ELUCIDATION OF RELATIONSHIPS BETWEEN CHLOROAROMATICS IN FULL SCALE INCINERATORS: HIGH TEMPERATURE FORMATION AND LONG-TERM CONCENTRATION INCREASE

<u>M. Blumenstock</u>[1], R. Zimmermann[1,2,3,*], K.-W. Schramm[1] and A. Kettrup[1,4]

[1] GSF-Forschungszentrum, Institut für Ökologische Chemie, D-85764 Neuherberg, Germany
[2] Lehrstuhl für Festkörperchemie Institut für Physik, Universität Augsburg, Universitätsstraße 1, D-86159 Augsburg, Germany
[3] BIfA-Bayerisches Institut für Angewandte, Umweltforschung und -technik GmbH, Abteilung, Umwelt- und Prozesschemie, Am Mittleren Moos 46, D-86167 Augsburg, Germany
[4] Lehrstuhl für Ökologische Chemie und Umweltanalytik, Technische Universität München, D-85748 Freising, Germany
*corresponding author address: ralf.zimmermann@gsf.de and blumenstock@gsf.de

Introduction

The formation of different chloroaromatics (CA) in combustion processes are under investigation for several years (1), (2), (3), (4). Until now there is no complete data available for the CA formation in full scale incinerators in the high temperature regime (1100K-900K) and the "classical" formation window between 500K-700K. This work is dealing with the relation between PCDD/F, PCBz and PCPh from 900K to 500K, the end of the so called formation "window", under normal and disturbed (CO-peaks) combustion conditions. To observe rapid and long-term changes in concentration profiles of PAHs real-time on-line monitoring with REMPI-TOFMS (Resonance-enhanced multiphoton ionisation - Time-of-flight mass spectrometry) was used (5), (6), (7).

Materials and Methods

Conventional isokinetically sampling and HRGC/HRMS analysing technique was used for the investigated CA (6). Parallel sampling were performed at 900K and 500K. The on-line real-time measurement with REMPI-TOFMS is described elsewhere in detail (8).

Results and discussion

Recent work pointed out that a significant part of the PCDD/F formation in incineration processes takes place already in the high temperature region (1000K-700K) (4), (10). However, the major part still is formed within the "classical" formation window at about 600K. In this work the influence of the combustion conditions on the ratio of high temperature PCDD/F formation (900K) and the PCDD/F formation in the classical 600K window is elucidated. In figure 1 the ratios between the concentrations of several CA at the 500K and the 900K sampling point are given as a function of the degree of chlorination. In the upper part of figure 1 the 500K/900K ratios are shown for the normal combustion conditions, in the lower part of figure 1 for disturbed combustion conditions.

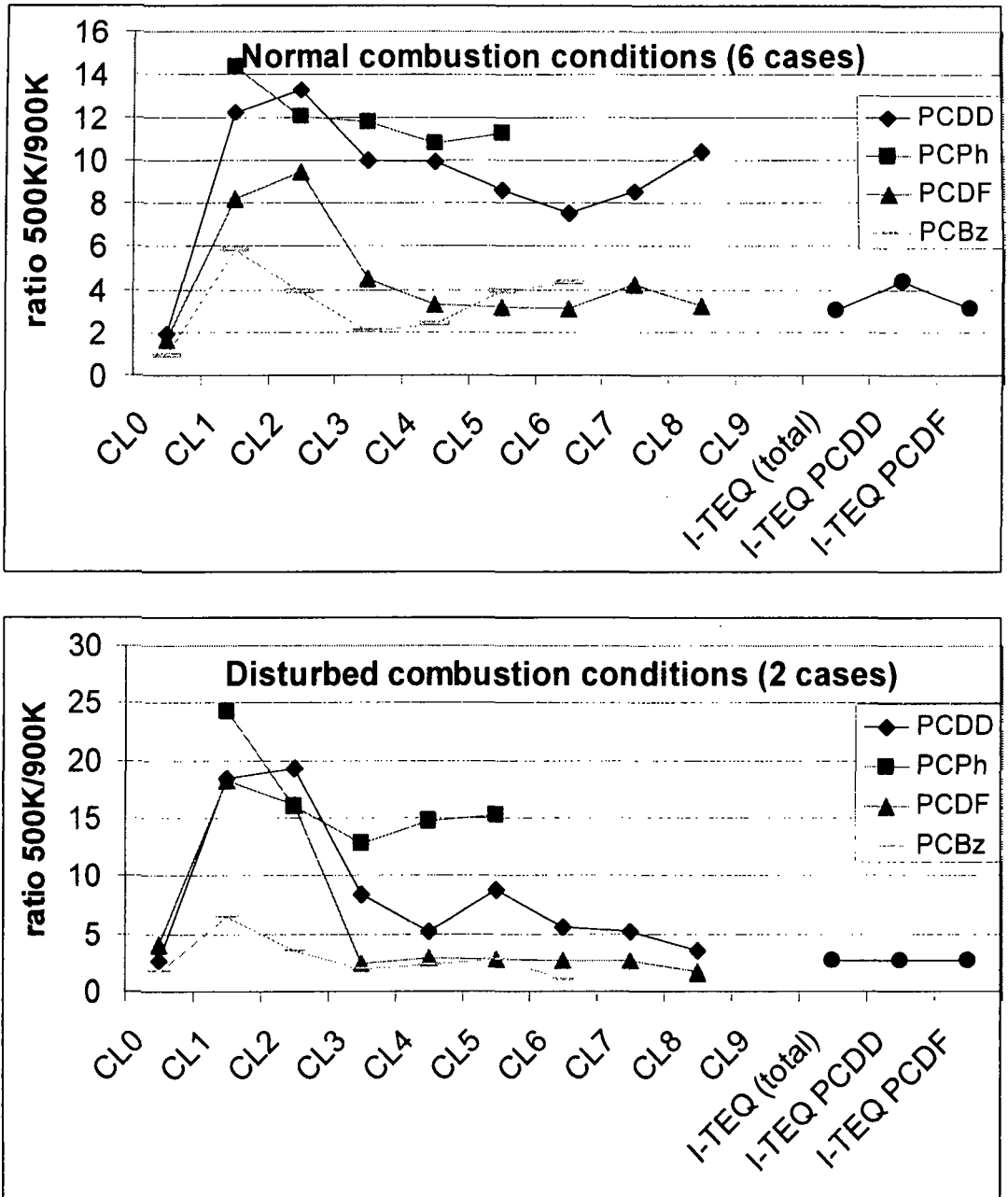**Figure 1:** Ratios for different CA between 500K and 900K at a waste incinerator under normal and disturbed combustion conditions.

Under normal combustion conditions similar formation ratios for PCDD and PCPh between 500K and 900K were found. This fact was reported previously for waste incineration plants (10) and labscale reactors (13). During disturbed combustion conditions the ratios between 500K and 900K are increased for the non chlorinated dibenzofuran (see also figure 4) and also for the mono- and dichlorinated PCDD/F. In contrast to that observation the ratios of the higher chlorinated CA decrease during disturbed combustion conditions, while the ratios for the I-TEQs keeps quite stabile. The strong influence of combustion conditions on the homologue profiles, especially of the lower chlorinated species was reported previously (7). The correlations between different CAs have been investigated by several authors (3), (2), (17), (6). These studies are interesting for the identification of surrogates of the I-TEQ. Recent work pointed out that chlorobenzene is the most suitable on-line measureable surrogate for the I-TEQ with REMPI-TOFMS (7). The fact that more than 60% of the whole toxicity of the I-TEQ is carried from the PCDF isomers (14), (6), (15) and the correlation between the concentrations from PCBz and the I-TEQ can be better understood with the similar behaviour of PCDF and PCBz in the formation process, which can be derived from figure 1.

Furthermore it was found that PCBz show very stable isomer ratios for a large data set (54 samples). In Figure 2 the isomer ratios for PCBz at different sampling points with their corresponding standard deviations were shown. Chlorinated benzenes have similar isomer ratios for the flue and stack gas. Furthermore the isomer with the lowest concentration in each degree of chlorination is the thermodynamic most stable one (1,4; 1,2,4 and 1,2,4,5 CBz).
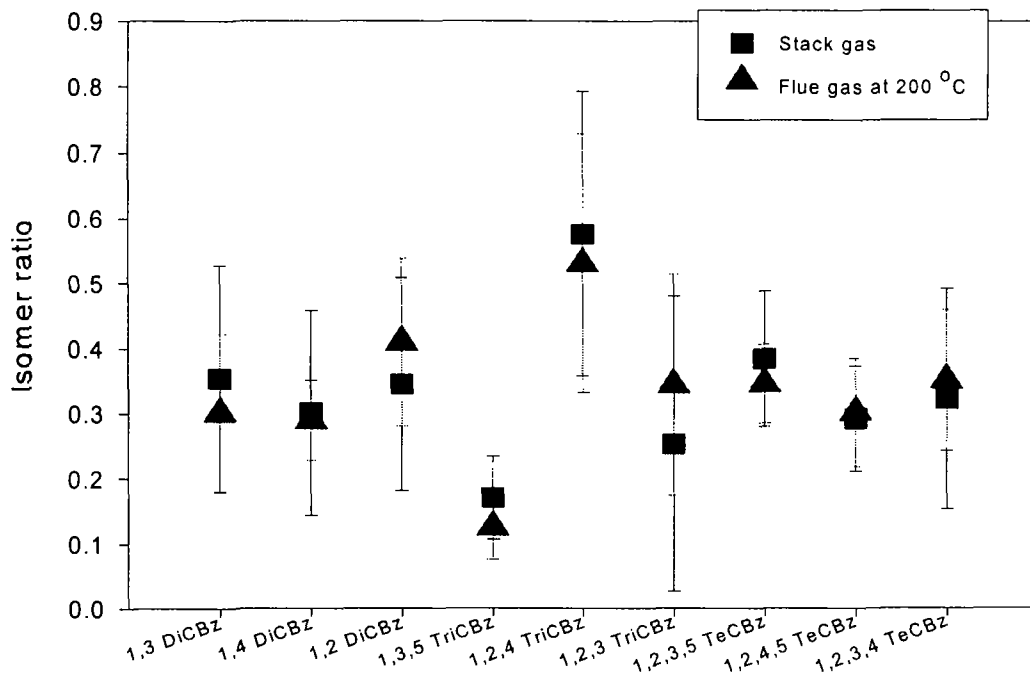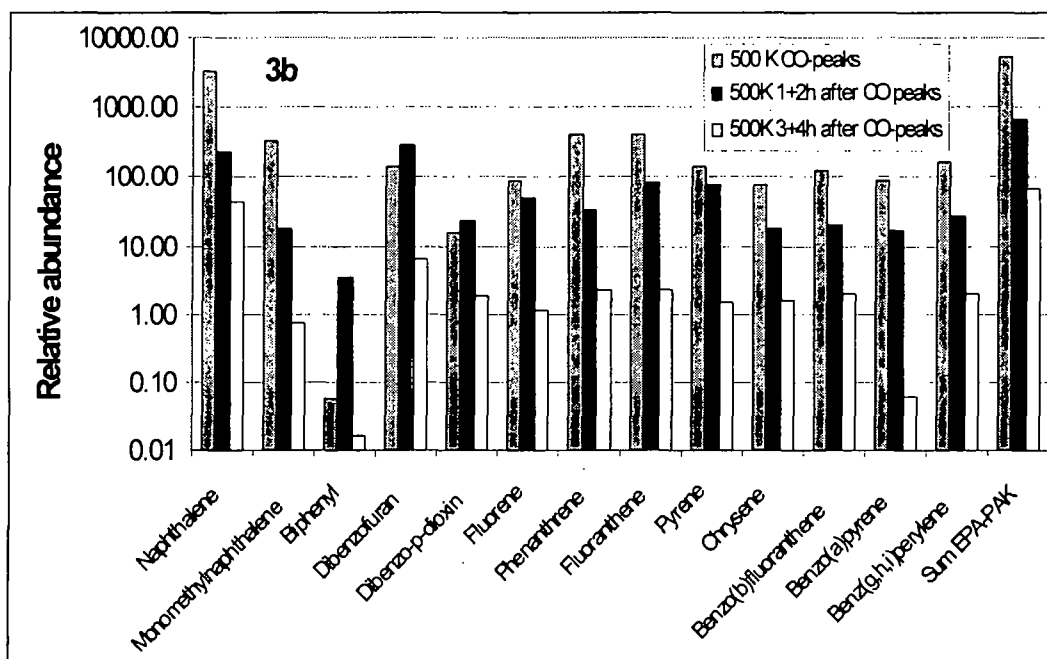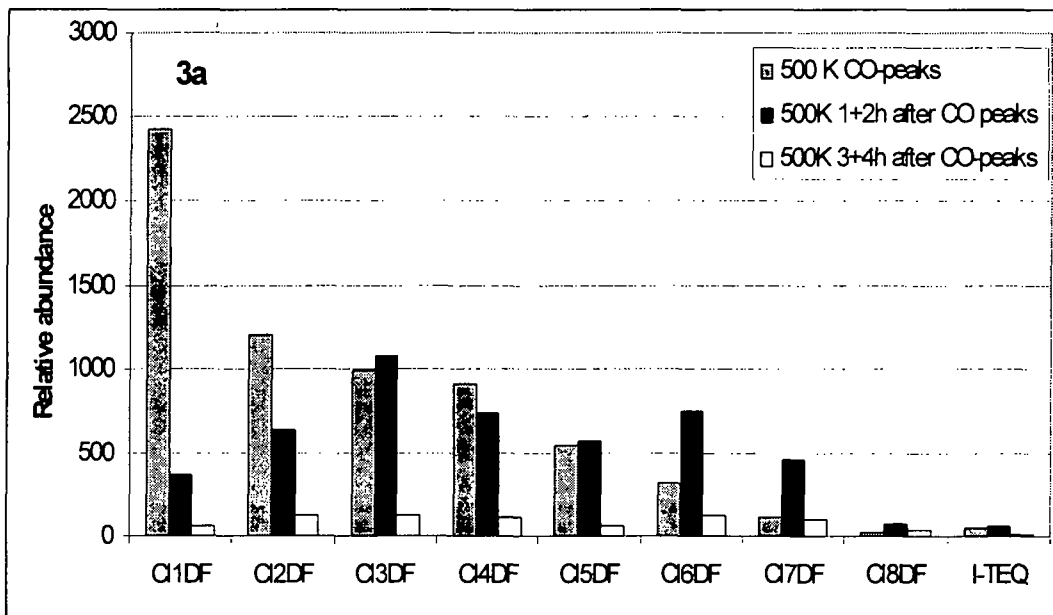

Figure 2: PCBz isomer ratios at different sampling points (total: 54 samples).

The observed stability in the isomer distribution for the PCBz may be an hint on an uniform formation mechanism. This stability can be used for an universal application of found surrogates for the indirect monitoring of the PCDD/F or I-TEQ concentration in flue and stack gases.

In figure 3 results from memory formation after disturbed combustion conditions from conventional analysis (3a, 3b) and on-line REMPI-TOFMS (3c) measurements at 500K are shown.

Figure 3a: Relative abundance vs ClDF congeners (Cl1DF–Cl8DF, I-TEQ). Legend: 500 K CO-peaks; 500K 1+2h after CO peaks; 500K 3+4h after CO-peaks.

Figure 3b: Relative abundance (log scale) for Naphthalene, Monomethylnaphthalene, Biphenyl, Dibenzofuran, Dibenzo-p-dioxin, Fluorene, Phenanthrene, Fluoranthene, Pyrene, Chrysene, Benzo(b)fluoranthene, Benzo(a)pyrene, Benzo(ghi)perylene, Sum EPA-PAK. Legend: 500 K CO-peaks; 500K 1+2h after CO peaks; 500K 3+4h after CO-peaks.
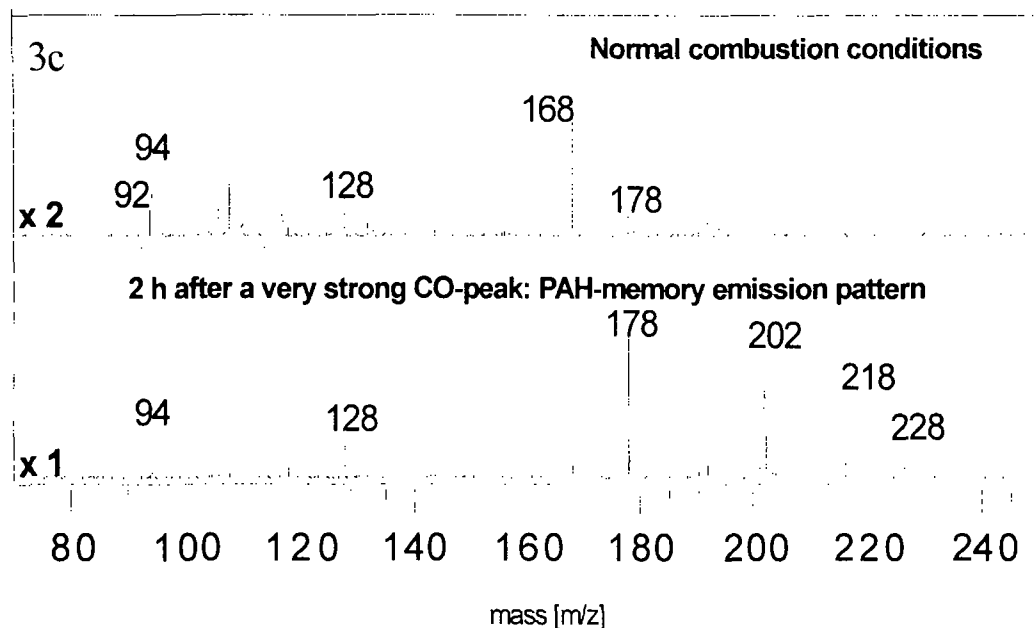
REMPI@266 nm signal

Figure 3: Long-term concentration increase of chlorinated and non-chlorinated substances from conventional sampling technique (PCDF and PAK, 3a+b) and on-line measurements with REMPI-TOFMS (mass spectra, 3c).

During the disturbed combustion conditions the most intensive concentration increase for PCDF was observed for the lower chlorinated homologues (figure 3a). Two hours after the massive CO-peak the three- up to octafold chlorinated homologues increase dramatically. This effect might be due to the freshly formed carbonaceous surfaces in the incinerator, which act as source and catalytic surface for the chlorination reaction after the disturbed combustion (high temperature memory effect) (16), (11). Results from conventional and REMPI-TOFMS PAH measurements are in good accordance with each other (3b, 3c). Two hours after the malfunction of the incinerator, the concentration of the higher condensed rings, like phenanthrene, is still higher than under normal combustion conditions. In combination with the PDCF concentration increase, this result support the theory of a slow thermal breakdown of carbonaceous surfaces formed during CO-peaks in the high temperature regime of the incinerator.

It can be concluded that the relationships between the different CA during formation processes, e.g. PCDF and PCBz, could be used for an surrogate monitoring of the I-TEQ via chlorobenzene. The stability of the isomer distribution of PCBz in different incinerators suggest to use this compound class as easy accessible surrogates for an indirect monitoring of PCDD/F concentrations in combustion. Short-term disturbances in combustion processes, like CO-peaks in a range of seconds up to minutes, can cause a long-term concentration increase of CA and aromatics over hours in incinerators. These memory effects due to rapid changes in combustion can be observed real-time on-line with REMPI-TOFMS. The REMPI-TOFMS instrument allows to monitor a great

number of nonchlorinated compounds (e.g. PAHs) on-line in real-time, which are associated with the memory emission and formation of PCDD/F (11), (5).

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