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Investigation of Polychlorinated Biphenyls Congeners in the Trikhlorbifenil Technical Mixture

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Abstract—Polychlorinated biphenyls contained in the Trikhlorbifenil technical mixture have been studied and identified. Content of the congeners in the mixture has been determined using the internal reference method. The results have been applied to determine qualitative and quantitative composition of polychlorinated biphenyls in contaminated soil.

Keywords: polychlorinated biphenyls, congeners, gas chromatography, gas chromatography–mass spectrometry, internal reference method

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Determination of the type and content of industrial wastes in the natural objects is among the topical issues of environmental monitoring. Organic contaminants, especially polychlorinated biphenyls, are considered the most dangerous components of industrial wastes [1]. According to the Stockholm Convention, polychlorinated biphenyls currently being used at the industrial facilities should be withdrawn and further utilized [2]. However, part of the contaminants has been accumulated in the environmental objects owing to the faulty operation of the facilities and further natural mass migration. In view of this, the set of persistent organic pollutants that should be monitored in the natural objects has been recently extended.

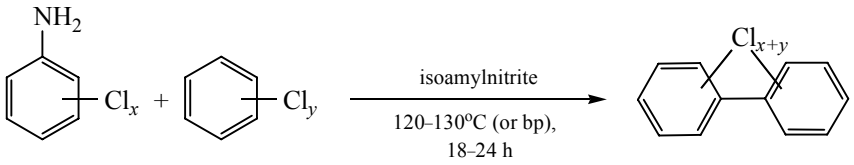
Identification and quantification of persistent organic pollutants, including polychlorinated biphenyls, is generally based on application of reference standards. As far as polychlorinated biphenyls are concerned, we have developed a State Reference Sample (Sovol mixture dissolved in hexane, GSO no. 7821-2000) [3, 4]. However, the Sovol mixture is not the only technical mixture of congeners of polychlorinated biphenyls produced in Russia; other widespread mixtures include Trikhlorobifenil and the Sovol-based mixtures: Sovtol (with trichlorobenzenes added), Nitrosovol (with α-nitronaphthalene added), and Geksol (with hexachlorobutadiene added). The reference standards for these mixtures are currently inavailable.

In this work we identified the congeners of polychlorinated biphenyls contained in the Trikhlorobifenil technical mixture and verified the possibility to determine the presence of those resistant contaminants in the soil. Gas chromatography in combination with various detection methods has been the major analytical tool applied to analysis of polychlorinated biphenyls mixtures. In particular, one-dimensional and multidimensional chromatography methods have been used, and the columns with different stationary phase types have been probed (cf. [1] and references therein). Separation of all the congeners of polychlorinated biphenyls using a single method is impossible: independently of the conditions and the stationary phase type, relative retention parameters remain the same, and certain congeners are eluted simultaneously.

The earlier performed identification of polychlorinated biphenyls of the Sovol mixture have revealed that it contains tri- (2%), tetra- (20%), penta- (55%), hexa- (19%), and heptachlorinated (2%) biphenyls [3]. The Trikhlorobifenil mixture (OST 6-01-43-79) is used in power capacitors and is therefore among the most widespread technical mixtures of polychlorinated biphenyls in Russia.

The Trikhlorobifenil technical product is a transparent viscous yellowish liquid. According to the elemental analysis data, the Trikhlorobifenil mixture

Scheme 1.



$x = 0 – 3$, $y = 0 – 2$.

contains 43.5% of chlorine (52.1% in the case of Sovol mixture). In order to reliably assign the peaks detected via gas chromatography (flame ionization detection) and chromato–mass spectrometry of the Trikhlorobifenil mixture, we applied the same chromatography conditions (column program and the stationary phase type) that were earlier used in the Sovol mixture studies.

Comparative analysis of the Trichlorobifenil and the Sovol mixtures dissolved in hexane using gas chromatography with flame ionization detection revealed that retention times of the components of the latter mixture were generally lower than those of the Sovol mixture components.

Chromato–mass spectrometry analysis of the Trikhlorobifenil mixture revealed that it contained di-, tri-, tetra, and pentachlorinated biphenyls. Mass spectra of the components were identical to those of the corresponding analogs from the NIST05 database (National Institute of Standards and Technology, version of 2005).

Basing on the reported data we concluded that the Trikhlorobifenil technical mixture contained mainly low- and intermediate-chlorinated biphenyls, in contrast to the Sovol mixture mainly consisting of the intermediate- and highly chlorinated biphenyls.

Quantification of the congeners of polychlorinated biphenyls in the Trikhlorobifenil mixture was performed taking advantage of the internal reference method using 4,4'-difluorobiphenyl (GSO 8534-2004). The method was based on addition of the known amount of the reference material to the studied samples and calculation of the mass concentrations of the polychlorinated biphenyls from the ratio of the peak areas corresponding to the polychlorinated biphenyls and the internal reference. Prior to the analysis, the relative correction factors should be determined, reflecting the ratio of the flame ionization detector signal per mass unit of the determined component and that of the internal reference.

In order to simplify identification and quantification of congeners of polychlorinated biphenyls contained in the Trikhlorobifenil mixture, we prepared a series of di- and trichlorinated congeners of polychlorinated biphenyls under conditions of the Gomberg–Bachmann–Hey reaction [5–8] from the corresponding chloroanilines and chlorobenzenes (Table 1); the commercial certified samples (Promochem, Germany) were also used: 2,4,4'-trichlorobiphenyl (PCB-28), 2,2',5,5'-tetrachlorobiphenyl (PCB-52), and 2,2',4,5,5'-pentachlorobiphenyl (PCB-101). Purity of the prepared congeners was confirmed by data of gas chromatography, chromato–mass spectrometry, and elemental analysis (Scheme 1).

In order to determine the correction factors, we prepared solutions of pure components (PCB-5, PCB-12, PCB-29, PCB-30, PCB-28, PCB-52, and PCB-101) with addition of the 4,4'-difluorobiphenyl reference and analyzed them by means of gas chromatography. The correction factors of the congeners with respect to the reference were calculated as follows [10]:

$$K_{kn} = c_k Q_{cmn}/c_{cm} Q_{kn}. \quad (1)$$

In Eq. (1): K_{kn}, the correction factor for the kth component and the nth chromatogram; c_k and c_r, concentrations of the kth congener and the reference, respectively, in the sample (mg/mL); Q_{kn} and Q_{rn}, peak areas corresponding to the kth congener and the reference, respectively, in the nth chromatogram (μV s).

The correction factors for each of the congeners were then averaged over the N recorded chromatograms:

$$\bar{K} = \sum_{n=1}^{N} \frac{K_n}{N}. \quad (2)$$

In order to determine the content of the congeners groups, a solution of the Trikhlorbifenil mixture containing the known amount of the reference was analyzed under the same conditions of gas chromatography. The measured peak areas were summed up accounting for the assignment to the congener groups (di-, tri-, tetra-, or pentachlorinated biphenyls). The correction factors

Table 1. Synthesis of congeners of polychlorinated biphenyls

Condensation components		The formed PCB congener (numbers according to IUPAC recommendations [9])
Aniline	1,2-Dichlorobenzene	PCB-5 (2,3-dichlorobiphenyl)
Aniline	1,2-Dichlorobenzene	PCB-12 (3,4- dichlorobiphenyl)
4-Chloroaniline	Chlorobenzene	PCB-8 (2,4'- dichlorobiphenyl
		PCB-13 (3,4'- dichlorobiphenyl)
		PCB-15 (4,4'- dichlorobiphenyl)
2,4,6-Trichloroaniline	Benzene	PCB-30 (2,5,6- trichlorobiphenyl)
4-Chloroaniline	1,4-Dichlorobenzene	PCB-31 (2,5,4'- trichlorobiphenyl)
2,4,5-Trichloroaniline	Benzene	PCB-29 (2,4,5- trichlorobiphenyl)

Table 2. Content of the polychlorinated biphenyls groups in the Trikhlorbifenil mixture (N 5, P 0.95)

Polychlorinated biphenyls group	Correction factor	Content, %	Relative standard deviation of the mean content, %
Dichlorinated biphenyls	1.5	14.5	2.4
Trichlorinated biphenyls	1.5	47.7	2.5
Tetrachlorinated biphenyls	1.6	29.3	2.6
Pentachlorinated biphenyls	2.1	3.8	3.0

were assigned to the groups according to the structures of the previously studied individual components. In particular, the correction factor for the dichlorinated biphenyls was the average one determined for PCB-5 and PCB-12, that for the trichlorinated biphenyls was calculated via averaging of the values for PCB-29, PCB-30, and PCB-28, and finally those for tetra- and pentachlorinated biphenyls were taken equal to those determined for PCB-52 and PCB-101, respectively. Such assumption was in line with the available reference data [11] stating that the correction factors to be applied for processing of gas chromatography data were practically the equal for the chlorinated biphenyls with the same number of chlorine atoms in the molecule. The content of congeners of each group was calculated as follows.

$$X_{gi} = K_g C_{cm}(Q_{gi}/Q_{cmi}). \quad (3)$$

In Eq. (3): g, the number of chlorine atoms in congeners of the considered group (2, 3, 4, or 5); Q_{gi}, total area of the peaks assigned to the considered congeners group in the ith chromatogram; K_g, correction factor for the considered congeners group.

The final result of the analysis $\overline{X}_g$ was the mean result of the N independent analysis runs X_i, Eq. (4). The relative standard deviation of the analysis was calculated using Eq. (5).

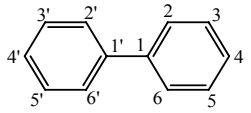
$$\overline{X}_g = \frac{\sum_{i=1}^{N} X_{gi}}{N}, \quad (4)$$

$$S_{\overline{X}}^{rel} = \frac{100}{\overline{X}} \sqrt{\frac{\sum_{i=1}^{N} (X_i - \overline{X})^2}{N(N-1)}}. \quad (5)$$

The obtained values of relative content of the congeners in the sample are collected in Table 2. From the collected data it followed that the Trikhlorobifenil technical mixture was close in the composition to the Arochlor 1242 product (USA) [12].

The congeners of polychlorinated biphenyls contained in the analyzed mixture were identified using the available reference data of the Arochlor 1242 mixture analysis [12–14]: the retention order, the peaks ratio, and the congeners fractions. Our data obtained in the

Table 3. Estimation of the fractions of congeners of polychlorinated biphenyls in the Trikhlorbifenil mixture and location of chlorine atoms in their molecules



Polychlorinated biphenyl number	Location of chlorine atoms	Relative fraction, %	Polychlorinated biphenyl number	Location of chlorine atoms	Relative fraction, %
4/10[a]	2,2'/2,6	2.8	47/48[a]	2,2',4,4'/2,2',4,5	2.0
7/9	2,4/2,5	0.3	44	2,2',3,5'	2.5
6	2,3'	0.9	37	3,4,4'	1.3
5/8	2,3/2,4'	7.5	42	2,2',3,4'	2.8
19	2,2',6	1.0	41/64[a]	2,2',3,4/2,3,4',6	1.2
18	2,2',5	9.1	40	2,2',3,3'	0.3
15	4,4'	3.2	74	2,4,4',5	0.7
17	2,2',4	3.1	76/70[a]	2',3,4,5/2,3',4',5	1.0
24/27[a]	2,3,6/2,3',6	0.7	66/95[a]	2,3',4,4'/2,2',3,5',6	2.2/1.4
16/32[a]	2,2',3/2,4',6	6.2	56/60[a]	2,3,3',4'/2,3,4,4'	1.0
26	2,3',5	1.3	101	2,2',4,5,5'	0.5
25	2,3',4	0.6	99	2,2',4,4',5'	0.2
31/28[a]	2,4',5/2,4,4'	18.6	97	2,2',3',4,5	0.1
20/33[a]	2,3,3'/2',3,4	4.7	87	2,2',3,4,5'	0.2
53	2,2',5,6'	2.6	85	2,2',3,4,4'	0.1
22	2,3,4'	1.8	110	2,3,3',4',6	0.6
51	2,2',4,6'	2.0	82	2,2',3,3',4	0.1
45	2,2',3,6	0.8	118	2,3',4,4',5	0.3
52	2,2',5,5'	2.4	105	2,3,3',4,4'	0.2
46	2,2',3,6'	2.2			

[a] Eluted together.

course of analysis of the congeners PCB-5, PCB-8, PCB-15, PCB-31, PCB-28, PCB-52, and PCB-101 were used as additional input information as well.

The results of qualitative identification and quantitative determination of the congeners content in the Trikhlorobifenil mixture are given in Table 3.

The obtained data were further used for identification of congeners of polychlorinated biphenyls in the contaminated soil. The gas chromatography analysis of the extract (cf. Experimental part for the details of the sample preparation) revealed the presence of congeners of polychlorinated biphenyls with the different chlorination degree. Comparison of the chromatographic parameters of the compounds present in the soil showed that it was contaminated with two technical mixtures of polychlorinated biphenyls: Trikhlorobifenil and Sovol. The total concentration of the detected congeners was of 485 mg/kg (with respect to the dry soil), about 8000 times above the highest permitted concentration (60 μg/kg) [15].

The reported study has demonstrated the general methodology of detailed analysis of the natural objects contaminated with technical polychlorinated biphenyls.

EXPERIMENTAL

The analysis was performed using a Shimadzu GC 2010 (Japan) gas chromatograph equipped with a flame ionization detector and a ZB-5 quartz capillary column [polydimethylsiloxane, 5 wt % of phenyl groups, l = 30 m, d = 0.25 mm, film thickness = 0.25 μm, initial column temperature 40°C (3 min incubation), programmed heating at 10 deg/min to 280°C (30 min incubation), injection temperature 250°C, detector temperature 300°C, 1.0 mL/min of nitrogen as carrier gas, split ratio 1 : 30].

Identification of the components was performed using a Trace GC Ultra DSQ II (USA) gas chromatograph–mass spectrometer equipped with a Thermo TR-ms quartz capillary column [polydimethylsiloxane, 5 wt % of phenyl groups, l = 30 m, d = 0.25 mm, film thickness = 0.25 μm, initial column temperature 40°C (3 min incubation), programmed heating at 10 deg/min to 280°C (30 min incubation), injection temperature 250°C, detector temperature 200°C, transition line temperature 200°C, 1.0 mL/min of helium as carrier gas, split ratio 1 : 50, sample volume 1.0 μL].

The correction factors were calculated using the results of analysis of the congeners solution in hexane (c = 0.05 and 0.1 mg/mL) containing 0.05 mg/mL of 4,4'-difluorobiphenyl as the internal reference.

For analysis of Trikhlorobifenil mixture, it was diluted with hexane (1 mg/mL for qualitative analysis and 0.1 mg/mL in the presence of 0.05 mg/mL of 4,4'-difluorobiphenyl for quantitative analysis).

The soil samples were collected at the industrial object intensively using the electrotechnical equipment. The samples were prepared for the analysis via extraction with a 1 : 1 (v/v) hexane–acetone mixture in the Soxhlet's apparatus, separation of the hexane fraction, and its purification with concentrated sulfuric acid according to the Procedure for determination of mass fraction of polychlorinated biphenyls in the working zone air, industrial wastes, natural and waste water, and soil by means of gas chromatography (the procedure was certified under no. 88-16358-25-2000).

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