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DETERMINATION OF PCB IN WATER USING MICROEXTRACTION AND CAPILLARY GAS CHROMATOGRAPHY

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Abstract: *Capillary gas chromatography and FID detector were used in the study of the recoveries of PCB microextraction of the Delor 103 mixture and selected congeners of PCB (8, 28, 52, 101, 118, 138, 153, 180, 203) from 1 litre of water (at 7 °C) into hexane and toluene (1 ml) by vigorous mechanical shaking for 5 minutes. The recoveries of PCB from the Delor 103 microextraction (at concentrations from 0.01 to 10 µg/l* H_20*) related to the internal standard 1,2,3,4-tetrachlornaphtalene (recovery = 100%) were above 60%. The similar results were obtained also in the case of the individual PCB congeners. The PCB recovery is influenced with number of chlorine atoms in biphenyl, concentration of the individual congeners in the mixture Delor 103 and their solubility in water. The results of recoveries showed, that the method described above can be used for the purposes of the routine PCB analysis in waters.*

Keywords: *capillary gas chromatography, polychlorinated biphenyls, microextraction, water analysis*

1. Introduction

PCBs have been identified in almost every environmental compartment or matrix. Detected levels depend on the nature and location of the particular environmental sample [1]. Environmental legislations approved by federal agencies like WHO, US EPA, or by European Commission Directives [2,3,4], aim at the most severe reduction of the PCB levels in water and soils (< 1 ng.kg^{-1} in the original sample). This implies, for a PCB analytical method to be validated, the achievement of very low detection limits (< 0.5 ng.kg^{-1} in the extract).

Analysis of polychlorinated biphenyls (PCB) is being discussed very often, as for the result evaluation several ways giving not always the same results can be used.

Technical mixtures of PCB are composed of tens of individual components (theoretically of 209 so called congeners), contents of which depends on a degree of chlorination and conditions of the respective reaction [5-8]. It is necessary to stress, that the composition of the technical mixtures produced in Chemko Strážske, Slovakia (Delor from 103 till 106) is markedly different from the compositions of the mixtures produced by another producers (Aroclor, Clophen, Kaneclor, etc.). This fact is a source of some problems arising in the quantitative evaluation of PCBs using capillary gas chromatography (GC).

Exact quantitative analysis of PCB in waters needs identification of all present congeners and on the base of a detector response also calculation of each concentration. From the practical point of view this fact means the necessity of using high resolution capillary GC and to dispose of all individual congeners or their mixtures applicable for calibration of each component, detector and the respective conditions. The result of analysis can be than calculated as the sum of the respective congener contents.

The work [9] is in the closest touch with this exacting evaluation. Its author used silica capillary column SE-54 (50 m x 0.2 mm) equipped with the electron capture detector (ECD) and was succeed in separation of 187 congeners PCB.

The work [10] has introduced a method for the quantitative analysis of PCB using the highly selective specific Hall´s electrolytic detector, response of which depends on the content of chlorine in PCB molecule. Application of this detector in certain conditions enables to analysis quantitatively the content of PCB isomers without a need of individual standards. Calibration is related mainly to the samples of Aroclor.

Because of the problems mentioned above some simpler methods are being used. I.e. all PCBs in the extract are chlorinated using the respective reactant and dekachlorbiphenyl is obtained. This compound has in the chromatographic spectrum the only one peak [11,12]. The procedure depends on the quality of reactant having been used for chlorination ($SbCl_2$, SO_2Cl_2) and on the degree of chlorination. Moreover, dekachlorbiphenyl determination can be disturbed with some accompanying compounds.

Next procedure being used for PCB determination is a summarizing of all identified peaks of the sample and standard giving the same response in detector. This method is best worked out for the Aroclor standard [13,14,15]. This method does not take into account the different degree of congeners transformation [16]. Thanks to the very different responses of individual congeners in ECD a standard choice must be done very carefully. Summarizing of all identified peaks is recommended by a lot of official methods.

Another widespread method of quantitative evaluation is the method of representative peaks. It is based on the choice of a few peaks, the highs or areas of which represent the whole quantity of PCB. As the representative peaks present in each chromatogram of PCB having been isolated from water are chosen. The authors have named these peaks as characteristic for each PCB mixture. Evaluation must be completed with the congeners, which are the results related to. Nowadays, these the most typical peaks are described in literature -28,52,101,138,153, 180. In the same conditions as an unknown sample also a PCB standard is analysed.

The most reliable method of PCB analysis is the combination of gas chromatography and mass spectrometry. A lot of works have been published, in which mass spectrometry (GS-MS) is presented as a method of individual PCB´s identification.

The most usable extractant of PCB´s from water is hexane, dichloromethane, toluene or petrol ether. Extraction is performed either in one batch with the biggest amount of extractant, or in multiplied batches with a smaller volumes of solvent [17-22].

A standardized method EPA 608 [23] uses for extraction of PCB together with organochloric pesticides dichlormethane as the extractant. 1 l of water is extracted 3 times with 60 ml of CH_2Cl_2. All extracts, poured together, are dried with natrium sulphate anhydride. In the Kuderna-Danish (KD) concentrator they are concentrated to the volume of 1 ml and after addition of 50 ml of n-hexane they are preconcentrated into hexane. PCBs are separated from chlorinated pesticides in the column packed with silicagel or fluorisil.

In a triple n-hexane extraction of 2 l of water or pouring together of two parallel hexane extracts and their concentrating together with using ECD a level 0.01 μg/l is achievable [24].

ECD is suitable first of all for multi-chlorinated PCB. For the components with less content of chlorine a combination of ECD and FID is advantagable [25].

PCB analysis in waters can be performed also with stripping in a close cycle. The work [26] describes, that the recovery of 2,2´,4,5,5´-pentachlorbiphenyl from water achieves nearly 20%, if these parameters are used: the volume of water sample is 3.8 litre, water sample temperature is 30 °C, stripping time 2 h. The pentachlorbiphenyl concentration in water was 21.4 ng.l^{-1}. In spite of the non-optimized conditions the recovery is surprisingly high, because pentachlorbiphenyl is not very volatile and has a high boiling point. Relatively high recovery is caused with the minimal solubility and thus with the high activity coefficient of PCB in water.

Recovery of PCB in the process of their separation from water can be improved with the sample temperature during stripping. In the same way also a temperature of a filter filled with charcoal is necessary to increase. Thus a condensation of water can be avoided. I.e. at the water sample temperature 70 °C (the charcoal filter temperature 90 °C and the stripping time 2 h) the recovery between 30 and 65% (related to the degree of biphenyl chlorination) was achieved. The method must be calibrated with the same mixture of PCB in a standard water solution as in the case of a contaminated water sample.

For the purposes of the charcoal extract analysis capillary columns wet with non-polar stationary phase on the base of polysiloxane (OV-101, SE-54, SE-52) are usually used. Detection is performed with ECD, however, the concentration factor of this method is so high, that the trace concentrations of PCB in water can be analysed either with FID (there is a danger of disturbing the analysis with the common hydrocarbons) or mass detector. With the help of GC-MS an identification of PCB and their differentiation from the possible interfering components is possible.

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Moreover, distinguishing of fractions with the different degree of biphenyl chlorination or identification of respective chemical individuals is possible.

Continual destilation and extraction are also possible to use for PCB extraction from water. If the concentrations of PCB were at about 10 μg/l, the average achieved recoveries of PCB in water (Aroclor 1260) were approximately 95%. The volume of sample was 50 ml, extractant (pentane) 2.5 ml and time of destilation-extraction one hour. GC analysis was done in a capillary column with OV-101 and ECD [27].

2. Experimental

2.1 Instrumentation

Gas chromatograph Carlo Erba (VEGA 6000) equipped with a FID detector and split-splitless capillary injector system was used.

For the chromatographic separation a silica capillary column DB-5 (30 m x 0.25 mm i.d.) wet with silicone stationary phase SE-54 was used. The column temperature during injection was 40 °C and after 1 min programmed at the temperature gradient 30 °C/min till 200 °C and then linearly programmed at 3 °C/min till 260 °C. At this temperature the column was kept 10 min.

The detector and injector temperature were 300 °C. FID detector was used together with nitrogen as the carrier gas and make-up. For injecting a splitless technique was used, i.e. during injection of extract (1.5µl) a sample splitter was closed within 30 sec. For the analysis of selected (representative) congeners the chromatographic conditions were the same. The only one change was in a linear programming of the column temperature from 200 °C. Program of 5 °C/min was used till the temperature value 270 °C. Chromatograms were integrated with DP 700 (Carlo Erba) integrator.

2.2 Chemicals

For the analysis of the mixture Delor 103 certified standards from the Slovak Metrology Institute were used. The concentration of Delor 103 in n-heptane was 1 mg/ml.

The mixture of selected (representative) congeners was produced in the Research Institute for Drugs in Modra and is being sold by the Slovak Metrology Institute. Concentration of the respective congeners was 15 µg/ml of n-heptane.

for extract (4) was connected to the extraction flask (**Figure 1**) [28]. In this case the n-hexane or toluene extracts are easily accessible and can be injected immediately by means of a syringe into a gas chromatograph.

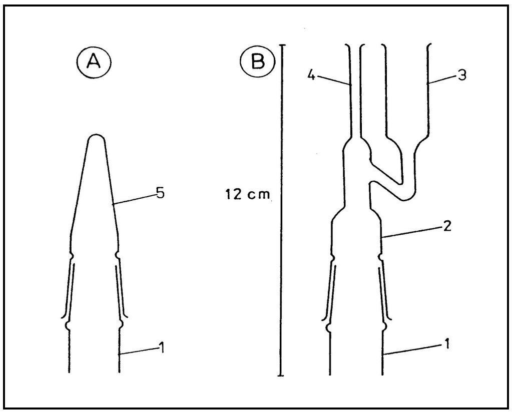

Fig.1 Solvent thin layer separator for microextraction of water

3. Results and discussion

Solvents (n-hexane, toluene) were highly purified and checked chromatographically. As the internal standard (IS) 1,2,3,4-tetrachlornaphtalene was used (purity at least 98%). A stock solution with the concentration of 1 mg/ml was prepared by weighing into hexane and toluene. Working solution was prepared by its gradual diluting to the concentration 0.1 µg/ml of n-hexane and toluene.

2.3 Microextraction

One litre of water containing defined content of organic substances was subjected to microextraction (at + 5-7 °C) with 1 ml of n-hexane or toluene containing internal standard (IS) by intense manual shaking 5 min.

The glass extraction flask, equipped with a male joint (1) and conical stopper (5) was used to extraction (A). After extraction (B) the solvent thin layer separator (2) containing side arm for water (3), capillary

For the analysis of polychlorinated biphenyls in waters a microextraction with the following capillary chromatography equipped with FID can also be used.

For the sake of the fact that in our country Delor 103 was mostly used (approximately 77% from the total production), this work pays attention to this mixture of PCB.

Figure 2 shows the gas chromatogram of Delor 103 (the PCB mixture with the content of chlorine between 42 and 43% with the prevailing content of trichlor derivatives) after microextraction of 1 litre H_2O into 1 ml of n-hexane with IS (0.1 µg. ml^{-1} 1,2,3,4-tetrachlornaphtalene).

Identification of Delor 103 components (elution peaks) is based on the data already published [29,30] and obtained standard from the Slovak Metrology Institute.

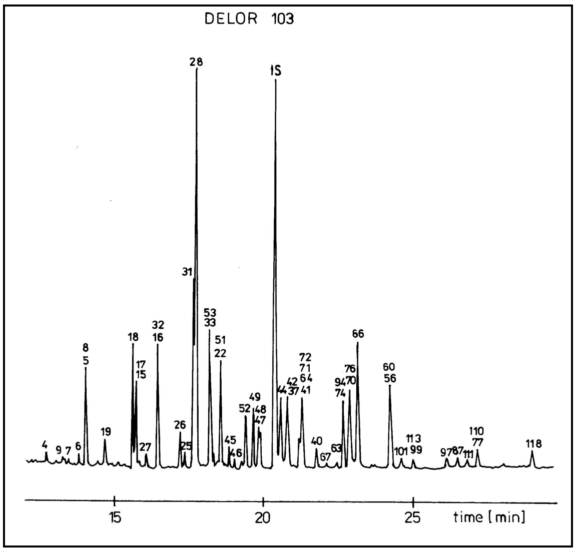

Fig. 2 Chromatogram of the Delor 103 mixture

Table 1 describes the relative recoveries of individual congeners of Delor 103 at the concentration of 1 µg/l of water related to the internal standard 1,2,3,4-tetrachloro-naphtalene (R=100%) obtained with the extraction of 1 l of water (at + 5-7 °C) into 1 ml of n-hexane with intensive hand shaking within 5 min. The recoveries are the arithmetical average values from 5 measurements.

Table 1 Relative recoveries of PCB congeners after microextraction into 1 ml of n-hexane.

Peak No.	Structure of congener	Recovery [%]	% RSD
4	2,2′	70.48	1.05
9	2,5	69.27	0.34
7	2,4	69.53	0.22
6	2,3′	73.15	0.23
5, 8	2,3 ; 2,4′	79.85	3.97
19	2,2′,6	75.78	0.31
18	2,2′,5	80.20	2.83
15, 17	4,4′ ; 2,2′,4	76.51	1.84
27	2,3′,6	76.32	0.42
16, 32	2,2′,3 ; 2,4′,6	80.43	2.72
26	2,3′,5	76.79	0.56
25	2,3′,4	74.88	0.45
31	2,4′,5	80.31	4.12
28	2,4′,4	79.36	7.98
33, 53	2′,3,4 ; 2,2′,5,6′	79.55	12.78
21, 51	2,3,4′ ; 2,2′,4,6′	80.14	2.14
45	2,2′,3,6	77.02	0.59
46	2,2′,3,6′	77.15	0.80
52	2,2′,5,5′	82.79	3.57
49	2,2′,4,5′	82.92	2.73
48, 47	2,2′,4,5 ; 2 ,2′,4,4′	80.25	3.06
44	2,2′,3 ,5	80.78	1.89
37, 42	3,4,4′; 2,2′,3,4′	78.63	2.10
41, 64, 71, 72	2,2′,3,4 ; 2,3′,4,6 ; 2,3′,5,5′ ; 2,3′,4,6	79.10	1.51
40	2,2′,3,3′	76.82	0.60
67	2,3′,4,5	72.34	0.19
63	2,3,4′,5	73.58	0.17
74, 94	2,4,4′,5 ; 2,2′,3,5,6′	77.28	1.34
70, 76	2,3′,4′,5 ; 2′,3,4,5	78.06	1.79
66	2,3′,4,4′	77.81	2.73
56, 60	2,3,3′,4 ; 2,3,4,4′	76.11	1.84
101	2,2′,4,5,5′	70.48	0.62
99, 113	2,2′,4,4′,5 ; 2,3,3′,5′,6	69.14	0.36
97	2,2′,3′,4,5	68.25	0.22
87	2,2′,3,4,5′	68.78	0.35
111	2,3,3′,5,5′	68.47	0.32
77, 110	2,3′,4,4′ ; 2,3,3′,4′,6	69.68	0.49
118	2,3′,4,4′,5	69.51	0.52

The individual recoveries of congeners in the mixture Delor 103 are influenced with the concentrations of respective congeners in the mixture and their solubility in water. From the data in Table 1 the possibility of using PCB separation from water (without concentration) and following extract analysis with capillary gas chromatography is apparent. The recoveries of individual congeners in the mixture Delor 103 are higher than 60%.

As PCB′s represent the rich mixture of chlorinated derivatives of biphenyl, the content of each of them can be determined from the areas (highs) of elution peaks belong to the respective components without the need of identification of each component. A lot of official methods recommend summarizing of all separated congeners.

That was the reason we studied the recoveries of microextraction of the mixture Delor 103 at the concentrations from 0.01 µ to 10 µg/l of water related to 1,2,3,4-tetrachlornaphtalene as the internal standard. Water with the defined content of Delor 103 was extracted into 1 ml of hexane containing 0.1 µg of 1,2,3,4-tetrachlornaphtalene.

Figure 3 shows the graphical dependence of the recoveries of PCB microextraction on the Delor 103 concentration.

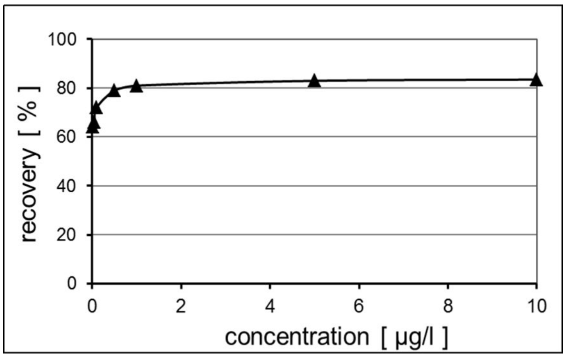

Fig. 3 Graphical dependence of the Delor 103 microextraction recoveries in dependence on the concentration.

The recoveries of Delor 103, calculated from the summarised area of its elution peaks, are at the concentration of Delor 103 above 0.5 µg/l higher than 60%. It can be concluded, that for the content of Delor 103 above 0.5 µg/l a microextraction into hexane can be used. It can also be seen, that at the Delor 103 concentration below 0.5 µg the recovery rapidly falls and is not a linear function of the concentration.

Figure 4 shows the analytical curve of the ratio of the area sum of elution peaks for the mixture Delor 103 ($P_{Delor\ 103}$) and area of the internal standard (P_{IS}) in the dependence of concentration.

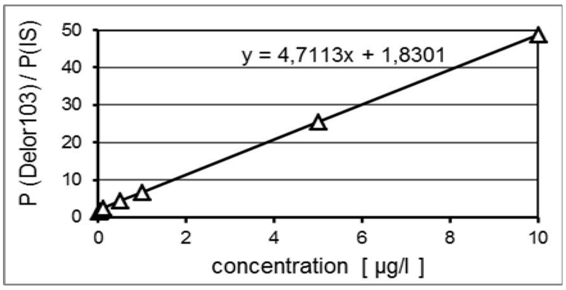

Fig. 4 Analytical curve of the mixture Delor 103 in the concentration range 0.01 - 10 µg/l H_2O.

Apart from the summarizing of all peaks a method of representative peaks nowadays often used. Literature describes the most typical congeners as the representative peaks. They are compared with analysed samples, whereas the chromatogram and the procedure of isolation were performed in the identical conditions. **Figure 5** shows the gas chromatogram of these congeners at concentration 50 ng/l of water.

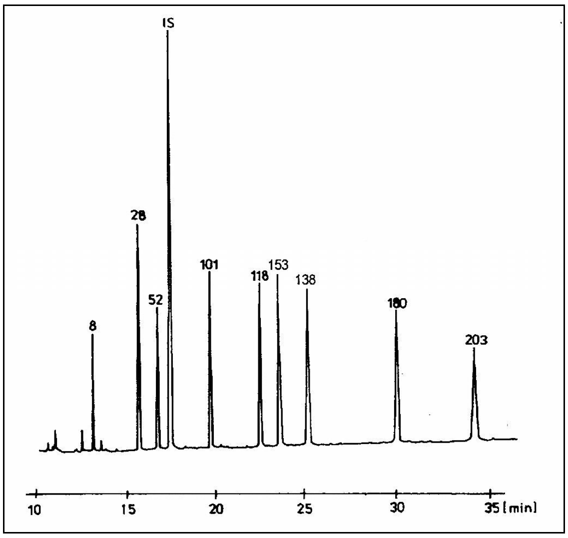

Fig. 5 Chromatogram of the selected PCB congeners in the concentration of 0.05 µg/l H_2O.

Table 2 shows the relative recoveries of the individual congeners mentioned above (concentration of each component is 50 ng/l of H_2O) related to the internal standard (0.1 µg 1,2,3,4-tetrachlornaphthalene). They were obtained with the microextraction of 1 litre of water (at 7 °C) into 1 ml of n-hexane or toluene performed by intensive hand shaking within 5 min. The recoveries are the arithmetical average values from 5 measurements.

As there is a need to have a continual control over these congeners, the proposed method can be used for the quantitative determination of PCB´s in waters (the recovery is above 75%).

The advantage of this method is in the fact, that in spite of its simplicity and speed, it is suitable for concentrations recommended as maximal acceptable in waters.

Table 2 Relative recoveries of the selected congeners at concentration 50 ng/l H_2O related to IS (R=100%) obtained with microextraction.

Peak no.	Structure of congener	Recovery [%]	
		1 ml n-hexane	1 ml toluene
8	2,4′	75.41	82.67
28	2,4′,4	76.38	83.58
52	2,2′,4,4′	81.66	85.09
101	2,2′,4,5,5′	85.92	89.14
118	2,3′,4,4′,5	84.69	91.86
138	2,2′,3,4,4′,5	89.78	92.11
153	2,2′,4,4′,5,5	88.02	91.58
180	2,2′,3,4,4′,5,5′	94.39	96.73
203	2,2′,3,4,4′,5,5′,6	91.27	95.14

Next conclusion of this table is the fact, that with increasing the number of chlorine in biphenyl the recovery of microextraction increases too. This is in accordance with the solubility of these compounds in water (see **Table 3**). The higher is the degree of chlorination the lower is the solubility of respective congeners in water.

The higher values of the recoveries were obtained using toluene as the extractant. When toluene was used for the extraction, the extract was concentrated (via dissolving the part of toluene in water). The higher recovery of toluene extraction is also caused with the similarity of the structures of extractant and biphenyl.

Table 3 Solubilities of the searched congeners in water [31,32,33]

Peak no.	Structure of congener	Solubility in water [µg/l]
8	2,4′	538 – 1880
28	2,4′,4	67 – 260
52	2,2′,4,4′	54.1 – 68
101	2,2′,4,5,5′	4.3 – 31
118	2,3′,4,4′,5	13.4
138	2,2′,3,4,4′,5	7.3
153	2,2′,4,4′,5,5	0.9 – 9.1
180	2,2′,3,4,4′,5,5′	3.85
203	2,2′,3,4,4′,5,5′,6	0.1 – 3.0

4. Conclusion

The results of recoveries showed, that the microextraction with n-hexane or toluene and capillary gas chromatography with detector FID can be used for the PCB analysis in waters. The PCB recovery is influenced with number of chlorine atoms in biphenyl, concentration of the individual congeners in the mixture Delor 103 and their solubility in water. When the analytical curve for the selected congeners is constructed, the method mentioned above can be successfully used, similarly as in the case of the mixture Delor 103, for the purposes of the routine analysis of PCB in water. Also a method of an internal standard is suitable for evaluation of the analysed components.

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