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Journal of Chromatography A, 845 (1999) 349–355

JOURNAL OF  
CHROMATOGRAPHY A

Short communication

## Comparison of the efficiency of extraction methods for polychlorinated biphenyls from environmental wastes

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### Abstract

Polychlorinated biphenyls (PCBs) from sludge coming from city sewage-treatment plants were extracted by different methods of extraction (in a Soxhlet apparatus, by sound amplification and by shaking) with the use of methylene chloride and hexane as solvents. Seven chosen PCB isomers with the following codes: 28, 52, 101, 118, 138, 153 and 180 (according to IUPAC) were determined by GC–MS. A universal method of extracting PCB isomers analyzed as tested standards could not be elaborated. Each method of extraction with the use of a particular solvent is effective and selective for particular PCB isomers. © 1999 Elsevier Science B.V. All rights reserved.

*Keywords:* Extraction methods; Environmental analysis; Sewage sludge; Polychlorinated biphenyls

### 1. Introduction

Polychlorinated biphenyls (PCBs) form a group of organic micropollutants of the environment, especially dangerous to living organisms due to weak biodegradability and high toxicity of some congeners and the possibility of bioaccumulation in adipose tissue [1–5]. Therefore, for many years they have been on lists of the main environmental pollutants requiring control, according to both the US Environmental Protection Agency (EPA) and the European Union (EU). The presence of PCBs in ecosystems is exclusively related to economic activity and results from using commercial products (such as Aroclor, Clophen, Fenclor, Delor etc.). Prolonged use of PCBs as dielectric liquids in transformers and condensers, as hydraulic liquids, as additives used in

the paint and lacquer industry and in manufacture of plastics has led to the spread of these compounds throughout the world [1–6]. The source of PCBs in sewage can range from used transformer oils or dielectric liquids to liquid waste which contains organic substances as a result of combustion processes [7]. Due to their weak solubility, PCBs are eliminated from water in the process of partitioning during sewage treatment. Its effect may be the formation of sludge with PCB concentrations ranging from 1 to 10 mg/kg. A large part of this sludge is used as an organic fertilizer for soil improvement. Obligatory standards permit the use of sludge in fertilizing the soil only when the heavy metal content is within permissible limits. Only the USA and some European countries (for example the Netherlands, Germany and Switzerland) introduced standards of tolerance or boundary PCB values allowable in sludge to be used in soil improvement [8,9]. Because of the proven harmful influence of PCBs on man and the fast spread of these compounds in the environ-

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ment, many countries have taken administrative actions leading to the restriction of human contact with these substances. Such actions have gone both in the direction of limiting PCB production and use, as well as towards establishing permissible concentrations of these compounds in water, food, air and sludge. PCBs were never produced in Poland and their use is limited only to the manufacture of electric insulation materials. However, a lot of equipment and materials containing these substances has been brought to Poland. At present, the main source of environmental pollution caused by PCBs in Poland is waste containing these compounds. The scale of the problem is not fully known yet, because there is no detailed record of such wastes. Also, there are no regulations in the Polish legislative system defining permissible concentrations of PCBs in the environment. Therefore, there is a need to work out both suitable regulations as well as standardised methods for determining these compounds, especially in water, soil and sludge used as a fertilizer in agriculture. For analyses described in this paper, sewage sludge samples from Częstochowa and Chorzów city sewage-treatment plants were used.

## 2. Experimental

### 2.1. Reagents

Throughout the study we used Ultra Resi-Analyzed hexane from J.T. Baker for gas chromatography–mass spectrometry (GC–MS), HPLC-grade methylene from Riedel-de Haën and silica gel from POCh (Gliwice, Poland). As a standard we used PCB mixture MIX 3 from Dr. Ehrenstofer at a concentration of 10 ng/μl and the following composition: 2,4,4'-trichlorobiphenyl (IUPAC No. 28), 2,2',5,5'-tetrachlorobiphenyl (IUPAC No. 52), 2,2',4,5,5'-pentachlorobiphenyl (IUPAC No. 101), 2,3',4,4',5-pentachlorobiphenyl (IUPAC No. 118), 2,2',3,4,4',5'-hexachlorobiphenyl (IUPAC No. 138), 2,2',4,4',5,5'-hexachlorobiphenyl (IUPAC No. 153) and 2,2',3,4,4',5,5'-heptachlorobiphenyl (IUPAC No. 180).

### 2.2. Instrumental analysis

We used a SUP4 universal-type drier, an LW-2

waterbath, a KS 125 shaker (Ikalabortechnik) working at 500 rpm, a vacuum rotary evaporator, a Techvamet UD20 ultrasonic disintegrator (Experimental Works, Warsaw, Poland) with 14 μm vibration amplitude at the concentrator tip and 1.65 kHz working frequency, a 150-ml volume Soxhlet apparatus and a solid-phase extraction (SPE) kit from J.T. Baker including Bakerbond SPE C<sub>18</sub> octadecyl columns (500 mg each).

For qualitative and quantitative analyses we used GC–MS [4,9–17]. Separation was achieved on a DB-5 column (30 m×0.32 mm, 1 μm). An MS 800 quadrupole mass spectrometer, working in selective ion monitoring (SIM) mode was used for detection. The analysis was conducted according to the following temperature program: 40°C/min to 40°C, 5°C/min to 120°C, during 15 min to 280°C.

An on-column feeder was used. Helium 5.0 (99.99%) was used as carrier gas. Its linear velocity was set at 14.73 cm/s (at 280°C) resulting in flow-rate of 0.33 ml/min. PCB quantitation was obtained (*m/z*) through SIM mode. For each PCB three representative ions were chosen:

Identifying ions (*m/z*) for chosen PCB

PCB 28	PCB 52	PCB 101	PCB 118	PCB 138	PCB 153	PCB 180
258	292	326	326	360	360	394
256	290	324	324	358	358	392
150	257	254	254	292	292	326

### 2.3. Testing methodology

For testing we used sludge from filter presses at city sewage treatment plants in Częstochowa and Chorzów. Sludge is a solid matter resulting from the processes of waste treatment and has high degree of humidity (up to 83.1%). The sludge used in this study had been dried to solid mass before the process of extraction.

Organic substances were extracted from the sludge either in Soxhlet apparatus or by means of sound amplification in the presence of solvent or by shaking with solvents. To perform analysis according to each extraction method a 5-g aliquot of dried sludge was weighed each time. Extracts obtained from Soxhlet apparatus, from ultrasonic disintegrating mill and from the shaking method were then passed through a silica gel-filled glass column and

next concentrated in a vacuum rotary evaporator to the volume of 0.1 ml. The extract obtained from the ultrasonic disintegrating mill was also prepared for chromatographic analyses by means of SPE.

### 2.3.1. Extraction in Soxhlet apparatus

Five g of dried sludge was weighed, extraction thimbles prepared and the extraction with 150 ml of methylene chloride or hexane was carried out for 6 or 9 h (4–6 cycles/h).

### 2.3.2. Extraction in ultrasonic disintegrating mill

Extraction in the ultrasonic disintegrating mill was performed sequentially for 15, 30 and 45 min for mixtures of 5g of sludge in 50 ml of either methylene chloride or hexane.

### 2.3.3. Shaking with a solvent

Dried and weighed sludge samples were shaken for 1, 2 and 3 h with 50 ml of either methylene chloride or hexane.

### 2.3.4. Extraction in an ultrasonic disintegrating mill and preparation of a sample for analysis by means of SPE

Forty-five min sludge extracts were prepared in the ultrasonic disintegrating mill according to the described methodology and the extracts were filtered. Next, 75 ml of distilled water and methanol was added to the concentrated extracts in order to get a clear solution (from 50 ml to 100 ml). Bakerbond SPE octadecyl C<sub>18</sub> columns (500 mg) were pre-conditioned with 2×3 ml of methanol and 2×3 ml of distilled water. A prepared sample was passed through the column with a constant speed flow of about 5 ml/min. The columns were washed with 3×3 ml of distilled water and dried in a stream of air under reduced pressure. PCBs were washed out from the sorbent with three 0.5-ml portions of methylene chloride. The obtained solution was concentrated under reduced pressure to the volume of 0.1 ml [4,16]. Extraction was repeated for new samples of sludge with the use of hexane. Simultaneously, with the above tests and according to the same methodologies, we performed extraction as well as qualitative and quantitative analyses of PCBs from sludge contaminated by a defined quantity of the standard PCBs (10 ng/kg). The extraction recovery has been calculated on the basis of the following formula:

$$\text{Recovery (\%)} = \frac{(a-b)x}{c} \cdot 100\% \quad (1)$$

where  $a$  = peak area of a given PCB isomer for a sample contaminated by a defined quantity of the standard,  $b$  = peak area of a given PCB isomer for a tested sample,  $c$  = peak area of a given PCB isomer for a standard and  $x$  = concentration of standard-containing sample divided by concentration of standard for a given volume of proportioning.

## 3. Results and discussion

### 3.1. Extraction in Soxhlet apparatus

The following values were determined in the sludge extract from a sewage-treatment plant in Częstochowa: 64.3% recovery of PCB 101 in case of extraction with methylene chloride; 75.2% recovery for PCB 28 and 68.6% for PCB 52 in the case of extraction with hexane. Increasing the extraction time (i.e., the number of solvent circulation cycles) caused an increase of concentration of PCBs being determined for methylene chloride. Total concentration of the determined PCBs 28 and 101 was 23 µg/kg of dried mass (d.m.) (Table 1). The recovery for a 6- and 9-h extraction was comparable for PCB 101 (64.3% and 62.8%) and within the limit of analytical error ( $\pm 3\%$ ). However, for the hexane extract, the determined quantities of PCB 28 and PCB 52 were close, both in a 6- and 9-h extraction (Table 1). The recovery for PCB 28 after a 6-h extraction was 75.2% and after 9 h it reached 70.4%. For PCB 52 after a 6-h extraction the recovery was 68.6%, after a 9-h extraction it was 69.2%. The limit of analytical error has ranged from  $\pm 7\%$  to  $\pm 2\%$ .

Using methylene chloride for PCB extraction from Chorzów sewage-treatment plant sludge was not effective; no PCB isomer was found. In hexane extracts PCBs of a higher degree of chlorination were been determined (PCBs 101, 118, 138, 153, 180) and their total concentration reached 481 µg/kg of d.m. after a 6-h extraction and 551 µg/kg of d.m. after a 9-h extraction, respectively (Table 2). The recovery after a 6-h extraction ranged from 64.3% for PCB 153 to 69.2% for PCB 118, while after a 9-h extraction it reached from 64.1% in case of PCB 153 to 71.0% for PCB 118.

Table 1  
Concentration of chosen PCB isomers in sludge samples from the city sewage-treatment plant in Częstochowa

Method			Solvent														$\Sigma$
			Methylene chloride ( $\mu\text{g}/\text{kg d.m.}$ )							Hexane ( $\mu\text{g}/\text{kg d.m.}$ )							
			PCB 28	PCB 52	PCB 101	PCB 118	PCB 138	PCB 153	PCB 180	PCB 28	PCB 52	PCB 101	PCB 118	PCB 138	PCB 153	PCB 180	
Soxhlet apparatus	6 h	no <sup>a</sup>	no	8	no	no	no	no	8	17	15	no	no	no	no	no	32
	9 h	8	no	15	no	no	no	no	23	13	18	no	no	no	no	no	31
Ultrasonic disintegrating mill	15 min	5	5	10	no	7	8	no	35	22	25	no	no	no	no	no	47
	30 min	9	8	10	no	14	6	no	47	20	13	no	no	no	7	no	40
	45 min	12	10	11	no	21	15	no	69	16	9	no	no	15	8	no	48
Ultrasonic/SPE		12	9	7	7	23	31	no	89	15	22	no	no	16	11	no	64
Shaking	1 h	no	7	no	no	no	20	no	27	14	6	no	no	no	6	no	26
	2 h	no	10	no	no	no	16	no	26	10	8	no	no	no	7	no	25
	3 h	no	10	no	no	no	18	no	28	10	11	no	no	no	7	no	28

<sup>a</sup> no = Not detected (below the limit of determination).

### 3.2. Extraction in ultrasonic disintegrating mill

In the case of sludge from sewage-treatment plant in Częstochowa we observed the influence of sound amplification time on the intensity of PCB extraction with the use of methylene chloride. In extracts we determined PCBs 28, 52, 101, 138 and 153. Their total concentration was 35  $\mu\text{g}/\text{kg}$  of d.m. (after 15 min of sound amplification), 47  $\mu\text{g}/\text{kg}$  of d.m. (after 30 min of sound amplification) and 69  $\mu\text{g}/\text{kg}$  of d.m.

(after 45 min of sound amplification) (Table 1). The recovery of PCBs determined ranged from 69.2% (PCB 180) to 77.2% (PCB 28); the analytical error being  $\pm 2\%$ . Extraction by means of hexane was less efficient: after 15 min of extraction only PCBs 28 and 52 were determined; their total concentration reached 47  $\mu\text{g}/\text{kg}$  of d.m. It was higher than the PCB concentration after extraction by means of methylene chloride. Raising extraction time decreases values of determined PCB 28 and 52 con-

Table 2  
Concentration of chosen PCB isomers in sludge samples from the city sewage-treatment plant in Chorzów

Method			Solvent														$\Sigma$
			Methylene chloride ( $\mu\text{g}/\text{kg d.m.}$ )							Hexane ( $\mu\text{g}/\text{kg d.m.}$ )							
			PCB 28	PCB 52	PCB 101	PCB 118	PCB 138	PCB 153	PCB 180	$\Sigma$	PCB 28	PCB 52	PCB 101	PCB 118	PCB 138	PCB 153	
Soxhlet apparatus	6 h	no <sup>a</sup>	no	no	no	no	no	no	–	no	no	78	49	96	138	120	481
	9 h	no	no	no	no	no	no	no	–	12	no	82	41	124	110	172	551
Ultrasonic disintegrating mill	15 min	no	no	no	no	no	no	no	–	no	52	32	16	28	30	20	178
	30 min	no	no	12	6	8	8	10	44	no	56	34	22	26	26	28	192
	45 min	10	15	32	41	30	47	54	229	206	146	126	110	166	188	150	1092
Ultrasonic/SPE		8	10	33	40	28	48	49	216	221	155	118	120	170	201	170	1150
Shaking	1 h	no	no	no	no	no	no	no	–	no	10	7	4	6	7	6	40
	2 h	no	no	no	no	no	no	no	–	no	15	12	6	10	14	7	64
	3 h	no	no	no	no	no	no	no	–	117	92	86	74	84	65	92	610

<sup>a</sup> no = Not detected (below the limit of determination).

centrations but raises the amount of various determined PCBs. The decrease of PCB 28 and 52 concentrations after a longer time may be related to extraction of organic compounds from the environmental matrix which leads to erroneously low results. This may be corroborated by the fact that preparation of sample for analysis by SPE methods allows an increase of concentration of determined PCB 52. After 45 min of extraction PCBs 28, 52, 138 and 153 were determined and their total concentration reached 48  $\mu\text{g}/\text{kg}$  of d.m. (Table 1). After 30 min of sound amplification the recovery of determined PCBs ranged from 75.6% (PCB 138) to 80.2% (PCB 28); after 45 min of sound amplification the recovery ranged from 79.0% (PCB 138) to 83.5% (PCB 28).

For sludge from the sewage-treatment plant in Chorzów the use of hexane as a solvent decidedly influenced the improvement of extraction effectiveness in the ultrasonic disintegrating mill. After 15 min of extraction six PCB isomers (52, 101, 118, 138, 153 and 180) were found and their total concentration reached 178  $\mu\text{g}/\text{kg}$  of d.m. (Table 2). We observed an increase of recovery for the PCBs under analysis along with the extraction time increase. The smallest recovery was obtained for PCB 180 (69.1%; analysis error  $\pm 4\%$ ), while the largest recovery was obtained for PCB 52 (75.3%). The increase of extraction time caused a concentration increase of determined PCBs (after 15 min of sound amplification it reached 178  $\mu\text{g}/\text{kg}$  of d.m.; after 30 min of sound amplification, 192  $\mu\text{g}/\text{kg}$  of d.m.; after 45 min of sound amplification, 1092  $\mu\text{g}/\text{kg}$  of d.m.). The recovery of determined PCBs increases also for extraction with the use of methylene chloride and it has higher values for a 45-min extraction. It ranges from 71.9% (PCB 101) to 81.0% (PCB 153). The largest analysis error for this method of extraction is  $\pm 5\%$  (PCB 180).

### 3.3. Shaking with a solvent

The results of PCB content analysis in methylene chloride and hexane treated sludge extracts from the sewage-treatment plant in Częstochowa have shown that the quantities of determined PCBs do not depend on extraction time. The kind of solvent used influences extraction effectiveness. After 1, 2 and 3 h of

extraction with methylene chloride PCBs 52 and 153 were determined and their total concentrations were, respectively, 27  $\mu\text{g}/\text{kg}$  of d.m., 26  $\mu\text{g}/\text{kg}$  of d.m. and 28  $\mu\text{g}/\text{kg}$  of d.m. After extraction with hexane PCBs 28, 52, 153 were determined; their total concentrations were 26  $\mu\text{g}/\text{kg}$  of d.m. (after 1-h shaking), 25  $\mu\text{g}/\text{kg}$  of d.m. (after 2-h shaking), 28  $\mu\text{g}/\text{kg}$  (after 3-h shaking) (Table 1). The smallest recovery after extraction with methylene chloride was obtained for PCB 52 (67.0%, 1-h shaking), the largest for PCB 153 (72.5%, 3-h shaking), but the differences were within error limits. After extraction with hexane the increase in recovery of determined PCBs was observed, but also in this case the differences were within error limits. After 1 h of shaking the recovery ranged from 66.2% (PCB 180) to 71.6% (PCB 28); the analysis errors were  $\pm 4\%$  (PCB 28) and  $\pm 2\%$  (PCB 180). The recovery after a 3-h shaking was greater than the recovery of determined PCBs after 1 and 2 h of shaking and reached 78.3% (PCB 28), 74.7% (PCB 52) and 68.9% (PCB 180).

In the case of hexane extracts from the sewage-treatment plant in Chorzów six PCB isomers were determined: (52, 101, 118, 138, 153, 180) after 1- and 2-h extraction and seven PCB isomers after 3 h of extraction. In extracts obtained with methylene chloride none of the determined PCB isomers were found (Table 2). In the extracts obtained after 1, 2 and 3 h of sludge shaking with hexane, the total concentration of determined PCB was 40  $\mu\text{g}/\text{kg}$  of d.m., 64  $\mu\text{g}/\text{kg}$  of d.m., 610  $\mu\text{g}/\text{kg}$ , respectively. The largest recovery (83.3%) was obtained for PCB 153 (after a 3-h shaking) while the smallest (65.2%) was for PCB 138 (after 1-h shaking). The largest analysis error was obtained for PCB 180 ( $\pm 7\%$ ).

### 3.4. Extraction in an ultrasonic disintegrating mill and preparation of a sample for analysis by means of SPE

Only PCB 180 was not found in the Częstochowa sewage-treatment plant sludge extract prepared by means of SPE (extraction with methylene chloride). The total concentration of the determined PCBs was 89  $\mu\text{g}/\text{kg}$  of d.m. The recovery for particular PCBs was as follows: 83.7% (PCB 101), 84.4% (PCB 28),

84.7% (PCB 153), 86.1% (PCB 52), 87.2% (PCB 138) and 87.5% (PCB 118). The use of hexane as a solvent has lowered extraction effectiveness, no PCB 101, 118 and 180 were found. The recovery for particular PCBs was as follows: 83.2% (PCB 153), 83.8% (PCB 28), 85.3% (PCB 52), 88.1% (PCB 138). The analysis error was  $\pm 4\%$  (Table 1).

In extracts from the Chorzów waste-treatment plant sludge all of the analyzed PCBs were found, when using either methylene chloride or hexane as solvents. Extraction by means of hexane substantially improved the effectiveness of separation of the analyzed PCBs from sludge and their total concentration reached 1155  $\mu\text{g}/\text{kg}$  of d.m. (Table 2). The recovery of the PCBs determined ranged from 73.9% (PCB 180) to 88.8% (PCB 28). In extracts obtained with methylene chloride the total concentration of the determined PCBs was 216  $\mu\text{g}/\text{kg}$  of d.m. The largest recovery (88.2%) was obtained for PCB 28 while the smallest (72.4%) was for PCB 180. The analysis error decreases for extraction with hexane reaching  $\pm 3\%$ .

#### 4. Conclusions

In the sludge from the sewage-treatment plant in Częstochowa six PCB isomers were found (28, 52, 101, 118, 138, 153) and their highest total concentration determined was 89  $\mu\text{g}/\text{kg}$  of d.m. In the sewage-treatment plant sludge from Chorzów seven PCB isomers were determined and their highest total concentration determined was 1155  $\mu\text{g}/\text{kg}$  of d.m. The cause of high PCB concentration in extracts from sewage-treatment plant sludge in Chorzów may be the fact that Chorzów is situated at the center of an industrial district with many chemical plants. Probably a lot of industrial waste also finds its way into this particular sewage-treatment plant.

The results of PCB content analysis in extracts from tested sludges obtained by using various extraction methods, extraction time and solvents show that as extraction time increases, concentration and recovery of the determined PCBs go up as well. An average standard deviation is comparable or it decreases with extraction time increase. The largest

analysis error has been recorded for the shaking method and it reaches  $\pm 7\%$ . Analysing the results obtained after extraction with different solvents shows that in almost all the cases use of hexane increases concentration, selectivity and recovery of the determined PCBs (with the exception of extract obtained from sewage-treatment plant sludge in Częstochowa). The use of methods and solvents tested shows that each tested standard is an individual entity and at least two methods of extraction should be used in order to confirm the correctness of quantitative and qualitative determination of the analyzed PCBs. The use of methylene chloride and hexane as solvents shows that each of these solvents is selective for particular PCB isomers.

#### Acknowledgements

This research was supported by State Committee for Scientific Research, Poland (Research Project No. 6PO4G09810).

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