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DEDUCTION OF A TYPICAL PATTERN FOR THE ISOMERS OF TETRA - TO HEPTACHLORO - DIBENZO-P-DIOXINS AND - FURANS FORMED IN COMBUSTION PROCESSES

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Abstract

A number of 121 different samples obtained in various combustion sources were analysed isomerspecificely according to their contents of tetra- to heptachloro-dibenzo-p-dioxins and -dibenzofurans (PCDD/F). The application of the principal component analysis (PCA) on the obtained data set shows the existence of a typical pattern for the isomers of each group of homologues.

Introduction

Isomerspecific seperation and quantification of PCDD/F is investigated using high resolution gas chromatography (HRGC) with cyanopropyl-siloxane phases in fused silica columns combined with high resolution mass spectrometrie (HRMS) [1,2]. Consequently the most toxic 2,3,7,8-isomers and all other isomers could be seperated [3], but in routine measurement some are only available in sums. Nevertheless the HRGC-spectrum of one group of homologues gives a pattern of seperated and not seperated isomers. Similarities in these patterns are found for some thermal processes [4], especially fly ash and car exhaust [5] or fly ash and OCDD/F-combustion on fly ash [6]. Suggesting a thermodynamically controlled formation mechanism for the PCDD/F [7], the isomer pattern of various thermal processes should be constant.

Experimental

Samples compared in this analysis are taken from five different municipal waste incinerators, two room fires and combustion of plastics under defined technical conditions. Different types of samples and sampling techniques are used (see Table 1). Clean up procedures and measurements used for sample preparation are described elsewhere [8,9].

Source	Number for PCA	Sample	Number for PCA	Sampling Technique	Number for PCA
municipal waste incineration	111	flue gas	67	adsorption on XAD	46
				adsorption on zeolith	12
				condensate	9
		fly ash	39	collected in an electrostatic filter	17
				collected in dust sinks	18
				fibre-filter	4
		slag	5	collected	5
room fires	6	soot	4	collected by wiping	4
		combustion residue	2	collected	2
combustion of plastics	4	computer boxes (polycarbonates)	1	collected	1
		computer devices (epoxy-resins)	1	collected	1
		PVC	2	collected	2

Table 1: Origin of samples analysed in this study

Results

According to different types of analysed samples a great variance of concentrations for PCDD/F were found (e.g. 2 ng/kg < TCDD < 20387 ng/kg). In Figure 1 the isomer pattern for TCDD of all of these samples is plotted against the isomer concentration. A general trend to build up two classes of parallel (proportional) patterns can be observed, but there are some differences too.

To get a better insight in similarities and differences, the data set of each group of homologues is transformed by a principal component analysis (PCA) [10]. Briefly, the data set for the TCDD-isomers consists of 15 isomers or sums of isomers, which span a 15-dimensional space. Concentrations of all samples (42 samples for the TCDD-isomers) constitute a swarm in this space. If this swarm is highly correlated, one might search for a vector, in whose direction most points of the swarm may be found. Mathematically, we search for a vector with the largest variance of distribution of measured points. This vector is called the first principal component. The second principal component is calculated orthogonal to the first one and describes the next largest variance. The higher principal components can be developed in the same way.

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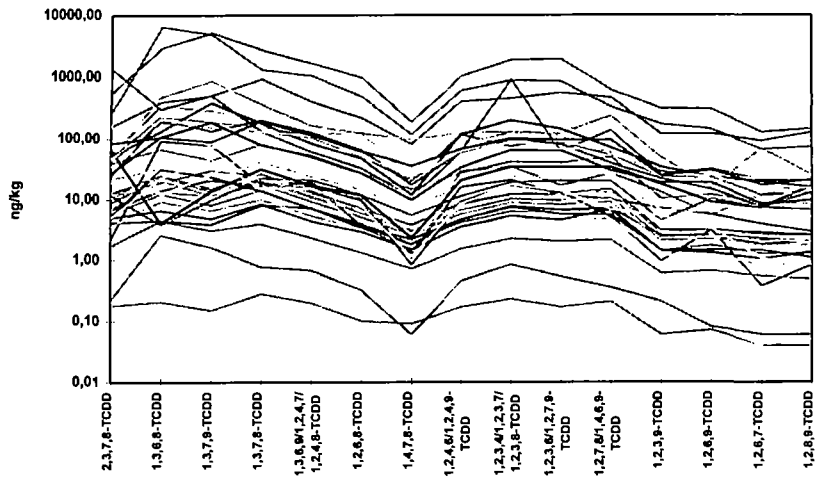

Figure 1: TCDD-isomers and their concentrations in different samples (lines in this plot) of combustion processes

Comparing this data set in a PCA, it is necessary to normalize the data set. Otherwise samples with high concentration would dominate the principal components. The concentration of each isomer per sample is divided by the square root of the sum of quadratic isomer concentrations in one group of homologues in this sample (Figure 2).

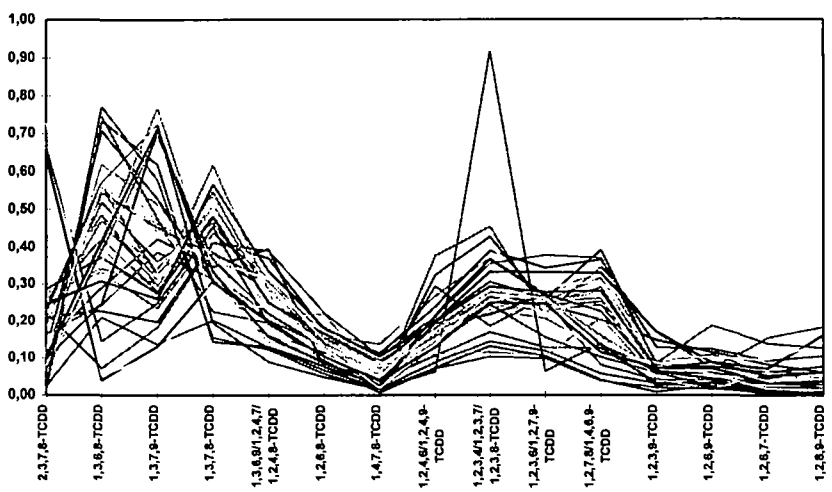

Figure 2: Normalized TCDD-isomer-distribution of samples coming from combustion processes

The normalized data set is analysed according to its principal components. Figure 3 shows a plot of the first and second principal component of the TCDD data set. The points in this plot represent different types of samples. It can be seen, that for most of these samples 'PRIN 1' is close to one; 91% of the TCDD-data set information (variance, not corrected for the mean) can be described by the first principal component. A nearly complete description is achieved by adding the second principal component, which contains 7% of the information.

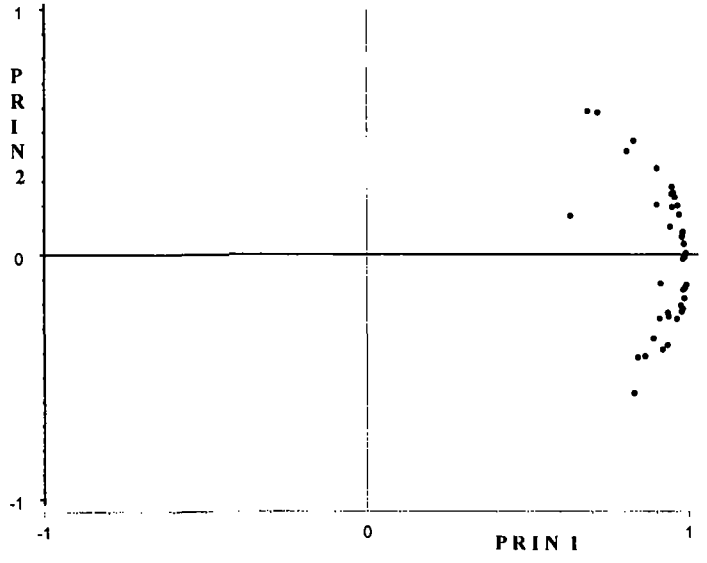

Figure 3: Principal component one ('PRIN 1') and two ('PRIN 2') of the TCDD-data set

This procedure described for the TCDD-isomers is performed for the other tetra- to hepta-dibenzo-p-dioxins and -furans, too. Similar results were obtained. For each of these eight groups of homologues the isomer distribution can be described by two principal components, at which the first principal component alone gives already a very good description (Table 2).
Note that the number of samples, which span the n-dimensional space, is different for each group of homologues, because only samples without missings in their isomer data set are included.

Group of Homologues	Number of Samples	1. Principal Component	2. Principal Component
TCDD	42	91 %	7 %
PCDD	63	92 %	5 %
HxCDD	85	92 %	4 %
HpCDD	121	95 %	5 %
TCDF	47	86 %	6 %
PCDF	70	83 %	13 %
HxCDF	66	85 %	7 %
HpCDF	111	98 %	2 %

Table 2: Percentage of the first and second principal component on the description of the isomer-data set of each group of homologues

Because of the large number of different samples included in this study, these results indicate a strong evidence for the existence of a typical pattern for the isomers of PCDD/F formed in various combustion processes.

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