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Journal of Chromatography A, 1071 (2005) 155–162
JOURNAL OF CHROMATOGRAPHY A
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Optimized method for the determination of 25 polychlorinated biphenyls in water samples using stir bar sorptive extraction followed by thermodesorption-gas chromatography/mass spectrometry

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Available online 9 February 2005

Abstract

An optimized method using stir bar sorptive extraction (SBSE) for the determination of 25 polychlorinated biphenyls (PCBs) from water samples among them three of the most toxic coplanar PCBs (PCB 77, PCB 126 and PCB 169) was developed. Since the investigated PCBs comprise all steps of chlorination (from PCB 1 as monochlorobiphenyl to PCB 209 as decachlorobiphenyl) the results should be representative for the total class of the 209 PCB congeners. For 8 ml spiked water samples with 2 ml methanol addition and 2 h exposure time of stir bars recoveries between 28% (PCB 209) and 93% (PCB 1, PCB 52, PCB 77) were found. Detection limits between 0.05 ng/l and 0.15 ng/l were calculated for the combination of SBSE and thermodesorption-GC/MS. The procedure was applied to the investigation of groundwater and river water samples from the industrial region of Bitterfeld northern Leipzig, Germany.

Keywords: Polychlorinated biphenyls; Stir bar sorptive extraction; Thermodesorption; Gas chromatography

1. Introduction

The class of polychlorinated biphenyls (PCBs), comprising 209 of congeners, is of environmental concern for more than three decades due to their wide dispersal, persistence, and toxic effects, e.g. as endocrine disruptors. Therefore PCBs are considered basic indicators for environmental quality and human health. In spite of their low solubility PCBs became target compounds of environmental codes such as POP-Convention, EC Water Directive, German Drinking Water Ordinance and German Federal Soil Act. Even though PCBs were banned many years ago, there is an urgent need for sophisticated PCB analysis in ground water, surface water, and leachate furthermore.

Since 1990 solid-phase microextraction (SPME) coupled to chromatographic systems has been arisen a growing interest, because liquid–liquid extraction and solid-phase extraction require large sample volumes and organic solvents. Besides liquid–liquid extraction is also a time-consuming technique. The application of SPME, headspace extraction and liquid extraction as well to PCB analysis in aqueous matrices has been described by some authors [1–3].

Other new techniques for the extraction of organics from aqueous samples like membrane-assisted solvent extraction [4], rod extraction [5], membrane-enclosed sorptive coatings [6] or semipermeable membrane devices [7] are subject of current scientific work or focussed on other tasks, such as passive sampling of organics in water.

When using SPME for the analysis of hydrophobic and semivolatile analytes, the stirring of the sample – usually using a Teflon-coated magnetic stir bar – is a necessity. There-

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doi:10.1016/j.chroma.2005.01.066

fore the use of a new stir bar for each sample is necessary to avoid carryover between the samples. Yang et al. [8] described a PCB carryover of up to 20%. These effects of adsorption on the extraction vial surface and on the Teflon-coating are quite significant for very non-polar compounds [9,10].

Due to this, the use of polymer coated stir bars followed by thermal desorption gas chromatography has started recently[11]. Together with the ease-of-use, the high amount of the stir bar polymer coating and the reduced risk of contamination are major advantages of this technique [12]. In the recent years, stir bar extraction (SBSE) combined with thermal desorption gas chromatography/mass spectrometry is of increasing interest in the development of new analytical techniques, especially for the monitoring of organic pollutants in water [13–17]. SBSE methods for the analysis of PCBs in body fluids are already established and known as very reliable [12].

The objective of this work was to develop a very sensitive method (detection limits below 1 ng/l) for the determination of 25 PCBs – among them three of the most toxic coplanar polychlorinated biphenyls (PCB 77, PCB 126 and PCB 169) – from aqueous matrices. The investigated PCBs comprise all steps of chlorination, what means the results should be representative for the whole class of the 209 PCB congeners. Furthermore investigations of complex contaminated ground and surface water have been completed and confirmed the performance of this new application.

2. Experimental

2.1. Chemicals and materials

The tested chemicals were 25 polychlorinated biphenyls (see Table 1). The standard solutions PCB-MIX 6 and PCB-MIX 20 (10 μg/ml isooctane) were obtained from Dr. Ehrensdorfer, Augsburg, Germany. The solutions were diluted in acetone and the HPLC-grade water (from Merck, Darmstadt, Germany) was spiked with concentrations between 0.1 ng/l and 100 ng/l of all PCBs investigated. A water sample volume of 8 ml and 2 ml of methanol were placed on a vial with septum cap (Supelco, Deisenhofen, Germany). The stir bars employed (so-called “Twisters” from Gerstel, Mülheim an der Ruhr, Germany) were 10 mm long, with a PDMS thickness of 0.5 mm.

2.2. Pre-treatment, extraction and desorption of the stir bars

For the PCB analysis, the stir bars were conditioned as follows: they were placed into a vial containing 1 ml of a 1:1 mixture of methylene chloride and methanol and treated for 5 min with sonication. Then the solvent mixture was rejected and this procedure repeated two times more. The stir bars were dried in a desiccator at room temperature and heated for 3 h at 280 °C in a nitrogen stream of about 100 ml min^{-1}. For the enrichment of the PCBs, 8 ml water samples together with 2 ml methanol were given in 10 ml glass vials and then extracted for 2 h at a stirring speed of 1000 rpm. After extrac-

Table 1
The 25 PCBs, their structure, the selected SIM ions and the retention times

PCB	Structure	SIM ions	Retention time (min)
PCB 1	2-Monochlorobiphenyl	188, 152	9.78
PCB 7	2,4-Dichlorobiphenyl	222, 152	11.71
PCB 28	2,4,4′-Trichlorobiphenyl	256, 186	15.82
PCB 30	2,4,6-Trichlorobiphenyl	256, 186	13.13
PCB 31	2,4′,5-Trichlorobiphenyl	256, 186	15.74
PCB 50	2,2′,4,6-Tetrachlorobiphenyl	292, 220	15.74
PCB 52	2,2′,5,5′-Tetrachlorobiphenyl	292, 220	17.93
PCB 77	3,3′,4,4′-Tetrachlorobiphenyl	292, 220	25.82
PCB 97	2,2′,3′,4,5-Pentachlorobiphenyl	326, 254	25.04
PCB 101	2,2′,4,5,5′-Pentachlorobiphenyl	326, 254	23.88
PCB 105	2,3,3′,4,4′-Pentachlorobiphenyl	326, 254	27.16
PCB 118	2,3′,4,4′,5-Pentachlorobiphenyl	326, 254	28.39
PCB 126	3,3′,4,4′,5-Pentachlorobiphenyl	326, 254	29.85
PCB 128	2,2′,3,3′,4,4′-Hexachlorobiphenyl	360, 290	30.64
PCB 138	2,2,3,4,4′,5′-Hexachlorobiphenyl	360, 290	29.48
PCB 143	2,2′,3,4,5,6′-Hexachlorobiphenyl	360, 290	27.50
PCB 153	2,2′,4,4′,5,5′-Hexachlorobiphenyl	360, 290	28.26
PCB 156	2,3,3′,4,4′,5-Hexachlorobiphenyl	360, 290	31.64
PCB 169	3,3′,4,4′,5,5′-Hexachlorobiphenyl	360, 290	33.13
PCB 170	2,2′,3,3′,4,4′,5-Heptachlorobiphenyl	394, 324	33.47
PCB 180	2,2′,3,4,4′,5,5′-Heptachlorobiphenyl	394, 324	32.34
PCB 183	2,2′,3,4,4′,5′,6-Heptachlorobiphenyl	394, 324	30.44
PCB 202	2,2′,3,3′,5,5′,6,6′-Octachlorobiphenyl	430, 179	31.56
PCB 207	2,2′,3,3′,4,4′,5,6,6′-Nonachlorobiphenyl	464, 392	35.37
PCB 209	2,2′,3,3′,4,4′,5,5′,6,6′-Decachlorobiphenyl	498, 428	38.25

tion the stir bars were removed in the usual way (with clean tweezers, followed by drying with a lint-free tissue). Each stir bar was then placed into an empty thermodesorption tube.

2.3. Instrumental

Thermodesorption-GC/MS analysis was performed on a HP 6980/5973 GC/mass-selective detector system (Agilent Technologies, Munich, Germany) equipped with a TDS-2 thermodesorption device and a TDSA autosampler (both from Gerstel). For cryofocusing the pollutants after thermal desorption, a cold injection system (CIS-4) from Gerstel with an empty liner was used, and the CIS was cooled to −20 °C. The transfer lines both from the thermodesorption device to the CIS and from the GC to the MS ion source were set to 250 °C. The following conditions were chosen for the thermodesorption of the analytes from the stir bars: desorption temperature, 250 °C; helium flow rate, 100 ml/min; desorption time, 10 min. After the desorption of the enriched compounds the CIS was heated to 250 °C at a rate of 12 °C/s, and the injector was used in the splitless mode with a splitless time of 2 min. An HP-5-MS-capillary column (30 m × 0.25 mm, 0.25 μm film thickness) was used under the following temperature program: 70 °C, 2 min isothermal, 15 °C/min to 180 °C hold for 10 min, 5 °C/min to 280 °C and hold for 10 min. The carrier gas used was pure helium with a linear velocity of 40 cm/s. A SIM mode acquisition method with two characteristic ions was chosen for the detection of the analytes. The 25 PCBs, the selected SIM ions and the retention times under the given experimental conditions are listed in Table 1.

3. Results and discussion

3.1. Optimization of cold injection system (CIS) and thermodesorption method

The studied PCBs cover a broad range of boiling points. So it was necessary carefully to optimize the initial temperature of the CIS and also the splitless time which is necessary to transfer the compounds completely to the GC column. Starting with a splitless time of 1 min the initial temperature of the CIS was chosen as −150 °C, −50 °C, −20 °C and 0 °C. The results showed, that an initial temperature of −150 °C results in low signals for all PCBs investigated. An initial temperature of −50 °C gives the highest peak area only in the case of PCB 1, and the highest temperatures (−20 °C and 0 °C) provide the best results for the other analytes. To check if the splitless time of 1 min was long enough to transfer the compounds into the column, for the temperatures of −150 °C and −20 °C the splitless time was increased to 2 min and 5 min. In both cases an increase of the peak area with the splitless time was observed. Only for PCB 1 the −150 °C initial temperature (at 2 min or 5 min splitless time) showed a higher peak area than the equivalent splitless time at −20 °C, indicating that −20 °C was not efficient enough to cryotrap this compound completely. For all other PCBs −20 °C and 2 min or 5 min splitless time were most favourably. For the following investigations the parameters −20 °C CIS temperature and 2 min splitless time were chosen. The temperature of 0 °C was not taken in consideration in the splitless time studies because the PCBs 7, 28, 30, 31 and 50 were not efficiently trapped and consequently the increase of the desorption time would result in no improvement of the recoveries.

A further pre-investigation comprised the optimization of the desorption flow between 50 ml/min and 200 ml/min. It was found, that a flow rate of 50 ml/min was not high enough to the transfer of the PCBs 50–209 from the thermodesorption device to the cold injection system; optimum flow rates were 100 ml/min and 150 ml/min. All the further investigations were done with 100 ml/min helium flow rate.

To investigate the dependence of the peak areas with the desorption time, the thermodesorption tube with the stir bars was first heated to 250 °C with a heating rate of 50 °C/min and then this final temperature of 250 °C was held for 2 min, 4 min, 6 min, 8 min, 10 min and 15 min. For the homologues with one to five chlorine atoms the peak areas were nearly independent of the desorption time, but starting with the hexachlorobiphenyls (see Fig. 1) it becomes evident that hold times of 2–6 min are not sufficient to completely desorb the PCBs from the stir bars. Consequently, a desorption time of 10 min was chosen for the following investigations.

3.2. Extraction time profiles

The extraction time profiles have been studied using a spiked HPLC-water sample containing with 50 ng/l of each PCB. Fig. 2 shows these profiles for 8 selected PCBs. The extraction time was varied from 30 min to 24 h. For the PCBs with 1–5 chlorine atoms the equilibrium is reached after 2 h and between 4 and 12 h for the PCBs with 6–10 chlorine atoms. An optimised extraction procedure should have short extraction times and high recoveries for the PCBs. A compromise could be a time of 2 h. In this case the recoveries are high enough to enable the determination of all PCBs with low detection limits.

3.3. Influence of carry over and matrix components

Carry-over was controlled by two consecutive desorption steps. A spiked water sample (10 ng/l of each PCB) was extracted for 2 h, the enriched stir bar was desorbed once (desorption time: 10 min; temperature: 250 °C) and then it was once more desorbed under the same desorption parameters. In this case no peak areas were found, meaning that the analytes are completely desorbed and no carry-over is detected.

The influence of some matrix components on the extraction yield was studied by addition of 20% methanol,

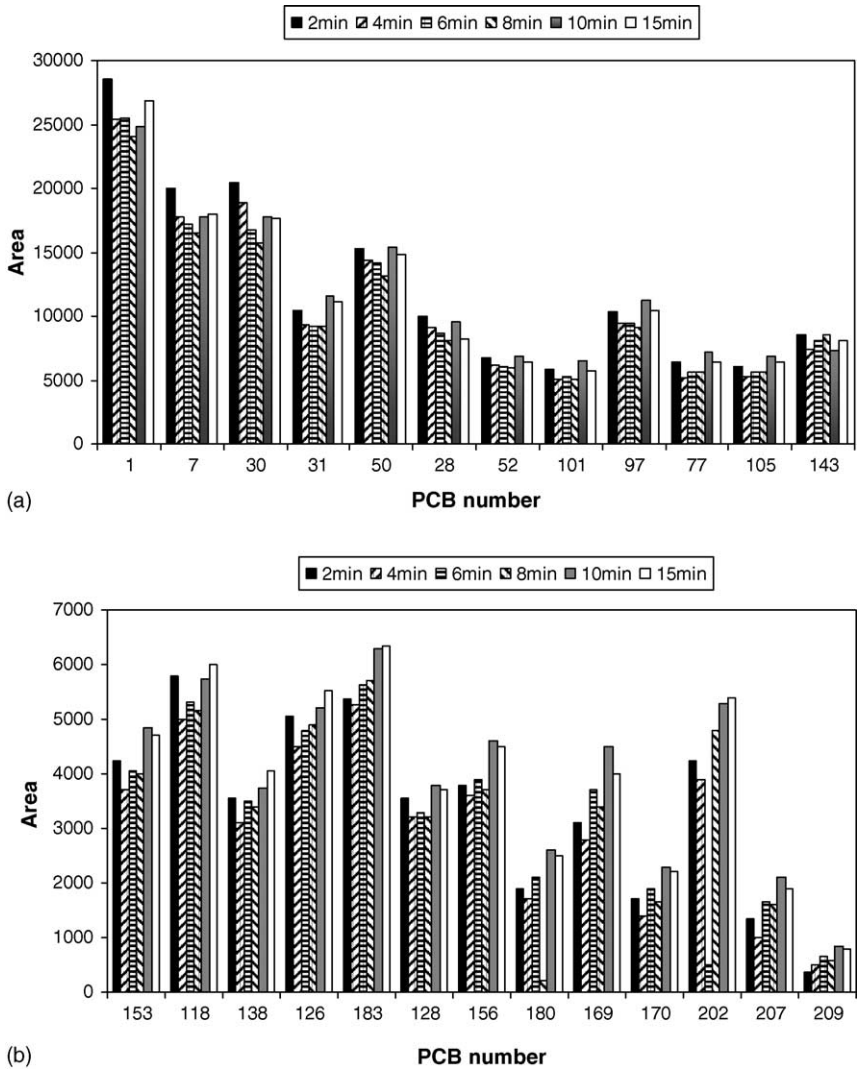

Fig. 1. (a and b) Variation of the desorption time—desorption flow: 100 ml/min; splitless time: 2 min; CIS temperature: −20 °C.

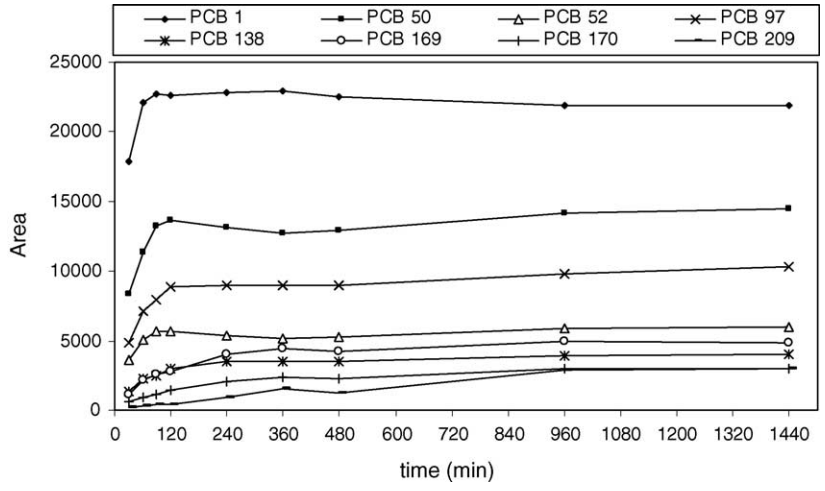

Fig. 2. Extraction time profiles of selected PCBs.

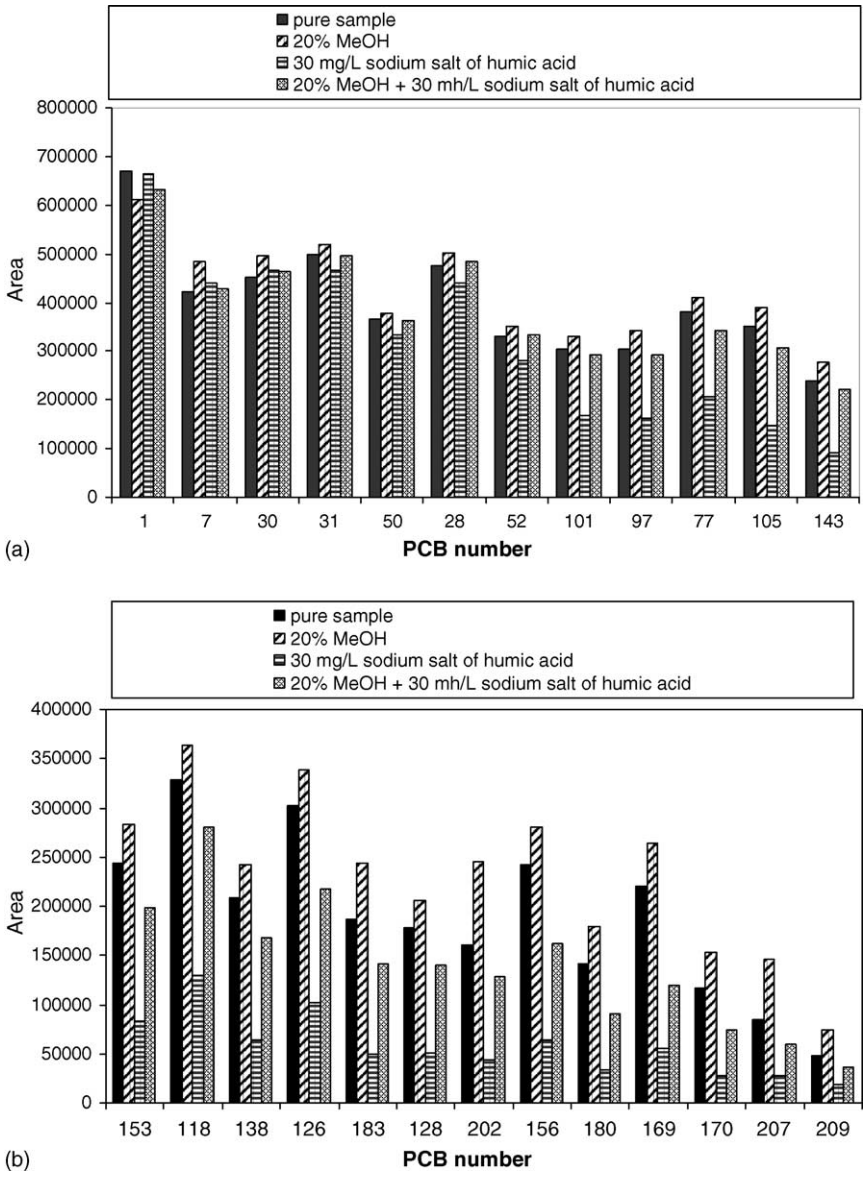

Fig. 3. Influence of matrix components on the peak areas.

30 mg/l sodium salt of humic acid and 20% methanol + 30 mg sodium salt of humic acid (Fig. 3). A positive salting-out effect was not expected because of the hydrophobicity of the PCBs. Besides, Schellin and Popp [4] showed that in case of membrane-assisted solvent extraction of PCBs the addition of salt decreased the extraction yield. So the influence of salt concentrations was not investigated. The results show that for all investigated PCBs excepting PCB 1 the addition of methanol increases the recoveries. This effect can be explained by the decreased adsorption of the PCBs on the glass walls of the extraction device [12]. The addition of organic matter especially for the higher chlorinated PCBs strongly reduces the recoveries but can be partially compensated by the addition of 20% methanol. As a consequence the validation of the procedure was performed with spiked water samples under addition of 20% methanol.

3.4. Figure of merit

The optimised SBSE procedure was validated with respect to precision, recovery, linear dynamic range and detection limits. To calculate its reproducibility, a sample of bidistilled water and 20% methanol was spiked with a concentration of 10 ng/l of the 25 PCBs and then extracted with 10 different stir bars. The results are given in the third column of Table 2. The relative standard deviations for PCB 1 to PCB 202 were between 3.3% (PCB 101) and 10.6% (PCB 30); only for the two PCBs with the highest boiling points and the lowest recoveries the RSD-values were 14.7% (PCB 207) and 29.7% (PCB 209). Taking into account that 10 different stirrers were used, the precision of the method (except for PCB 209) is satisfactory. These stir bars were used for calibration and for the analysis of real samples.

Table 2
Performances of the SBSE method for the selected PCBs (extraction time: 2 h)

Compound	Recovery (%)	Reproducibility (%)	Detection limit (ng/l)	R^2
PCB 1	93	6.2	0.10	0.996
PCB 7	88	8.6	0.10	0.999
PCB 28	90	4.6	0.10	0.997
PCB 30	85	10.6	0.10	0.996
PCB 31	88	5.1	0.10	0.997
PCB 50	85	6.5	0.05	0.997
PCB 52	93	3.7	0.05	0.998
PCB 77	93	4.1	0.10	0.996
PCB 97	91	3.4	0.10	0.997
PCB 101	89	3.3	0.10	0.998
PCB 105	90	4.2	0.10	0.996
PCB 118	92	4.6	0.10	0.997
PCB 126	88	5.5	0.10	0.997
PCB 128	83	6.0	0.08	0.997
PCB 138	87	5.7	0.05	0.997
PCB 143	87	4.7	0.05	0.997
PCB 153	88	5.1	0.05	0.997
PCB 156	86	6.6	0.05	0.997
PCB 169	84	8.4	0.05	0.997
PCB 170	78	9.1	0.05	0.994
PCB 180	79	8.2	0.05	0.995
PCB 183	78	7.1	0.05	0.994
PCB 202	75	8.8	0.08	1.000
PCB 207	51	14.7	0.08	0.992
PCB 209	28	29.7	0.15	0.997

Recoveries were calculated by comparing the peak areas of the extracted compounds with a standard solution injected on a glass-wool filled thermodesorption tube. The results are given in Table 2, column 2. The values for the investigated PCBs were between 28% (for PCB 209) and more than 80% for the PCBs 1, 7, 28, 30, 31, 50, 52, 77, 97, 101, 105, 118, 126, 128, 138, 143, 153, 156 and 169.

Calibration was performed by extracting spiked water–methanol samples at 7 calibration levels (0.1, 0.5, 2.5, 5, 10, 50 and 100 ng/l). For all the investigated PCBs no peak areas in the blanks (extraction of bidistilled water) were found and the limit of detection was defined as the concentration giving a signal-to-noise ratio of 3. The results are listed in Table 2, column 3. Linearity was investigated within the range between the detection limit and 100 ng/l, and the R^2 values were found to be between 0.992 and 1.000. A comparison with some recent papers for the determination of PCBs in waters shows that the detection limits for a 8 ml sample are exceptionally low (between 0.05 and 0.15 ng/l). Westbom et al [18] used the solid-phase extraction coupled to GC/ECD and a water sample of 1 l to obtain LODs between 0.25 and 1.0 ng/l. Cortazar et al. [19] used the SPME with a 30 μm PDMS fibre in combination with GC/MS and calculated for 6 PCBs at a 30 ml water sample LODs between 30 and 110 ng/l. Schellin and Popp [4] obtained with the membrane-assisted solvent extraction and a 15 ml water sample for the PCBs 28, 52, 101, 138, 153 and 180 LODs between 2 and 10 ng/l.

3.5. Environmental samples

The procedure was tested for contaminated river water and groundwater samples from the region of Bitterfeld northern Leipzig, Germany. The river “Spittelgraben” is a wastewater channel of a chemical industry plant from the former GDR located in the town Bitterfeld. In the water of this river no PCBs were found. Therefore the samples were spiked with the 25 selected PCBs with a concentration of 10 ng/l for each PCB. The recoveries of the PCBs represent an average of three measurements for each sample. The results (extraction recoveries in reagent water are considered as 100%) are given in Table 3 with recoveries between 89% and 100%. The result shows that in this case the method is nearly independent from the matrix.

The second sample was a contaminated groundwater of the Bitterfeld region, taken from a depth of 2.5–5.6 m. Three of

Table 3
Recovery of the spiked samples in river water (concentration: 10 ng/l)

PCB	Recovery (%)	PCB	Recovery (%)	PCB	Recovery (%)
1	96	101	99	169	91
7	97	105	97	170	90
28	97	118	96	180	93
30	99	126	96	183	94
31	100	128	94	202	93
50	97	138	96	207	89
52	99	143	97	209	95
77	97	153	97		
97	98	156	94		

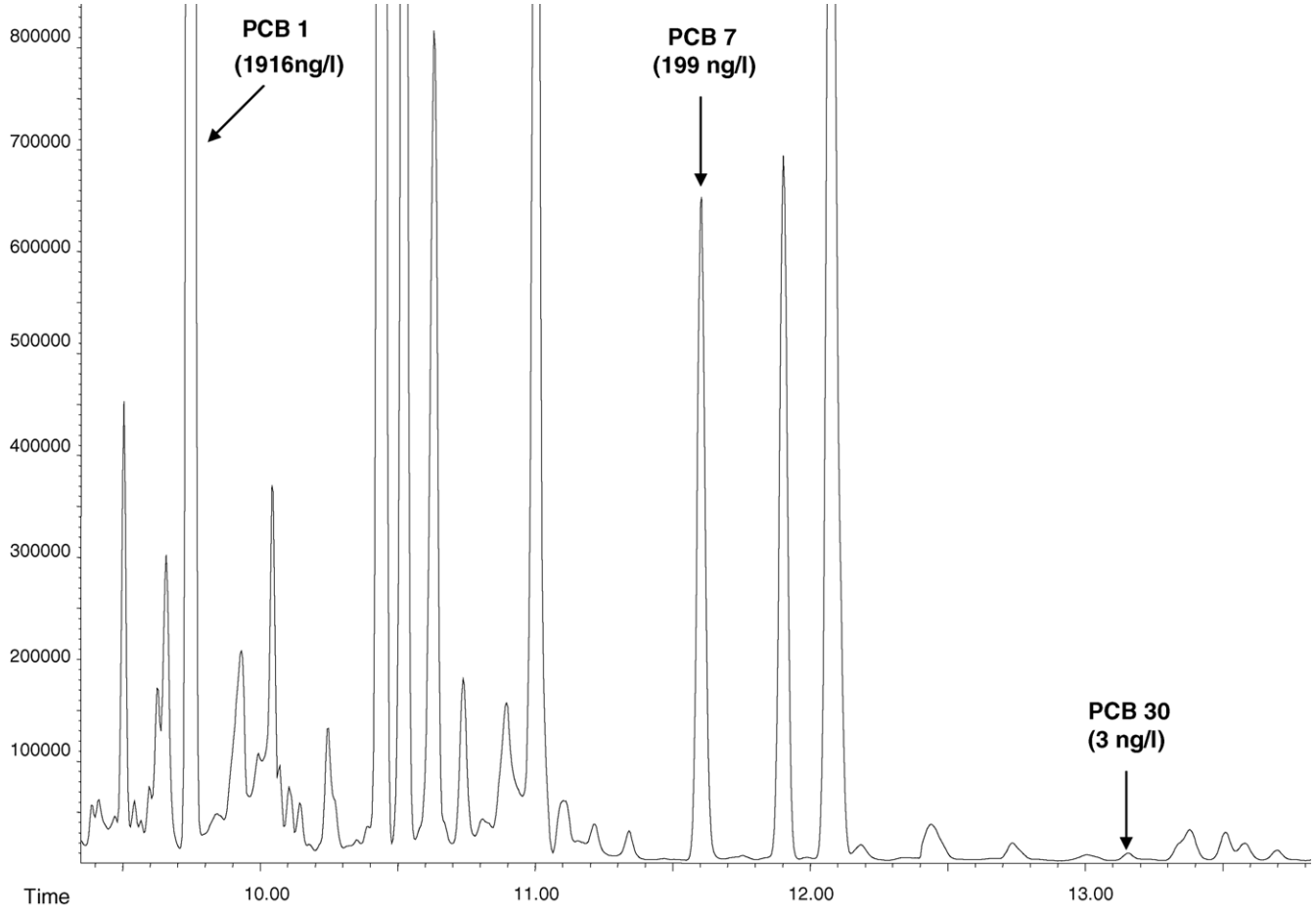

Fig. 4. Determination of PCBs in a contaminated groundwater sample.

the investigated compounds (PCB 1, PCB 7 and PCB 30) were found in very different concentrations (see Fig. 4). The original sample was injected to determine PCB 30, PCB 7 and PCB 1 were quantified from a dilution of 1:10 and 1:100, respectively. The concentrations were 1916 ng/l (PCB 1), 199 ng/l (PCB 7) and 3 ng/l (PCB 30).

4. Conclusion

The developed method enables the determination of PCB concentrations in water samples down to the pg/l range. Because the investigated PCBs comprise all steps of chlorination (from PCB 1 as monochlorobiphenyl to PCB 209 as decachlorobiphenyl) the results should be representative for the total class of the 209 PCB congeners.

Acknowledgement

We thank Mrs. Ursula Winkler for the excellent technical assistance.

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