

## On-Line Real-Time Measurement of PAHs and PCDD/F Surrogates in the Flue Gas of Industrial Waste Incineration Processes

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### Abstract

A mobile resonance-enhanced multiphoton ionization time-of-flight mass spectrometer (REMPI-TOFMS) with direct inlet has been developed. The instrument allows real-time on-line measurements of e.g. traces of aromatic species in complex gaseous matrices like flue gases. REMPI-TOFMS measurement results from a 22 MW industrial hazardous waste incinerator are reported. Products of incomplete combustion have been on-line measured at ppbv to pptv levels in the flue gas. This includes monitoring results on polycyclic aromatic hydrocarbons (PAH) as well as on monochlorobenzene, which represents a reliable surrogate for PCDD/F.

### Introduction

Laser induced Resonance-Enhanced Multi-Photon Ionization Time-Of-Flight Mass Spectrometry (REMPI-TOFMS) represents a highly selective and sensitive two-dimensional analytical technique, combining UV-(laser)-spectroscopy and mass spectrometry [1]. Briefly, the technical realization is as follows: A molecular beam, containing the sample molecules is generated. The molecular beam is directly in the ion source of the TOF mass spectrometer irradiated with short (e.g. 10 ns) UV laser pulses (e.g. with 20 Hz repetition rate). The power density of the pulses is in the 10<sup>6</sup> W/cm<sup>2</sup> range. During the laser pulse, intermediate states of molecules can be selectively excited by laser photon absorption when the wavelength of the laser is in resonance with an UV-transition. The resonance condition introduces the UV spectroscopic selectivity of the ionization process, as only excited molecules can subsequently be ionized by absorption of an additional laser photon from the (same) laser pulse. The formed ions are accelerated by electrostatic fields into the Time-of-Flight mass analyzer, where they are detected with mass resolutions of 2.000-3.000. In particular aromatic compounds are efficiently ionizable by the REMPI-method. The high optical selectivity makes the technique to an ideal instrument for direct on-line analysis of e.g. aromatics from complex samples [2]. However, the degree of optical REMPI selectivity depends from the sample inlet technique. The more complex jet inlet technique [3] allows the highest selectivity due to adiabatic cooling of the analyte molecules in the jet, while the more robust effusive beam inlet technique is a bit less selective [4]. The REMPI technique for selective ionization of molecules initially was introduced

in the late seventies, early eighties by different groups (see e.g. [5]). With exception of some REMPI applications in combination with GC, the technique was used for fundamental research solely in the following decade. This was mainly due to the fact that laser technology was still very sophisticated at this time. However, this has changed, robust and compact laser systems are available nowadays. Thus lasers now are more and more frequently applied for analytical purposes. In 1993 REMPI firstly was used for on-line analytical applications, namely the direct analysis of internal combustion engine exhausts [6].

In this contribution, the recent progresses in application of laser induced mass spectrometry in the field of on-line analysis of traces of pollutants, including PCDD/F surrogates, in industrial process gases are described [7,8]. The direct, on-line monitoring of trace chemicals from highly complex real-world samples as, e.g., off-gases from combustion or pyrolysis processes, required a lot of development work in the field of sampling methods and on-line sample preparation/inlet techniques [4]. For industrial process gas analysis, in most cases, we prefer the use of the effusive molecular beam technique for sample inlet rather than the more complex jet inlet technique. The selectivity performance of effusive beam inlets in most cases is sufficient, while its easier handling under the harsh conditions usually present at industrial sampling sites is beneficial. The first application of a REMPI-TOFMS laser mass spectrometer for on-line analysis of combustion byproducts in a pilot plant scale facility was in 1996/1997 [2,4]. In 1998 firstly an industrial scale waste incineration plant was investigated [7]. In the same year also on-line REMPI measurements at a pilot plant by another research group have been reported [9]. In addition to the development of the REMPI technique, also an extensive research program, using conventional analytical techniques, was started [10,11] in order to figure out suitable surrogate compounds for e.g. the dioxin emission or the general process status, which are on-line measurable by REMPI-TOFMS.

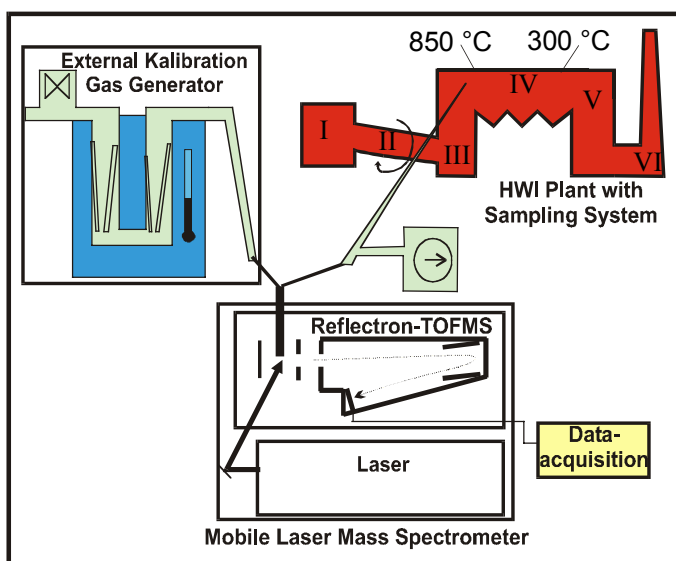


Figure 1: Schematic representation of the 22 MW hazardous waste incinerator, the sampling system and the on-line REMPI-TOFMS instrument.

## Experimental

The here presented conventional and REMPI-TOFMS measurements have been performed at a South German hazardous waste incineration facility. The plant consists of two rotary kilns, leading into one post-combustion chamber. After the boiler section several flue gas cleaning measures are installed. The overall thermal power of the plant is 22 MW. The on-line REMPI-TOFMS measurements have been performed at two sampling sites, closely after the post-combustion chamber

(sampling point #1, flue gas temperature 900°C) and at the end of the boiler section, prior to the first emission reduction devices (sampling point #2, flue gas temperature 300°C). As we intend to supervise the primary combustion process, the location of the sampling site in the raw flue gas is essential.

The principle of REMPI-TOFMS laser mass spectrometry and the sampling technique is described in detail elsewhere [1,4] (see also Introduction). External calibration was performed via a portable calibration gas cell (permeation- and diffusion standards), supplying ppbv-concentrations of naphthalene, monochlorobenzene and other compounds. For registration of the PAH species pattern, the fourth harmonic frequency of a Nd:YAG laser (266 nm) was used. The energy of 266 nm photons wavelength is in a region, where most of the PAH with three or more annealed rings exhibit broad absorption band systems ( $S_2$  or  $S_n \pi^* \leftarrow \pi$  transitions). Thus a more or less PAH-selective ionization can be performed with 266 nm. For a simultaneous monitoring of a specific smaller aromatic systems (e.g., a benzene derivative), it is necessary to tune the laser wavelength in resonance with an optical UV transition of this target compound. In this contribution monochlorobenzene (MCB), which represents a good surrogate for the PCDD/F emission, was monitored continuously, using a laser wavelength of 269.8 nm.

The identification of potential PCDD/F surrogates for on-line REMPI-TOFMS monitoring was performed as follows. For sampling of PCDD/F, an isokinetic sampling unit was used. The compounds were adsorbed on two cartridges, the first was filled with quartz glass wool for separation of particulate matter. The second cartridge was filled with a XAD-2 resin for the adsorption of gas phase PCDD/F. The quantification of the PCDD/F was done by isotope dilution, using a HRGC/HRMS in the MID mode [10]. Due to their low volatility, the lower chlorinated compounds as well as the xylenes and naphthalene were adsorbed on Carbotrap. The chlorinated benzenes, the xylenes and naphthalene were measured subsequently by direct thermal desorption followed by HRGC/LRMS. The standards for isotope dilution were spiked before sampling [10]. The more polar chlorinated phenols were measured after derivatization (acetylation) with HRGC/LRMS. The acetylated sample was injected without any previous cleanup and detected in the MID mode.

## Results and Discussion

In the first campaign, the flue gases were on-line sampled and analyzed by REMPI@266nm-TOFMS directly after the post combustion zone, prior to the boiler section. Flue gas temperatures are in the range of 750 to 900 °C at this sampling point. In contrast to previous results, where sampling was performed directly in the post combustion zone, a large number of aromatic compounds at trace levels were observed. Particularly interesting is that long progressions of methylated species are observed in the mass spectra. Thus the spectra obtained at this sampling site are quite dense. However, most peaks can be assigned clearly to a basic PAH mass or a corresponding methylated homologue. Note that isomeric species (e.g. benzo[a]pyrene versus perylene) can often not be discriminated without using a tunable laser and a jet inlet technique. Figure 2 shows two REMPI@266nm mass spectra obtained at this sampling point. The right spectrum was recorded during normal operation conditions with hazardous waste as fuel. A temporary change to mineral oil based fuel caused the change in the observed PAH pattern. During hazardous waste combustion the spectrum is dominated by phenanthrene and its methylated homologues while during mineral oil combustion naphthalene and methylated naphthalenes are the

most prominent species. Shifts in the patterns of the PAH also are observed for different temperatures (i.e. different sampling positions in the flue gas current) or during non optimal combustion conditions (i.e. during substoichiometric conditions).

These results suggest that the PAH pattern is containing a broad variety of informations about the process. However, the decoding of the chemical and process related information hidden in the PAH patterns is a future project and will require extensive use of chemometric data analysis methods.

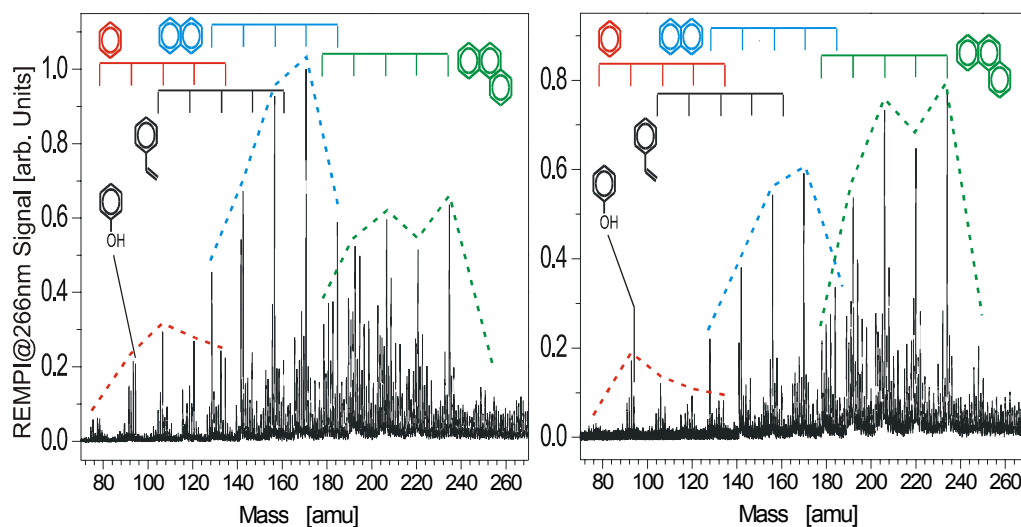


Figure 2: REMPI-TOF mass spectra of on line sampled flue gas from the hazardous waste incinerator (sampling point #1 at 900°C) recorded with the laser wavelength 266 nm. **left**) PAH profiles registered during combustion of mineral oil. **right**) PAH profiles registered during combustion of hazardous waste.

Table 1: Correlation between the logarithm of the I-TEQ value and the logarithm of the concentration of different compounds in the flue gas of the hazardous waste incinerator.

$R^2$	MCB	1,2 DCB	2,4 DCPh	2,4,6 TCPPh	MCDD	DCDD	MCDF	DCDF	naphthalene	xylenes
I-TEQ (PCDD/F)	0.82	0.62	0.54	0.66	0.28	0.55	0.13	0.25	0.07	0.16

In addition to the on-line measurement of the PAH patterns, which are describing the general process status, a further goal was the on-line REMPI-monitoring of specific hazardous compounds. This may be precursors in the NO<sub>x</sub> formation process like NH<sub>3</sub>, HCN or the HCNO isomers. In this contribution we are focusing on indicators for the PCDD/F emission. Based on previous work, reporting that penta- and hexachlorinated benzenes are indicators for the emission of PCDD/F I-TEQ [12,13], extensive conventional studies on correlation of different compounds have been started. For REMPI-TOFMS monitoring non or low chlorinated species are suited best

[14]. In Table 1, data on the correlation of different molecular species in the flue gas with the I-TEQ value at the investigated hazardous waste incinerator are given. Note, that a high correlation does not mean necessarily that the respective compound is a direct chemical precursor of the PCDD/F. We rather assume that parallel reaction paths exist for the different compound classes. Thus a good correlation more likely is caused by similar dependencies of the formation reaction pathways on process conditions and similar formation regions in the flue gas channel. Monochlorobenzene (MCB) has been identified as a well suited surrogate substance for the PCDD/F I-TEQ. For sensitive REMPI-TOFMS-monitoring of MCB, the wavelength of the laser has to be tuned onto a vibronic resonance absorption band of MCB. An intense resonance is the  $0^0$  origin transition of the  $^1B_2$  first electronic singlet state ( $S_1$ ) of MCB at 269.82 nm. This wavelength is located relatively close to the wavelength used for detection of the PAH patterns (266 nm). Due to the broad absorption bands of the PAH in this wavelength region, a very similar PAH-pattern can be recorded at 269.82 nm. The figure 3 shows two on-line recorded REMPI-mass spectra of flue gas from the hazardous waste incinerator, recorded at 266 and 269.82 nm respectively. On-line sampling was performed at the second sampling port at flue gas temperatures of about 300 °C. Here the patterns of the observed aromatics is much less dense in comparison to the REMPI spectra observed at the previous measurement point at 900 °C (figure 2). This depletion is caused on one hand by oxidation and other catalytical and thermal degradation processes and on the other hand by reactive adsorption of the molecular species on aerosol particles (fly ash and soot). The insets in figure 3 show an enlarged view on the molecular ion region of MCB. No MCB signal can be obtained with REMPI at 266 nm, while REMPI with 269.82 depicts a clear MCB signal. The figure 4 shows a time to intensity diagram of the MCB concentration.

The calibration of the REMPI signal was performed via an external standardization procedure as described in detail in reference [4]. Using the correlation diagram between MCB and the PCDD/F I-TEQ value as published in [10], a MCB concentration of about 400 pptv corresponds to a PCDD/F I-TEQ value of ca. 0.5 ng/Nm<sup>3</sup> at this particular plant. However, note that the results shown in figure 4 are representing a flue gas measurement, where sampling was performed prior to the flue gas cleaning measures. Thus, stack emission are considerably lower, meeting the stack gas emission limit of 0.1 ng/Nm<sup>3</sup>. The time to concentration diagram displayed in figure 4 shows a transient peak of the MCB concentration. The FWHM of this emission peak is between 10 and 20 seconds range. This demonstrates that changes in formation rate of chloroaromatic compounds can be very rapid, even at large industrial facilities. During the transient increase of the MCB concentration most likely also the formation rate of PCDD/F is increased. However, due to their low volatility, these additionally formed PCDD/F congeners will emit delayed because of absorption/desorption effects in the colder parts of the plant. A multiple occurrence of transient emission peaks can be responsible for an increased average PCDD/F emission level of the facility. Strategies for a further PCDD/F emission reduction thus may include advanced on-line measurement techniques like REMPI-TOFMS for diagnostics and feed back process steering. Similar highly dynamic emission effects have also been observed for non chlorinated aromatics, as reported previously [2,4].

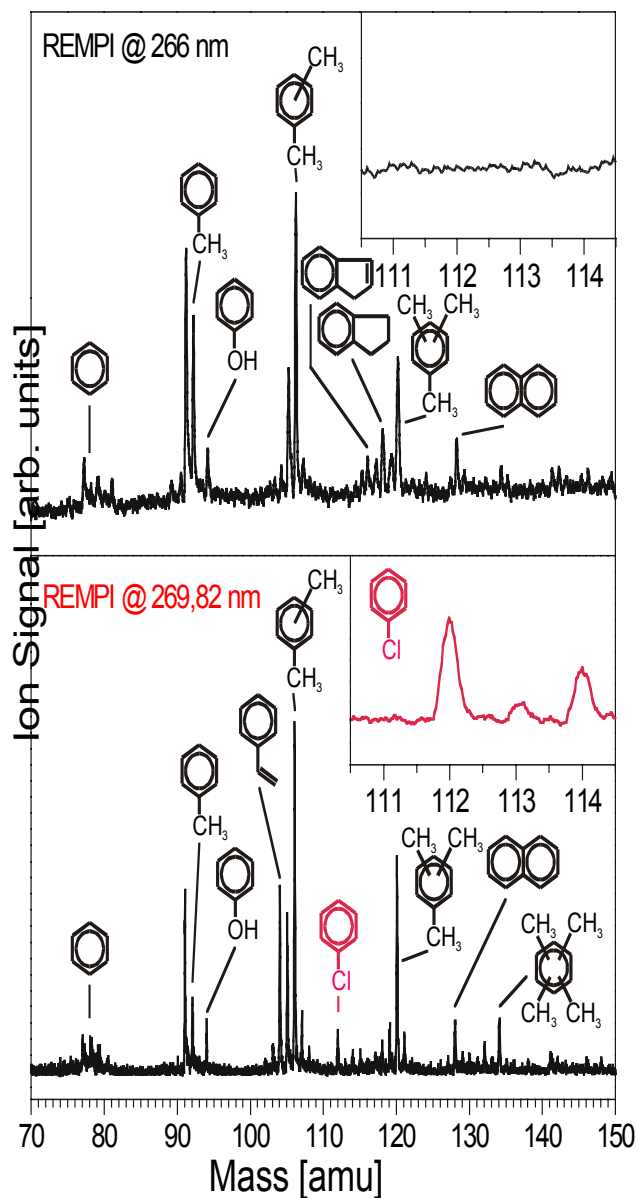


Figure 3: REMPI-TOF mass spectra of flue gas from the HWI, on-line sampled at sampling point #2 at 300°C. Upper part) Laser wavelength 266 nm. Aromatic compounds as benzene or naphthalene are detected. Lower part) Laser wavelength 269.82 nm (S1 origin transition of monochlorobenzene). Monochlorobenzene (MCB) is detectable additionally (see inset).

### Conclusion

The here depicted measurements are the first on-line real-time measurements of PAH-patterns and a dioxin indicator in the ppbv-concentration range (and below) from flue gases of an industrial waste incineration plant. Particularly important is the fact that REMPI-TOFMS allows a simultaneous monitoring of both informations. The technique thus may be useful for industrial applications, e.g. for feed back process control. However, although the instrumentation is mobile, it is still too bulky and sophisticated for a routine application in industry. In the framework of a recently started research and development project more compact and robust REMPI-TOFMS devices are under construction.

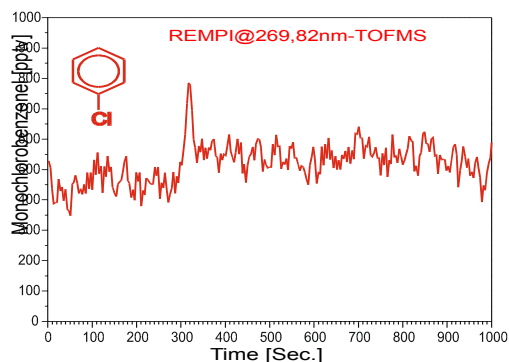


Figure 4: REMPI-TOFMS time to intensity profile for monochlorobenzene.

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