A SENSOR CONCEPT FOR ON-LINE DETECTION OF PCDD/F-MEMORY FORMATION IN WASTE INCINERATOR FLUE GAS

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Introduction

The PCDD/F stack emission of waste incineration (WI) plants has been considerably reduced in the last years by modern secondary measures, like improved de-dusting and flue gas scrubbing methods. Modern WI plants meet the 0.1ng I-TEQ/m^3 emission limit, which is now valid in several industrialized countries. The secondary measures, however, do not, in most cases, destroy PCDD/F, but are transferring the PCDD/F burden in the solid residues. The fly ashes are in particular PCDD/F contaminated (*see Table 1*).

Table 1. Typical PCDD/F concentrations and frights for different WI residues and stack gas

Waste incineration outputs	bottom ash	boiler ash	fly ash	stack gas
amount residues/ t waste	200 kg	5 kg	30 kg	5000 m^3
typical PCDD/F concentration	20 ng/kg	200 ng/kg	1 µg/kg	0.05 ng/m^3
PCDD/F freight / t waste	4 µg	1 µg	30 µg	0.25 µg

The sensor concept is based on the observation that there are phases, in particular after disturbed combustion conditions, with increased PCDD/F formation (and thus also increased PCDD/F concentrations in the residues). If phases with high PCDD/F-formation rates can be identified by an on-line measurement technique, the particularly heavy contaminated fractions of the residues fly/boiler ash can be separated for further treatment. By separation of up to 50 % of the material with the peak PCDD/F-contamination, the PCDD/F contamination of the remaining fly ash should be significantly decreased. A favorable way of treating the separated, highly contaminated fraction of the fly/boiler ash is its re-introduction into the WI combustion chamber, where the PCDD/F and other organic contaminants are destroyed.

The selective re-introduction of the fly/boiler ash fractions (process integrated technique) combined with the MARTIN®-SYNCOM® process is a potential approach to meet the total PCDD/F emission limit for waste incineration of 5 µg/t waste (Japan). The feasibility-study concerning this aim is subject of a current Bavarian research project. The MARTIN®-SYNCOM® process consists of a combination of oxygen enrichment of underfire air, flue gas recirculation and infrared thermography of the waste bed temperatures[1].

PCDD/F SURROGATES

A prerequisite for a selective separation is the availability of an on-line sensor, which can indicate the phases with increased PCDD/F formation. In the last years several on-line mass spectrometric methods for on-line monitoring of trace compounds in complex process gases, like WI flue gas, have been developed and were successfully applied for on-line monitoring of products of incomplete combustion (PIC) in flue gases of industrial combustion processes. This include laser based techniques like the resonance-enhanced multiphoton ionization-time-of-flight mass spectrometry (REMPI-TOFMS)[2-6], single photon ionization-time-of-flight mass spectrometry (SPI-TOFMS)[7] as well as techniques based on chemical ionization-Mass spectrometry (APCI-ITMS)[8] A drawback of the techniques based on mass spectrometry (MS) is the very complicated and sensitive instrumental set-up, requiring vacuum pumps, special inlet techniques, electronics and last not least sophisticated, non-standard ionization techniques for selective ionization of the PCDD/F. Although the MS techniques have already successfully applied for research projects it will be very challenging to realize a 365d/year working PCDD/F surrogates continuous monitoring MS instrument.

A more practicable alternative for detection of increased PCDD/F concentration in the raw gas can be the use of a REMPI-sensor based on the detection of the integrated ion signal which is obtained by ionization of PAHs at different excitation wavelengths. Hereby, it will be made use of the fact, that during and after disturbed combustion conditions typical patterns of PAH concentration profiles are observed in the flue gas of waste incineration plants. These patterns can also serve as an indicator for phases with increased PCDD/F formation[9]. Figure 1A shows the PCCD/F I-TEQ and the added up concentrations of EPA-PAHs and PAHs with higher molecular masses, respectively.
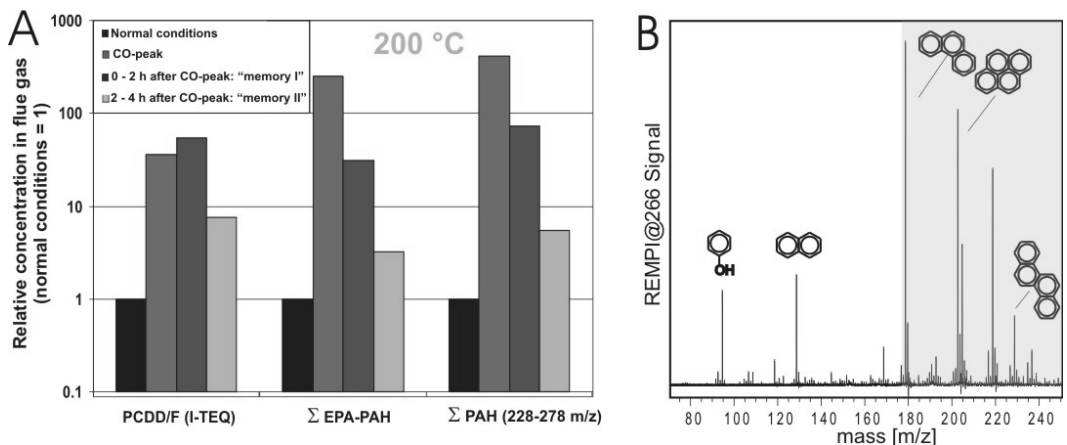

Figure 1. A Memory formation in of PCDD/F-TEQ and PAH flue gas after disturbed combustion conditions (relative to normal conditions). B REMPI@266nm mass spectrum of PAH from the "memory phase"

During non stationary combustion conditions, indicated by a short-term increase in CO-concentration, a drastic increase in dioxin as well as PAH concentration can be observed. Furthermore, it is remarkable, that these increased concentrations can still be monitored several hours after the combustion disturbance. The figure also reveals that this so called memory-effect is mainly due to the PAHs with higher molecular weight such as phenanthrene and pyrene. Figure 1B shows a typical REMPI@266nm mass spectrum from the memory phase, which exhibits the high concentrations of the PAHs with masses higher than 180 m/z.

Experimental

The concept of the REMPI sensor is founded on REMPI ionization of PAHs combined with the detection of the integral ion signal at different wavelengths. Figure 2 shows an exemplary implementation of the sensor. The flue gas of the waste incineration plant is sampled and carried to the ionization cell. Concepts for probing, sampling and inlet system technique are described in detail elsewhere[2,4]. The ionization cell as well as the sampling system have to be heated to 300°C to avoid condensation of tar and acid material of the flue gas. Furthermore, this ensures the desorption of the PAHs from the fly ash particles to obtain a covered correlation between sensor signal and pollutant concentration. Ionization of the PAHs should be carried out with alternating laser beams with wavelengths of 248 nm and 308 nm, respectively. Therefore, an special excimer laser with two tubes (KrF and XeCl) will be used, which can be triggered independently and will be build by the project partner (TUI-Laser AG, Germany). Hereby, the detection of small aromatic compounds such as benzene, toluene and naphthalene as well as the detection of PAHs with three and more rings should be possible simultaneously. The first group serves as an indicator for minor fluctuations of the combustion conditions, the latter indicates the memory effect, which is observed after more pronounced instationary behavior. The integral ion signal derived from the REMPI-ionization should be detected by means of either a Faraday-cup or Micro Channel Plates. The obtained current can be measured by e.g. an electrometer. Triggering and data acquisition is provided by a PC.
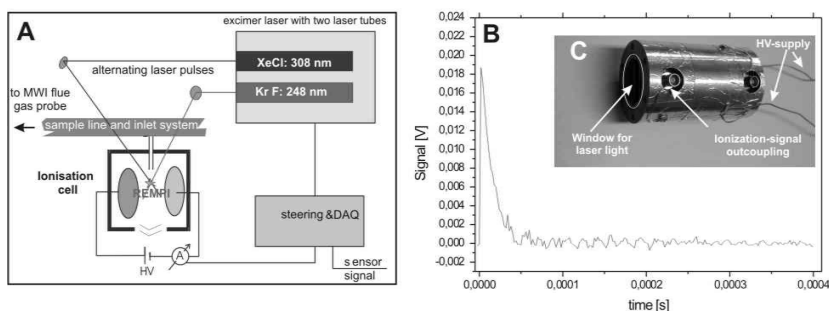

Figure 2. An exemplary concept of the REMPI sensor for PAH detection using an excimer laser with two tubes. B Typical response signal of the integrated ion current,C Photograph of the laser ionization cell.

Results and Discussion

In Figure 2 C a photograph of a first prototype of the ionization cell is depicted. This cell could also serve as a source for ions generated by single photon ionization using VUV light[7,10]. Figure 2B shows a typical curvature of the integrated ion signal derived from ionization of NO with a VUV beam at 118 nm. The area below the curve corresponds to the amount of formed ions. The practicality of the usage of the selected laser wavelengths (248 nm and 308 nm) to obtain distinct patterns of either the small aromatic compounds or the higher molecular ones is proved in Figure 3, that shows REMPI-TOFMS spectra of PAHs from laser desorbed carbonaceous material detected after post-ionization with these two wavelengths. The REMPI@248nm spectrum exhibits signals of all arenes starting with a mass of 178 m/z, which can be assigned to phenanthrene.

Gas phase REMPI-TOFMS measurements depict that also the smaller monocyclic aromatic (like benzene, toluene and the xylenes) and naphthalene are accessible with 248 nm[2]. On the other hand, in the REMPI@308nm spectrum of the laser desorbed PAH (Figure 3, right) only signals from the PAHs with masses higher than 180 m/z can be observed. Phenanthrene is not longer visible applying REMPI@308nm, neither are the smaller aromatics (like e.g. benzene, toluene, xylenes and

naphthalene, not shown here). This is due to the decreasing ionization potential with increasing size of the aromatic molecules.
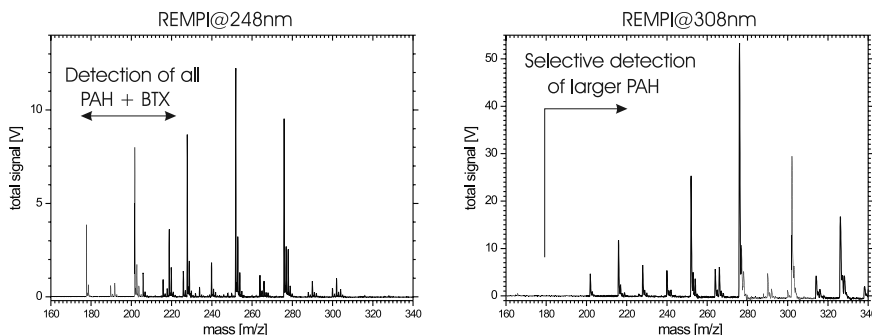

Figure 3. REMPI-TOFMS spectra of laser desorbed carbonaceous material at 248nm and 308 nm excitation wavelengths

Therefore, by applying these two wavelengths in an alternating manner for ionization of the different aromatics in the flue gas within the REMPI sensor, two subgroups of aromatic compounds can be distinguished. Hereby, REMPI@308nm serves as a selective detection method for larger PAHs, which indicate the memory phase. With this approach it should be possible to monitor phases of memory formation conditions that lead to increased PCCD/F concentration levels in the flue gas. However, one has to keep in mind that memory formation is only one PCDD/F formation pathway among several others. Thus, the REMPI sensor as pictured above will be an integral part of a larger sensor array for prediction of the dioxin formation, which will also detect other crucial species for the description of PCCD/F formation like CO, Cl_2, C_xH_y and SNVOX (Semi-/Non Volatile Organohalogen Compounds)[11].

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