

PCBs DETERMINATION IN WATER, SOILS AND BIOTA BY PERCHLORINATION AND GC-ECD

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Introduction

Most of the PCB pollutions are caused by industrial application. PCB-containing mixtures whose compositions are well known and constant should be rapidly and precisely analyzable as total PCB to monitor real pollution exposure. Consequently, a simple but reproducible and cheap method for operative control is needed which should be periodically controlled by standard analytical methods.

So it is advisable to have a rapid method that will allow PCBs determination in wide range of quantities by simple instrumentation with internal standards. The method based on perchlorination of PCBs considerably simplifies the detection of PCB congeners as compared to other techniques. In this practice all polychlorinated derivatives are converted into decachlorobiphenyl (DCB).

This is followed by gas chromatography with electron capture detector (GC-ECD), which is highly sensitive for the substances of interest. Currently EPA procedure #508a (1989) is the only official screening method for detection of PCBs using perchlorination. This uses SbCl_5 and powdered Fe mixture as reagent at 270 °C without internal standard.

We reported about using of perchlorination reagent based on mixture of powdered duralumin, sulphur and SO_2Cl_2 heated at 105°C for 2 h for detection of PCBs as decachlorobiphenyls in a wide range of concentration: 16.4 ng/sample to 164 µg/sample. 4,4'-difluorobiphenyl was proposed as internal standard that allowed to control all steps of sample preparation including perchlorination reaction [1]. In the present work we extended our experience of perchlorination to detect the PCBs.

Methods and Materials

GC-ECD measurements were conducted on a gas chromatograph Hewlett-Packard 5890A equipped with ECD (^{63}Ni , β -particles ionisation); carrier gas – nitrogen, 25 ml/min; HP-1column 20 m, 0.32 mm i.d., 0.52 µm film thickness; constant flow of carrier gas (nitrogen) 2ml/min; injector temperature, 240 °C; detector temperature, 300 °C. The GC was programmed as follows: 150 °C isothermal for 2 min, heating to 300 °C at the ramp of 10 °C/min, isothermal for 4 min. 1µl of the sample was injected in splitless mode with 0.1 min delaying of injector gas washing.

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GCMS measurements were conducted on Finnigan MAT ITD 700 with gas chromatograph Varian 2400; DB-5ms, 30 m column, 0.25 mm i.d., 0.25 μm film thickness; constant flow of carrier gas (helium) 1 ml/min. Ionisation by 70 eV electron impact, scan velocity – 1 spectra/ sec, m/z range – 41-450; GC injector temperature, 240 °C; transfer line temperature, 200 °C. The GC was programmed as follows: 100 °C isothermal for 2 min, heating to 220 °C at the ramp of 10 °C/min, then to 280 °C at the ramp of 5 °C/min. 1 μl of the sample was injected in splitless mode with 0.1 min delaying of injector gas washing.

For perchlorination studies the following solutions were prepared:

- PCBs mixture Sovol (analogue of Arochlor-1254 in Russia [2]) in hexane with c = 820; 82; 8.2 $\mu\text{g/ml}$; 820; 82 ng/ml;
- surrogate standard 4-fluodiphenyl ether (FDE) in acetone with c = 0,52 mg/ml;
- external standard for GC-ECD analysis of 2-fluoro-3-bromo-6,7,8,9-tetrachlorodibenzo-*p*-dioxin (FBrTCIDD) with c = 1 mg/ml;
- Aliquat-335 in hexane with c = 25 mg/ml.

All reactions were conducted in Fisherbrand® 4 ml screwthread vials with rubber-lined caps, provided with self-made Teflon lining. All solvents used were of PCB-grade. Sulphur and SO_2Cl_2 were ordered from Fluka. Industrial duralumin alloy D18™ brand (Russia) was used in all reactions. This aluminum alloy contains: Cu 3.8-4.9%, Mg 1.2-1.8%, Mn 0.4-0.8%, Fe <0.5%, Si <0.5%.

Water, soils and sediments extract preparation

5 μg of FDE was added to soils 10 g samples before extraction on continuous-flow extractor [3] by 150 ml of hexane at 65 °C.

One litre of water containing no PCBs was spiked by 1.64 μg of "Sovol". 5 μg of FDE was added before extraction with 2 x 80 ml of dichloromethane. Organic layer was separated and dried over MgSO_4 .

All extracts were rotary-evaporated with isooctane to 2 ml, then treated on a multilayer column filled from below upwards with 2 cm^3 of activated silica gel¹, 2 cm^3 K_2SiO_3 , 0.5 cm^3 MgSO_4 , 3 cm^3 $\text{H}_2\text{SO}_4/\text{SiO}_2$ (44%), 0.5 cm^3 MgSO_4 , then eluted with 40 ml of hexane and rotary-evaporated to 1-2 ml.

Perchlorination procedure

PCBs calibration solutions, 5 μg of FDE, 5 mg of Aliquat-336 were put into reaction vials. Then solvents were evaporated in airflow at 45 °C (sample extracts were evaporated in the same way, but without addition of FDE). 40 mg of powdered duralumin, 9 mg of sulphur and 150 μl of SO_2Cl_2 were added; vials were filled with dry gas (nitrogen, argon), tightly closed and heated at 105 °C for 35 min. Then SO_2Cl_2 was evaporated in airflow at 50 °C. The reaction mixture was extracted under sonication by 5 x 2 ml of hexane. Extract was passed through a small multilayer column filled from below upwards with 1 cm^3 of activated silica gel, 2 cm^3 K_2SiO_3 , 0.5 cm^3 MgSO_4 , 3 cm^3 $\text{H}_2\text{SO}_4/\text{SiO}_2$ (44%), 0.5 cm^3 MgSO_4 , 1.5 cm^3 Na_2SiO_3 , then eluted with 30 ml of hexane, rotary-evaporated to ~1 ml, transferred to Al_2O_3 micro column (Pasteur pipette filled with 1 cm^3 of Al_2O_3)

¹ Silica gel was activated according to US EPA Method 3630C.

and eluted by 3 ml of hexane into spear-bottomed test-tube. 10 µg of FBrTCIDD was added to the sample before GC-ECD analysis.

Results and discussion

Reported combination of duralumin, sulphur, SO₂Cl₂ and tridecane as keeper heated at 105°C for 2 h [1] appeared to be uncertain and insecure for multiple analyses and frequently lead to extremely high chromatographic noise that didn't allow DCB and standards peaks determination. We modified perchlorination procedure by using of Aliquat-336 (methyl-*tri*-capryl-ammonium chloride) both as keeper and catalyst. This allowed us to conduct PCBs perchlorination with 95% yield of DCB for 35 min at 105°C.

We found that in new reaction conditions 4,4'-difluorobiphenyl used as internal standard converted to DCB with 1-10% yield. Thus we applied FDE as new internal standard. Under reaction condition (duralumin, sulphur, SO₂Cl₂, Aliquat-336, 105°C, 35 min) this compound yields to 4-fluorononachlorodiphenyl ether and octachloro-di-cyclo-pentadien (identified by NIST mass spectra library). While calibration we took into account chromatographic peaks of both substances yielded from FDE. As shown in Fig. 1 there is a good linear correlation between "Sovol" amount and standard used in five-order interval of PCB quantities involved in the reaction.

The elaborated procedure was applied for perchlorination of real organic matrix extracts. The extracts of water spiked by 1.64 and 0.164 µg of PCBs were subjected to perchlorination. Results presented in table 1. It can be seen that error under determination not exceeded 15% that allow application of this method for PCBs determination in water samples.

We also tested perchlorination method for analysis of soils (table 2) and biological samples (table 3).

Soils samples, which were analyzed for mono-*ortho*- and non-*ortho*-substituted PCBs congeners (GCMS, "Typhoon" lab, Obninsk, Russia) and for total PCBs (GCMS, IPEE RAS), were subjected to perchlorination (fig. 2). Results of these comparison experiments presented in table 2. Results obtained by perchlorination are overvaluated if comparing with GCMS data on total PCBs. We can propose several reasons of this. First, because of interferences of unsubstituted biphenyl from fuels that under perchlorination yields DCB. Second, when analyzed PCBs mixture doesn't correspond to one used for calibration.

Extracts of chicken liver, chicken legs and chicken breasts from hens exposed by PCBs (20 mg/kg of food for 45 days) were but into perchlorination. Results presented in table 3.

Conclusion.

1. Proposed new perchlorination agent and conditions for perchlorination of PCBs to DCB with high yield for short time for amounts range from 16 ng/sample to 164 µg/.
2. 4-fluorodiphenyl ether proposed as internal standard for PCBs determination. It was injected into the samples and passed through all sample preparation steps including perchlorination.
3. Elaborated method was tasted for PCBs analysis in water, soils and biota.

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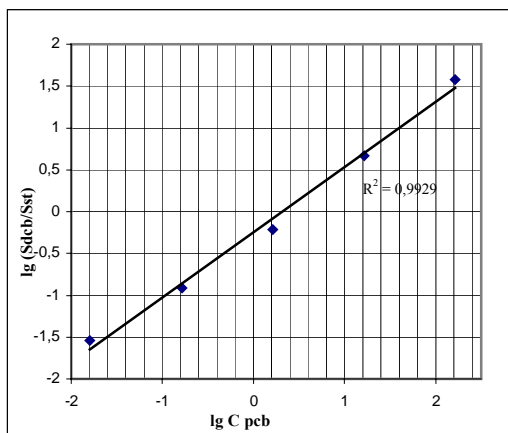


Fig. 1. Calibration curve.

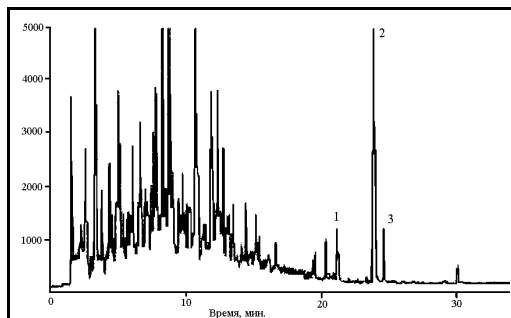


Fig. 2. Chromatogram of perchlorinated soil extract.
 1 – 2-fluoro-3-bromo-6,7,8,9-tetrachloro-dibenzo-*p*-dioxin,
 2 – internal standard,
 3 – decachlorobiphenyl.

Table 1.

Water extracts perchlorination data.

Spiked by PCB, μg	№	found, μg	% from spike
1,64	1	1,46	89,1
	2	1,83	111
	3	1,55	94,6
0,164	4	0,189	115,4
	5	0,14	85

Table 2.

Soils samples perchlorination data

Sample code	Found, Ng/g		
	Perchlorination	GCMS IPEE RAS	GCMS "Typhoon"
BRS-2	101	-	4

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BRS-3	44	-	0,46
BRS-4	40	-	2,33
BRS-5	55	21,7	0,74
BRS-6	31	11,4	7,87
	21		
BRS-7	36	12,8	4,12

Table 3.

Biological samples perchlorination data

	PCBs contamination, ng/g	
	perchlorination	GCMS
Chicken legs	607	302
Chicken breasts	412	210
Chicken liver	569	850