GENERATION OF BROMINATED DIOXINS AND FURANS IN A MUNICIPAL WASTE INCINERATOR (MWI) - RESULTS OF A CASE STUDY

Michael Wilken, Andreas Beyer, Johannes Jager
ITU-Forschung, Ansbacher Str. 5, D - 1000 Berlin 30

Introduction

Within a two year research programme about "practical concepts for reducing the generation of PCDD and PCDF within municipal waste incinerators (MWI)", the authors studied the emission of PXDF and PXDD after the addition of organobromine compounds to the input (1).

Recent publications show that brominated and mixed-halogenated dioxins and furans can be formed after thermal reaction of several brominated compounds. The chlorine-source can either be organic or inorganic (2, 3). Some authors propose that the amounts of PCDD/PCDF found in municipal incinerator fly ash is even formed by PBDD/PBDF (4), which themselves are formed by pyrolysis of flame retardants (5) or plastic materials containing flame retardants (6).

On the other hand, bromo compounds are regarded as at least as and possibly more reactive towards the formation of PXDD/PXDF (7). The generation brominated compounds in a higher portion than their chlorinated analogues seems in addition probable with regard to reaction of chlorine with bromide within drinking water disinfection (8). Here, the increase of bromine input led to an increase in several organochlorine compounds (9).

Experimentals

We selected CBr_4 as bromine carrier, because it is combustible and therefore not used as flame retardant, is no direct precursor for PXDD/PXDF and has a high content of bromine (about 96 % of mass). CBr_4 is a solid substance and does not melt before reaching the furnace.

The experiment took place on the 10th of March, 1989 in a MWI. Five polyethylene boxes, each containing 1 kilogram of CBr_4, were bound toghether, put in a bag and then thrown into the waste feeding hopper of line 2 of the MWI. The boxes-in-bag-system was chosen in order to make sure that CBr_4 enters the furnace all at once.

The bromine mass entering the furnace amounted to 4831 g. In the same time about 5 tons of waste were burnt, resulting in an increase of bromine content of this waste of 966 g/t. As waste normally contains about 20 - 90 g/t bromine, the bromine supply was increased more than ten-fold and amounted to about a tenth of the usual content of chlorine.

As the Air Pollution Control (APC) has a levelling influence, short time measurements in this test were conducted with crude gas. 21 samples were taken and nine of them (corresponding to bromide-

maximum) were analyzed for brominated and chlorinated dioxins, furans and benzenes. Bromide served as leading parameter in crude gas.

Results

Bromide maximum in the dust occured about 20 minutes later than in the gas. The lapse of total bromide concentration (dust + gas) corresponds very well to a theoretical idealized curve. Using a Gaussian function, one can calculate the bromine mass in crude gas. Estimating the average exhaust gas stream to amount to 50.000 m^3/h, the bromine mass stream amounts to 1260 g resp. 26 % of the added input.

The results of the PXDD/PXDF-analyses are of great interest: We found mainly monobromo-polychloro *compounds, while polybromo-(poly)chloro and only brominated compounds could not* be detected, or traces of them could not be quantified. Detection limit of brominated compounds was somewhat higher than of the chlorinated ones, because of technical problems (not enough standards for all chlorination degrees of brominated dioxins and furans, too small dust sample size). The bromo-chloro dioxins and furans are named Br_1Cl_xD resp. Br_1Cl_xF, their sum Br_1Cl_xDF. The index x means 2 to 7 chlorine substituents.

Tab. 1: Br_1Cl_xD and Br_1Cl_xF - content in dust and gas

No.:	Monobromo-polychloro-dibenzofurans, in dust, in ng/g: Br_1Cl_2F	Br_1Cl_3F	Br_1Cl_4F	Br_1Cl_5F	Br_1Cl_6F	Br_1Cl_7F	Br_1Cl_xF	Monobromo-polychloro-dibenzodioxins, in dust, in ng/g: Br_1Cl_2D	Br_1Cl_3D	Br_1Cl_4D	Br_1Cl_5D	Br_1Cl_6D	Br_1Cl_7D	Br_1Cl_xD	Sum PXDD/F
4 :	< 0,50	< 0,50	0,79	1,02	0,75	< 0,50	< 4,06	< 0,50	< 0,50	< 0,50	< 0,50	< 0,50	< 0,50	< 3,00	< 7,06
5 :	< 0,50	1,53	2,66	4,32	2,58	< 0,50	< 12,09	< 0,50	< 0,50	< 0,50	< 0,50	< 0,50	< 0,50	< 3,00	< 15,09
6 :	< 0,50	1,78	3,57	5,76	3,78	0,50	< 15,90	< 0,50	< 0,50	< 0,50	< 0,50	0,79	2,00	< 4,79	< 20,69
7 :	< 0,50	1,16	1,91	4,74	5,03	0,78	< 14,11	< 0,50	< 0,50	0,67	< 0,50	0,99	2,65	< 5,80	< 19,91
8 :	0,57	1,66	4,22	7,66	6,95	1,25	22,30	< 0,50	< 0,50	< 0,50	0,66	1,42	3,23	< 6,81	< 29,11
9 :	< 0,50	1,65	3,32	5,48	3,51	0,61	< 15,07	< 0,50	< 0,50	< 0,50	< 0,50	1,46	2,29	< 5,75	< 20,82
10 :	< 0,50	0,97	2,12	4,74	2,37	0,50	< 11,20	< 0,50	< 0,50	< 0,50	< 0,50	1,30	1,65	< 4,95	< 16,15
11 :	0,78	0,53	1,20	1,88	2,29	< 0,50	< 7,18	< 0,50	< 0,50	< 0,50	0,59	0,55	1,22	< 3,86	< 11,04
12 :	< 0,50	< 0,50	0,53	0,66	0,67	< 0,50	< 3,36	< 0,50	< 0,50	< 0,50	< 0,50	< 0,50	< 0,50	< 3,00	< 6,36
Phs:	< 0,20	< 0,20	0,33	0,53	0,74	0,35	< 2,35	< 0,20	< 0,20	< 0,20	0,27	0,54	0,25	< 1,69	< 4,04

	Monobromo-polychloro-dibenzofurans, in gas, in ng/m^3							Monobromo-polychloro-dibenzodioxins, in gas, in ng/m^3							
4 :	< 1,00	< 1,00	< 1,00	< 1,00	< 1,00	< 1,00	< 6,00	< 1,0	< 1,0	< 1,0	< 1,0	< 1,0	< 1,0	< 6,0	< 12,0
5 :	< 1,00	< 1,00	1,05	2,45	2,12	< 1,00	< 8,62	< 1,0	< 1,0	< 1,0	< 1,0	< 1,0	< 1,0	< 6,0	< 14,6
6 :	< 1,00	< 1,00	1,10	3,20	1,97	< 1,00	< 9,27	< 1,0	< 1,0	< 1,0	< 1,0	< 1,0	< 1,0	< 6,0	< 15,3
7 :	< 1,00	< 1,00	1,47	1,95	2,06	1,05	< 8,53	< 1,0	< 1,0	< 1,0	< 1,0	< 1,0	< 1,0	< 6,0	< 14,5
8 :	< 1,00	< 1,00	1,05	1,12	< 1,00	< 1,00	< 6,17	< 1,0	< 1,0	< 1,0	< 1,0	< 1,0	< 1,0	< 6,0	< 12,2
9 :	< 1,00	< 1,00	< 1,00	< 1,00	< 1,00	< 1,00	< 6,00	< 1,0	< 1,0	< 1,0	< 1,0	< 1,0	< 1,0	< 6,0	< 12,0
10 :	< 1,00	< 1,00	< 1,00	< 1,00	< 1,00	< 1,00	< 6,00	< 1,0	< 1,0	< 1,0	< 1,0	< 1,0	< 1,0	< 6,0	< 12,0

A comparison of the bromide concentration and of monobromo-polychlorinated dioxins and furans (CxDF) shows bromide and dioxins/furans having two maxima, the second occurring at a time, where the bromide maximum has passed. The reason for the second maximum is mainly the high content of dust-bound CxDF. A view at the original data confirm the later occurrence of CxDF in the dust.

As the dust-bound maximum occurs about 22 min. later, an explanation with different transport velocities cannot suffice. We think, the explanation has to be sought at the grate. Entering the fron-

going into the gas phase. Bromine-containing fly ash is not released here, but later on after reaching the ignition temperature in the middle of the grate. Here the main part of CBr_4 burns up and leaves the furnace bound in the fly ash. Under this aspect, the plateau in the CxDF-line of the dust is of special importance: This first (relative) maximum occurs simultaneously to the maxima of the gas phase, although there has been no release of bromine-containing dusts up to then. The cause for this could lie in the transfer of those PBDD/F, which were generated in the gasphase, into the dust. The amounts of the second maximum represent, in contrast, another production process, namely the generation of dioxins and furans directly in the fly ash, corresponding to the laboratory tests of Stieglitz et al. (10).
In order to compare the amounts of mixed halogenated dioxins and furans resulting from the addition test and during regular operation (phase 3) with amounts found in the dust of other facilities, table 2 shows the percentage of these compounds in relation to PCDD/PCDF in dust.

Tab. 2: Percentage of mixed halogenated dioxins and furans related to the corresponding PCDD/PCDF-concentrations in dust, in ng/g

Sample No.	4	5	6	7	8	9	10	11	12	Phase3
Sum Br_1Cl_xO+F	7,1	15,1	20,7	19,9	29,1	20,8	16,2	11,0	6,4	4,0
Sum PCDD/F	81,5	92,7	88,8	87,5	138,5	123,2	101,6	91,2	79,6	95,9
% of PCDD/F	8,7	16,3	23,3	22,7	21,0	16,9	15,9	12,1	8,0	4,2

The average of the short phase analyses (no. 4 - 12) during addition test amounts to 16,1 %, whereas longterm measurement (phase 3) results in 4,2 % in dust. This agrees well with measurements of dusts from other facilities (2,0 - 4,9 % during regular operating) (1).

Conclusions

The results of the PXDD/PXCF-analyses implicate several conclusions:

1. The enlargement of the bromine-input resulted in an increase of mixed-halogenated dioxins, furans and benzenes in the exhaust gas. Bromine has not necessarily to be offered in form of precursors to dioxins, furans and other.

2. Mixed-halogenated dioxins and furans found in the exhaust gas are most probably generated during the incineration process. These compounds could not be found in the input of MWIs, as observed at another MWI.

3. The occurrence of two succeeding concentration maxima indicate two different generation processes of polyhalogenated dioxins, furans and benzenes. While dioxins and furans have a good correlation with the bromide-content of the dust, the respective benzenes show the same with the gas-phase. One can conclude, that in addition to the experimentally proved synthesis in fly ash there is a generating process in the gas phase.

4. The increase of the bromine input in waste is accompanied not only by an expected increase of mixed-halogenated dioxins, furans and benzenes, but in addition by an unexpected increase of their chlorinated analogues in the exhaust gas. This is of special importance in regard to an expected increase of bromine input via brominated compounds in waste via electronic scrap including flame protected plastics and conductive plates.

References

1) Wilken M., Jager J., Beyer A.: ITU - Forschung. Endbericht F & E - Vorhaben "Praktische Konzepte zur Verminderung der Bildung von PCDD und PCDF bei kommunalen Muellverbrennungsanlagen" an der Ruhleben (Berlin), April 1990
2) Munslow W. D., Sovocool G.W., Donnelly J.R., Mitchum R.K.: Chemosphere 16, 1661 - 1666 (1987)
3) Thoma H., Hauschulz G., Hutzinger O.: Chemosphere 16, 1579 - 1581 (1987)
4) Schwind K.,H., Hosseinpour J., Thoma H.: Chemosphere 17, 1875 - 1884 (1988)
5) Thoma H., Rist S., Hauschulz G., Hutzinger O.: Chemosphere 15, 649 - 652 (1986)
6) Thoma H., Rist S., Hauschulz G., Hutzinger O.: Chemosphere 16, 297 - 307 (1987)
7) Buser H.-R.: Chemosphere 16, 713 - 732 (1987)
8) Hwang S-C., Larson R.A., Snoeyink V.L.: Chemosphere 17, 1337 - 1342 (1988)
9) Stachel B., Lahl U., Schröer W., Zeschmar B.: gwf-wasser/abwasser 126, 356 - 360 (1985)
10) Stieglitz L, Zwick G., Beck H., Roth W., Vogg H.: Chemosphere 18, 1219, 1989