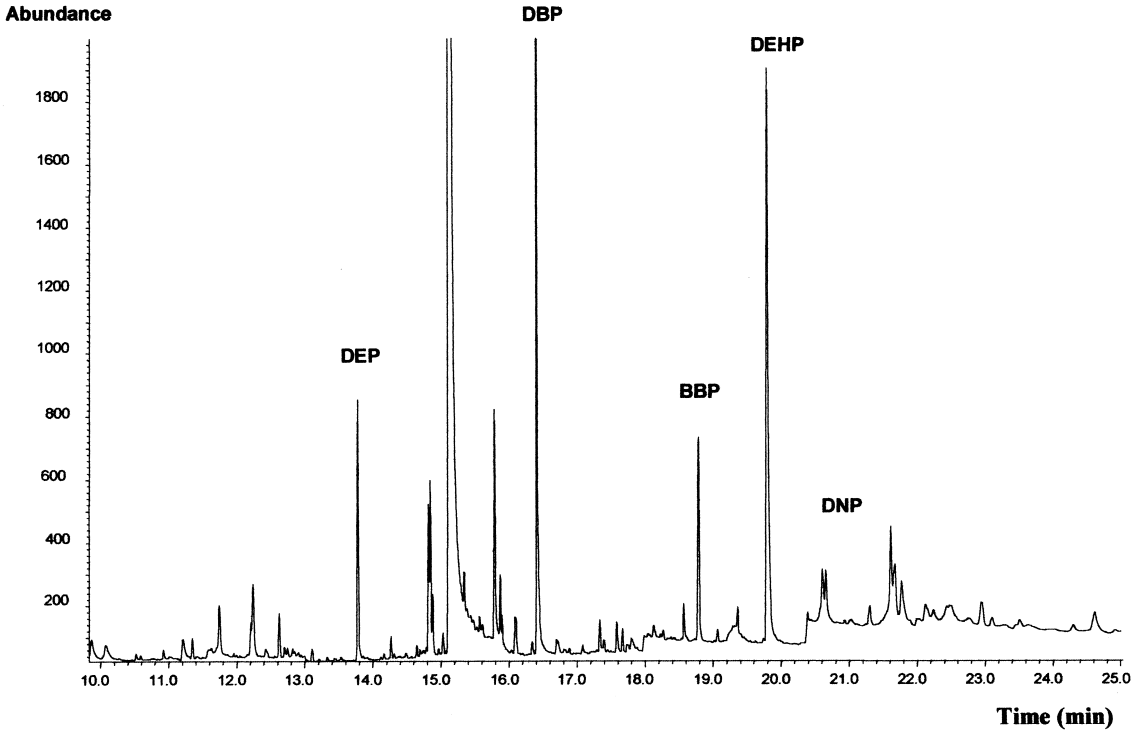

Fig. 2. Chromatogram obtained by the SPME–GC–MS (SIM) analysis of drinking water collected in Leipzig. Chromatographic conditions are given in the text.

tively (more than 60%) and they are convenient for the extraction of DMP and DEP as well. The fibres with the PDMS phase are the most suitable for DEHP extraction. When taking a selection criterion into consideration, the investigated phthalates can be determined with different fibres, and these are the fibres containing DVB phase. If we consider another important factor — repeatability of the extractions — then CW–DVB fibre can be recommended for phthalates.

Application of the optimised SPME–GC–MS procedure with the use of CW–DVB fibres to real-world water samples allowed us to detect phthalates at low $\mu g\ l^{-1}$ concentrations in drinking waters.

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