

## PXDF/D in Flue Gas from an Incinerator Charging Wastes Containing Cl and Br and a Statistical Description of the Resulting PXDF/D Combustion Profiles

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### Abstract

Five reference trials were carried out on chlorine-containing input materials and nine co-combustion trials on chlorine and bromine-containing plastic input materials at a test facility for solid waste incineration<sup>(1)</sup>.

Emission samples taken from raw gas were analysed for polyhalogenated dibenzo(p)dioxins and dibenzofurans (PXDF/D: X = Cl, Br, ClBr). The total concentrations of PXDF/Ds were found to fluctuate by a factor of approximately 4, but concentrations determined for the halogen inputs fluctuated by a factor of about 1.5. No correlation between these parameters was found. On average, the furan concentrations were found to be twice as high as those measured for the dioxins. In the reference samples mostly PCDF/Ds are detected, while in the samples from the co-combustion trials up to 45% of the total PXDF/Ds consisted of PBCDF/Ds. The percentage of those congeners correlated well with the bromine content of the total halogen input.

It is possible to calculate PXDF profiles using simple statistical functions from the knowledge of the bromine and chlorine content of the input materials. These profiles are comparable to those received from the analytical results. Comparing such calculated profiles to PCDF analytical data allows the estimation of the concentrations of the remaining PXDFs.

### Introduction

Reference trials were carried out with plastic waste materials containing chlorine, and co-combustion trials were carried out with electrical and electronic wastes containing various amounts of both chlorine and bromine. These took place in July and December 1995 at the test facility for solid waste incineration 'TAMARA' at Karlsruhe Research Centre (FZK Germany).

PXDF/Ds are trace substances in the flue gases of incineration plants normally generated by a process known as de novo synthesis<sup>(2)</sup>, which is based on gas or particle phase reactions<sup>(3)</sup> usually taking place at temperatures between 200°C and 400°C. Typical so-called PXDF/D combustion profiles<sup>(4)</sup> are consistently found for flue gases after the de novo synthesis temperature zone. This suggests the statistical formation of PXDF/Ds without the influence of precursors. PXDF/D profiles were calculated<sup>(5)</sup> with the aid of simple statistical functions, which are based on the bromine/chlorine ratio during the synthesis, describing well the analytical results from real combustion processes.

Following, the PXDF/D analytical results from the raw gas samples, which were extracted during the trials at TAMARA and determined by GfA, are presented, and compared with the chlorine and bromine contents of the input materials. Particular attention is paid to the quantitative ratios of the PCDF/Ds, PBCDF/Ds and PBDF/Ds. The analytical PXDF/D profiles are compared with the calculated combustion profiles. In

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conclusion, a method is presented which uses the analytical PCDF concentrations in the flue gas and the chlorine and bromine content of the input materials to assess the profiles and concentrations of the PBDF and PBCDF.

## Methods

### Combustion trials

Five reference trials and nine co-combustion trials were carried out on the TAMARA test facility at FZK during two campaigns in July and December 1995. Municipal waste was burnt during the reference tests, containing significant amounts of chlorine in the percentage range, with no significant amounts of bromine.

During the nine co-combustion trials additional electrical and electronic waste plastic (E&E material) containing chlorine and bromine was added. The E&E material consisted of shredded electrical and electronic plastic material from computers, electrical switches, communications and data-processing equipment taken from household and industrial waste. The E&E material contained various plastics with different amounts of chlorine and bromine; the bromine originates mostly from brominated organic compounds which are originally added to the equipment as flame retardants because of fire and safety requirements.

The input material was examined to determine the chlorine and bromine content by FZK and GfA in parallel using various techniques (Microwave Digestion - TRFA; Schöniger Combustion - Ion Chromatography).

The different analytical techniques led to comparable results - if the accuracy of the analytical method and the difficulties encountered when extracting representative samples from an inhomogeneous mixture are taken into account. Accordingly, 128 - 208 kg/h input material containing between 0.56 and 1.00 % wt chlorine and <0.01 and 0.18 % wt bromine was used in each trial (see Table 1).

In addition, the combustion residues were analysed by FZK. The halogen concentrations of the input materials were assessed from the values of the individual combustion residues, as shown in Table 1. The contents found for chlorine and bromine show good agreement with the results for the input analysis.

The table also shows that by far the largest halogen content, both chlorine and bromine, was found in the fly ash and gas phase, which indicates that they are available for the de novo synthesis of PXDF/Ds.

table 1: Chlorine- and bromine-concentrations in combustion matrices and the input material (calculated in weight-% of the input material)

trial-N <sup>o</sup> (chronological) Reference Co-combustion	matrix 1 bottom ash		matrix 2 grate sifting		matrix 3 boiler ash		matrix 4 fly ash <small>after boiler</small>		matrix 5 gas phase <small>after boiler</small>		matrix 1-5		analysis of input material	
	Cl	Br	Cl	Br	Cl	Br	Cl	Br	Cl	Br	Cl	Br	Cl	Br
No.	%wt <sup>(1)</sup>		%wt <sup>(1)</sup>		%wt <sup>(1)</sup>		%wt <sup>(1)</sup>		%wt <sup>(1)</sup>		%wt <sup>(1)</sup>		%wt <sup>(1)</sup>	
R1	0,033	0,003	0,002	< 0,001	0,000	< 0,001	0,108	0,003	0,477	0,002	0,620	0,008	0,580	0,006
C1	0,032	0,006	0,003	< 0,001	0,001	< 0,001	0,146	0,012	0,510	0,007	0,690	0,025	0,574	0,019
C2	0,033	0,006	0,002	< 0,001	0,001	< 0,001	0,174	0,046	0,502	0,152	0,713	0,206	0,636	0,137
C3	0,033	0,006	0,002	< 0,001	0,001	< 0,001	0,147	0,026	0,575	0,056	0,758	0,088	0,585	0,043
C4	0,018	0,007	0,001	< 0,001	0,001	< 0,001	0,177	0,044	0,463	0,090	0,661	0,142	0,589	0,086
R2	0,017	0,002	0,001	< 0,001	0,000	< 0,001	0,100	0,002	0,447	0,002	0,566	0,007	0,580	0,006
R3	0,076	0,001	0,006	< 0,001	0,002	< 0,001	0,107	< 0,001	0,672	0,003	0,862	0,005	0,615	0,003
R4	0,086	0,001	0,007	< 0,001	0,002	< 0,001	0,087	< 0,001	0,623	0,003	0,815	0,004	0,615	0,003
C5	0,086	0,002	0,007	< 0,001	0,003	< 0,001	0,109	0,003	0,766	0,081	0,972	0,066	0,810	0,055
C6	0,084	0,001	0,006	< 0,001	0,003	< 0,001	0,135	0,004	0,892	0,120	1,121	0,125	1,002	0,106
C7	0,073	0,002	0,007	0,001	0,002	< 0,001	0,102	0,007	0,636	0,141	0,820	0,151	0,644	0,083
C8	0,073	0,002	0,006	< 0,001	0,003	< 0,001	0,089	0,013	0,728	0,306	0,898	0,321	0,673	0,183
C9	0,081	0,004	0,008	0,001	0,002	< 0,001	0,080	0,004	0,555	0,121	0,724	0,130	0,564	0,072
R5	0,060	0,001	0,005	< 0,001	0,002	< 0,001	0,091	< 0,001	0,535	0,003	0,694	0,004	0,615	0,003

(1) referring to input material

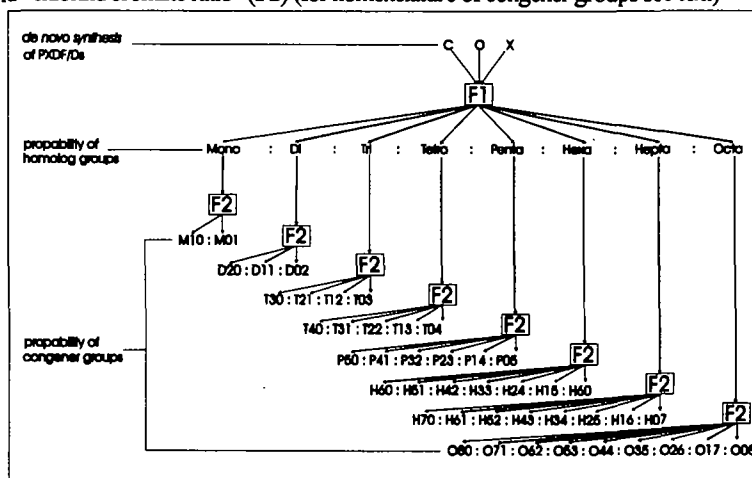
### Calculation of PXDF/D profiles

According to theory, 1700 different PXDD and 3370 PXDF congeners can be formed during the de novo synthesis. These congeners can be arranged into 44 "congener groups" (each with the same number of Cl and/or Br substituents) and into 8 "homolog groups" (with the same total number of substituents). In the

following, the congener groups will be identified in each case by the first letter of the "homolog group" to which it belongs (e.g. M for Mono), and two numbers (the first number = the number of Cl substituents and the second number = the number of Br substituents). The process on which the following profile calculation is based was described in a paper given at the "DIOXIN '93" meeting in Vienna <sup>(5)</sup>. The probability of formation of congener groups is described by two binomial functions, which on the one hand are influenced by a "hypothetical reactivity" of the halogen atoms and on the other hand by the "chlorine/bromine ratio" in the flue gas during PXDF/D formation.

The first binomial function (F1) describes the probability of formation of the mono- to octa-halogenated homolog groups, based on the "reactivity" parameter. The second binomial function (F2) describes the probability of formation for congener groups with different degrees of chlorination or bromination within a homolog group, using the "chlorine/bromine ratio" at the time of formation. A schematic profile calculation curve, using the binomial functions F1 and F2, is presented in Figure 1.

figure 1: Calculation of probability for the formation of homolog and congener PXDF/D-groups in a de novo synthesis using binomial distributions influenced by "reactivity" of halogens (F1) and "chlorine/bromine ratio" (F2) (for nomenclature of congener groups see text)



## Results

### PXDF/D analytical results

PXDF/Ds were found in all the samples examined, the furan concentrations generally varied between 1.5 and 2 times as high as those of dioxin. The total PXDF/D concentrations were found to vary between 24.3 ng/m<sup>3</sup> (sample R2) and 97.2 ng/m<sup>3</sup> (sample C6). With this fourfold variation the total PXDF/D concentrations were subject to greater variation than the concentrations of the total halogen input, as also shown in Figure 2.

In general Figure 2 shows that there is no specific relationship between the total PXDF/D concentrations and the absolute amount of halogens added.

In Figure 3 the percentages of PBCDF/D and PBDF/D for all PXDF/Ds detected compared with percentages of Br in the total halogen input. With the exception of sample R5 a very low percentage of brominated/mixed halogenated dioxins or furans was found. In the raw gas samples from the co-combustion trials C2-4 and C5-9, brominated/mixed halogenated congeners were found in high concentrations; these concentrations show a good correlation with the bromine content of the input material. With increasing bromine content in the input materials, the percentage PBCDF/D and PBDF/D of the total PXDF/Ds increased to 45% (C8). In the reference sample R5, where the amount of bromine in the input material was

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negligible, the proportion of these components found in all PXDF/Ds in the raw gas amounted to around 17%. A kind of "bromine hysteresis" in the facility after the preceding co-combustion trials C5-9 could be a possible explanation, although this effect was not observed in sample R2.

figure 2: PXDF/D-raw-gas concentrations in relation to halogen-input ( $C_6=100\%$ ) and Br [% of  $\Sigma(Cl+Br)_{molar}$ ] in 5 reference trials (R1-5) and 9 cocombustion trials (C1-9)

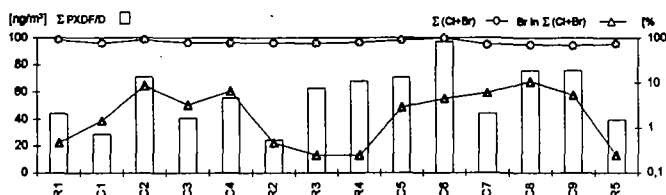
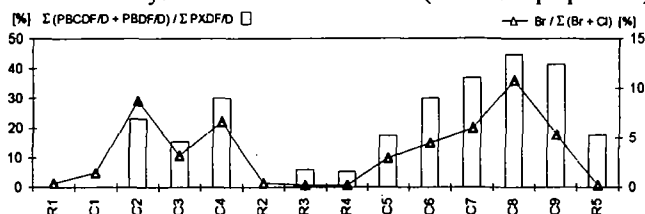


figure 3: Portion Br in the total Cl- and Br-input in relation to portion of PBCDF/D- and PBDF/D in the analysed PXDF/D concentrations (both molar proportions)



## Comparison of calculated PXDF profiles with analytical PXDF profiles

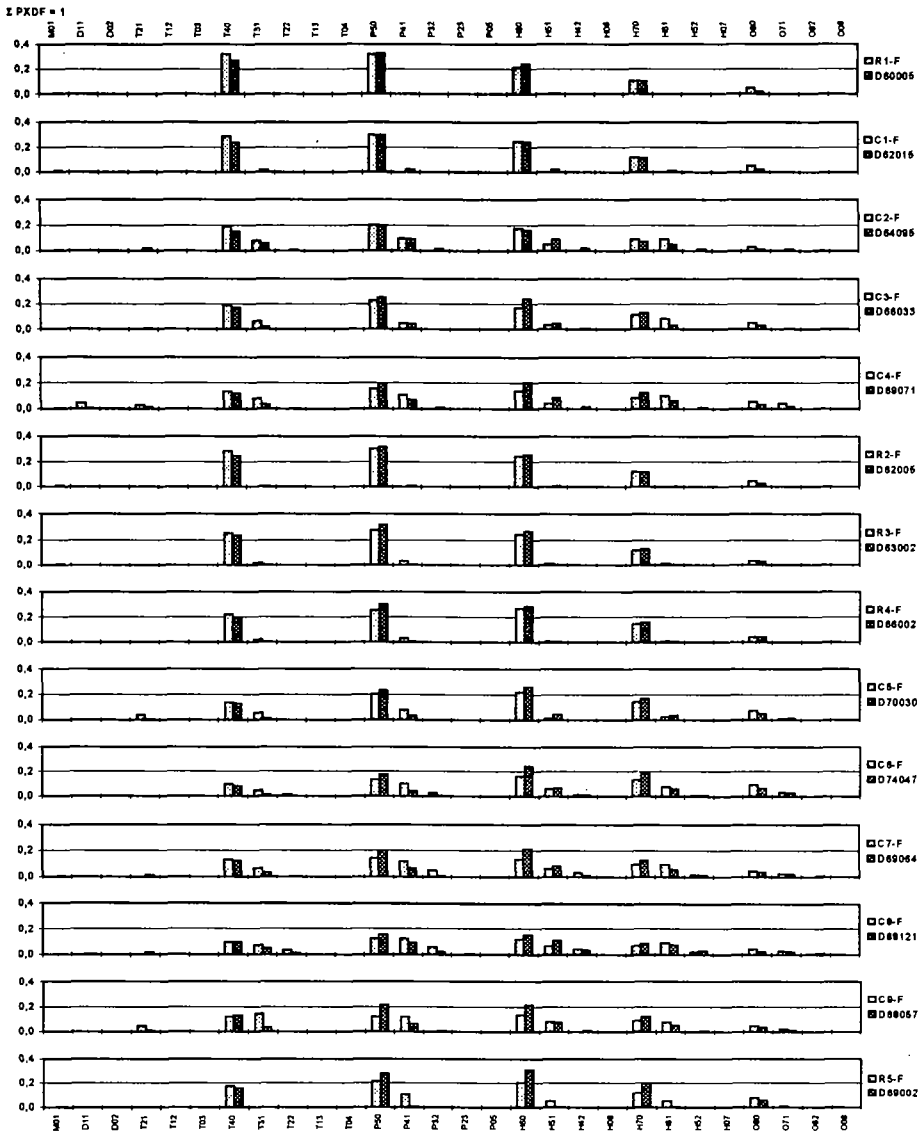
As described under the section "PXDF/D analytical results", the furan concentrations were, in part, considerably greater than those of the dioxins. PBDDs and PBCDDs in the majority of samples could not be found. The following profile comparisons, for which the most congener groups have been detected, were only carried out for the furans therefore. In principle, these observations should also be possible for the dioxins. However, in the case of the matrices examined here, they require an analytical technique with lower than standard detection limits, especially where mixed halogenated species. Until today, a low resolution MS has been used for these components. There are no labelled standards and only a limited number of native standards for analysis are available.

For the following investigations, 100 combustion profiles were calculated for each combustion trial using "Cl/Br ratio" of the input material (see "input analysis" in Table 1) and graded "reactivities" from 0.01 to 1.00 (see the section "Methods" for the calculation). Using pattern recognition software (Principle Components Analysis) on calculated profile with the best fit was assigned to PXDF analytical results. As Figure 4 shows, it was possible to fit a calculated distribution to each sample very satisfactorily. The diagram of the calculated distribution shows the "reactivity" on which it is based in each case (e.g. D60006 = reactivity 0.60) as well as the molar "Br/Cl ratio" used in the calculation (e.g. D60006 = Br/KCl ratio 0.6%).

## Estimation of the PBCDF/PBDF concentrations using PCDF analytical data

The PXDF profiles, calculated in accordance with the previous section can be used to estimate the concentrations of PBCDF and PBDF with existing PCDF analytical data. For this purpose, normalised profiles for the PCDF are extracted from the 100 PXDF profiles which were calculated for each combustion trial (with the relevant "Cl/Br ratio" in the input material and "reactivities" of 0.01 - 1.00). Using the pattern recognition software, the calculated profile was found which best fitted the PCDF analytical data. After this, the relevant complete calculated PXDF profile was assigned to the PXDF analytical data of the sample.

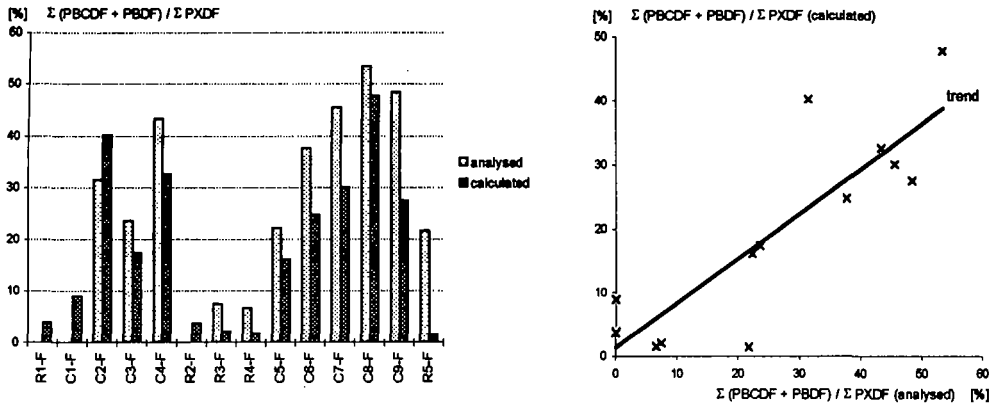
Figure 4: Associating calculated combustion profiles to analysed furan concentrations in the raw gas during 14 combustion trials using pattern recognition (profiles are standardized)



In Figure 5, the amounts of the PBDF and PBCDF in the assigned calculated profiles are compared with the analytical data. With the exception of sample R5 (for this see also section 'PXDF/D analytical results' - "bromine hysteresis" in the facility after the previous co-combustion trials C5-9), the compared values have the same order of magnitude, the calculated amounts tending to be slightly below the analytical values, as the curve in Figure 5 also shows.

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Figure 5: Comparison of analytical PBCDF-, PBDF-results (white columns) to calculated concentrations using known profiles of PCDF congener groups and Cl/Br ratio of the input-material



Knowing the analytical PCDF raw gas concentrations, the percentage amounts of the brominated or mixed halogenated congener groups in the assigned calculated profiles were converted to  $\text{ng/m}^3$ . In Table 2, they are compared with analytical results for the Mono Bromo CDF congener groups, as for example. They also tend to agree. An analytical technique with lower detection limits, especially for the mixed halogenated species, (see also section "Comparison of calculated profiles with analytical PXDF profiles") would probably improve the agreement between the "model" and the analytical data.

table 2: Associating calculated concentrations of MonoBromoCDFs to analytical results

trial-N <sup>o</sup> (chronological) Reference Co-combustion	PXDF-raw gas concentration									
	T31		P41		H51		H61		O71	
	analysed $\text{ng/m}^3$	calculated $\text{ng/m}^3$	analysed $\text{ng/m}^3$	calculated $\text{ng/m}^3$	analysed $\text{ng/m}^3$	calculated $\text{ng/m}^3$	analysed $\text{ng/m}^3$	calculated $\text{ng/m}^3$	analysed $\text{ng/m}^3$	calculated $\text{ng/m}^3$
R1	a (<0,17)	0,10	a (<0,21)	0,18	a (<0,24)	0,15	a (<0,26)	0,08	a (<0,29)	0,02
C1	a (<0,18)	0,16	a (<0,21)	0,27	a (<0,23)	0,27	a (<0,27)	0,15	a (<0,30)	0,04
C2	2,39	1,77	3,23	3,16	1,87	3,35	3,63	1,96	a (<0,36)	0,49
C3	1,08	0,42	0,91	0,86	0,70	0,90	1,85	0,86	a (<0,25)	0,15
C4	2,01	1,02	3,06	2,12	1,27	2,63	3,29	1,80	1,47	0,52
R2	a (<0,14)	0,05	a (<0,23)	0,08	a (<0,25)	0,08	a (<0,29)	0,04	a (<0,32)	0,01
R3	0,53	0,06	1,06	0,09	0,47	0,09	0,41	0,05	a (<0,10)	0,01
R4	0,66	0,04	0,93	0,08	0,33	0,09	0,25	0,06	a (<0,10)	0,02
C5	1,90	0,48	2,98	1,25	0,62	1,95	1,18	1,67	0,42	0,61
C6	2,21	0,51	5,21	1,60	3,42	3,76	4,55	4,33	2,11	2,13
C7	1,38	0,75	2,76	1,58	1,52	1,97	2,55	1,35	0,68	0,40
C8	2,32	1,54	4,53	3,36	2,46	4,36	3,81	3,12	1,10	0,95
C9	4,63	1,04	4,14	2,20	2,94	2,76	3,07	1,91	0,81	0,56
R5	a (<0,05)	0,03	1,95	0,06	1,02	0,07	1,10	0,05	0,26	0,01

a no congener detectable (detection limit for one congener of the congener group)

The method described above can be adapted, for example, to determine the bromine/chlorine ratio of input material from a knowledge of the PXDF/D raw gas concentrations. The bromine concentration in the input can be determined from the PXDF/D raw gas concentrations and the chlorine content of input material, and the chlorine contents of the input materials from the known PXDF/D raw gas concentrations and the bromine content of the input material.

## References

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