

FORMATION CONDITIONS OF SEVERAL POLYCHLORINATED COMPOUND CLASSES ON FLY ASH OF A MUNICIPAL WASTE INCINERATOR

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ABSTRACT

Decomposition of inorganic carbon, catalyzed by copper, is the first reaction step in formation of a variety of polychlorinated compounds on fly ash of waste incinerators. The observed concentrations depend on the relative reaction speed of formation, decomposition and vaporization as competing processes.

INTRODUCTION

In 1986 Stieglitz et al (1) suggested, that the de novo synthesis of PCDD and PCDF proceeds from residual carbon and inorganic chlorine at temperatures of about 300°C on the surface of the fly ash.

In our experiments we extend these investigations to other chlorinated compounds in order to define general conditions of formation. Besides PCDD and PCDF we determined the quantities of polychlorinated naphthalenes, benzenes, phenols, benzofurans, benzonitriles, thiophenes and benzothiophenes depending on temperature.

EXPERIMENTAL

Materials: The fly ash, obtained from the electrofilter system of a MWI, was ground and refluxed 12 hours at portions of 20g with 200ml toluene. The fly ash was filtered, combined and dried at 80°C under reduced pressure (50mbar) for 5h and divided into identical fractions.

Experiments: Fly ash samples of 10g each were heated in a furnace for two hours at temperatures of 250, 300, 350, 400, 470 and 550°C (see fig. 1). The temperature of the fly ash was measured by a thermocouple to $\pm 5^\circ\text{C}$. During thermal treatment a stream of synthetic air

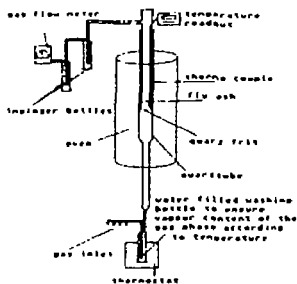


Fig 1 Experimental set up for thermal treatment

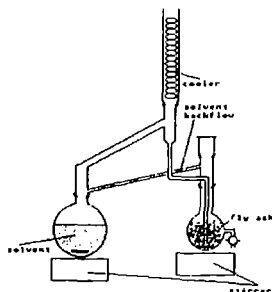


Fig 2 Extraction method

(50 ml/min) containing 120mg water vapor per liter was passed through the samples. To ensure close contact between the gas phase and the fly ash, the sample was placed in a quartz tube with a lit at the bottom, using an ascending gas flow. At the gas outlet of the arrangement two impinger bottles were installed to trap volatile compounds, the first filled with 100ml benzene and the second with the same amount of cyclohexane.

Sample preparation The treated fly ash was digested with 60ml of 4N HCl, the residue centrifugated, washed two times with water and freeze dried as reported by Vogg and Sieglitz (2). The weight loss of the fly ash by this procedure was determined by weighing to be about 65%. Extraction was performed with 3 to 4g of the residue, under addition of potassium fluoride to complex iron ions. To avoid chemical reactions on the surface of the fly ash during extraction we used the setup described in fig 2, with 250ml benzene for 24 hours and additionally the same time with 250ml cyclohexane. By this method, the solvent temperature in the extraction flask was adjusted to 40°C.

Clean up For quantitation the solutions were concentrated to about 500µl. Fractionation into two parts was carried out by semipreparative high pressure liquid chromatography using an RP18 column (250mm length, 10µm ϕ) and methanol as mobile phase with UV detection at 254nm wavelength.

After concentration of the two methanol solutions to 1ml, 50ml cyclohexane were added and again concentrated up to 100µl to substitute the alcohol. As internal standard 1500ng dinitroterfluorobenzene were added to the solutions.

GC/MS was performed on an Carlo Erba Gaschromatograph with splitless on column injector on an uncoated precolumn (5 m) coupled to a DB5 column (30m length, 0.25 mm i.d., 0.2µm film thickness) using helium as carrier gas. The temperature program was: 3 minutes isothermally at 75°C, 5°C/min to 150°C, 10°C/min to 300°C, 10 min isothermally.

A Finnigan Mat mass spectrometer with an Ineos data system operated in electron impact mode was used at 0.75s/cycle. To get higher sensitivity, the observed mass range was changed during the run as follows. Mass 122 to 320 from start to 27min, 245-443 from 27 to 35min and 294 to 492 until 50 min retention time.

Identification of the compounds was carried out by retention time, isotope ratio of the parent masses and by the mass spectra. Quantitation was made by integration of the two most intensive parent masses, corrected for relative response to the dibromotetrafluorobenzene which was determined by standard solutions.

RESULTS AND DISCUSSION

Table 1 shows the concentrations of different chlorinated compounds in ng/g heated fly ash depending on temperature. The first row of each compound class contains the sum of all degrees of chlorination. As the fly ash was extracted before thermal treatment, the presence of these newly formed compounds is a proof for the de-novo synthesis from residual carbon and inorganic chlorine.

Table 1: Concentrations of Chlorinated Compounds (ng/g) in Dependence of Temperature

Temperature	250	300	350	400	470	550		250	300	350	400	470	550
Benzenes	1819	27410	27800	20484	37549	3181	Naphthalenes	134	2318	1589	2340	4227	472
Dichloro-	24	1720	2050	884	603	98	Dichloro-	24	430	967	596	563	2
Trichloro-	193	6180	7230	4050	3670	538	Trichloro-	37	700	1150	845	1710	50
Tetrachloro-	752	12020	10800	7540	21764	1460	Tetrachloro-	44	810	1040	672	1590	228
Pentachloro-	710	6670	6150	6430	10600	789	Pentachloro-	25	320	387	207	323	159
Hexachloro-	140	820	1570	1580	912	296	Hexachloro-	4	58	42	20	41	31
							Heptachloro-	n.d.	n.d.	3	n.d.	n.d.	2
Thiophenes	167	770	287	323	363	17							
Dichloro-	8	122	33	20	n.d.	n.d.							
Trichloro-	79	456	118	133	67	n.d.							
Tetrachloro-	80	192	136	170	296	17							
Benzothiophenes	94	936	866	569	1388	212	Benzofurans	115	856	1880	1888	5144	317
Dichloro-	10	143	200	104	58	n.d.	Dichloro-	6	214	450	313	587	n.d.
Trichloro-	26	250	256	175	517	6	Trichloro-	28	377	550	525	1880	36
Tetrachloro-	32	315	237	180	570	81	Tetrachloro-	44	223	472	640	2200	93
Pentachloro-	21	193	147	96	155	107	Pentachloro-	28	36	330	346	403	156
Hexachloro-	5	35	26	14	88	18	Hexachloro-	9	6	78	64	74	52
Benzonitriles	40	765	1499	1074	2051	105	Phenoles	340	8	53	188	308	n.d.
Dichloro-	4	316	717	441	327	n.d.	Dichloro-	1	1	14	88	65	n.d.
Trichloro-	9	353	567	392	1100	70	Trichloro-	29	2	14	57	100	n.d.
Tetrachloro-	22	93	189	211	524	16	Tetrachloro-	234	5	25	29	163	n.d.
Pentachloro-	5	3	26	30	100		Pentachloro-	76	n.d.	n.d.	14	n.d.	n.d.
PCDD	53	1149	468	109	246	60	PCDF	131	4380	5801	3405	9242	3771
Dichloro-	3	31	75	19	78	n.d.	Dichloro-	15	530	1520	1340	3135	138
Trichloro-	1	96	157	49	79	10	Trichloro-	37	1045	2270	1116	3610	2870
Tetrachloro-	4	144	100	29	46	31	Tetrachloro-	38	1330	1350	668	1950	568
Pentachloro-	8	287	58	8	28	16	Pentachloro-	25	972	480	219	451	151
Hexachloro-	12	346	45	4	12	3	Hexachloro-	16	503	180	62	96	44
Heptachloro-	21	222	31	n.d.	3	n.d.	Heptachloro-	n.d.	n.d.	1	n.d.	n.d.	n.d.
Octachloro-	4	23	2	n.d.	n.d.	n.d.	Octachloro-	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

The chlorobenzenes are the most favoured compound class followed by PCDF and chloronaphthalenes. According to the ratio between PCDD and PCDF, monobenzodioxins are not detectable whereas the monobenzofurans and -thiophenes occur in all degrees of chlorination. The chlorophenols which are discussed as precursor compounds of PCDD and PCDF, show only small concentrations.

For the chlorobenzenes the highest concentrations are found for the tetrachloro-compounds independent of temperature. Benzofurans and benzothiophenes show according to their comparable chemical structure a similar pattern with the highest concentrations for the tri- and tetrachloro-compounds. At temperatures above 350°C the amounts of the benzofurans increase much more than those of the benzothiophenes. The thiophenes reach the highest concentrations for the maximum possible degree of chlorination. For a better understanding of the mechanisms of formation we also determined di- and trichlorodioxins and -furans, although they are of minor toxicological interest. The data show, that the decrease in degree of chlorination at higher temperatures, as described by several authors, does not stop at the tetrachloro-compounds, but is continued to the di- and trisubstituted congeners. An unambiguous explanation of this effect by dechlorination reactions is not yet possible, as in dependence of substitution pattern some isomers should decompose faster than others. A qualitative comparison of the chromatograms for different temperatures shows no significant differences. In comparable experiments we found, that at temperatures above 350°C more than 90% of the tetra- and penta-furans occur in the impinger bottles. The decrease in degree of chlorination can be explained by the relative reaction speed of decomposition on one hand and vaporization on the other. The lower chlorinated compounds evaporate, according to their lower boiling points and survive in the impinger, whereas the high chlorinated dioxins and furans get destroyed on the hot surface of the fly ash.

Some general trends can be drawn from the data. At 250°C only small formation for all compound classes can be found. Besides the chlorophenols, which show a different pattern, there are two maxima of formation: the first at 300°C and the second at 470°C. For the PCDD and PCDF this second maximum occurs especially for the low chlorinated congeners, whereas the other cited compounds show no significant change in degree of chlorination with increasing concentrations at 470°C. A comparison of the values at 300°C and 470°C shows the largest increase of concentration for the benzofurans from 856 to 5144 ng/g, followed by the benzothioles with values of 765 and 2051 ng/g. The naphthalenes reach an increase by a factor of two, benzothiophenes and benzenes by a factor of 1.4 to 1.5. At 550°C nearly quantitative destruction occurs for all compound classes.

LITERATURE

1. H. Vogt, L. Steglicht, *Chemosphere* 15, 1373 (1986)
2. L. Steglicht, G. Zwick, J. Deck, W. Roth, H. Vogt, *Chemosphere* 18, 1219 (1989)