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On-line real-time measurements at incineration plants: PAHs and a PCDD/F surrogate compound at stationary combustion conditions and during transient emission puffs

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Abstract

Laser mass spectrometry has been applied for on-line monitoring of traces of aromatic compounds from flue gas of incineration plants. The experiments have been carried out at two sampling sites in an industrial hazardous-waste incinerator. With laser mass spectrometry resonance-enhanced multiphoton ionization (REMPI) with time-of-flight mass spectrometry (TOFMS) (REMPI–TOFMS), using the group selective multi-component monitoring approach, aromatic compounds are selectively ionized from the complex flue-gas matrix. In this case, the result of an REMPI–TOFMS on-line measurement is a distinct pattern of aromatic compounds. These patterns are dependent on: (i) the point of measurement, (ii) the incineration plant, (iii) the temperature, and (iv) the fuel. This contribution focuses on the fuel dependence of the pattern. The most transient behavior can be observed when containers filled with hazardous waste are burnt, leading to puffs. Real-time monitoring results of puffs are given. Furthermore, as an approach towards on-line monitoring of the TEQ (PCDD/F toxicity equivalent), REMPI–TOFMS on-line analysis results of chlorobenzene are presented.

Keywords: REMPI; TOFMS; Online; PAH; Dioxin; Monitoring; Combustion

1. Introduction

The toxic by-products emitted from combustion processes in trace amounts are of still growing public interest, since more than 90% of the total energy worldwide (including traffic) is generated by combustion processes (Warnatz et al., 1996). In industrial combustion plants, several flue gas-cleaning measures ensure that the legal emission limits are not exceeded. Flue gas-cleaning units are expensive to build and run, and often generate hazardous waste themselves. In fact, a major part of the investment and operational costs of modern incineration plants is due to the emission-reduction devices (Thomé-Kozmiensky, 1994).

Recent developments focus on the optimization of the primary combustion process (Beckmann et al., 1997). For improving the knowledge about the process, time-resolved flue-gas analysis has to be performed. So far, on-line analysis methods existed only for small molecules in high concentrations, e.g. carbon monoxide. The measurement of the organic pollutants in trace amounts requires a sensitive and selective method, as otherwise, interferences would prevent a peak allocation or quantification.

In general, laser-based methods can provide a high degree of selectivity. Several methods have been

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successfully applied to on-line measurements of flue gas (Dreizler et al., 1997). For larger, aromatic molecules at ppb concentrations and lower, laser mass spectrometry has proven to be a successful method for on-line analysis from the complex flue-gas matrix (Zimmermann et al., 1997b). In the following, laser mass spectrometry results are presented and analyzed with respect to the influence of the fuel composition.

Additionally, an indirect monitoring of the international toxicity equivalent (I-TEQ, summed toxicity of the polychlorinated dioxin and furan congeners) by using chlorobenzene as the indicator parameter compound is performed. By this, the formation of chlorinated organic species is also observable.

2. Materials and methods

Laser mass spectrometry combines the selective ionization method resonance-enhanced multiphoton ionization (REMPI) with time-of-flight mass spectrometry (TOFMS). The method is described in detail in several publications, e.g. Lubman (1990), Boesl et al. (1994), Zimmermann et al. (1994), Gittins et al. (1997) and Heger et al. (1999b). REMPI can be carried out in two degrees of selectivity, depending on the spectroscopic properties of the molecules which can be influenced by the molecular beam-inlet system into the mass spectrometer. The two achievable selectivities are (i) group-selective ionization of a group of molecules out of a substance class (effusive beam sample inlet, (Heger et al., 1999b)), and (ii) species-selective ionization of one single species (supersonic beam sample inlet, (Zimmermann et al. (1994)). In the experiments described in this contribution, the first approach has been applied. Note that both degrees of REMPI selectivity are highly selective compared to, e.g. direct inlet mass spectrometry with electron-impact ionization.

The substance class of molecules is chosen by the spectral range of the laser light utilized for ionization. Here, UV light in the range of absorption of the π electron system of aromatic compounds has been used (Nd:YAG Laser, 266 nm). A group of aromatic molecules is thus selectively ionized, each molecule with an individual cross-section depending on its UV spectrum. Emphasis can be laid on a target compound by using a tunable laser system and tuning the wavelength to the maximum REMPI cross-section of this compound to enhance sensitivity. This combination of group-selective analysis and target compound monitoring has been developed and applied to the simultaneous measurement of PAHs and chlorobenzene (Zimmermann et al., 1999a). A detailed discussion on the two concepts is given by Heger et al. (1999a).

With a novel data-acquisition concept, the complete information about the group-selective REMPI–TOFMS measurement have been recorded (i.e. every single shot mass spectra is available for data processing). Further, data processing allows different presentations of the results as e.g., time-concentration profile or contour plot. A detailed description of the instrument and the data analysis including quantification is already published elsewhere (Heger et al., 1999b).

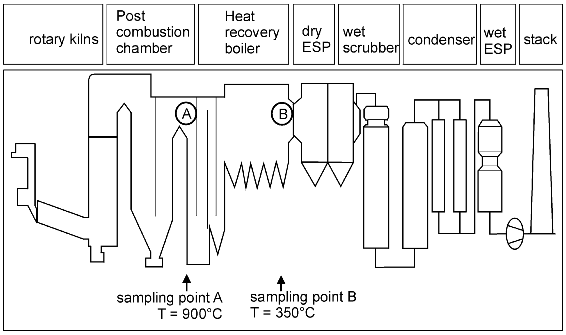

Fig. 1. Setup of the hazardous waste incineration plant (ESP). The thermal power of the plant is about 22 MW. The two sampling points for the on-line measurement are marked as A and B.

The measurements have been performed at an industrial hazardous-waste incinerator (22 MW). The setup of the plant is depicted in Fig. 1. This plant consists of rotary kilns and a separate post-combustion chamber. A boiler is applied for steam generation. These parts of the primary combustion process are followed by flue-gas cleaning devices (dust precipitator, washer, etc.)

In previous on-line monitoring experiments, it turned out that the dust precipitator will cause extensive memory effects in the plant, i.e. a short concentration peak due to a short deviation of the primary combustion process will cause an increased concentration after the dust precipitator for a longer time (Zimmermann et al., 1997b). Thus, the points of measurement have been chosen close to the exit of the post combustion chamber (A) at a flue-gas temperature of 950°C and in the boiler in front of the first dust precipitator (B) at a flue-gas temperature of 350°C.

The sampling has been performed by drawing flue gas through a heated quartz-glass tube and a specially developed glass-wool dust filter into the MS. Details of the sampling system are described in Heger et al. (1999b). It should be emphasized here that the amount of analyte molecules adsorbed on particles can be neglected, since all the target compounds are nearly completely in the gas phase due to the high flue-gas temperatures.

3. Results and discussion

Results of two conceptionally different on-line experiments are presented. The aim of the first experiment was to gain information about the combustion process using the PAHs as products of incomplete combustion. The latter experiments aimed at achieving an indirect on-line measurement of the I-TEQ and thus, to measure the dioxin/furan-related toxicity on-line.

3.1. Incomplete combustion: Patterns of polycyclic aromatic compounds

For a group-selective measurement of aromatic compounds, REMPI at 266 nm was performed using the fourth harmonic of a Nd:YAG laser (10^7 W cm^{-2}).

Fig. 2 shows two mass spectra obtained with REMPI at 266 nm at sampling point 1. The mass range covers the one to five-ring aromatics; the dominant peaks are naphthalene and phenanthrene, and their alkylated derivatives. Next to these, benzene, styrene and phenol are the most prominent peaks. In case of ambiguous peak allocation, the REMPI cross-section and the abundances of isobaric substances in waste-incineration flue gas (taken from Jay and Stieglitz (1995)) was taken into account. In the following, peaks are assigned according to the most contributing substance. A note on the fragmentation observed under laser-analytical conditions should be added: alkylated aromatic compounds (mass M) show little fragmentation to $M - 14$ amu and $M - 15$ amu, as well as to $M - 1$ amu fragments. Compared to the electron impact, these fragment peaks are very small. No fragmentation into a mass smaller than 78 amu has been observed. In summary, fragmentation only makes a small contribution to the mass spectra.

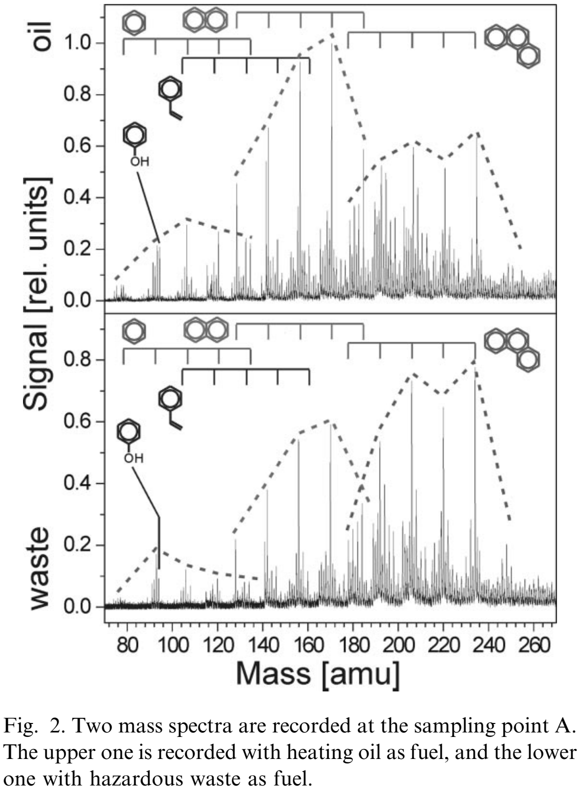

Fig. 2. Two mass spectra are recorded at the sampling point A. The upper one is recorded with heating oil as fuel, and the lower one with hazardous waste as fuel.

The upper mass spectrum was recorded when the plant used heating oil as fuel for at least 3 h, the lower one was recorded after using hazardous waste as fuel for at least 3 h too. A shift in the different aromatic skeletons can be clearly observed: with heating oil, the peaks of the alkylated naphthalenes are more abundant in the spectrum, while with hazardous waste, there is a slight predominance of phenanthrenes. Furthermore, a difference in alkylation can be observed for benzenes: with heating oil, xylene is the most prominent peak among the alkylated benzenes, while with hazardous waste, the highest peak is that of toluene. This result shows that the pattern of the products of incomplete combustion depends on the fuel used. A process optimization for a specific plant has to consider the fuel properties and, especially for inhomogeneous fuels such as, for e.g., waste, on-line monitoring is an important tool for process understanding and optimization.

A prominent example for inhomogeneous fuel feeding are containers filled with liquid hazardous waste that are directly put into the rotary kiln leading to strong puffs. The problem is well known and special containers have been suggested to reduce the puffs (Wendt, 1994). However, a research on the exact behavior of the containers during incineration is difficult without highly time-resolved on-line data for more complex products of incomplete combustion.

In Fig. 3, REMPI–TOFMS on-line measurements of a transient puff due to barrel uptake are presented. The mass spectra of the single measurement are arranged in a contour plot to show the development of the pattern with time. The measurements have been performed with 10 Hz repetition rate, allowing a time resolution of 200 m. The main puff is observed at about 50 s measurement time with a strong peaking of the aromatic skeletons from benzene (78 amu) to naphthalene (128 amu), and phenanthrene (178 amu). Of these, only phenanthrene shows a broad emission peak. This is in accordance with previous measurements, where larger PAHs showed a memory effect in the plant that was interpreted as an effect of the wall surface. An effect of the sampling system can be excluded (Heger et al., 1999b). The alkylated benzenes show, furthermore, a delayed maximum emission output. This is a hint that there are different temperature zones involved in the formation of these compounds, as degrees of alkylation vary with temperature (Blumer, 1976).

Besides the degree of alkylation, there are further differences between the "on-peak" chemistry and the "after peak" chemistry of formation of aromatic trace compounds: during the puff, a strong peak of an

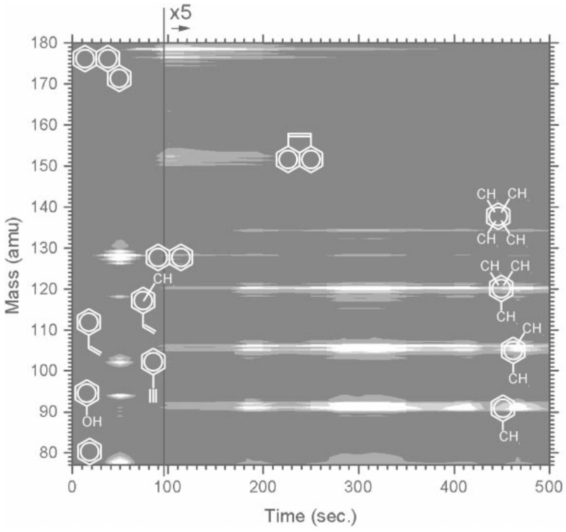

Fig. 3. Contour plots recorded at the sampling point B. The peaks at 50 s are due to a puff from container incineration. Following the puff, the concentration of methylated aromatics was raised for a few minutes. Peaks recorded after 100 s are enhanced five times.

oxygenated compound, phenol, is observed and a series of products that can be interpreted as intermediates in the formation of higher aromatics from benzene show concentration peaks as well. Examples are styrene and phenylacetylene. The most prominent peaks are marked in the contour plot.

The variety in the behavior of individual compounds observed during and after the puff shows the complexity of the process, and the ability of on-line REMPI–TOFMS measurements to monitor such complex processes using multiple parameters that are measured simultaneously with every laser shot.

3.2. On-line measurement of MCB as "PCDD/F" indicator

The polychlorinated dioxin and furan congeners are in the ppqv-concentration range and thus, are far beyond the detection limits of today's on-line methods. Furthermore, the determination of the most interesting value, the I-TEQ, would require a simultaneous but selective measurement of all toxic congeners. Although REMPI–TOFMS selectivity would help solving a task like this, and might be applied to improve analysis time by using it as a selective detector for HRGC–MS (Zimmermann et al., 1997a, 1999b), a real-time on-line measurement of the I-TEQ requiring the simultaneous measurement of the 17 toxic PCDD/F congeners is not possible.

Owing to the complexity of TEQ-analysis, the idea of using indicator parameter compounds for the I-TEQ for a fast screening came up, first proposed by Öberg and Bergström (1989) and investigated in detail by Kaune et al. (1994). With this concept, I-TEQ analysis is reduced to the analysis of one target compound, which should be easily accessible with conventional analysis, e.g. HPLC methods. In these investigations, mainly highly chlorinated benzenes have been considered to be TEQ indicator compounds.

A further development is to analyse an indicator compound for I-TEQ on-line. To apply REMPI for selective ionization of chlorinated aromatics in combustion flue gases had been proposed a decade ago (Rohlfing, 1988); REMPI detection limits for a variety of candidates for on-line measurement in a combustion flue gas have been determined by Cool and coworkers (Williams et al., 1992; Tanada et al., 1994). Recent developments have improved the detection limit to the pptv range (Oser et al., 1996; Heger et al., 1999b). The REMPI spectra of chlorinated aromatics have been investigated in detail (Zimmermann et al., 1994, 1996) and it turned out that, for spectroscopic reasons, mono and dichlorobenzenes are the best suited for REMPI on-line measurement.

Recent conventional GC-MS measurements revealed that monochlorobenzene is a good indicator parameter for the 1-TEQ (Blumenstock et al., 1999, 2000; Zimmermann et al., 1999a).

The REMPI spectrum of monochlorobenzene (effusive inlet) has been recorded (Heger et al., 1999a), and the maximum UV absorption of the 0_0^0-transition of the $^1B_2(S_1) \leftarrow {}^1A_1(S_0)$ band at 269.82 nm has been identified as a suited intermediate state for REMPI–TOFMS detection. A dye laser was tuned to the respective wavelength for the following on-line measurement, performed at sampling point 2.

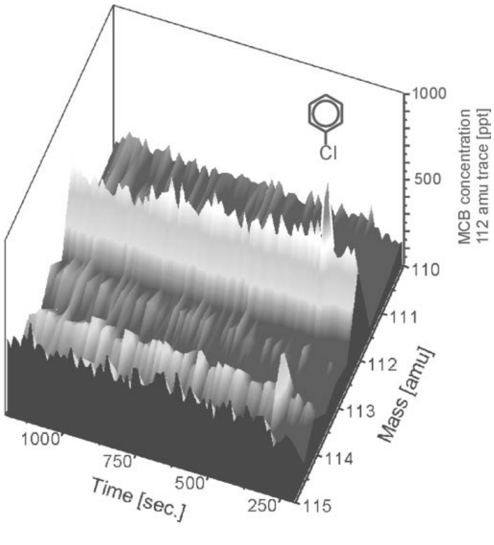

Fig. 4. Monochlorobenzene (a surrogate compound of the I-TEQ) measured on-line with REMPI–TOFMS.

Fig. 4 shows the time-concentration profile of the chlorobenzene molecular peak (112 amu) and the ^{37}Cl isotope (114 amu). The development in time, of the signals of the mass range 110–115 amu is depicted in 3-d presentation. The chlorobenzene concentration has been quantified using an external gas standard and is in the range of 500 ppt in the depicted trace. A transient behavior at about 300 s measurement time can be observed at both 112 and 114 amu. Via the indicator parameter relation (Blumenstock et al., 1999, 2000)), an estimation of the I-TEQ is possible on-line, in real-time.

In summary, the results show that a comprehensive characterization of combustion processes can be achieved by REMPI–TOFMS on-line monitoring.

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