

PCB EMISSION IN THE COMBUSTION PROCESSES

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Introduction

Polychlorinated biphenyls (PCBs) are known to be one of the most harmful environmental pollutants. Their production is prohibited in most countries but their high stability leads to long term conservation and transfer of the pollution.

It is regarded that PCBs impact into environment is mainly due to spills or evaporation of PCB technical formulations¹. Nevertheless, it was noticed that in gas emissions in the combustion processes, among various chlorinated compounds such as PCDD/PCDFs etc., PCBs are present^{2,3}.

In the present work, PCB composition in gas emission of various industrial plants using combustion processes is studied. Gas emission samples were collected in Krasnoyarsk industrial plants: power, non-ferrous metallurgy, aluminium production, cement manufacturing. PCB composition was compared with that of in technical formulations Arochlors and Sovol.

Experimental

Gas emission samples were collected using sample collector "Air Sampler" TFIA-2 from "Staplex" with thin silica filter and sorbent XAD-2. The filter was spiked by isotope labeled standards (5 ng ¹³C₁₂-PCB 77, 101 and 153) were added.

The filter was crashed, placed in the extraction cartridge and extracted by a acetone:hexane (1:1) mixture at 70 °C and pressure 0.5 atm. The extract was rotary evaporated up to 30 ml, 100 ml of DCM-hexane (1:1) mixture was added and cleaned up on the "multilayer" column with length 200 mm and inner diameter 14 mm contained from top to bottom - 1 cm³ K₂SiO₃, 1 cm³ MgSO₄, 5 cm³ 40 % H₂SO₄/SiO₂, 1 cm³ MgSO₄, 10 cm³ 44 % H₂SO₄/SiO₂, 1 cm³ MgSO₄, 3 cm³ K₂SiO₃ and 1 cm³ MgSO₄, which was eluted by 40 ml of petroleum ether (40-70°C).

The analyses were performed on GC-MS (Hewlett Packard HP 6890 Plus, Finnigan MAT 95XL) at resolution 10000 in the mode of selected ions detection. Fused silica capillary column 30 m x 0.18 mm with stationary phase DB-5ms (0,25 μm) was used. Temperature was programmed from 150 °C (1 min hold) to 220 °C, rate 10°C/min, then to 300 °C, rate 5 °C/min. Injector temperature was 240 °C. 1 ml of the sample was injected in splitless mode with purge start in 0,5 min.

PCB concentrations were evaluated by internal standard method. Detection limit was calculated as a concentration at which signal to noise ratio is 3:1 and is equal to 1 ng/m³.

Results and discussion

Congener PCBs concentrations in the gas emissions are presented in the Table 1.

Table 1. PCB congeners concentration in the gas emissions (ng/m³).

12 – power plant

13 - power plant

16 – non-ferrous metallurgy plant

22 – cement plant

25 – aluminum plant, calcination furnace,

29 - aluminum plant, entry into electrostatic filter

<i>Congener</i>	<i>RT, s</i>	12	13	16	22	25	29
1	450	83.8	-	-	3.9	26.3	-
9/7	485	12.8	-	-	-	8.3	-
6	535	46.7	12.5	117.7	1.8	11.5	-
5/8	543	103.6	21.8	217.4	5.8	30.5	-
13	582	13.3	1.1	-	-	1.9	-
15	589	42.6	-	-	3.0	6.9	-
18	602	64.8	12.0	133.6	3.0	20.8	2.9
24	624	3.8	5.8	85.9	2.6	10.8	-
32	633	-	3.0	-	1.0	1.7	-
26/25	652	-	5.3	52.1	3.8	11.0	-
31/28	661	147.7	30.4	237.2	7.4	46.3	7.7
20/33	673	43.4	11.4	95.3	1.2	10.5	-
22	681	7.8	1.5	15.6	2.0	8.6	-
22	684	88.5	-	-	-	-	-
35	707	38.7	26.7	-	6.8	11.0	-
52	708	111.6	39.3	265.2	5.6	51.7	4.4
49	713	38.0	13.8	152.2	3.4	28.6	-
47/48	732	53.8	18.2	117.0	5.5	23.0	0.0
44	746	47.2	11.7	90.6	2.0	17.6	2.4
41	754	7.8	2.6	-	0.9	-	-
74 (70)	781	230.1	61.8	445.6	12.2	74.1	4.6
66	786	-	-	-	3.1	34.3	9.9
56/60	802	33.2	11.8	60.2	3.8	8.5	-
100	766	-	7.1	20.7	0.8	-	-
95	787	92.5	19.8	127.3	5.1	29.4	6.9
91	793	19.6	3.7	27.1	1.8	5.8	1.6
92	810	30.4	4.8	60.0	2.2	12.2	2.8
101	818	153.8	23.4	184.6	9.0	40.4	9.9
99	824	105.0	20.9	148.6	5.0	31.5	6.7

<i>Congener</i>	<i>RT, s</i>	12	13	16	22	25	29
119	835	4.6	0.0	11.5	2.5	0.9	-
97	841	38.9	7.0	51.3	1.8	9.0	-
115	846	65.0	17.1	88.1	4.9	23.2	-
85	850	26.3	-	44.7	-	-	5.9
110	858	-	29.6	185.5	8.9	44.6	10.4
123	872	-	37.5	25.0	1.1	-	1.7
82	876	-	1.2	6.9	-	-	-
118	894	173.8	-	-	8.1	40.5	7.5
105	924	59.49	-	-	2.6	11.7	3.1
136	879	-	2.1	-	-	0.8	-
149	893	17.2	1.3	356.3	1.1	6.4	1.5
146	923	8.9	17.9	-	-	-	-
153	928	49.2	3.8	66.1	2.9	14.4	-
138	963	41.9	-	49.1	1.0	9.7	-
156	1037	-	-	-	-	1.2	-
157	1054	-	-	-	-	-	-
187	992						
183	1001						
180	1070	2.5	-	-	-	-	-
170	1123	1.9	-	-	-	-	-
Cl₁		162.8	17.9	113.5	10.5	93.4	-
Cl₂		214.0	40.2	812.2	40.5	217.4	4.1
Cl₃		520.8	60.4	1244.6	78.0	523.5	17.2
Cl₄		927.4	199.5	1318.0	37.9	236.7	14.9
Cl₅		783.4	151.5	1279.0	70.4	196.8	60.9
Cl₆		130.7	28.9	207.3	25.8	46.8	4.8
Cl₇		8.9	-	25.6	3.6	-	-
Σ, ng/m³		2748	498	5000	2677	1315	102
Emission factor, μg/t		31871	5780	694999	31368	15251	3359

PCB concentration in flue gas is rather high – from 0.1 to 5 μg/m³. To compare PCB congener profile in flue gas to that of in technical PCB formulations, which are at first sight, very similar, principal component analysis was used. It was done for experimental data set with added data for some Aroclor mixtures⁴ and Russian PCB formulation – Sovol. Total dispersion very smoothly changes with factor number increasing. The first three principal components characterize about 70 % of the total dispersion. On the plane of the two principal components points corresponding to flue gas samples are located in compact cluster, that indicates that PCBs in all these samples have similar congener profile (Fig.1). Only the sample 29 is outside of the cluster. This cluster includes also the point of Aroclor 1248. Other clusters fall together with lines 60-69, Dioxin 2009 Boston, MA 1016, 1232,

1242, and heavy – Aroclors 1260, 1262. A separate cluster is formed by Aroclor 1254 and alike is Sovol. Therefore it can be concluded that PCB congener profiles in flue gas is not different from that of technical PCB formulations having the same chlorination degree. The actual chlorine content in the flue gas PCB mixture is 41-50 % (average of 47 %).

PCB emission factors were calculated for studied plants analogously to calculations for PCDD/PCDFs⁵. Emission factors for various plants ranged from 3 to 700 mg/t of raw materials or fuel expended. Thereby contribution of flue gases to environmental PCB pollution is not so small and it does not vanish when PCB production was finished.

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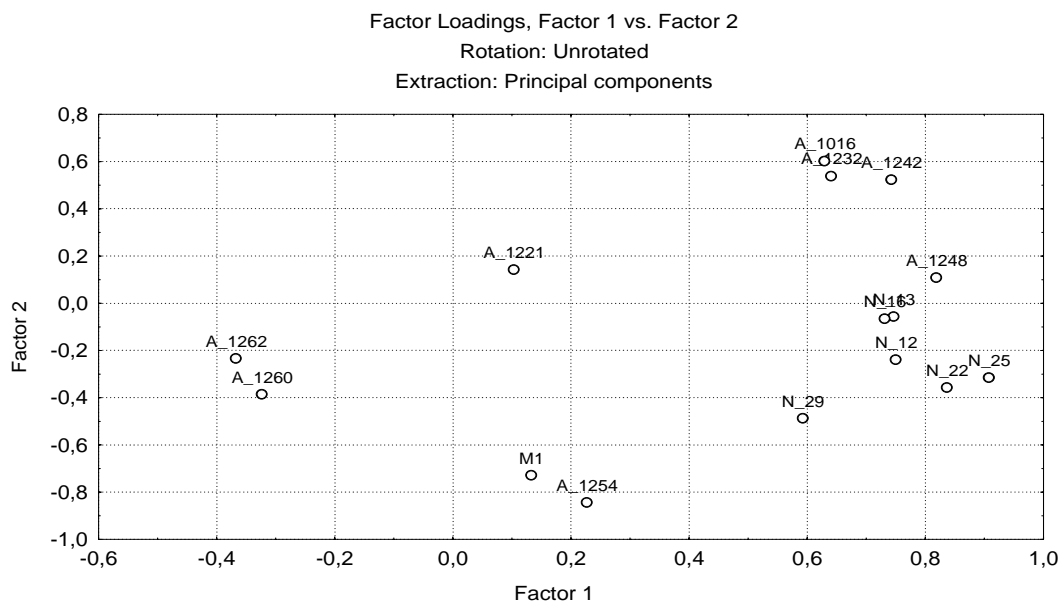


Fig.1. Factor scores of PCBs in flue gases in combustion processes (N12 – N29), Aroclors (A-1221 – A-1262) and Sovol (M1).