

ON-LINE LASER MASS SPECTROMETRY FOR ANALYSIS OF COMBUSTION PROCESSES: PCDD/F SURROGATES IN WASTE INCINERATION FLUE GASES

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Introduction

In the last years the applicability of Resonance-Enhanced Multi-Photon Ionization – Time-of-Flight Mass Spectrometry (REMPI-TOFMS) [1-3] for on-line monitoring of polychlorinated dibenzo-p-dioxins/-furans (PCDD/F) in flue gases of industrial combustion processes was discussed controversially. A direct on-line measurement of the toxic PCDD/F most likely is impossible due to REMPI spectroscopic reasons. Recent investigations, however, pointed out that there are valid surrogate compounds for PCDD/F-emission from waste incineration (e.g. monochlorobenzene [4] or some PAH species during “memory” emission phases [5]). It was demonstrated that some PCDD/F surrogates are on-line measurable by REMPI-TOFMS instruments in the flue gas of waste incineration plants [4-6] (see also *Figure 4* and *Figure 5*). However, the REMPI-TOFMS technique still is in a rather experimental development stage and the task for next years is the development of more rugged REMPI based process monitoring systems. The here presented REMPI-TOFMS instrumentation with continuous effusive or jet-inlet (needle inlet [6, 7]) as well as with fixed frequency ($\lambda=266$ or 248 nm [6]) or tunable laser [4, 7] is already sufficiently robust for short term field applications at waste incineration plants or comparable industrial measurement sites.

Experimental

The principles of the Resonance-Enhanced Multi-Photon Ionization – Time-of-Flight Mass Spectrometry (REMPI-TOFMS) technique were discussed thoroughly in several publications.[1, 6, 8-12]. *Figure 1* depicts a schematic representation of the REMPI-process and of a time-of-flight mass spectrometer. Briefly, UV laser pulses (typically with pulse energies of some mJ, pulse power densities at the ionization region of $10^6 - 10^7$ W/cm², pulse widths of about 10 ns and pulse repetition rates of about 10 Hz) are used for two-photon ionization of molecules. The two-photon ionization process is mediated by the energetic position of molecular excited states (i.e. UV-spectroscopic selectivity is involved).The REMPI-ionization process with intense laser pulses can be extremely efficient (if not being quenched by intermolecular relaxation processes [12]). Ionization yields of some 10 % in the laser focus have been reported [13]. Furthermore, in most cases a soft ionization (without fragmentation) can be achieved [14].

ORGANOHALOGEN COMPOUNDS

In summary, REMPI ionization allows a highly selective ionization (i.e. with respect to the applied laser wavelength) combined with a very high ionization yield (in particular for many aromatic species) and low fragmentation rates. These properties make REMPI to an ideal ionization technique for direct inlet mass spectrometry in order to on-line monitor specific trace compounds or substance classes from complex mixtures [6, 15-17].

- a) REMPI = resonance-enhanced multiphoton ionization b) Time-of-Flight mass spectrometer

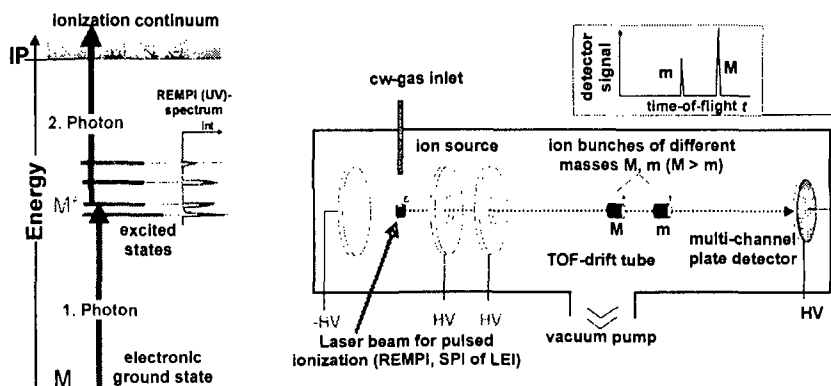


Figure 1: a) Schematic representation of the REMPI-process, using a two photon absorption for ionization. b) Schematic representation of a linear Time-of-Flight mass spectrometer with effusive needle gas inlet.

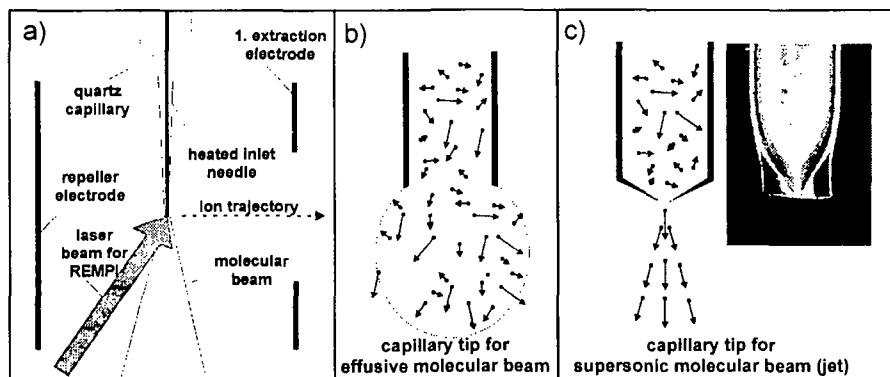


Figure 2: a) Detailed scheme of the capillary based needle inlet system (continuous molecular beam). b) Schematic representation of the quartz capillary tip without restriction for formation of an effusive („warm“) molecular beam. c) Schematic representation and photo of the quartz capillary tip with restriction for formation of supersonic molecular beams (jet) for cooling of sample molecules ([7], patented [18]).

The selectivity of the REMPI technique depends on the molecular beam source used for the sample gas inlet. If the gas expands through a nozzle and a supersonic jet expansion is formed, the molecules are cooled down to cryogenic temperatures (30 – 3 K [19]). Due to this cooling effect, features in the UV spectrum are narrowed and an increased optical selectivity of the REMPI ionization process can be achieved (e.g. discrimination of isomers is possible). The supersonic jet inlet technique commonly is used with sophisticated pulsed inlet valve systems [11, 20, 21]. If the sample inlet is performed without a restriction nozzle, an effusive molecular beam is formed. No cooling is observed in this case and the optical REMPI selectivity is lower. However, it turned out, that for many application the use of the effusive molecular beam technique for REMPI-TOFMS

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for many application the use of the effusive molecular beam technique for REMPI-TOFMS still gives sufficient selectivity [6, 22]. In order to achieve a high sensitivity it is important to perform the REMPI ionization process close to the origin of the molecular beam, where the gas density still is high. This is realized by a needle inlet, as shown in *Figure 2a*. The hollow needle (stainless steel) reaches directly in the center of the ion source between the repeller- and the first extraction-electrode. Inside of the hollow needle runs a quartz capillary with chemically deactivated inner walls. The sample gas current flows through the quartz capillary, forming a molecular beam at its tip. Directly underneath the capillary tip (orifice), laser pulses are crossing the molecular beam for REMPI-ionization. The tall design of the inlet needle helps to minimize disturbances of the electrostatic field in the ion source. Sensitivities in the ppbv to pptv-region have been reached with this type of inlet. Due to the simple setup, the constantly running flow and the inertness of quartz, possible contamination of the inlet system is minimized [6]. By using capillary with a nozzle restriction at the tip also a continuous supersonic jet, as described above, can be formed (see *Figure 2c*) [18]. The nozzle is made by melting the tip of the quartz capillary with a O_2/H_2 -torch until closure. Subsequently the nozzle is re-opened by controlled abrasion of the tip. For details see [18]. This procedure allows to manufacture a very smooth inner surface of the glass nozzle. Thus extremely good jet-cooling properties are obtained even at very low gas flow rates. With this type of continuous (cw) jet inlet, using the same flow rate as with the effusive molecular beam (about 10 ml/min), for example rotational temperatures of 15 K were achieved for benzene vapor in air. This novel cw-jet inlet recently was applied for Jet-REMPI detection of monochlorobenzene in the flue gas of a waste incineration plant [7].

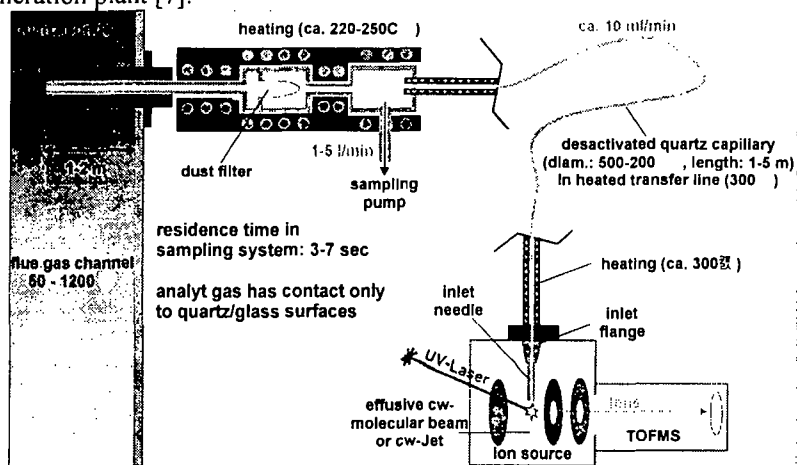


Figure 3: Sampling and inlet system for REMPI-TOFMS based process monitoring instruments

A further advantage of the REMPI-TOFMS setup is the very open design of the ion source. The molecular beam crosses the ionization region and falls directly into a turbo pump and thus has minimal interaction with parts of the ion source. This open setup largely avoids the risk of contamination of the ion source region. However, in addition to a thorough design of the inlet technique and ionization region of the TOFMS-instrument also the concept and realization of the sampling system is crucial for monitoring of complex process gases. *Figure 3* shows schematically the setup of the sampling and inlet techniques as used for monitoring of combustion flue gases. For details on the sampling technique see e.g. ref. [6, 7].

Results and Discussion

The REMPI-TOFMS technique is used for detection of aromatic species in the flue gas of incinerators (first application in 1996 [16]). Analysis of several on-line REMPI sequences, recorded at incineration plants during process steering measures or induced disturbances of the combustion conditions, revealed typical patterns of aromatic species. During unstable, disturbed combustion conditions, smaller aromatic systems, like benzene, toluene and xylenes (BTX) or naphthalene, are transiently increased. ("direct emission"). Further typical "molecular growth" intermediates from the building-up process of polycyclic aromatics and soot (i.e. from aliphatic C₂ and C₃ units), like indene and phenylacetylene, are detected. Particularly important was the finding that after a short disturbance of the combustion conditions (i.e. lack of oxygen) an increased concentration of specific PAH species was detectable for a rather long time (memory emission). This effect was already observable in the hot flue gas (>600 °C) [5]. In some cases memory emission of PAH was detectable over time spans of hours (by REMPI and conventional HPLC or GC-MS measurements [23]).

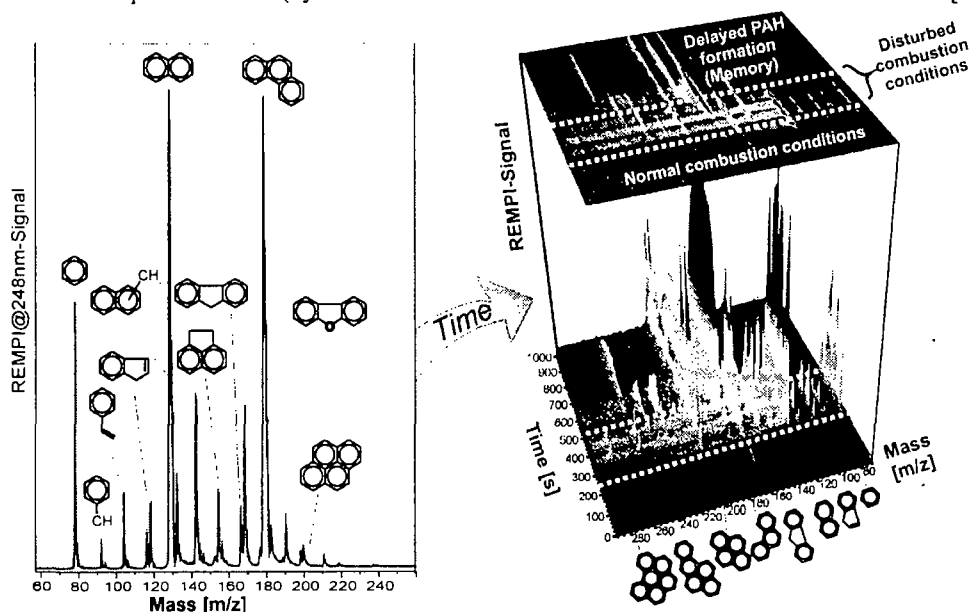


Figure 4: On-line measurement of the signature of the polycyclic aromatic hydrocarbons (PAH, typically in ppbv concentrations) from flue gas of an incineration plant: left) REMPI-TOFMS flue gas mass spectrum (effusive inlet). right) 3-dimensional representation (time x mass x REMPI-signal) of a REMPI-TOFMS on-line measurement sequence (landscape- and contour-plot), recorded during process steering measures. A short disturbance of the combustion conditions due to process steering measures is indicated. After the disturbed combustion conditions, which are characterized by "direct emission" of several aromatic species (benzene, naphthalene, indene, phenylacetylene etc.), a sustained formation of specific PAH species is observed (memory emission, [5]).

Further it was observed by GC-MS that during the phases of PAH memory emission the homologue profiles of the polychlorinated dibenzodioxins/furans (PCDD/F) were changed drastically [5] and (in some cases) the I-TEQ of the PCDD/F emission was significantly increased. Particularly interesting is that these memory emission effects are induced in the high temperature zone of the incineration plants. A likely explanation of the observed memory emission is the formation of car-

bonaceous surface layers on the plant inner wall during disturbed combustion conditions. The decomposition of the layer may be responsible for the PAH memory while the shift of the PCDD/F homologue patterns is due the catalytic activity of the formed carbonaceous layers or high temperature de novo formation. The memory emission effects of PAH (which is correlated with memory emission of PCDD/F) was observed at up to now 3 different incineration plants. The latter mentioned results implicate, that the on-line measurement of PAH species in the flue gas of incinerators can give information about the long term variation (hours/days) of the PCDD/F emission (i.e. caused by the above mentioned memory effects), while the short term variations (seconds/minutes) could be observed via the on-line measurement of a direct PCDD/F surrogate (for which monochlorobenzene seems to be a good candidate). The right part of Figure 4 shows a three dimensional (3D) representation of a REMPI-TOFMS flue gas on-line measurement sequence (time x molecular mass x intensity). The sequence was recorded during a change of process condition at a pilot incineration plant and shows the changes in the signature of PAH species with time. During the phase of disturbed combustion conditions "direct emission" of benzene, naphthalene, indene and other aromatic species is observed, after the phase of disturbed combustion conditions memory emission of specific PAH species is detectable (e.g. phenanthrene).

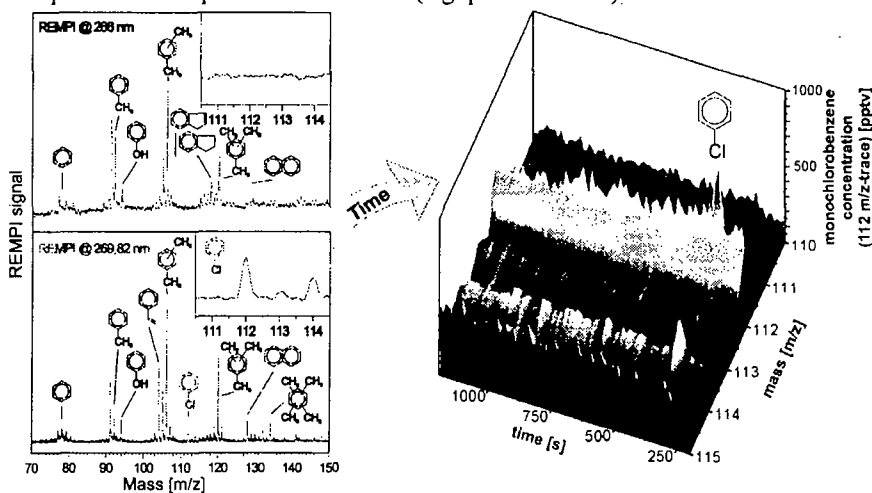


Figure 5: On-line REMPI-TOFMS measurement of monochlorobenzene (MCBz) in the flue gas of a hazardous waste incinerator. Monochlorobenzene is a surrogate for the emission of polychlorinated dibenzodioxins/-furans (PCDD/F) [4, 24, 25]: left) Flue gas REMPI mass spectra, on-line recorded at a hazardous waste incineration plant (effusive inlet). In the upper trace, recorded with 266 nm laser pulses, MCBz is not detected (see inset). The lower trace is recorded with 269.82 nm (resonance wavelength of the origin band of MCBz's first excited singlet state). MCBz in the pptv concentration range is detectable (see inset). right) Three dimensional landscape plot (time x mass x REMPI-signal) of the MCBz traces (112 and 114 m/z) from an on-line measurement sequence, recorded at an hazardous waste incineration plant.

On line monitoring of monochlorobenzene (MCBz) requires a tunable laser system. For efficient ionization of MCBz the laser has to be tuned to its S_1 origin transition (269.82 nm). In Figure 5 an on-line measurement sequence of MCBz, recorded at a hazardous waste incineration plant is shown. At the MCBz resonance wavelength also several other aromatic species can be detected. This includes several indicators for "direct-" and "memory emission" as e.g. on the one hand toluene, naphthalene, indene and on the other hand phenanthrene and pyrene. Therefore a comprehensive

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monitoring of surrogates/indicators by REMPI-TOFMS may be a feasible concept for on-line combustion control.

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