Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Chromatography A, 1071 (2005) 155–162
JOURNAL OF CHROMATOGRAPHY A
www.elsevier.com/locate/chroma

Optimized method for the determination of 25 polychlorinated biphenyls in water samples using stir bar sorptive extraction followed by thermodesorption-gas chromatography/mass spectrometry

P. Popp [a,*], P. Keil [a], L. Montero [a], M. Rückert [b]

[a] *Department of Analytical Chemistry, UFZ-Centre for Environmental Research, Permoserstrasse 15, Leipzig 04318, Germany*
[b] *Interdisciplinary Department of Industrial and Mining Landscapes, UFZ-Centre for Environmental Research, Permoserstrasse 15, Leipzig 04318, Germany*

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-

* Corresponding author. Tel.: +49 341 235 2408; fax: +49 341 235 2625.
E-mail address: peter.popp@ufz.de (P. Popp).

0021-9673/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
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