Determining Polychlorinated Biphenyls in Soil Using Accelerated Solvent Extraction (ASE)

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Abstract

Contamination of the environment with compounds belonging to the persistent organic pollutants (POPs) group constitutes a global problem. According to the Stockholm Convention adopted in 2001, much effort should be put into the minimisation of its presence not only in soil, water, and residues, but also in living organisms where these compounds are accumulated. As a consequence of research conducted in the area of environmental matrices involving wide ranges of chemical compounds, a growing demand for various certified reference materials has been observed. This study was focused on finding the most efficient extraction conditions for six polychlorinated biphenyl congeners: Nos. 28, 52, 101, 138, 153, and 180, with the accelerated solvent extraction (ASE) method and with the use of CRM963 manufactured by RTC. Analyte recovery was examined by the application of the following solvents: hexane, hexane/acetone, and acetone/dichloromethane at 150ºC and 170ºC. The best recovery (88.5-106%) and the lowest standard deviation (2.1-5.7%) values were obtained for hexane at 170ºC. The method was further employed to determine the homogeneity and stability of soil being the candidate for CRM. Moisture and organic carbon content in both the CRM963 as well as the soil examined were determined.

Keywords: polychlorinated biphenyls, soil, certified reference materials, gas chromatography, accelerated solvent extraction

Introduction

Polychlorinated biphenyls (PCBs) belong to the group of persistent organic pollutants (POPs). The POPs are chemical substances that exhibit certain toxic properties which, in contrast to other contaminants, are degradation-resistant. The POPs are particularly harmful to humans and the environment. They undergo bioaccumulation in living organisms and distribution by air, water, and migratory species; they also get accumulated in terrestrial and aquatic ecosystems. POP-caused contamination is a transnational problem and therefore requires international cooperation and actions. PCBs are classified to this group due to the properties they present, e.g. high thermal conductivity, intermediate vapour pressure, stability at high temperatures, and resistance to acids and bases. In the 1970s, owing to the above-mentioned properties, PCBs were commonly used in industry. Among others, their applications involved the production of condensers, transformers, printing ink, or plastics. The manufacture and use of those products resulted in the problem of waste disposal, and thus environmental contamination. The contamination of water, soil, and residue with PBCs as well as their tendency to bioaccumulate in living organisms constitutes a problem serious enough to result in the reduction of their industrial application as a result of the Stockholm Convent adopted in 2001, which issued limitations to the POPs applications for industrial purposes. Despite the reduction of the PCB application, the problem of environmental contamination still exists [1-3].

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A significant number of studies currently carried out deals with environmental contamination with compounds of the POPs group. To perform an analysis that gives reliable results, certified materials (CRM) are used in order to check and validate the examination procedure, measuring equipment calibration, and to provide internal and external control over laboratories. The CRMs ensure homogeneity, stability, and well-known physical and chemical properties [4, 5].

Extraction using the accelerated solvent extractor (ASE) is a commonly employed method of separating numerous compounds from the POPs group, e.g. the polycyclic aromatic hydrocarbons (PAH), pesticides, and PCBs from various environmental matrices. The method is often used due to the use of small amounts of solvents, small weighed amounts, short analysis time, and satisfactory repeatability [6-10].

Our research was aimed at finding and validating the most efficient conditions for the method of extracting six PCB congeners with the use of a commercial reference material. It also focused on determining those compounds' content, homogeneity, and stability in natural soil, which is a candidate for the certified material of soil used in PBC determination.

Experimental Procedures

Experimental Materials

We used a standard substance, PCB Mix 1 (Dr. Ehrenstorfer GmbH, Germany) with PCB Nos. 28, 52, 101, 138, 153, and 180 congeners in isooctane, each at a concentration of 10 ng/μl. Standard solutions were prepared in the range from 2.5 to 500 ng/ml by diluting in hexane. In order to find appropriate extraction conditions, certified material manufactured by RTC CRM963-50G was used. GC analytical-grade organic solvents and silver nitrate were purchased from Avantor Performance Materials (Poland). Sand required for extraction was repeatedly rinsed with distilled water and heated at 600ºC for four hours. Silica gel for chromatographic applications, 100-200 mesh (Merck, Germany), was activated at 130ºC for 16 hours.

Soil Moisture and Organic Carbon Analysis

Materials' moisture was checked with the use of a moisture analyzer (Sartorius MA35). Organic carbon content was determined with a total organic carbon analyzer (TOC 5000 Shimadzu).

Particle Fraction

Particle fraction was determined by test sieve in CRM963 and in candidate for the certified material of soil. Fractions were collected in the range 05 – <0.025 mm.

Sample Extraction and Clean-Up

The extraction method was based on the EPA 3545a method [11]. The ASE 100 Dionex was applied for the extraction of six PCB congeners. The soil was earlier crushed and lyophilized, and in this form delivered to laboratory. The mass of the sample was approximately 1 g. The recovery of the method was checked for various solvents (i.e. hexane, acetone/dichloromethane in 1:1 ratio, acetone/hexane in 1:1 ratio) and for three temperature values (i.e. 120ºC, 150ºC, 170ºC). Three static cycles were performed, each held for five min. Nitrogen purge was carried out for 100 s. The obtained extracts were concentrated to the volume of approx. 1 ml and purified in SPE columns packed with $AgNO_3$ silica gel. It was used hexane to elution [12]. The obtained extracts were concentrated in gentle stream of nitrogen at the temperature 50ºC to the volume of 1 ml.

PCB Analysis

Concentrated extracts were analysed by an Agilent GC 6890N combined with an Agilent MSD 5975 in the SIM mode. The column was ZB 5MS, 30 m × 0.25 mm × 0.25 μm. The injector temperature was set at 265ºC, and the oven temperature started at 50ºC (holding time one min.), increased to 150ºC at 20ºC per minute (holding time two minutes), then to 280ºC at 5ºC (holding time six min.). Helium was a carrier gas with flow of 1.1 ml/min. The injecting volume was 1 μl. The temperature of the ion source was 300ºC.

Homogeneity and Stability

Homogeneity was calculated for five packages, each containing 50 g of the examined soil. Five samples were prepared from each of the packages; for each sample, three GC/MS analyses were performed. The homogeneity determination was conducted on the basis of within-the-bottle and between-bottles coefficients of variability (1). The examined analyte stability determination was based on the six PBCs' content analyses. The experience lasted four months with one month periods.

$$CV = \frac{SD}{\bar{x}} \tag{1}$$

...where: CV – coefficient of variability, SD – standard deviation, $\bar{x}$ – average concentration [ng/g].

Results

Water Content

The moisture content in the CRM963 was 1.82%. The examined soil was characterized by low water content ranging from 1.65% to 1.87%.

Table 1. Percentage distribution [%] of particle fraction [mm].

Material	>0.5	0.5<x<0.25	0.25<x<0.1	0.1<x<0.063	0.063<x<0.045	0.045<x<0.025	<0.025
CRM963	1.28	7.8	34.9	19.9	10.7	13.9	5.9
Candidate for CRM	0	2.2	48.9	19.8	10.5	8.8	5.6

Table 2. Equations of calibration curves, correlation coefficients R^2 and determined LOD and LOQ values of applied GC/MS system for six PCB congeners.

Congener PCB No.	Calibration equation	R^2	LOD [ng/g]	LOQ [ng/g]
28	$y = 174.25x + 0.15$	0.9998	3.28	9.84
52	$y = 173.77x - 27.91$	0.9999	0.82	2.45
101	$y = 170.05x - 21.22$	0.9994	3.11	9.32
153	$y = 136.08x - 12.68$	0.9995	8.70	26.09
138	$y = 130.43x - 13.95$	0.9997	2.86	8.58
180	$y = 104.32x - 88.59$	0.9994	2.62	7.85

Carbon Content

The percentage value of carbon content in the CRM was between 0.48% and 0.72%. The examined soil contained from 1.35 to 1.55% of organic carbon.

Particle Fraction

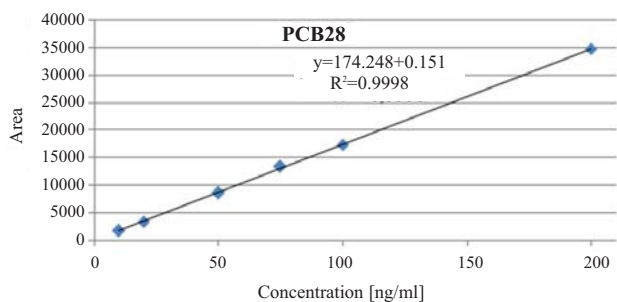Particle fraction distribution is presented in Table 1.

Fig. 1. Calibration curve of applied GC/MS system (SIM mode) for PCB No. 28.

Validation

For each examined analyte, the linearity coefficients found for the calibration curves is close to 1. Fig. 1 presents a calibration curve for PCB No. 28 and Fig. 2 presents a chromatogram obtained from the CRM963 analysis. Based on equations, the detection and quantification limits of six PCB congeners were calculated. The values of the above-mentioned parameters are presented in Table 2. Jurowski et al. [13] described how an important step in method validation is calibration.

On the basis of the analyses carried out and certified values, the recovery value for each particular analyte was found (Table 3). Both recovery as well as standard deviation values are essential when choosing the most efficient method conditions.

Homogeneity and Stability

In order to analyse soil that was a candidate for the certified material, hexane was applied as the solvent. The extraction was carried out at 170ºC. The choice was
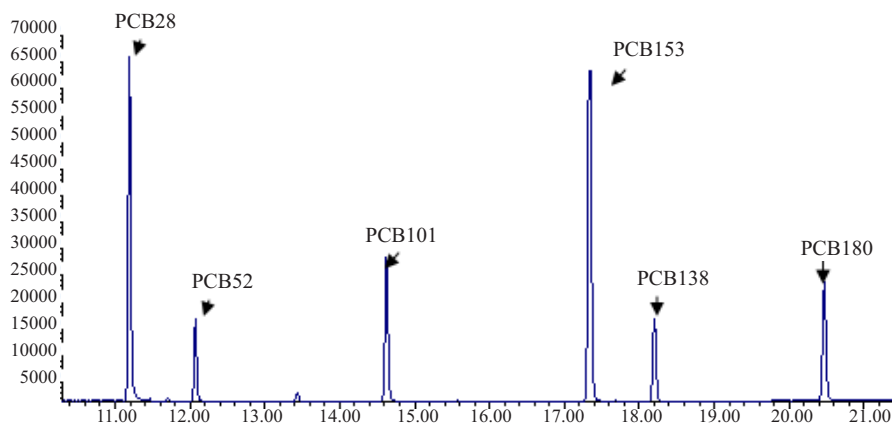

Fig. 2. Chromatogram of CRM963.

Table 3. Contents of PCB congeners in certification of CRM963, recoveries (Recov.) and standard deviations (SD) [%] for used conditions of method.

| PCB		No. 28		No. 52		No. 101		No. 153		No. 138		No. 180	
Certified contents[ng/g]		148±25.5		40.3±3.26		77.3±11.3		290±28.1		84.5±3.98		135±20.0	
Solvent	Temp. [ºC]	Recov.	SD	Recov.	SD	Recov.	SD	Recov.	SD	Recov.	SD	Recov.	SD
Hexnae	150	91.3	7.1	102.1	9.1	96.0	4.2	102.4	3.8	92.0	2.7	110.1	2.3
	170	90.4	3.6	99.0	5.7	94.3	4.6	99.9	5.3	88.5	4.0	106.0	2.1
Hexane/ Acetone (1:1)	150	91.3	10.5	84.5	6.7	88.9	0.3	96.7	1.8	82.2	5.5	114.9	14.3
	170	95.0	10.1	94.3	7.7	105.3	3.6	117.2	2.8	104.6	0.8	138.5	17.7
Acetone/ DCM (1:1)	150	109.8	13.7	104.3	8.0	115.4	12.0	124.3	12.4	115.1	13.4	145.9	8.4
	170	96.6	3.7	102.7	3.1	106.6	2.7	118.5	4.4	109.2	8.7	142.6	10.4
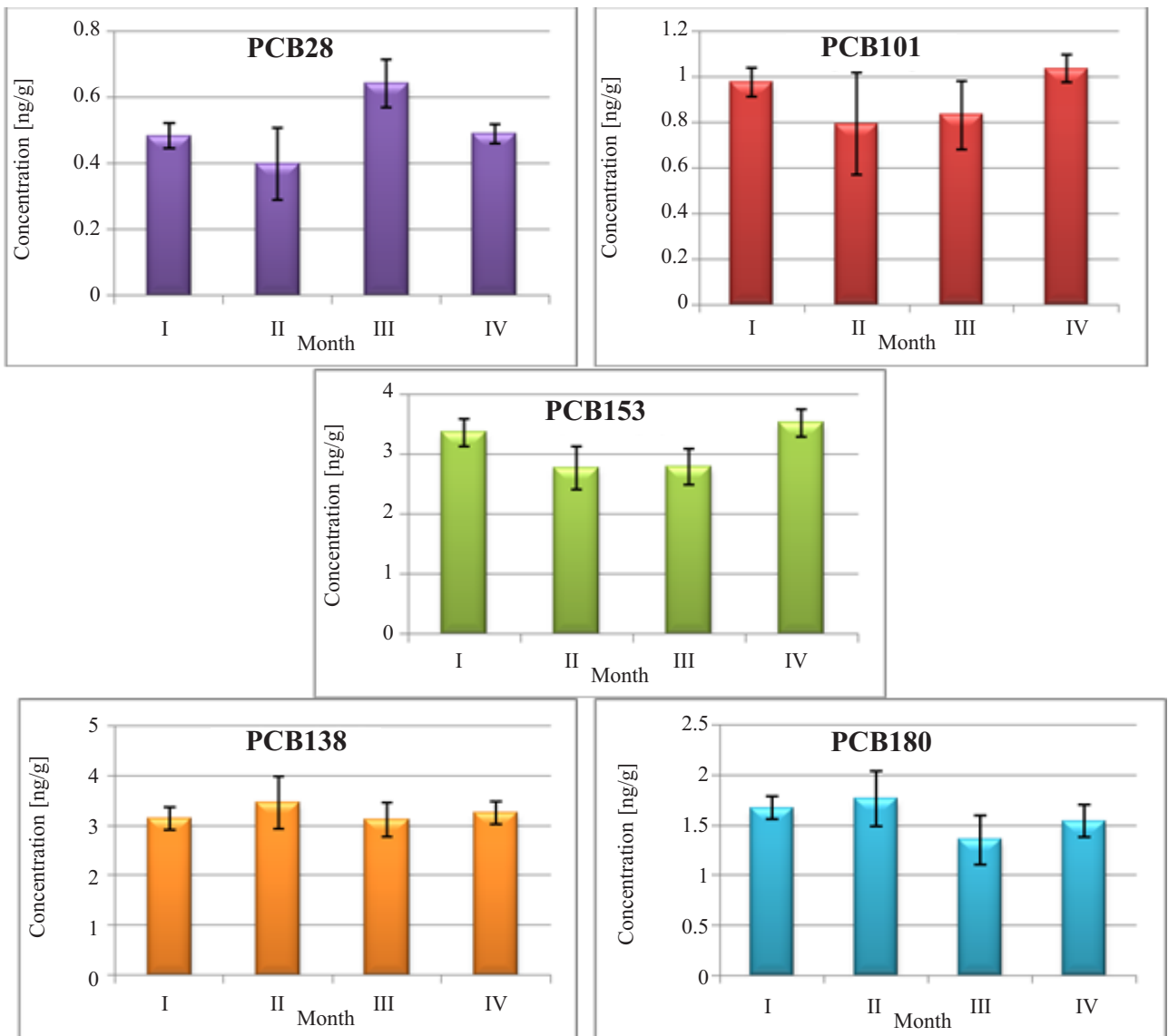
Fig. 3. Comparison of concentration congeners of PCBs over four months.

Table 4. Coefficients of variability within-the-bottle CV_{WB} and between-bottles CV_{BB}.

Congener of PCB	CV_{WB} [%]	CV_{BB} [%]
No. 28	49.0	14.9
No. 52	ND	ND
No. 101	45.4	34.4
No. 153	41.6	18.4
No. 138	34.7	32.8
No. 180	40.8	47.0

ND – not detected

justified by high recovery values and lowest standard deviations obtained for each of the analytes examined. With regard to low content levels of particular congeners, it was necessary to increase the weighed amount to 1.5 g and concentrate the sample to the volume of 100 µl. PCB No. 52 was not detected. Coefficient of variability values are presented in Table 4.

Fig. 3 shows charts comparing the analyze contents in one of the five packages examined within four months. As can be seen from the charts, there is no decrease in PCB congener concentrations. The analyze content is constant; standard deviations are on a comparable level.

Results and Discussion

The levels of both moisture and organic carbon were at comparable levels in the cases of the environmental matrices examined. Particle fractions were also similar. Therefore, the choice of the CRM to study the method conditions was confirmed to be suitable for the determination of PCBs in soil. The method was further used to separate six PCB congeners from the soil being the candidate for the reference material. The linearity, detection, and quantification limits – as well as recovery and repeatability calculations performed – allowed us to find the most efficient method conditions. Hexane was applied as the solvent and the temperature was set at 170ºC due to the recovery values close to 100% and ranging from 80 to 120%, which is required for the analytical method. Also, the standard deviation values were lower than 10% for each of the analytes.

In the case of soil being a candidate for reference material, it was found that the total amount of the analytes examined does not exceed 20 ng/g. The values of the CV which were calculated in order to determine the homogeneity within-the-bottle and between-bottles are 34.7-55.4% and 14.9-47%, respectively. It is necessary to take these values into account when estimating the uncertainty of the certified values. The comparison of the analytes contents examined every month for four consecutive months shows that these values undergo no changes. Thus it can be stated that, in terms of the PCB congeners, the material content is stable.

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