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EVALUATION OF PCDF/D, PBDF/D AND PBCDF/D PROFILES IN FLUE GAS OF COMBUSTION FACILITIES USING A STATISTICAL DISTRIBUTION FUNCTION

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Introduction

Chlorinated, brominated and bromo/chloro-substituted dibenzo(p)dioxins and dibenzofurans (PXDF/Ds; x = Cl, Br) are trace substances in the flue gas of combustion facilities, normally generated at temperatures of 200 to 400 °C by the so-called *de novo synthesis*[1].

Several research groups discuss mechanisms of the *de novo synthesis* based on reactions in the gas phase or the particulate phase[2]. Results from real combustion processes indicate, that tetra- to octaXDF/D homolog groups reproducibly show typical so-called *combustion profiles*[3]. These profiles indicate a statistical distribution of the halogenated dibenzo(p)dioxins (PXDDs) and dibenzofurans (PXDFs) in the flue gas behind the temperature zone of the *de novo synthesis*.

The paper presented here covers the calculation of *combustion profiles*, based on a simple statistical relation, not only for PCDF/Ds but also for PBDF/Ds and PBCDF/Ds. The results are in good accordance to real PXDF/D distributions received from flue gas analysis.

Method

During *de novo synthesis* of halogenated dibenzofurans (PXDFs) and dibenzo(p)dioxins (PXDDs) theoretically 1700 PXDDs and 3320 PXDFs congeners can be formed. These congeners belong to 44 groups of congeners and 8 homolog groups (see Table 1).

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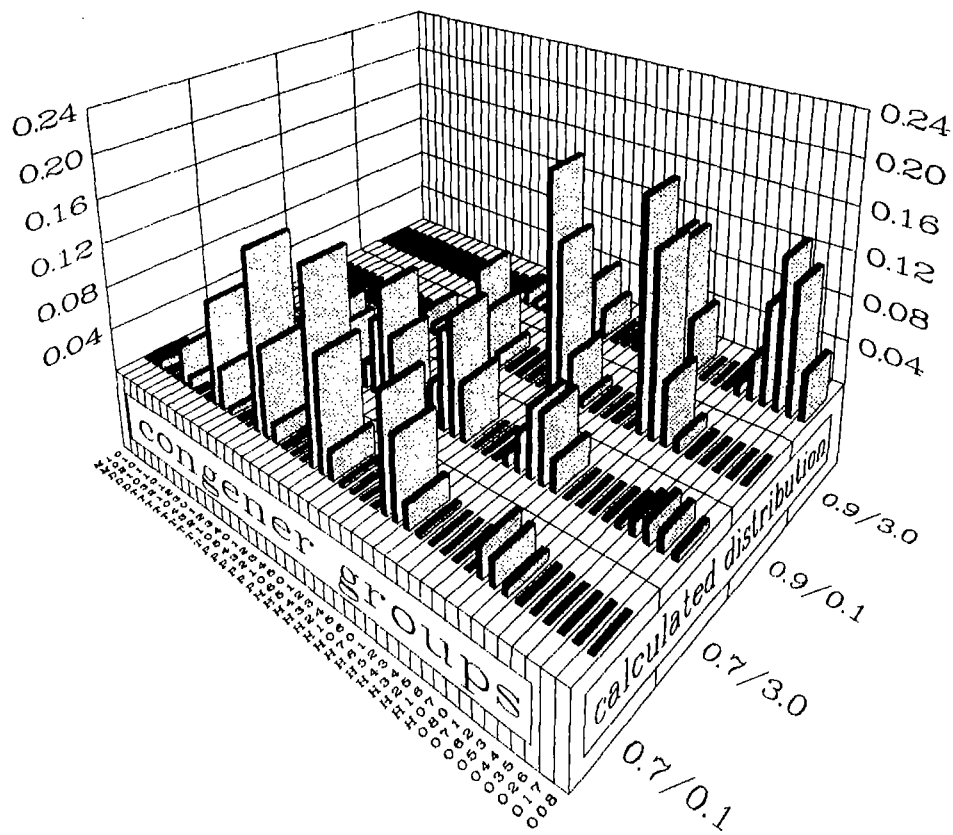
Table 1: Possible PXDF/D congener groups (x = Cl, Br)

Homolog group	Congener group			Nomen-clature	Homolog group	Congener group			Nomen-clature
Mono	Monochloro-		DD/DF	M10	Hexa	Hexachloro-		DD/DF	H60
		Monobromo-	DD/DF	M01		Pentachloro-	Monobromo-	DD/DF	H51
						Tetrachloro-	Dibromo-	DD/DF	H42
Di	Dichloro-		DD/DF	D20		Trichloro-	Tribromo-	DD/DF	H33
	Monochloro-	Monobromo-	DD/DF	D11		Dichloro-	Tetrabromo-	DD/DF	H24
		Dibromo-		D02		Monochloro-	Pentabromo-	DD/DF	H15
							Hexabromo-	DD/DF	H60
Tri	Trichloro-		DD/DF	T30					
	Dichloro-	Monobromo-	DD/DF	T21	Hepta	Heptachloro-		DD/DF	H70
	Monochloro-	Dibromo-	DD/DF	T12		Hexachloro-	Monobromo-	DD/DF	H61
		Tribromo-	DD/DF	T03		Pentachloro-	Dibromo-	DD/DF	H52
						Tetrachloro-	Tribromo-	DD/DF	H43
Tetra	Tetrachloro-		DD/DF	T40		Trichloro-	Tetrabromo-	DD/DF	H34
	Trichloro-	Monobromo-	DD/DF	T31		Dichloro-	Pentabromo-	DD/DF	H25
	Dichloro-	Dibromo-	DD/DF	T22		Monochloro-	Hexabromo-	DD/DF	H61
	Monochloro-	Tribromo-	DD/DF	T13			Heptabromo-	DD/DF	H70
		Tetrabromo-	DD/DF	T04					
					Octa	Octachloro-		DD/DF	O80
Penta	Pentachloro-		DD/DF	P50		Heptachloro-	Monobromo-	DD/DF	O71
	Tetrachloro-	Monobromo-	DD/DF	P41		Hexachloro-	Dibromo-	DD/DF	O62
	Trichloro-	Dibromo-	DD/DF	P32		Pentachloro-	Tribromo-	DD/DF	O53
	Dichloro-	Tribromo-	DD/DF	P23		Tetrachloro-	Tetrabromo-	DD/DF	O44
	Monochloro-	Tetrabromo-	DD/DF	P14		Trichloro-	Pentabromo-	DD/DF	O35
		Pentabromo-	DD/DF	P05		Dichloro-	Hexabromo-	DD/DF	O26
						Monochloro-	Heptabromo-	DD/DF	O17
							Octabromo-	DD/DF	O08

The calculation of the profiles is based on two binomial functions, one describing the linkage of congener groups to homolog groups by the parameter "reactivity", the other the coordination inside the homolog groups by the "bromo/chloro ratio". The "reactivity" is a characteristic of the halogen sustituents and is indicated by values between 0 and 1. Low "reactivity" leads to increased formation of members of homolog groups with low degree of chlorination. For the formation of PXDF/Ds two halogens (Cl, Br) are available which leads to n + 1 congener groups per homolog group with n degrees of halogenation. Figure 1 shows four examples of calculated propability distributions of the 44 groups of congeners based on different "reactivities" and "Br/Cl-ratios".

Figure 1: 4 examples of calculated propability distributions ("reactivity": 0.9 and 0.7; "Br/Cl ratio": 3.0 and 0.1)



Emission samples received from combustion facilities were analyzed for PCDF/Ds, PBDF/Ds and PBCDF/Ds. According to the nomenclature of Table 1 the following distributions of the congener groups were found in six samples:

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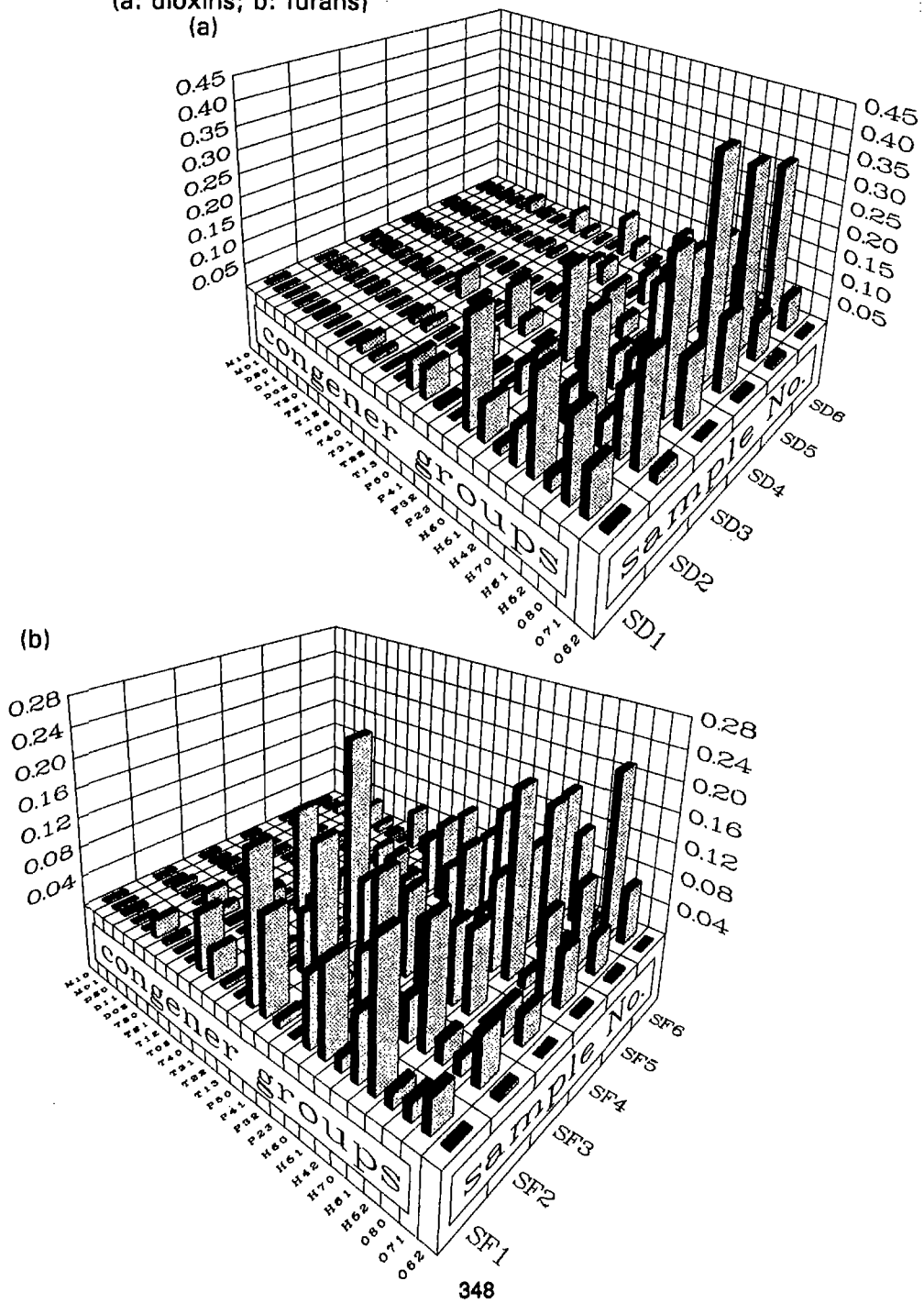
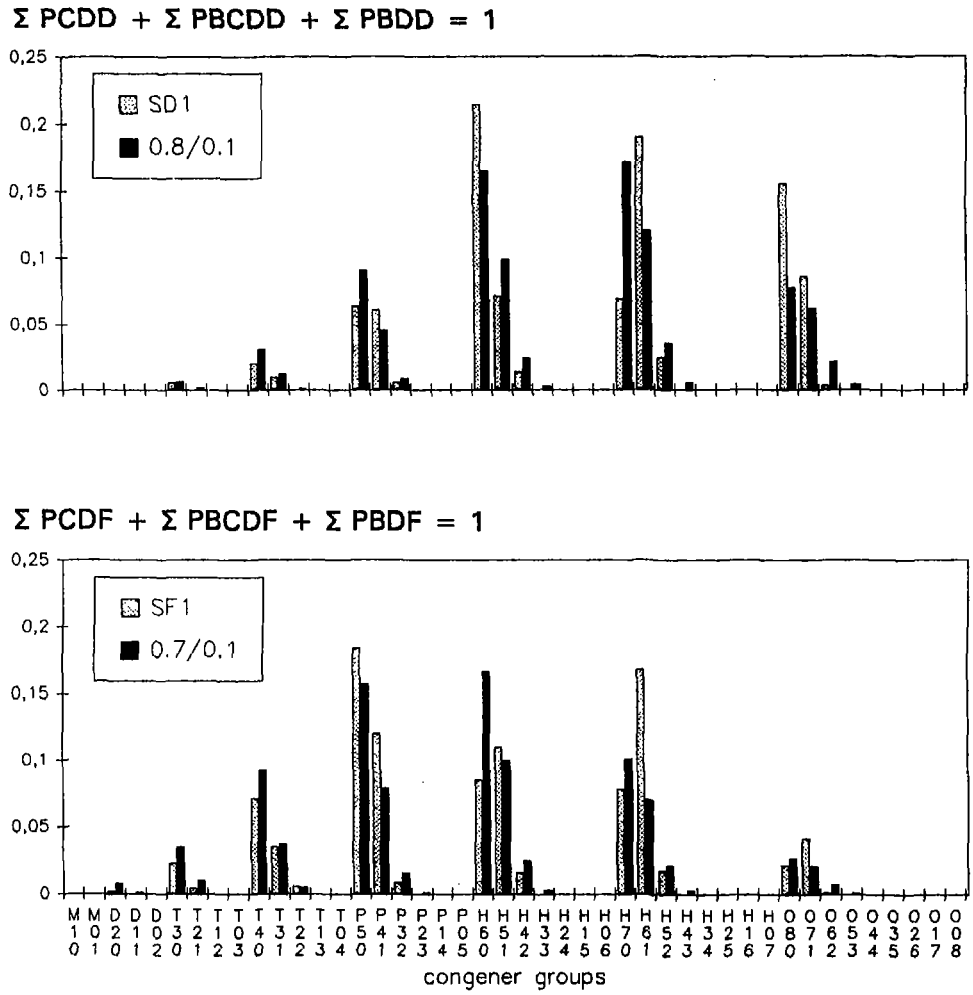
Figure 2: Distribution of PXDF/D congener groups in emission samples (a: dioxins; b: furans)



Using a pattern recognition software[4] one calculated distribution out of several thousand calculations based on different "reactivities" and "Br/Cl ratios" is associated to each sample. The results are shown graphically in figure 3.

Figure 3: Comparison of calculated distribution profiles (black columns) with results from sample SD1 and SF1 (white columns)



In certain cases the method allows the estimation of concentrations and distribution patterns of PBDF/Ds and PBCDF/Ds, based on known PCDF/D concentrations and distributions.

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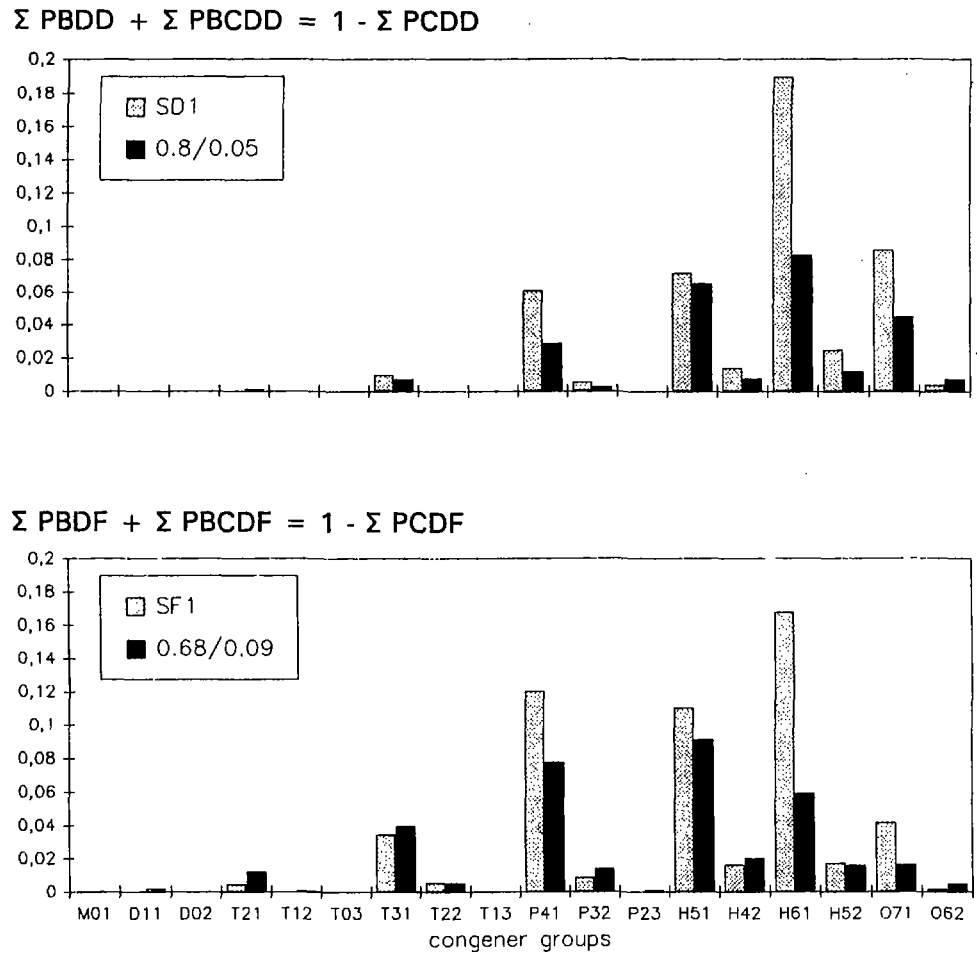
Figure 4: Comparison of calculated distributions of brominated and bromo/-chloro halogenated congener groups (black columns) from known distributions of chlorinated congener groups with analytical results from sample SD1 and SF1 (white columns)



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