FORMATION OF PAH AND PCDD/F IN INDUSTRIAL INCINERATION PLANTS: MEMORY EFFECTS AFTER DISTURBED COMBUSTION CONDITIONS DUE TO DEPOSITS IN THE HIGH TEMPERATURE REGION

R.Zimmermann[1,2], M.Blumenstock[1], K.-W.Schramm[1], A.Kettrup[1,2]

[1] GSF-Forschungszentrum, Institut für Ökologische Chemie, D-85764 Neuherberg, Germany
[2]Lehrstuhl für Ökologische Chemie und Umweltanalytik, Technische Universität München, D-85748 Freising

Introduction and Experimental

Products of incomplete combustion (PIC) from different waste incineration facilities have been analyzed on-line by REMPI-TOFMS (*Resonance-Enhanced Multi-Photon Ionization Time-Of-Flight Mass Spectrometry*) and by conventional analytical methods. It was observed by REMPI-TOFMS that after disturbed combustion conditions a sustained release of some PAH species occur in the high temperature region of the flue gas channel. This PAH-memory was also confirmed by conventional PAH analysis. PCDD/F-measurements (GC-MS) pointed out that during PAH memory emission phases the homologue profiles of the PCDD/F are drastically changed. These effects could be explained in terms of carbonaceous surface deposits on the walls of the combustion chamber and flue gas channel, which are formed during instationary combustion conditions. REMPI-TOFMS represents a highly selective and sensitive laser based analytical technique, well suited for on-line analysis of target compounds in ppbv to pptv concentrations from e.g. combustion flue gases. The principle of REMPI-TOFMS is described in detail elsewhere[1]. The first application of REMPI-TOFMS for on-line flue gas analysis at an incineration plant was in 1996[2]. Other applications at different industrial scale and pilot plants followed[3,4]. PCDD/F measurements were performed by HRGC/HRMS (isokinetic sampling[5] with XAD-2 resin as adsorbent) using the isotope dilution technique, PAH were analyzed by HPLC [6,7]. Low volatile compounds like naphthalene were adsorbed on *Carbotrap* adsorbent and measured by direct thermal desorption-GC/MS.

Results and Discussion

Under stable combustion conditions, only minor changes in the PAH and PCDD/F signatures of flue gas samples are detected. On the other hand, highly dynamic changes of the concentrations of several aromatic species are observed during disturbed combustion conditions[2]. Disturbed combustion conditions may occur from time to time in industrial scale incineration plants, either due to steering measures, feeding artifacts or malfunctions. Nevertheless it should be noted that the measurements illustrated in this paper do not allow general conclusions to be drawn about plants of this type under normal operation. This is the case as e.g. for the MWI-plant adverse operating conditions were intentionally selected for test purposes. REMPI results show that intense deviations from optimal combustion conditions within a time span of minutes can cause a long term emission of aromatic species, which sometimes lasts even for time spans of up to hours. It is important to mention here that these emissions are not indicated by an increased CO level. In Fig. 1 on-line recorded REMPI-TOF mass spectra (266 nm) of flue gas from an incineration pilot plant (IPP, left) and a municipal waste incineration plant (MWI, right) are shown. The respective upper spectra are recorded during instationary combustion conditions, while the lower one were acquired some time after the disturbances. The flue gas was sampled prior to the emission reduction devices at temperatures of 800 °C (IPP) and 200 °C (MWI), respectively (raw gas). During unstable combustion conditions benzene (78 m/z) and naphthalene (128 m/z) are prominent (Fig. 1, top). Further, typical indicators for the flame chemistry of generation of aromatic compounds like phenylacetylene (102 m/z), indene (116 m/z) and acenapthylene (152 m/z)[8] are detected.

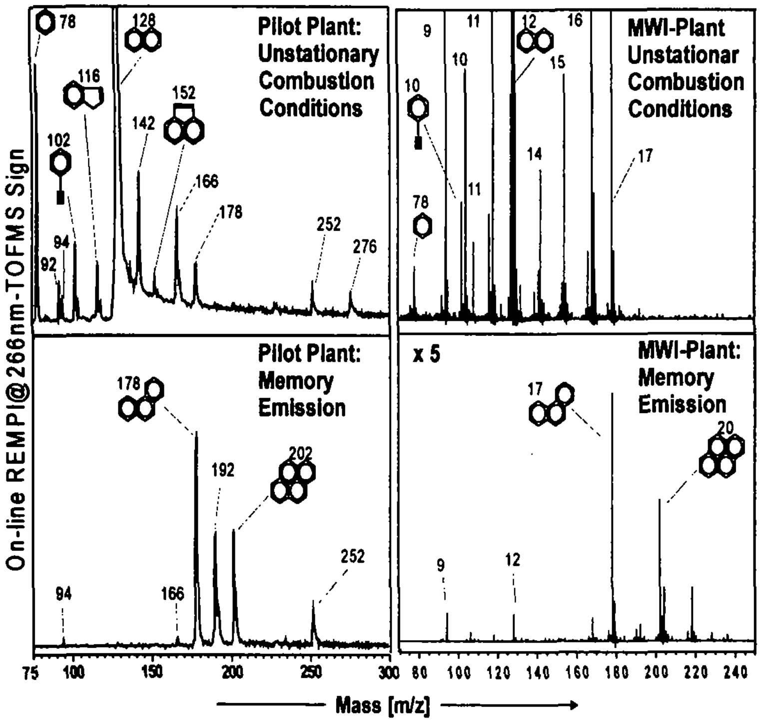

Figure 1: REMPI flue gas mass spectra, on-line recorded during and after disturbed combustion conditions.

Some time after the disturbance most compounds already are decreased, while the concentrations of some specific aromatic compounds, like phenanthrene and pyrene, are still further increasing (Fig. 1, bottom). Similar PAH memories was detected in several cases at different combustion plants.

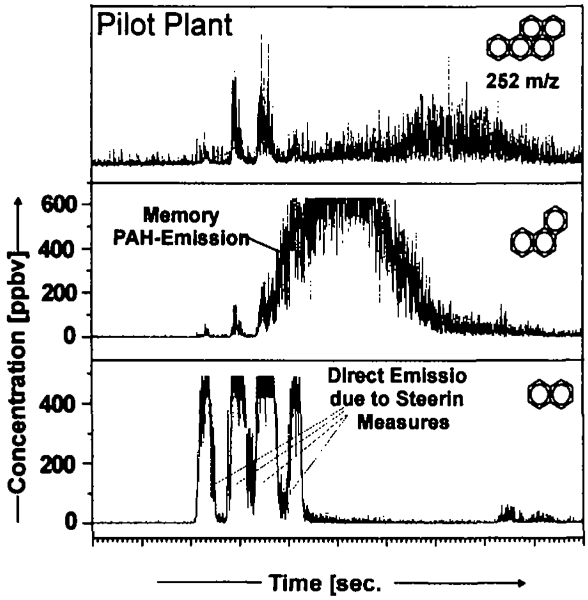

Figure 2: REMPI-TOFMS profiles of naphthalene, phenanthrene and isomeric 252 m/z PAH (pilot plant)

In Fig. 2 REMPI-TOFMS time to concentration profiles of naphthalene (bottom), phenanthrene (middle) and the isomeric 252 m/z PAH (top), on-line recorded at the 1 MW pilot plant during process steering measures are shown (flue gas 800 °C). The four transient emission peaks in the naphthalene trace are due to the steering measures. The phenanthrene trace shows a different behavior, the first two emission peaks are resolved, afterwards a timely broad emission continuum can be observed. At the mass trace 252 m/z (Fig. 2, top) the four transient emission peaks are observed, followed by a weak delayed emission continuum. However, after more drastic deviations from optimal combustion conditions, the time span of this delayed emission of PAH species is considerably enlarged and can be detected by conventional analytical techniques (one hour sampling time). In Fig. 3 conventional results on PAH concentrations (naphthalene, phenanthrene, pyrene and chrysene) are given for the municipal waste incinerator (MWI) and the pilot plant (IPP). A sequence of concentrations values is depicted (1h averages, respectively). The respective first bar is due to the concentration during normal conditions. The second and third bars reflect the concentrations during disturbed- and 1h after disturbed combustion conditions. During phases with disturbed combustion conditions PAH concentration are increased.

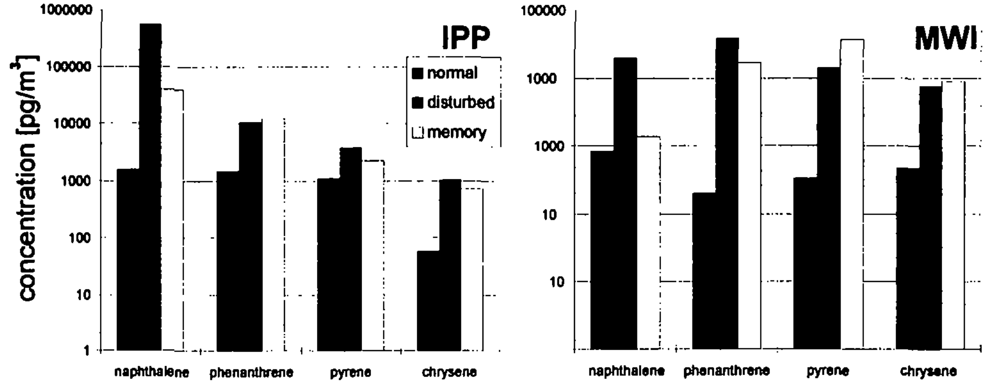

Figure 3: PAH memory after disturbed combustion conditions: Flue gas measurements of PAH (HPLC, 1 h average) prior, during and after disturbed combustion conditions from the IPP- and MWI-plant.

One hour later, the concentrations are still at a very high level or are increased even further (phenanthrene at the IPP and pyrene and chrysene at the MWI). This type of emission memory effect (i.e. in the high temperature region of the flue gas channel), which has been observed firstly by REMPI-TOFMS, thus has been confirmed by conventional analytical methods. The long lasting, intensive memories at high flue gas temperatures observed after a short period ofinstable combustion conditions implicate that the walls of the plant's flue gas channel are involved. A plausible explanation for the observed behavior is that during substoichiometric combustion conditions (substantial lack of oxygen), carbonaceous layers, with embedded further elements, are formed at the plant's inner wall. The formation of the layers most likely is analogous to the formation ofpyrocarbon by the chemical vapor deposition process (CVD)[9]. This carbonaceous coatings are probabaly of a highly polymeric structure, resulting in a high stability against thermal and chemical degradation. A slowpyrolytic decomposition of the layer can explain the increased PAH concentrations during memory emission phases. The degradation of the layer and the formation of specific degradation products may be supported by metal species embedded in the layer matrix. The presence of carbonaceous layers with embedded metal species is supported also by conventional PCDD/F measurements of performed prior during and after disturbed combustion conditions. Drastic changes of the homologue profiles of the PCDD/F are observed during the time span of the PAH memory. In Fig. 4 the PCDF homologue profiles are shown (same measurement intervals as in Fig. 3). During and after disturbed combustion conditions in particular the concentration of the low chlorinated PCDF is dramatically increased. For the MWI-plant the increase for the highly chlorinated homologues is considerably lower, while for the IPP even a decrease of the highly chlorinated homologues observed. The PCDD show a similar behavior as the PCDF. The observed PCDD/F homologue profile shifts and memories are most likely associated with catalytic effects (shift of the dechlorination/chlorination equilibrium) and high temperature de novo synthesis PCDD/F from the carbonaceous layers.

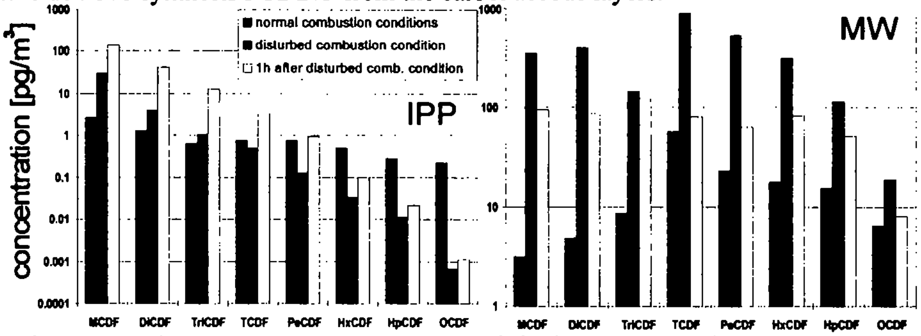

Figure 4: The PCDD/F homologue profiles show drastic shifts during phases of PAH memory emission: Flue gas measurements of PCDF (GC-MS, 1h average, same measurement intervals as in Fig. 3) prior, during and after disturbed combustion conditions from the IPP- and MWI-plant. All concentrations illustrated refer to measurement points upstream of the flue gas cleaning system. The corresponding clean gas emissions are significantly lower than the above and meet the regulations. The MWI-plant measurements illustrated do not allow conclusions to be drawn about plants of this type under normal operation (test operation).

Conclusion

Short disturbances of the combustion conditions at industrial combustion facilities can cause significant memory emission of PIC-compounds like PAH and PCDD/F for time span of at least hours. The reason for this memory emission is located in the high temperature region of the plants (<600 °C) and is most likely associated with surface deposits formed during unstable combustion conditions. However, such phases of increased emission of toxic compounds are not visible by the conventional process analytical techniques used for supervision of the combustion plants (e.g. CO, NOx and SOx monitoring systems). The here presented findings, in particular the emission memory effects from the high temperature region of large scale incinerators due to surface deposits and the high temperature formation (T >> 300°C) of PIC compounds (PCDD/F and PAH) stand in a line with recent findings from laboratory incinerators[10,11] and experiments on relationship of PAH and PCDD/F[12] the by other research groups.

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References

(1)Heger,H.J.; Zimmermann,R.; Dorfner,R.; Beckmann,M.; Griebel,H.; Kettrup,A.; Boesl,U. *Anal. Chem.* 1999, *71*, 46.
(2)Zimmermann,R.; Heger,H.J.; Kettrup,A.; Boesl,U. *Rapid Commun. Mass Sp.* 1997, *11*, 1095.
(3)Thanner,R.; Oser,H.; Grotheer,H.-H. *Eur. Mass Spectrom.* 1998, *4*, 215.
(4)Zimmermann,R.; Heger,H.J.; Blumenstock,M.; Dorfner,R.; Schramm,K.-W.; Boesl,U.; Kettrup,A. *Rapid Commun. Mass Spectrom.* 1999, *13*, 307.
(5)Lehnardt,R.; Kaune,A.; Schramm,K.-W.; Kettrup,A. *Organohal. Compd.* 1998, *36*, 77.
(6)Blumenstock,M.; Zimmermann,R.; Schramm,K.W.; Kaune,A.; Nikolai,U.; Lenoir,D.; Kettrup,A. *J. Anal. Appl. Pyrol.* 1999, *49*, 179.
(7)Blumenstock,M.; Zimmermann,R.; Schramm,K.-W.; Kettrup,A. *Chemosphere* 2000, *40*, 987-993.
(8)Melton,T.R.; Vincitore,A.M.; Senkan,S.M. In *27th Symposium (International) on Combustion*, 1998, pp 1631.
(9)Brüggert,M.; Hu,Z.; Hüttinger,K.J. *Carbon* 1999, *37*, 2021.
(10)Wikström,E.; Tysklind,M.; Marklund,S. *Environ. Sci. Technol.* 2000, *in press.*
(11)Lee, C. W.; Kilgroe, J. D.; Raghunathan, K. *Environ. Eng. Sci.* 1998, *15*, 71-84.
(12)Iino, F.; Imagawa, T.; Takeuchi, M.; Sadakata, M. *Environ. Sci. Technol.* 1999, *33*, 1038-1043.