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 formulations[1]. 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 $^{13}C_{12}$-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 cm^3 K_2SiO_3, 1 cm^3 $MgSO_4$, 5 cm^3 40 % H_2SO_4/SiO_2, 1 cm^3 $MgSO_4$, 10 cm^3 44 % H_2SO_4/SiO_2, 1 cm^3 $MgSO_4$, 3 cm^3 K_2SiO_3 and 1 cm^3 $MgSO_4$, which was eluted by 40 ml of petroleum ether (40-70^oC).

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 um) was used. Temperature was programmed from 150 ^oC (1 min hold) to 220 ^oC, rate 10^oC/min, then to 300 ^oC, rate 5 ^oC/min. Injector temperature was 240 ^oC. 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/m^3.

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/m^3).
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

Congener		***RT, s***		**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

Congener	*RT, s*	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	-	-	-	-	-
Cl_1		162.8	17.9	113.5	10.5	93.4	-
Cl_2		214.0	40.2	812.2	40.5	217.4	4.1
Cl_3		520.8	60.4	1244.6	78.0	523.5	17.2
Cl_4		927.4	199.5	1318.0	37.9	236.7	14.9
Cl_5		783.4	151.5	1279.0	70.4	196.8	60.9
Cl_6		130.7	28.9	207.3	25.8	46.8	4.8
Cl_7		8.9	-	25.6	3.6	-	-

Σ, ng/м^3	**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/m^3. 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 mixtures[4] 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 light Aroclor-1221, medium – Aroclors-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/PCDFs[5]. 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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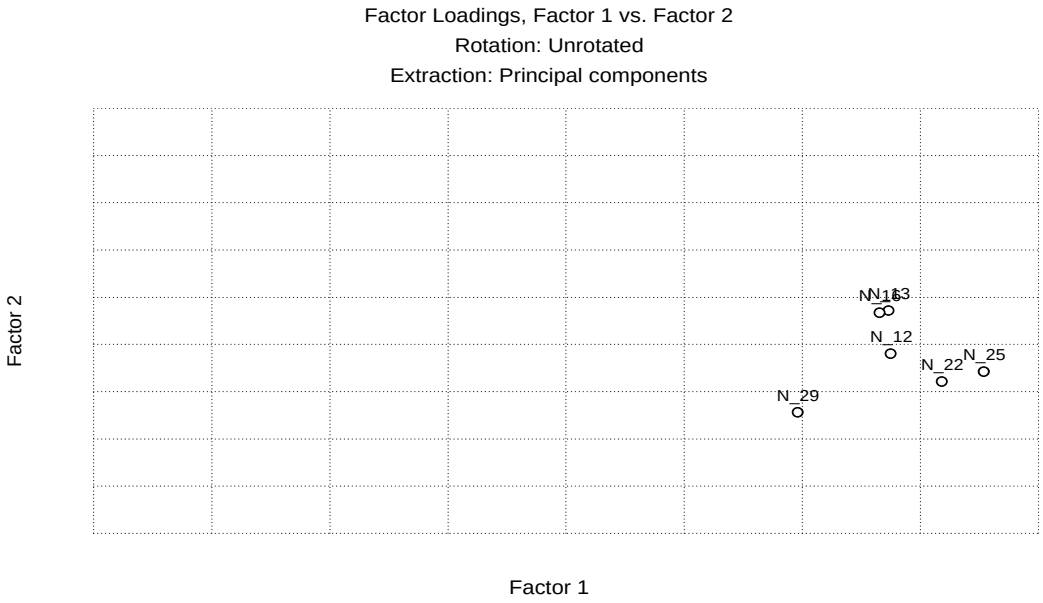

Fig.1. Factor scores of PCBs in flue gases in combustion processes (N12 – N29), Aroclors (A-1221 – A-1262) and Sovol (M1).