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Original Research

Validation of an Analytical Procedure for Selected Polychlorinated Biphenyls Determination in Sediment Samples

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Abstract

This paper describes the method for determining 15 individual polychlorinated biphenyls in sediments, using fexIKA extraction. The analytical procedure included extraction and clean-up of extracts with concentrated sulfuric acid and solid phase extraction (SPE) on Florisil. The identification and quantification of analytes were carried out by capillary gas chromatography (GC) with electron capture detector (ECD) and/or low resolution mass spectrometry (LRMS). The method detection and quantification limits varied from 0.06 to 0.12 and from 0.2 to 0.4 ng/g dry weight, respectively. The relative standard deviations in repeatability and intra-laboratory reproducibility studies varied from 3.2 to 11.2%. Recoveries of analytes from spiked sediment samples were between 74.0% and 108.8%. The method was linear and characterized by good correlation coefficients (>0.99) for all compounds studied. The quality of the method under validation was verified by the analysis of certified reference material and by participation in an interlaboratory exercise.

Keywords: PCB, sediments, method validation

Introduction

Polychlorinated biphenyls (PCBs) have been included in the Stockholm Convention list of pollutants since 2001 [1] due to their ubiquity, persistence and toxicity. In the aquatic environment PCBs tend to accumulate in sediments and biota because of their hydrophobic character and consequently low solubility in water [2, 3]. The need to identify individual PCB congeners in environmental and biological matrices results from the fact that they are characterized by very different levels of toxicity [4-6].

Although PCBs have been measured for over 40 years, the accurate and precise determination of selected congeners in multicomponent environmental matrices (sediments, biota) might continually present some problems [7, 8]. The 34th round of QUASIMEME interlaboratory exercises showed that only 28-52% of the results of PCB determination in marine sediments (depending of congener) were classified as satisfactory ($|z|<2$) [9].

A large number of various isolation procedures for PCB from several matrice types has been described [10-12]. Soxhlet extraction has been the traditional method used for the extraction of PCB congeners from sediments and other environmental samples [9, 12-14]. In recent years, new extraction techniques have been established in order to reduce the solvent volume used for extraction, to improve the precision of analyte recoveries and to reduce extraction time [11, 15-18]. To ensure the quality of results, all analytical procedures should be validated in laboratory experiments according to the requirements of modern analytical chemistry [19, 20].

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The aim of this work was to evaluate and validate the method of the determination of select PCB congeners in sediment samples using the fexIKA 200 apparatus for the extraction of analytes.

Experimental

Chemicals

Individual chlorobiphenyls used as primary standards (PCB IUPAC Nos: 28, 52, 74, 101, 105, 114, 118, 128, 149, 138, 153, 156, 170, 180 and 187), PCB 30 and 209 (internal standards) were purchased from Dr. Ehrenstorfer Laboratories (Augsburg, Germany). The various working standard solutions were prepared by adding the appropriate amounts of primary standards to isooctane (Baker ® Ultra-resi analysed quality) or to acetone (Baker ® Ultra- resi analyzed quality). All measurements were made by mass.

Copper powder (Baker grade) was pre-treated prior to use: 20 g of Copper powder was washed with 3 x 50 ml of water rinsed with hexane, 3 x 50 ml of acetone, and 3 x 50 ml of hexane [21]. The remaining solvent was evaporated on the rotary evaporator and the powder was kept under hexane.

Concentrated H_2SO_4 (Merck®), n-hexane (Mallinckrodt Nanograde®), granulated sodium sulphate anhydrous (Baker Ultra-resi Analyzed) and Florisil® (for residue analysis, Baker Analyzed) were used.

Florisil was activated at 650°C for 4 hrs, stored in a desiccator and kept at 130°C for two hours before use [22]. Florisil and sodium sulphate were loaded into solid phase extraction (SPE) borosilicate glass columns (500 mg) before each elution.

Sediment Samples

Three types of sediment samples were used to evaluate and validate the examined analytical procedure.

Spiked Lake Sediments

The sediment samples used for development and validation of analytical procedure were collected at Lake of Swarzedz, situated near Poznań, Poland. To determine the efficiency of extraction, it is imperative that the contaminant is bound to the matrix in a similar configuration as in the environment [12]. Therefore, the dried sediment samples (about 2 g), were passed through a 0.09 mm sieve and dosed with known amounts of selected PCB congeners dissolved in acetone. The spiked samples were put in an ultrasonic bath for 1 hr and allowed to stand 72 hrs prior to extraction.

Certified Reference Material

The freshwater harbour sediment (BCR-536) available from the Institute for Reference Materials and Measurements (IRMM, Geel, Belgium) was used for confirmation of the accuracy and the precision of developed analytical procedure. It was certified for thirteen PCB congeners [23].

Samples for the Interlaboratory Exercise

Two test materials of river sediments were supplied by the organizers of interlaboratory proficiency studies WCH PG PCB 1 (Wydział Chemiczny, Politechnika Gdańska – Faculty of Chemistry, Gdansk Technical University) in December 2003 [24].

Analytical Procedure

Extraction

The extraction of analytes was performed in a fexIKA 200 apparatus. The principles of the fluidized-bed extraction were described by Gfrerer *et al*. [25,26]. In our studies a sample of dried sediment (circa 2g) was placed in a mortar and then 4 g of anhydrous sodium sulphate and 4 g of Copper powder were added. The mixture was blended to yield a dry powder and then transferred into an extraction tube of the extractor. 25 ml of the hexane:acetone (1:1) mixture was filled into the basic vessel and a magnetic stirring rod was put in. The second 25 ml of the same solvent mixture was then fed into the extraction tube which, in the mean time, was mounted onto the basic vessel. The successive steps of the operating cycle of the extractor are shown in Fig.1.

The heating system started at 25°C, the boiling temperature was maintained at 85°C and the heating and cooling times were 3 min. and 2 min, respectively. In all cases the time of filtration was 5 min. For optimizing the extraction procedure, the boiling time in one operating cycle as well as the number of operating cycles were evaluated.

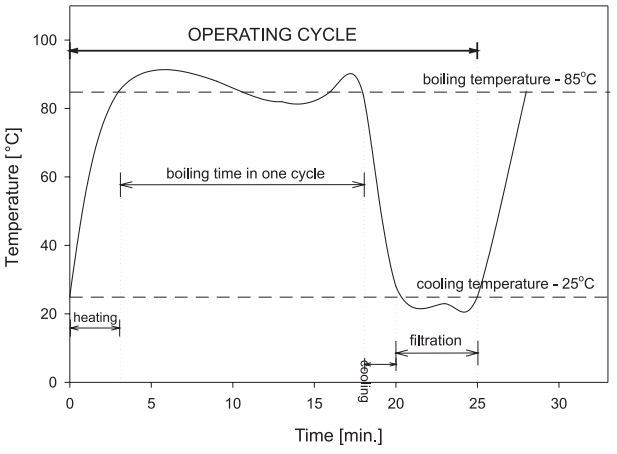

Fig. 1. Processing sequence of fexIKA extractor.

Clean Up of Extracts

The extract was evaporated on a rotary evaporator and concentrated to circa 2 ml under a stream of nitrogen gas. The concentrated extract was transferred into a centrifuge tube and agitated 2 min. with 4 ml of concentrated H_2SO_4. The hexane and acid layers were separated by centrifugation (15 min., 4000 rpm). The hexane layers were collected in a centrifuge tube. The volume of hexane solution was reduced to about 1 ml by evaporation in a nitrogen atmosphere. The extract was transferred on the preliminary conditioned SPE column filled with 500 mg of Florisil. After drying the column, the elution of analytes with 5 ml of hexane was carried out. The fraction containing PCBs was collected and reduced to the volume of about 1 ml. PCB 30 and 209 as internal injection standards were added to the extract before GC analysis.

Chromatographic Separations

The PCB identification and quantification were performed by GC with electron capture detector (ECD) on a Shimadzu GC-14A gas chromatograph equipped with a ^{63}Ni ECD and a split/splitless injector. Chromatographic separation of the examined PCB congeners was carried out on a 60 m RTx-5®, Restek Corporation (0.25 mm I.D.; film thickness 0.25 μm) fused silica capillary column (5% diphenyl polysiloxane, 95% dimethyl polysiloxane). The injector and detector temperatures were 250°C and 300°C, respectively. The nitrogen as make-up gas was used at a flow rate of 48.0 ml/min. The sample extract (3 μl) was introduced to the chromatograph with a syringe (split mode). The temperature program of the column was 2 min. at 125°C; 7.5°C/min. until 190°C and 2°C/min. until 280˚ C, holding for 15 min. The retention times were measured with accuracy of 0.001 min. using a Chrompack integrator. Each congener was identified by a comparison of the relative retention times ($RRT_{PCB30+PCB209}$) of the peaks from calibration standards with peaks from cleaned-up extracts of sediment. The repeatability of the $RRT_{PCB30+PCB209}$, expressed as relative standard deviation (R.S.D.), calculated from eighteen replicate analyses of a standard mixture of the PCB congeners was between 0.02 and 0.37**%.** The following elution order of congeners was established PCB: 30 (IS), 28, 52, 74, 101, 149, 118, 114, 153, 105, 138, 187, 128, 156, 180, 170 and 209 (IS). The linearity of the ECD response for each congener was determined by plotting calibration graphs of peak height/mass injected *versus* mass injected [27]. The linear ranges used for PCB quantification varied between 2 to 350 ng/ml, depending on the congener. The repeatability of the peak heights calculated from five replicate analyses of a standard mixture of the PCB congeners was between 3.8 and 6.5%.

For the confirmation of the results, the extracts were additionally analyzed by GC with LRMSD (low resolution mass spectrometry detector) on a Perkin Elmer AUTOSYSTEM XL, equipped with autosampler, splitsplitless injector and connected *via* direct interface to a Turbomass detector [28]. The measurements were carried out with fused silica capillary column Rtx-5MS®, Restek, USA (60m, 0.25 mm I.D., 0.25 μm film thickness; 5% diphenyl – 95% dimethyl polysiloxane). Helium was used as the carrier gas at a flow rate of 1 ml/min. The injector was operated in the splitless mode at 250°C. The electron impact ionization MS source, 70 eV nominal was employed, with the source set at 300°C. Mass spectra data acquisition was initiated directly after sample injection. The dwell time was set at 100 ms and the multiplier voltage at 450. The mass spectra were scanned from 100 to 650 amu every one second in full scan mode and compared to the spectra of PCB standards. The sample extract (1 μl) was introduced to the chromatograph with syringe by an autosampler (splitless mode). The temperature profile used in our experiments was: 0.5 min. at 80°C; 7.5°C/min. until 140°C and 3°C/min. until 300˚ C, holding for 10 min. The retention times were measured with accuracy of 0.001 min. by using Turbomass Data System, Perkin-Elmer. The repeatability of the $RRT_{PCB30+PCB209}$, expressed as relative standard deviation (R.S.D.), calculated from eighteen replicate analyses of a standard mixture of the PCB congeners was between 0.01 and 0.04%.

Quantitative measurements of PCB congeners in sediment extracts were carried out on the basis of peak heights. Quantification was performed by external standard. The concentrations were calculated by interpolation on the linear curve corresponding to each compound.

Blank experiments were included in each batch of samples to minimize the risk of introduction of any artifacts.

Results and Discussion

Development and Evaluation of Extraction Procedure

The evaluation of the extraction procedure, using the fexIKA 200 apparatus was performed with sediment samples, spiked with the specific congeners (PCB – 28- tri; 52, 74 – tetra; 101, 105, 114 and 118 – penta; 128, 138, 149, 153 and 156 – hexa; 170, 180 and 187 – hepta substituted).

Initially the efficiency of the extraction of analytes was examined as a function of various boiling time in one operating cycle. The recovery of congeners ranges from 40% for PCB 187 to 100% for PCB 28, depending on total boiling time. It is worth noting that the recovery level was well correlated with chlorine atom number in PCB molecule. The decrease of extraction efficiency in the order penta-, hexa- and hepta substituted homologue groups was observed. A similar trend was reported by Yang *et al.* [29], who demonstrated that the lower chlorinated biphenyls are easier to extract than the higher chlorinated congeners.

The effect of cycle numbers on PCB recovery was examined in the next step because, according to Brühl and Matthaüs [30], the recovery of analytes in the fexIKA extractor is influenced by the number of operating cycles in the extraction processes. The quantity of each congener extracted from spiked sediments after 5 and 10 operating cycles at the same total boiling time (150 min.) was determined. There was a general trend that the extraction efficiency for most congeners was better when 10 operating cycles were carried out.

Taking into account the results of preliminary studies, we have recognized that the optimum conditions of PCB extraction by the fexIKA extractor are attained when extraction is proceeded in 10 cycles and the total boiling time of the solvent mixture is 150 min.

Validation

The optimized analytical procedure was evaluated for detection and quantification limits, linearity, accuracy/recovery and precision. The quality of PCB determinations in environmental sediment samples was verified in interlaboratory exercises.

Instrumental and Method Detection and Quantification Limits

The instrumental limit of detection (LOD) and limit of quantification (LOQ) were expressed as a concentration of specified PCB (ng/ml) at a signal-to-noise ratio equal 3:1 or 10:1 respectively [19]. As it results from the data presented in Table 1, LOD for PCBs analyzed by GC-ECD ranged from 0.4 to 0.8 ng/ml and corresponds well to these presented by Jaouen-Madoulet *et al.* (0.20 – 2.65 ng/ml) [31]. The obtained values of LOQ (1.3 – 2.7 ng/ml) are in good agreement with the limits given for PCBs by Dabrowski *et al.* (1.8-2.8 ng/ml) [16] for the GC-MS method.

On the other hand the method detection limit (MDL) and the method quantification limit (MQL) were estimated from LOD or LOQ respectively. This means that the LOD or LOQ value was multiplied by the final volume of cleaned up extract and divided by the sediment sample weight and the volume of the extract injected on the GC column [MDL(MQL) = (LOD or LOQ x final volume)/(sample weight x injected volume) [17]. The obtained MDLs range from 0.2 to 0.4 ng/g dry weight of sediment (Table 1) and are comparable to estimated detection limits given for PCBs in sediment and soil by Thal (0.3-0.6 ng/g sediment) [32].

Linearity

The linear dependence between PCB concentration determined in spiked sediment samples and the quantities of congeners, added to the sample, was examined.

The parameters *a* and *b* of linearity equation (y = ax + b, where y is PCB determined in ng/g dry weight and x is

Table 1. Limit of detection (LOD) and quantification (LOQ) by the GC-ECD system and method detection (MDL) and quantification limit (MQL) of selected PCBs determination in sediment with the fexIKA extractor.

PCB IUPAC No	LOD (ng/ml)	LOQ (ng/ml)	MDL (ng/g dry weight)	MQL (ng/g dry weight)
28	0.8	2.7	0.12	0.4
52	0.4	1.3	0.06	0.2
74	0.8	2.7	0.12	0.4
101	0.6	2.0	0.09	0.3
149	0.8	2.7	0.12	0.4
118	0.6	2.0	0.09	0.3
114	0.4	1.3	0.06	0.2
153	0.6	2.0	0.09	0.3
105	0.4	1.3	0.06	0.2
138	0.4	1.3	0.06	0.2
187	0.6	2.0	0.09	0.3
128	0.4	1.3	0.06	0.2
156	0.4	1.3	0.06	0.2
180	0.6	2.0	0.09	0.3
170	0.6	2.0	0.09	0.3

PCB spiked in ng/g dry weight) and their standard errors (Δa and Δb) as well as the correlation coefficients for all congeners studied were calculated. As it results from the data presented in Table 2, the linear regression gives good correlation coefficients (>0.99) in the PCB content range of 5-22 ng/g dry weight, for all analytes.

Accuracy/Recovery and Precision

Spiked Sediment Samples

The accuracy (trueness and precision) [19] of the evaluated method was calculated for concentrations from 5 to 22 ng/g dry weight of each congener in spiked sediment, using 2-4 samples for each spiking level. The trueness was expressed by the percentage difference between the mean PCB content determined and spiked: error (%) = (|mean content determined – spiked content|) x 100%)) spiked content. The recovery of analytes was calculated as the percent of the mean content of congener determined and its spiked content in sediment sample.

As shown in Table 3, the mean recovery of PCBs from spiked sediment samples varied from 74.0% for PCB 170 (intra-laboratory recovery) to 108.8% for PCB 101 (repeatability study). Therefore, the recent requirement [19, 33] concerning the acceptable recovery percentage of analytes on 10 ppb level (60-115%) for all examined congeners was met. Also the results of recoveries were comparable to those reported by other authors for the same matrix and the same analyte concentrations [15, 31].

The repeatability and intra-laboratory reproducibility precision measurements were estimated for the same range of PCB content as for evaluation of accuracy and recovery. They were expressed as R.S.D.[R.S.D.(%) = (S.D. mean determined content) x 100/spiked content]. The obtained results were compared to acceptable R.S.D. values according to Horwitz and the AOCA PVM (Association of Official Analytical Chemists – Peer Verified Methods) requirements for the precision of analytical methods [19]. As it results from the data presented in Table 3, the R.S.D. values for all examined congeners were below 22.6% (Horwitz% R.S.D.) and 21% (AOCA PVM% RSD).

Certified Reference Material

The triplicate analysis of natural sediment certified reference material BCR-536 was performed to confirm the accuracy/recovery and precision of the whole analytical procedure, as established in the studies of spiked sediment. The typical GC-ECD chromatogram of cleaned-up extract is shown in Fig. 2.

The quantitative results of BCR-536 analysis are presented in Table 4 alongside the certified content of each analyzed congener.

A comparison of PCB recovery levels (Table 3 and Table 4) shows that the recovery of all congeners except PCB 128, PCB 180 and PCB 170 were from 3.5% (PCB 149) to 35.1% (PCB 101) lower in the case of natural matrix than in the case of spiked sediment samples. This is in good agreement to the data presented by other authors [12, 34] showing that some PCB fractions can be tightly

Table 2. Parameters of the linearity of the method of selected PCB determination in sediments with the fexIKA extractor.

PCB IUPAC No	n	a ±Δa	b ± Δb	R
28	8	0.8802 ± 0.0251	0.6442 ± 0.3481	0.9975
74	5	0.6923 ± 0.0242	0.4155 ± 0.3703	0.9982
101	6	0.8749 ± 0.0581	1.7047 ± 0.8812	0.9913
149	8	0.7669 ± 0.0229	0.1536 ± 0.3162	0.9973
118	7	0.9157 + 0.0533	0.2867 ± 0.7768	0.9916
114	6	0.7435 ± 0.0442	2.1792 ± 0.6680	0.9930
153	7	0.7576 ± 0.0353	2.5823 ± 0.5008	0.9945
105	6	0.8907 ± 0.0564	0.6593 ± 0.7272	0.9920
138	8	0.7971 ± 0.0350	1.4767 ± 0.4805	0.9943
187	7	0.7554 ± 0.0461	1.2488 ± 0.6734	0.9908
128	7	0.8042 ± 0.0220	0.5372 ± 0.3197	0.9981
156	7	0.7864 ± 0.0323	0.4512 ± 0.4704	0.9958
180	8	0.7575 ± 0.0238	1.0013 ± 0.3291	0.9970
170	7	0.7331 ± 0.0324	0.1097 ± 0.3943	0.9951

Table 3. Validation parameters of the method for selected PCB congeners in sediment with the fexIKA extractor.

PCB IUPAC No	Repeatability (n=4) [a]			Intra-laboratory reproducibility [b]			
	Trueness (error,%)	Recovery (mean,%)	Precision (R.S.D.,%)	n	Trueness (error,%)	Recovery (mean,%)	Precision (R.S.D.,%)
28	3.9	96.1	3.2	8	6.1	93.9	3.6
52	-	-	-	7	10.8	89.2	7.1
74	-	-	-	6	1.6	76.4	7.4
101	8.8	108.8	5.5	6	23.6	101.5	9.3
149	21.0	78.9	5.4	8	21.9	78.2	4.3
118	2.8	97.2	5.0	7	6.6	93.3	7.8
114	0.6	99.5	3.9	7	5.3	94.7	8.8
153	5.9	105.9	8.6	7	1.0	101.0	11.4
105	3.2	96.8	6.2	6	5.0	95.0	5.7
138	3.0	97.0	5.5	8	6.1	93.9	6.8
187	10.5	89.5	6.2	7	14.0	86.0	6.6
128	15.5	86.5	3.6	7	15.0	85.0	3.5
156	15.6	84.3	3.6	7	17.8	82.2	4.9
180	15.3	84.7	4.3	8	14.2	85.8	7.3
170	23.7	76.3	3.5	7	25.9	74.0	6.1

[a] Range of spiked congeners – 10.5-11.5 ng/g dry weight
[b] Range of spiked congeners – 5.0-22.0 ng/g dry weight

Table 4. Content of selected PCB congeners in freshwater harbour sediment BCR-536.

PCB IUPAC No	Content (ng/g dry weight)		Recovery [%]	R.S.D[2] [%]
	Certified (mean ± μ[1])	Determined (mean ± μ[1])		
28	44 ± 5	31.9 ± 2.2	72.4	3.5
52	38 ± 5	25.4 ± 1.3	66.7	2.6
101	44 ± 4	29.2 ± 2.5	66.4	5.6
149	49 ± 4	36.6 ± 6.1	74.7	8.4
118	28 ± 3	21.7 ± 2.1	77.5	4.9
153	50 ± 4	37.5 ± 3.8	75.0	5.0
105	3.5 ± 0.6	2.4 ± 0.3	69.2	5.7
138	27 ± 4	23.1 ± 3.8	85.7	8.3
128	5.4 ± 1.2	6.1 ± 0.4	112.2	3.1
180	22 ± 2	20.9 ± 1.8	95.2	4.4
170	13.4 ± 1.4	12.6 ± 0.9	93.7	3.5

μ[1] – uncertainty expressed as the half width of the 95% confidence interval [23 and this study]
R.S.D[2] – relative standard deviation of the determined values (n=3)

bound to sediment (*slow cites*) and not accessible to extraction in standard conditions.

Nevertheless, it is worth noting that the recovery of each analyte was in an acceptable range (from 60- 80% to 100-115%) for analytes on 10-100 ppb levels [19].

The high precision of evaluated procedure obtained for spiked sediment, expressed as R.S.D. (Table 3), was confirmed by the results of BCR-536 analysis. The calculated R.S.D. values presented in Table 4 ranged from 2.6% for PCB 52 to 8.4% for PCB 149. The R.S.D. values obtained to BCR-536 were lover or similar to R.S.D. values obtained in repeatability assessment of the results of PCB determination in spiked sediment samples (Table 3), except PCB 149 and 138. For all examined congeners the precision has been satisfactory according to the AOCA PVM% RSD criterion (R.S.D.< 15% – value acceptable for analytes on 100 ppb level) [19].

Additionally, the accuracy of the developed method was assessed by comparing the measured values with the reasonable estimation of the true value (C_{CRM}) according to Luque-Garcia *et al.* method [17]. The mean value ($C_{measured}$) and the standard deviation ($S_{measured}$) were calculated. Whether the method is accurate for examined congener or not, the following two equations must be fulfilled:

$$S.D._{measured}\, n^{-0.5} < \mu_{CRM} \quad (1)$$

$$C_{CRM} - \mu_{CRM} < C_{measured} < C_{CRM} + \mu_{CRM} \quad (2)$$

where C_{CRM} is the congener certified content in the reference material, μ_{CRM} is the uncertainty (the 95% confidence interval) of the CRM, $C_{measured}$ is the mean content of analyte in measured sample, $S_{measured}$ is the standard deviation of the PCB content in measured sample and n is the number of measurements.

Table 5 shows that the evaluated procedure meets the first criterion (equation 1) for each congener and both criteria (equation 1 and 2) for PCB 138, PCB 128, PCB 180 and PCB 170. Relatively low recoveries (<80%) of PCB 28, PCB 52, PCB 149, PCB 118, PCB 153 and PCB 105 from natural matrix indicate that for quantification of these congeners in environmental sediment samples their recovery factors should be taken into account.

Interlaboratory Exercise

The performance of a new analytical method should be verified in an interlaboratory study [19]. Therefore, the developed procedure was tested in interlaboratory proficiency exercise WCH PG PCB1 organized in 2003 by CEEAM (Centre of Excellence in Environmental Analysis and Monitoring), Department of Analytical Chemistry of the Technical University of Gdańsk (Poland), LCG-Promochem Ltd and RefMat Association.

The participating laboratories were asked to analyze the sediment samples for five congeners (PCB 52, 101, 118, 138, 153 and 180), by their own meth-

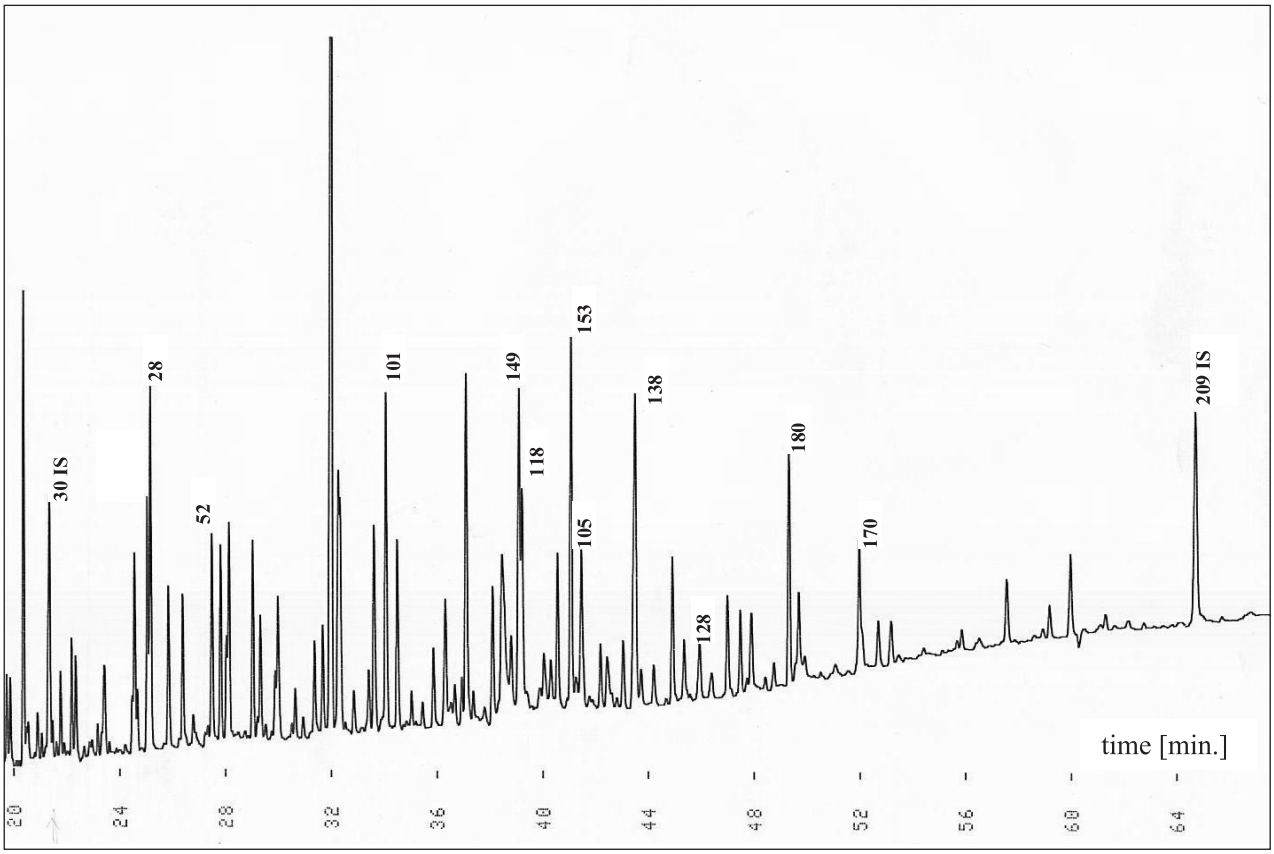

Fig. 2. GC-ECD chromatogram of the extract of sediment certified reference material BCR-536.

od using a supplied PCB standard solution. Data for exercise were returned by 18 of the 25 laboratories. As it resulted from the WCH PG PCB1 report [24], both test materials supplied by organizers were the same reference sediment METRANAL 2, from ANALYTIKA®Ltd. It was a secondary river sediment reference material (laboratory control material) for calibration, prepared for use in a national scheme of traceability. Analyte concentrations and uncertainties were verified by several metrological laboratories associated in METROCHEM group [35].

The mean content of each congener determined in the two test materials by an individual laboratory was compared to the assigned value (certified value) using two independent methods of the data assessment: one, based upon the uncertainty of assigned and measured value and a second, using the robust statistics Z-score [24].

In the inter-lab study, we have used the evaluated and validated method described above, as well as our own standard solutions for the determination not only of the five congeners indicated by organizers but also PCB 28 and PCB 101. The data assessment based on Z-score statistics have shown that our results (lab cod 23) were satisfactory ($|Z|<2$) for all examined congeners [24]. Consequently, it demonstrates the good performance of developed procedure.

The interlaboratory test material was also used in additional verification of the accuracy of the examined method. Similar to the BCR-536 analysis, the same criteria of the accuracy assessment have been taken into consideration [17].

Table 6 presents the content of seven congeners and the results of the accuracy test for the PCBs measured in the METRANAL 2 (test material), showing that the method is accurate and both equations (1 and 2) are fulfilled.

Table 5. PCB content (ng/g dry weight) and results of the accuracy test for the congeners in the BCR-536 sediment.

PCB IUPAC No	S.D. $_{measured}$	S.D. $_{measured}/n^{0.5}$	μ_{CRM}	$C_{CRM} - \mu_{CRM}$	$C_{measured}$	$C_{CRM} + \mu_{CRM}$
28	1.1	0.6	5	39	31.9	49
52	0.7	0.4	4	34	25.4	42
101	1.6	0.9	4	40	29.2	48
149	3.1	1.8	4	45	36.6	53
118	1.1	0.6	3	25	21.7	31
153	1.9	1.1	4	46	37.5	54
105	0.1	0.1	0.6	2.9	2.4	4.1
138	1.9	1.1	4	23	23.1	31
128	0.2	0.1	1.2	4.2	6.1	6.6
180	0.9	0.5	2	20	20.9	24
170	0.4	0.2	1.4	12.0	12.5	14.8

Table 6. PCB content (ng/g dry weight) and results of the accuracy test for the congeners determined in the METRANAL 2 sediment.

PCB IUPAC No	S.D. $_{measured}$	S.D. $_{measured}/n^{0.5}$	μ_{CRM}	C_{CRM}	$C_{CRM} - \mu_{CRM}$	$C_{measured}$	$C_{CRM} + \mu_{CRM}$
28[1)]	2.7	1.2	6.8	23.3	16.5	21.4	30.6
52[2)]	3.8	1.9	9.0	29.2	20.2	31.7	38.2
101[1)]	7.6	3.4	7.6	28.1	20.5	23.6	35.7
118[2)]	1.0	0.5	5.4	12.2	9.0	10.6	15.4
153[2)]	5.1	2.6	19.8	70.2	50.4	78.8	90.0
138[2)]	9.8	4.9	15.4	61.3	45.9	55.3	76.7
180[2)]	6.4	3.2	15.4	63.6	48.2	70.5	79.0

[1)] – congeners not included in interlaboratory exercise (n=5)

[2)] – congeners determined in interlaboratory exercise (n=4)

Conclusions

FexIKA extraction has proved to be a successful technique for extracting PCBs from sediments.

Evaluation of the developed method by in-house and interlaboratory validation has shown that it fulfills the requirements of modern analytical chemistry and that our results do not much differ from these demonstrated by other authors [36, 37] for other extraction techniques.

Maintaining efficient extraction of PCBs, the amount of organic solvent was reduced from 300 to 60 ml and the extraction time was minimized from 24 h to 250 min. compared to the classical Soxhlet extraction technique [12, 13, 38].

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