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On-Line Emission Analysis of Polycyclic Aromatic Hydrocarbons down to pptv Concentration Levels in the Flue Gas of an Incineration Pilot Plant with a Mobile Resonance-Enhanced Multiphoton Ionization Time-of-Flight Mass Spectrometer

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A newly developed, mobile laser mass spectrometer (resonance-enhanced multiphoton ionization – time-of-flight mass spectrometer, REMPI-TOFMS) was applied to on-line measurements at a waste incineration pilot plant. REMPI-TOFMS combines the optical selectivity of resonance-enhanced multiphoton ionization with a time-of-flight mass analysis to give a two-dimensional analytical method. Special care was taken to build up a sampling and inlet system suitable for on-line measurements of large, semivolatiles polycyclic aromatic hydrocarbons (PAHs). An effusive molecular beam inlet in combination with a fixed frequency UV laser (Nd:YAG at 266 nm or KrF excimer at 248 nm) was used. Under these conditions, many different PAHs can be ionized selectively from the complex flue gas matrix. For example, the achieved detection limit for naphthalene is in the 10 parts-per-trillion by volume (pptv) concentration range. Calibration was performed by using external concentration standards supplied in low ppbv concentrations. The instrumentation is sufficiently robust to be operated under industrial conditions at incineration plants, for instance. The REMPI mass spectra can be acquired at 5–50 Hz. Time profiles of the concentrations of different PAHs in the flue gas were monitored with a time resolution of 200 ms. Significant variations in the concentration profile of several PAHs up to mass 276 amu (e.g., benzo[ghi]perylene) and methylated PAHs have been observed while combustion parameters were changing. In summary, it was demonstrated that laser mass spectrometry (REMPI-TOFMS) enables a real-time on-line trace analysis of combustion flue gases or industrial process gases.

Fire is one of the most fascinating physicochemical phenomena in daily life, and the comfort of today's society relies on controlled firing processes in many ways. Energy for industrial and personal use (heating, traffic) is mainly generated by combustion of organic

material, especially wood and fossil fuels such as coal and oil. Hazardous compounds from combustion have a considerable impact on human health and ecosystem health.¹ Risk assessment studies point out that the limitation and reduction of toxic emissions formed at trace levels in combustion devices is of public interest, resulting in a number of national laws and acts imposing limits for emissions of toxic byproducts.²

In general, the pollutants in the combustion flue gas can be divided into two groups according to their origin. On one hand, there are the fuel-related emissions, e.g., SO_x, HCl, and heavy metals. On the other hand, there are the process-related emissions, e.g., NO_x, CO, and organic compounds such as polycyclic aromatic hydrocarbons (PAHs) and halogenated aromatic compounds. The hazardous potential of the organic part of the exhaust gas from burning wood or fossil fuels is mainly due to PAHs. In the case of burning waste, heavy metal species and halogenated hydrocarbons also make a notable contribution to the hazardous emissions. Attention is paid especially to the polychlorinated dioxins/furans (PCDD/PCDF) because of their high toxicity, although they constitute only a minor part of the total chlorinated hydrocarbon emission.

With regard to reduction of pollution concentrations, in the past the emphasis was on the development of an efficient purification of flue gas and the posttreatment of residuals (i.e., secondary measures). Currently equipped plants now generally

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comply with the legally required limits concerning the discharge or the disposal of noxious matter in air, water, and soil.

Further reduction of stack emissions is expected to be achieved by optimizing the thermal process by primary measures, leading to reduction of fuel-related emissions. Particularly waste incineration and biomass combustion have to deal with a very inhomogeneous fuel composition, frequently resulting in incomplete combustion, with process parameters adjusted to mean values for the whole process. Application of primary measures for reduction of process-related emissions on one hand requires construction of the plant which makes it possible to react to fast-changing combustion situations. On the other hand, special parameters should be available which reliably represent the actual combustion conditions and are measurable by online analytical methods. Currently, species-selective on-line measurement techniques are available for small molecules that are emitted in relatively high concentrations, such as CO, CO₂, and NO_x, and for the FID value (flame ionization detector signal, representing the overall content of carbon). The CO concentration is used as an indicator of incomplete combustion conditions. Since incomplete combustion is the main source of toxic byproducts, the CO concentration is assumed to be a parameter for the formation of PAHs. But this assumption is not proved experimentally, because only time-integrated measurements of PAH concentrations were available up to now. Accordingly, there is a strong demand for on-line analytical instrumentation for selected species at trace levels in the flue gas.³

The conventional analytical methods for measurement of the PAH emissions in the stack gas of incineration plants commonly use sample enrichment on a trap, solvent extraction, and subsequent analysis using a two-dimensional analytical method, e.g., high-resolution gas chromatography/mass spectrometry (HRGC/MS) or high-performance liquid chromatography/UV detection (HPLC/UV).^{4,5} The major drawback of these methods is the time-consuming and cost-intensive cleanup step. The results are available hours or even days after the sample has been taken and only represent integrated measurements, as mentioned above.

On-line measurements of trace compounds in complex exhaust gases require methods that combine selectivity with sensitivity. A soft ionization without fragmentation is decisive for successful on-line mass spectrometry. Recent developments of ionization methods for on-line analysis involve chemical ionization (CI)⁶ or resonant laser ionization (REMPI).⁷ These methods have in common that they can be adjusted so that no or little fragmentation occurs because the excess energy upon ionization, i.e., the energy difference between the ionization potential and the energy supplied for ionization, is very low. Direct inlet (DI) mass spectrometry with electron impact ionization would result in congested mass spectra due to fragment peaks. Both methods, CI and REMPI, provide additional selectivity: the ionization potential or proton affinity and the gas-phase UV spectroscopy.

With proton-transfer mass spectrometry (PTR-MS), a suppression of the bulk compounds but a presentation of nearly all organic trace molecules is possible. It has been applied for on-line measurements successfully.⁸ REMPI may be extremely sensitive (e.g., one-atom detection by Hurst et al. in the 1970s⁹) and selective (isomer-selective ionization of jet-cooled molecules¹⁰). The REMPI selectivity can be tuned from substance class selectivity to isomer selectivity by varying of the laser wavelength and the molecular beam source. Thus, the two methods are complementary in their results in terms of selectivity. For particularly high selectivity, a resonant multiphoton process (REMPI) is best suited. In addition, pulsed laser ionization is an ideal ionization method for time-of-flight mass spectrometry because of the well-defined temporal and spatial parameters of the laser pulse. In combination with TOFMS, a time resolution of up to 20 ms is achievable, mainly dependent on the laser system.

Since the first REMPI mass spectra of aromatic molecules,¹¹ several analytical developments for REMPI analysis of PAHs have been successfully performed; examples are coupling with gas chromatography¹²⁻¹⁵ or flame sampling.¹⁶⁻¹⁸ The highly time-resolved measurement of small aromatic molecules (benzene, toluene, and xylenes, the so-called BTX aromatics) in the exhaust gas of automotive combustion engines¹⁹ and the on-line measurement of volatile and semivolatile compounds in the off-gas during the roasting of coffee beans²⁰ show the variety of applications of REMPI-TOFMS for on-line trace gas analysis. In the following we investigate the application of REMPI-TOFMS for on-line measurement of PAHs in the highly complex, dusty, and corrosive waste incineration flue gas and report, in detail, the first REMPI on-line monitoring experiments at an industrial-scale facility.

EXPERIMENTAL METHOD

For the REMPI detection of aromatic compounds, usually a one-photon resonant/two-photon ionization process is used. The first photon is absorbed, and the molecule is in an excited state. This step is similar to gas-phase UV absorption spectroscopy. In the measurements described below, a second photon is absorbed, ionizing the molecules of interest. For strong transitions in the first excitation step, the yield can be in the range of several percent of the illuminated molecules.²¹

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For molecules, the selectivity can be tuned by varying of the temperature of the molecules, which determines the number of populated rotational and vibrational states in the molecular ground state. The temperature is determined by the inlet system used. Here, two different approaches are possible. Within a supersonic expansion, the rotational temperature of the molecules can be cooled to about 5 K. As a result, only a very few rovibronic states are populated, leading to very sharp UV spectra. This allows isomer-selective ionization. However, despite isomer selectivity, simultaneous ionization of other unwanted molecules cannot be suppressed in complex gas mixtures with thousands of compounds. For this reason, the second mass spectrometric dimension is necessary, even if a supersonic beam inlet system is used. Of course, the effort of supersonic beam cooling is only justified if ultrahigh selectivity is required. One should notice, however, that this is possible only where UV spectroscopy allows sharp spectra. For PAHs, this is the case only for $S_1 - S_0$ transitions.

The second approach is to use effusive molecular beams (no cooling). As opposed to cold molecules, in hot molecules rotational and vibrational states are excited, resulting in broad absorption bands. For a given wavelength, a whole substance class may have overlapping absorption bands and will be ionized effectively by REMPI. From an analytical point of view, there are arguments for both, depending on the application.

Accordingly, there are three strategies for the application of REMPI for on-line measurements: (i) using a narrow-band tunable laser in combination with a supersonic jet inlet, (ii) using this laser with an effusive molecular beam inlet, and (iii) using a fixed-frequency laser in combination with the effusive molecular beam inlet.

The first strategy optimizes the selectivity and is necessary if isomer-selective ionization is desirable. It requires a sophisticated setup, especially a supersonic jet nozzle that is heatable up to at least 300 °C to transport larger PAHs into the mass spectrometer without memory effects or decomposition.

The second strategy leads to medium substance-specific selectivity. The complexity of the device is reduced, although it is still difficult to run a tunable laser under the industrial environment conditions of an incineration plant.

The third strategy is the most robust and reliable setup. Depending on the chosen laser, a substance class of molecules with similar UV absorption bands will be ionized, resulting in a good overview of the concentrations of these molecules in one laser shot. Comparing the sensitivity using a jet inlet (strategy one) with that using an effusive inlet (strategy two), a general statement cannot be made. On one hand, in the cold jet the population is in the ground state, leading to a better ionization yield, while on the other hand, the sample is often diluted with carrier gas and the geometric overlap of molecular and laser beam is worse than that for an effusive molecular beam. While the effusive molecular beam setup allows ionization directly under the inlet orifice (distance < 1 mm), a common supersonic jet arrangement consists of a nozzle and a skimmer, leading to a distance between nozzle inlet and ionization region of about 70 mm and thus to a lower density of target molecules. This can be overcome using a free-jet setup, but still at least 4 mm distance is necessary for building up the jet and for developing the cooling.²²

Developing a mobile REMPI-TOFMS device for on-line measurements at incineration plants primarily means building a very robust device for operation in a hot, dusty, and vibrating environment. For the first on-line measurements in the flue gas of a waste incinerator, the third strategy, using a small and reliable fixed frequency laser with simple and robust effusive molecular beam inlet, is applied. For target analysis of mono- and polycyclic aromatic hydrocarbons, there are two common commercially available fixed-frequency lasers that emit in the suitable range: the KrF excimer laser with emission at 248 nm and the Nd:YAG, using the fourth harmonic at 266 nm. The individual ionization yield for aromatic molecules may be different; e.g., comparing the effusive molecular beam REMPI spectra of benzene and toluene,¹⁹ it turns out that with KrF benzene is more effectively ionized than toluene and with the fourth harmonic Nd:YAG vice versa.

For optimum selectivity, REMPI has to be performed using the sharp structured $S_1 - S_0$ transition of the target molecule. It is important to pay attention to this fact, especially for comparison of detection limits. There may be stronger transitions with better ionization yield using higher electronic states, but the selectivity of the ionization process is reduced. Using fixed-frequency lasers, one can take advantage of reduced selectivity due to warm molecules with broad absorption bands to achieve substance class-selective ionization. The $S_1 - S_0$ transition of the PAHs is above 300 nm, but the broad S_n structures of these molecules are in the range around 250 nm, allowing an effective ionization of warm molecules with medium selectivity.

Laser ionization with pulsed lasers is ideally suited for combination with time-of-flight mass spectrometry, allowing the registration of the total mass spectrum with every laser shot. Additionally, time-of-flight mass spectrometers have an outstanding transmission, and due to their simple setup they are very robust and insensitive to vibrations, which is particularly important for field applications.

The setup for the on-line monitoring of PAHs in the flue gas is schematically depicted in Figure 1. The lower part of the figure shows the laser mass spectrometer with data acquisition. To achieve a very compact setup with a maximized transmission, a home-built linear TOF with a Wiley-McLaren ion source²³ and a 50-cm drift tube was used. The achieved mass resolution, $\Delta m/m$, of 330 is sufficient for the desired application. A two-stage multichannel plate is used for detection of the ions. The mass spectra were recorded using an 8-bit, 500-MHz transient recorder PC card (Signatec DA500) to write every mass spectrum on the hard disk of the PC (P100, SCS). With the storage of the whole mass spectrometric information, there is no limitation in the subsequent data processing, allowing, e.g., addition of n mass spectra for enhancement of the signal-to-noise (S/N) ratio with the square root of n and preserving the possibility of finding unexpected peaks in the MS, which is impossible using selected ion monitoring with a limited number of integrators. Mass spectra have been recorded with a repetition rate of 5 Hz, corresponding to a time resolution of 200 ms. The data acquisition and

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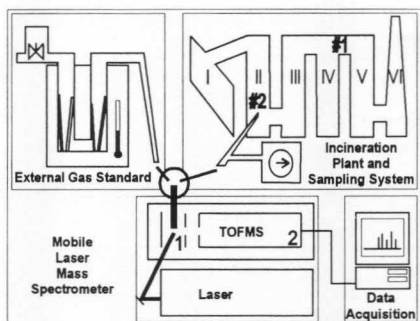


Figure 1. Scheme of the laser mass spectrometer with data acquisition (lower part), the calibration gas standard (upper left), and the pilot incineration plant with sampling system (upper right). The heatable sample inlet of the laser mass spectrometer can be coupled to either the dynamic gas standard (diffusion/permeation tubes under constant gas flow in a water bath) or the flue gas sampling system (quartz glass tube and pump depicted) of the pilot incineration plant (I, grate; II, postcombustion chamber; III, heat exchanger; IV, cloth dust filter; V, activated coke filter; VI, stack). The two sampling points are indicated. The main parts of the ion optics of the linear time-of-flight mass spectrometer, the Wiley-McLaren ion source (1) and the separated flight tube liner (2), are depicted.

processing routines are home-built using the LabVIEW programming environment (National Instruments). Additionally, a digital storage oscilloscope (LeCroy 9361) was used for adjustment and storage of snapshot mass spectra.

A very important part of the instrumental design is the setup of the probing and sample inlet system for real-time on-line acquisition of the complex sample. The waste incinerator flue gas consists of corrosive inorganic substances, e.g., HCl, NO_x, SO₂, and a variety of organic substances of different volatility up to tarry, low-volatile compounds and is loaded with dust particles. The requirements for direct probing of PAHs from the combustion flue gas are (i) avoidance of condensation of low-volatile compounds, (ii) minimization of memory effects for the semivolatile compounds, (iii) reduced catalytic activity of the surface, and (iv) a rugged and reliable design. A detailed view of the developed sampling system is shown in Figure 2. The sample inlet system is built with quartz glass surface from the stack right into the MS. It consists of a quartz glass tube, quartz wool filter paper, and a capillary (Figure 2a). The quartz glass tube with a diameter of 10 mm is used for the first part from the sampling point in the flue gas of the plant to the splitting point for on-line and conventional measurements. The filter is integrated in the tube. Behind the filter, the tip of a quartz capillary (inner diameter 0.25 mm) is set in the center of the tube (Figure 2a) and splits the flow into the part flowing to the mass spectrometer and the part being pumped through a trap for simultaneous conventional measurements. A flue gas sampling stream of 100 L/h is pumped through the sampling system. The transition time from the stack into the MS is about 3 s.

The whole inlet system is heatable up to 200 °C to avoid memory effects for larger PAHs. The quartz tube and filter housing are heated by heating tape, and the capillary between

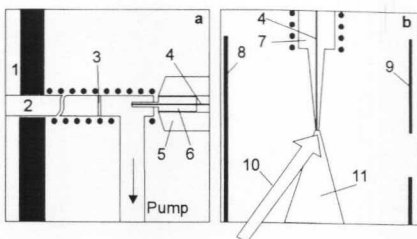


Figure 2. Detailed view on the sampling system. In part a of the figure, the part from the flue gas (1) through the heated quartz glass tube (2) with quartz wool filter (3) to the capillary transfer line (4) is depicted. The transfer line is heated with a commercial heating tube (5), and the tip of the capillary is heated via heat conduction through a metal interface (6), from which a part is heated in the heating tube. Part b of the figure shows the effusive molecular beam sample inlet of the mass spectrometer. Again, the capillary (4) is heated via heat conduction along the conical metal needle (7), which is heated to the entrance into the ion source. Thus, the needle is at zero potential, while the repeller (8), draw-out plate (9), and flight tube (see Figure 1) are adjusted to the corresponding potentials. The laser beam (10) is crossing the effusive molecular beam (11) right under the needle tip.

the glass tube and the mass spectrometer is inside a heating pipe. Special care was taken to avoid cold spots at the tips of the capillary in the quartz tube behind the filter (Figure 2a) and in the center of the ion source of the time-of-flight mass spectrometer (effusive beam inlet, Figure 2b). This was realized by using a tight metal tube that was heated at one end. Heat conduction provided sufficient temperatures at the other end. The setup for an effusive molecular beam inlet is shown in Figure 2b. The sample is introduced through a quartz capillary inside a metal cone. This is positioned between the two acceleration plates of the first stage of the ion source. The emitted sample gas is ionized by the laser beam, which crosses the molecular beam right under the cone tip.

Since the cone reaches into the accelerating field of the ion source, the potential of the capillary tip has to be chosen, so that the distortion of the accelerating electric field (repeller, +300 V; first and second extraction plates, -200 and -1900 V, respectively) of the MS is minimized. In the common setup, the needle that is introducing the sample is electrically isolated and set on a carefully adjusted high-voltage potential. Since the thermal conduction of electrical insulators is insufficient, the tip of the capillary in the ion source would be the coldest part of the inlet system. The ion optics of the mobile laser mass spectrometer for on-line trace gas analysis are designed to avoid this problem by defining the tip of the capillary as zero potential. A separate flight tube within the vacuum system is set to negative potential (-1900 V). With zero potential at the capillary, good heat conductors can be used for the inlet system and the tip can be sufficiently heated via heat conduction. For optimization of the heat conduction, a cone instead of a needle was used.

Another typical problem for mass spectrometers used for analytical application is the contamination of the ion source. The TOFMS ion source was set up in an open design, using plates with 75 mm outer diameter and a distance between the plates of

the first stage of 20 mm. With this setup, there was no contamination effect observed.

The whole instrument, including the laser, vacuum pumps, and electronics, is set up in a rack of 0.8 × 1.0 m length and 1.5 m height. The weight is about 250 kg, and the box has wheels and hooks for crane lifting. Additionally, a PC is required for data acquisition. The modular setup can be equipped with compact excimer or Nd:YAG lasers.

INCINERATION PILOT PLANT

The setup of the incineration plant is outlined only briefly. A detailed description of the incineration pilot plant is published elsewhere.^{24,25} The structural principle of a municipal waste incinerator plant can be broken down into the main thermal process and the flue gas purifying unit. In the field of thermal waste treatment, stoker firing systems are frequently applied for incineration processes. Today's flue gas purifying plants are able to keep the emission limits, irrespective of the quality of the results in the main thermal process. But considerably high costs of construction and operation of the plant result from extensive application of these so-called secondary measures. Recent developments focus on the optimization of energy efficiency and the extent of exhaust gas and residual waste flows using primary measures, i.e., optimization of the main thermal process itself. For a review of methods in discussion, see Scholz et al.²⁶ From the technical point of view of the combustion process, coarse waste materials are more difficult to treat than gaseous, liquid, and powdered fuels. For very different successive tasks, like conversion of solid matter and combustion of gases generated, the separation into different process units provides opportunities for individually optimizing each task. To minimize flue gas heat loss and total flow rate and to avoid carbon-loaded residuals, the solid combustibles should be gasified in the first unit. The gas generated in this way can then be independently burned in the second unit with a low total excess air ratio and without additional fuel.

For the optimization of the combustion and gasification in grate systems by primary measures, a pilot plant with a thermal power of about 0.5 MW was developed.^{24,25}

The three steps of the main thermal processes—(i) gasification of solid matter on the grate with air (λ -value_{grate} ≈ 0.4–0.8; the λ -value represents the ratio of the supplied oxygen to the stoichiometric amount required for complete combustion) (I in Figure 1), (ii) postcombustion of the gases almost stoichiometrically (λ -value_{total} ≈ 1.2–1.4) in a combustion chamber system (II in Figure 1), and (iii) heat exchange (III in Figure 1) separately—are shown schematically in the upper right part of Figure 1. The flue gas cleaning system consists of a dust precipitator (IV) and an activated coke filter (V).

The results discussed here were obtained at this pilot plant at two sampling points. The first sampling point (1 in Figure 1) was situated behind the dust precipitator (low temperature) the second one (2 in Figure 1) at the outlet of the combustion chamber (high temperature).

Note that the postcombustion chamber is geometrically separated from the grate. Thus, the postcombustion process can be adjusted independently from the grate conditions. The postcombustion is a gas-phase reaction with a fast response to changes in parameters, e.g., oxygen supply. Therefore, a fast feedback steering of the combustion process is possible if a fast sensor for relevant parameters, e.g., PAHs, is available.

As already mentioned, the pilot plant can be operated using both combustion and gasification modes on the grate with postcombustion in the combustion chamber. Process change from combustion to gasification on the grate is ideally suited for the observation of dynamic processes in the incineration plant. Both time-resolved on-line measurement sequences presented in this paper are recorded during the switch from combustion to gasification on the grate. The CO concentration is registered continuously by the plant's gas analysis system. It should be emphasized that the flue gas purifying plant ensure that the legal emission limits have not been exceeded during such changes of process parameters.

CALIBRATION METHOD AND DETECTION LIMIT

Multiphoton processes are nonlinear optical processes. The theoretical ionization yield is proportional to the product of the laser intensities. Due to unknown REMPI cross sections, the ionization yield cannot be estimated from a laser intensity measurement in general. An adequate calibration procedure therefore is important for analytical applications. Quantification methods can rely on the linearity of the REMPI-TOFMS signal with the concentration of the standard, which has been proven for orders of magnitude down to the parts-per-trillion by volume (pptv) concentration range.^{27,28}

In general, there are two ways for quantifying REMPI-TOFMS analysis results. The first one is off-line comparison to an external calibration standard, and the second one is on-line addition of an internal calibration standard. In the first case, an analyte standard can be used with a well-defined standard sampling. The standard signal is not disturbed by interfering mass peaks, and the integrated peak intensity is well related to the concentration. However, external calibration standards can be used only occasionally. Using internal calibration, the short-term variations of the instrument (e.g., laser intensity and spatial laser beam profile) can also be compensated. The latter is performed either by adding a nonanalyte calibration gas¹⁹ or by using a standard addition method with alternating measurements of the sample and of the sample with an additional standard.¹⁸ The first method allows highly time-resolved measurements, but the possible differences in the spectroscopic properties of analyte and nonanalyte molecules have to be considered. The second method uses an analyte standard, but every second shot has to be used for calibration purpose, and shot-to-shot variations in the signal of the analyte or interfering substances may disturb the differential calibration.

Examining the short-term variations of the setup used here, it turned out that the system's stability is better than ±5% maximum deviation for shot-to-shot signal variations. Thus, the external

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calibration method can be applied. The long-term variations can be supervised by frequent use of the external calibration standard. This analysis has been performed before and after every sequence of measurement, and it turned out that the signal is sufficiently stable over time.

The measurements have been calibrated with ppbv standards prepared dynamically with permeation and diffusion devices²⁹ as indicated in Figure 1. Details of the in-house-designed microdevices will be published elsewhere. Naphthalene has been directly quantified using the external calibration standard. The REMPI signal of the standard has been integrated in a window of 1 amu width. The concentration-to-peak area factor has then been calculated. One sequence of measurement is calibrated by dividing the integrated signal by this calibration factor. Other compounds can be quantified if the relative REMPI cross section at the specified laser wavelength is known. The calibration factors for other PAHs have been determined from GC-REMPI-TOFMS measurements with KrF excimer laser experiments³⁰ and with Nd:YAG laser experiments.¹⁴ These have been adapted to our procedure of measurement in combination with the naphthalene calibration. The latter has been performed in our setup as well as in the setup of the experiments cited above. In the case of different isobaric species, an unambiguous peak identification can be performed using the relative REMPI cross sections and the abundance in incinerator flue gas known from conventional measurements.⁵ Often isobaric molecules differ considerably in one of these properties. Pyrene and fluoranthene have similar flue gas concentrations, but the cross section (REMPI at 266 nm) for pyrene is an order of magnitude larger than that for fluoranthene.¹⁴ For phenanthrene/anthracene, which have similar REMPI cross sections, the peak assignment can be justified using the concentrations in the flue gas, where phenanthrene is abundant (1.09 $\mu\text{g}/\text{m}^3$), while anthracene has not been detected (<0.05 $\mu\text{g}/\text{m}^3$).

The detection limits of REMPI-TOFMS have been determined from several research groups using REMPI-TOFMS devices with a supersonic molecular beam/tunable laser setup. In the following, all detection limits refer to a signal-to-noise relation (S/N) = 1. Cool and co-workers have investigated the detection limits for numerous toxic combustion byproducts.^{27,31} Detection limits in the low ppbv (5 ppbv for naphthalene at 301.6 nm) and 10 pptv ranges (50 pptv for toluene at 266.7 nm) have been achieved for highly selective ionization of aromatic compounds using the S_1 state of the jet-cooled target molecules.²⁷ With improved free-jet setups, reductions in the distance between the nozzle and ionization region and use of different, less selective REMPI transitions detection limits in the low pptv range have been reported.^{28,32}

However, these results cannot be applied for a REMPI-TOFMS setup with effusive molecular beam inlet and fixed-frequency laser ionization. The detection limit for our particular instrument was determined according to the method of Williams et al.³¹ from a TOF mass spectrum of the naphthalene permeation standard. The

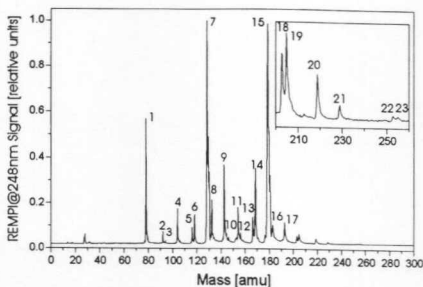


Figure 3. REMPI at 248 nm mass spectrum recorded at sampling point 1 behind the cloth dust filter while the plant was fed with a mixture of wood chips and shredded combustible car parts. The spectrum is averaged over 50 single-shot mass spectra. Please notice that resonance ionization is a soft ionization method with little or no fragmentation. The peak assignment is given in Table 1.

noise level was determined using the variance σ of the amplitude of the signal between mass peaks; the mean value of the noise was defined as baseline. The variance was compared to the signal peak height p of the target molecule in the mass spectrum. The concentration c of the target molecule (naphthalene) was derived from the constant loss of substance due to permeation and from the gas flow through the permeation cell. A value of 58 ppbv has been determined. Finally, the detection limit d is calculated according to

$$d = \frac{c}{p - \bar{m}\sigma}$$

A detection limit of 86 pptv was derived for naphthalene at 248 nm using the KrF excimer laser, and 94 pptv was achieved for naphthalene at 266 nm using the fourth harmonic of the Nd:YAG laser. From mass spectra recorded in the flue gas of the incineration plant with naphthalene concentrations in the 100 pptv range (quantification using the integrated signal as described above), even a detection limit of 25 pptv can be estimated.

These results are not comparable with the results for naphthalene of Cool and co-workers,^{27,31} since we use the strong S_n absorption bands of naphthalene beyond 300 nm, while they use the weak S_1 state as the intermediate state in the REMPI process. For high selectivity, the S_1 has to be used, while for medium selectivity (substance class selective ionization), preferably the overlapping S_n bands of the PAHs are involved in the REMPI process.

It can be summarized that detection limits in the low pptv concentration range have been achieved with several REMPI-TOFMS devices and that the method is thus suitable for on-line monitoring of trace compounds down to pptv concentrations.

ON-LINE MEASUREMENTS

A mass spectrum obtained at the sampling point 1 (Figure 1) behind the heat exchanger and the dust precipitator is shown in Figure 3. The KrF excimer laser at 248 nm was used for ionization, and the mass spectrum is averaged over 50 laser shots,

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Table 1. Peak Allocation of the REMPI at 248 nm Mass Spectrum*

no.	amu	substance
1	78	benzene
2	92	toluene
3	94	phenol
4	104	styrene
5	116	indene
6	118	methylstyrene, indan
7	128	naphthalene
8	132	dimethylstyrene
9	142	methylnaphthalene
10	152	acenaphthylene
11	154	biphenyl, acenaphthene
12	156	dimethylnaphthalene
13	166	fluorene
14	168	methylbiphenyl, dibenzofuran
15	178	phenanthrene, anthracene
16	182	dimethylbiphenyl
17	192	methylphenanthrene, methylanthracene
18	202	pyrene, fluoranthene
19	204	phenylnaphthalene, dihydropyrene
20	218	phenylmethylnaphthalene
21	228	chrysene, benz[a]anthracene, triphenylene, benzo[c]phenanthrene
22	252	benzopyrene, perylene, benzofluoranthene
23	254	dinaphthyl

* Due to the spectroscopic selectivity of the resonance ionization, only aromatic compounds contribute to the signal in the mass spectrum.

with a laser repetition rate of 50 Hz. It is recorded during a short deviation from optimum combustion conditions in the post-combustion chamber. For the assignment of the mass peaks given in Table 1, the following spectral information has been taken into account. With the applied wavelength of 248 nm, most likely only aromatic molecules are ionized, as for 266 nm. Aliphatic molecules without any chromophores exhibit a much larger energy gap between S_1 and S_0 (excitation step) and a higher ionization potential. Further on, chromophores have a distinct spectral region of absorption.³³ Therefore, most organic molecules cannot contribute to the REMPI mass spectra of given laser wavelength since they do not fulfill the resonance conditions. Aromatic molecules in general are likely to be ionized with wavelengths of 248 or 266 nm, but many substituted aromatics, e.g., halogen-substituted aromatics, can be excluded due to spectroscopic reasons.³⁴ The mass spectrum shows benzene, toluene, PAHs, and methylated PAHs as well as some oxygenated compounds, e.g., phenol. The incinerator was fed with wood and shredded combustible car parts, and in comparison to the mass spectra obtained with a painted wood feedstock³⁵ this mass spectrum shows a styrene peak additionally, probably a decomposition product of the polystyrene present in the shredded car parts. The isobaric substances (up to mass 202 amu) in Table 1 are listed according to their abundance in the flue gas taken from conventional measurements of volatile organic compounds in the emissions of waste incineration plants.⁵ For convenience, in the

following only the most abundant substance will be used to describe the laser mass spectrometric information. In the mass spectrum, small peaks due to molecules in high concentration (e.g., N_2 and CO , 28 amu) appear also. These molecular ions are formed not by resonant multiphoton ionization but by laser-induced electron ionization. Since the laser crosses the molecular beam right under the needle tip (Figure 2), electrons are released by photons from the edge of the laser beam.

The first sampling point represents stack gas conditions. The temperature of the flue gas is 320–380 K. This is close to the dew point, and the temperature of the probing system is carefully adjusted to avoid condensation effects. The capillary sample inlet of the laser mass spectrometer from the quartz glass tube (Figure 2a) into the ion source (Figure 2b) is heated to 530 K anyway.

Due to the re-formation of PAHs after combustion in the colder parts of the plant, benzene and some PAHs can be detected (even under optimum combustion conditions). However, due to the relatively low temperature in the flue gas cleaning system and the large surfaces in, e.g., the cloth dust filter, no transient emission changes from the primary combustion process can be observed here. Deviations from optimum combustion conditions, causing strong emission peaks with a duration of a few minutes in the raw gas, are registered as broad emission maxima with a time range of 30–50 min.³⁵ Thus, the first sampling point is well suited for examination of the behavior of the devices behind the combustion chamber. This point of measurement, however, cannot be used for observation of transient phenomena in the combustion dynamic itself. A measurement point for that purpose has to be close to the combustion process.

Thus, the sampling point 2 has been chosen directly in the postcombustion chamber. The flue gas temperature is 900–1000 K. During changes of the combustion conditions, the formation of PAHs can be observed, and a variety of PAHs and related compounds can be found.

The time-resolved on-line measurements shown in Figure 4 are recorded using the KrF excimer at 248 nm (Figure 4a) and the fourth harmonic of a Nd:YAG laser at 266 nm (Figure 4b) for one-color REMPI. In both experiments, conversion from combustion to gasification on the grate with short emission peaks of PAHs is observed. While reducing the primary oxygen supply through the grate to achieve gasification, malfunctions occurred. The secondary oxygen supply in the postcombustion chamber obviously was not in the optimum range for a short time, resulting in a lack of oxygen in the combustion process. This leads to production of PAHs, which is visible from the REMPI-TOFMS on-line measurements depicted in Figure 4. While the group of substances ionized at 266-nm wavelength is qualitatively almost the same as that ionized at 248 nm, the individual ionization cross sections of the compounds may be different, and the peak heights in the mass spectra are not comparable. In Figure 4, parts of the sequences of measurement are depicted in a three-dimensional plot, with the coordinates mass, time, and signal intensity showing the highly transient behavior of PAHs and the multitude of information that is acquired in a sequence of REMPI-TOFMS on-line measurements. The temporal development of the concentration of particular compounds can be realized at one glance, as well as the a whole mass spectrum at a particular time. Note that in Figure 4a and b, only a small section of a measurement

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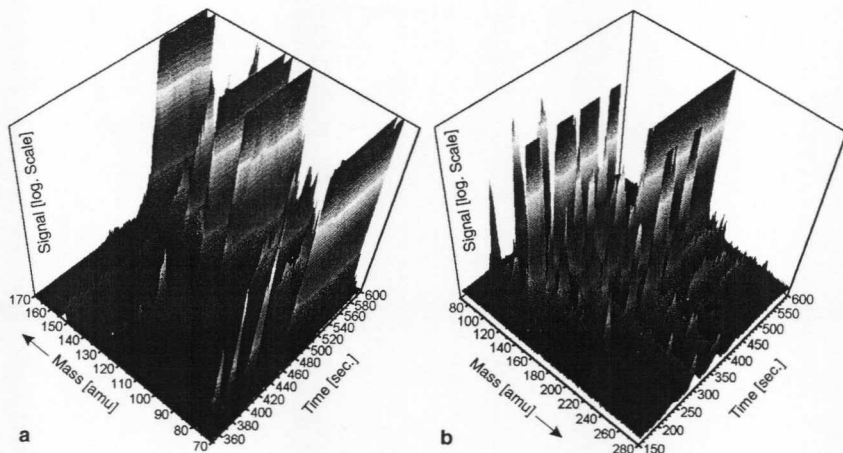


Figure 4. REMPI on-line monitoring of dynamic processes in the incineration plant (sampling point 2). The 3D plots show the signal in the dimensions mass and time; the signal is scaled logarithmic. Plot a (REMPI at 248 nm) shows flickering-like processes for benzene (78 amu) and naphthalene (128 amu) and in the background signal peaks indicating nonoptimum combustion conditions. Plot b (REMPI at 266 nm) shows transient behavior of different PAHs during a change of combustion conditions. Note that, for better presentation of the high masses, the mass scale in plot b is reversed. The multitude of different time behaviors of PAHs can be seen.

sequence is shown on an enlarged scale in order to allow a detailed view of the emission dynamics and time resolution of the measurement. In particular, transient phenomena, such as the three short benzene emission peaks (78 amu) in Figure 4a, are more readily recognizable in this form of data presentation.

To emphasize a couple of PAH time concentration profiles of individual substances, cuts through these 3D plots are made parallel to the time axis. Quantification of the signal can be performed for these concentration-to-time profiles of individual substances. These profiles are created from the set of stored mass spectra by setting the desired mass windows, integrating over a window with 1 amu width, and representing the results for the sequence of measurements.

In Figure 5, four concentration-to-time profiles from the REMPI at 266 nm measurement (see Figure 4b) generated in the way described above are depicted. The data are not averaged; the time resolution is 200 ms. The naphthalene trace shows four strong peaks; additionally, there are some deviations from baseline at the end of the sequence. Fluorene shows only three major peaks, and the fluorene peaks are shifted toward the naphthalene peaks. Phenanthrene exhibits a completely different behavior: while the first two peaks are small in comparison to that of naphthalene, the third one is huge and is the broadest peak observed in this sequence. The first four peaks of pyrene are similar to those of naphthalene, but the fifth and the sixth peaks are unique to the pyrene trace, and the following two peaks can be found as very small peaks in the naphthalene trace only. Looking at the fast changes in the pyrene trace, e.g., $fwhm = 4$ s for the first peak, a memory effect or deception through retention of phenanthrene in the inlet system can be excluded.

The concentration-to-time profiles in Figure 6 are recorded using the KrF excimer laser at 248 nm for the ionization process (see Figure 4a). The transient recorder settings have been optimized for highly sensitive measurement. As a consequence, the upper limit for the concentration that can be recorded is reduced due to the limited dynamic range of the transient recorder (8 bit). With a new revision of the data acquisition software, this can be overcome by shot-to-shot changes of the transient recorder card settings for alternating measurement of different concentration ranges. With the most sensitive settings, the beginning of the process conversion on the grate can be observed best. The first change in combustion parameters results in a step of about 100 pptv in the naphthalene trace at about 150–200 s after starting the measurement, followed by three short peaks with low ppbv concentrations. The uppermost trace in Figure 4 represents an enlarged view on the first 500 s of the naphthalene trace (Figure 4, second trace). This enlarged trace is generated by averaging over 10 mass spectra and shows the 100 pptv concentration step and combustion process-related fluctuations (particularly significant at 245 and 275). About 250 s after the slight increase in the naphthalene concentration, the flickering of the naphthalene trace indicates that the process starts to get instationary. At 500 s, a sudden rise of the naphthalene trace shows that the postcombustion has ceased to work acceptably. As shown in the first 300 s of this sequence, under optimum combustion conditions, only phenanthrene (178 amu) has a strong signal in a single-shot mass spectrum. During the first part of the malfunction starting at 500 s, naphthalene has maximum values, while the larger PAHs are showing just short and small peaks. The rise of fluorene is slightly delayed toward the rise of naphthalene, and the trace shows a

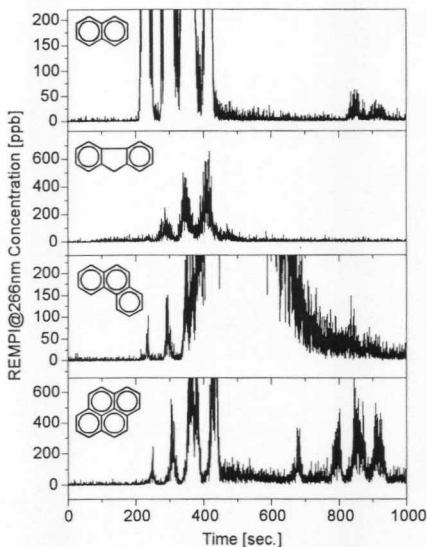


Figure 5. REMPI at 266 nm concentration–time profiles of selected PAHs during the dynamic process depicted in Figure 4b. The profiles are generated by integration of the single-shot mass spectra within a window of 1 amu width for selected masses, here 128, 166, 178, and 202 amu, respectively. The time resolution is 200 ms. The first peak in the pyrene trace has a fwhm of 4 s. The quantification has been performed using the external gas standard (see Figure 1).

fluctuating signal that indicates that there are dynamic processes while the naphthalene concentration is high. A steep increase in the fluorene concentration shows the peak of the malfunction; afterward naphthalene and fluorene are falling simultaneously to nearly normal values, while a slow rise of phenanthrene indicates a qualitatively different second part of the malfunction. In the second part, phenanthrene rises and later on dominates with a broad emission peak. This is in agreement with the previously shown profile (Figure 5) and other measurements. The phenanthrene concentration changes very slowly and is the only trace without any sudden changes in the signal.

The CO concentration of the flue gas in the postcombustion chamber has been recorded continuously by the emission control device of the plant with a time resolution of 1 min. The flue gas is transferred via a heated transfer line to the sensor. Due to this transfer, a time delay of about 2 min between the appearance of the concentration change and the registration of the change through the sensors occurred. For comparing the conventional measurements with the REMPI on-line PAH analysis in Figure 7, this time delay was corrected. But it is important to emphasize that the reaction of the sensor is 2 min after its registration by on-line REMPI-TOFMS. The upper trace of Figure 7 represents the CO concentration and the lower traces the naphthalene (black) and phenanthrene (gray) concentrations, respectively, all of them on a large time scale. The CO concentration is increasing with the beginning of the registration of aromatic compounds. During

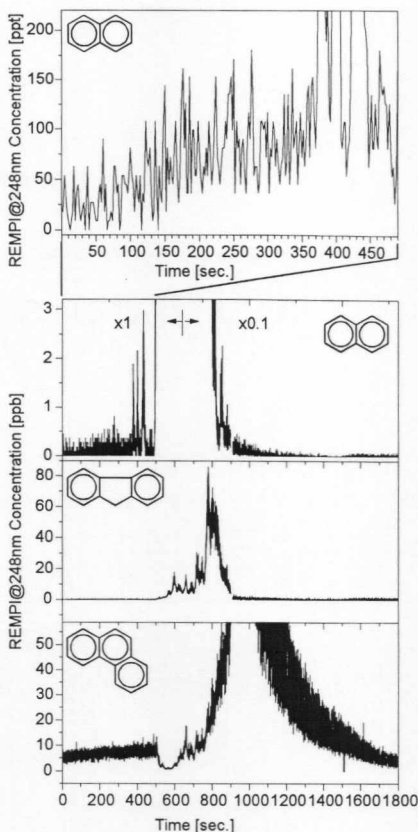


Figure 6. REMPI at 248 nm concentration–time profiles. Data analysis and quantification are similar to those of the profile in Figure 5. Two 128-amu traces (top and second one), one 166-amu trace (third trace), and one 178-amu trace (bottom) are shown. The uppermost trace shows an enlarged section of the second trace (naphthalene). The data here are averaged over 10 laser shots (0.5-Hz time resolution) in order to show the presence of combustion process-related fluctuations on a 100 pptv concentration scale such as the 100 pptv step at approximately 200 s. Please note that the second trace (naphthalene) is depicted in two different scalings.

the malfunction, the CO sensor is saturated. The equivalent PAH pattern exhibits a broad maximum for naphthalene, while fluorene shows a structured dynamic behavior as discussed already (see Figure 6). Afterward, phenanthrene is rising. Obviously the phenanthrene peak is not correlated with the CO concentration, which is falling to normal level while the 178 amu peak reaches its maximum. As a consequence, the CO concentration is not a good indicator of PAH-related toxicity of the flue gas. The lower part of Figure 7 demonstrates on a short time scale of 120 s that, with on-line REMPI-TOFMS, dynamic emission processes can be

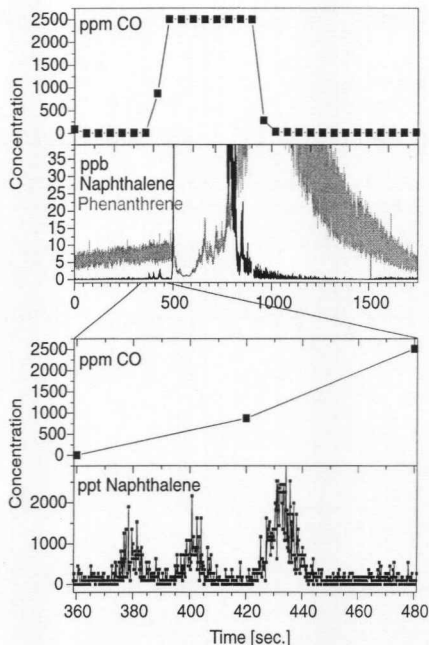


Figure 7. Conventional on-line monitoring of CO (upper traces) versus REMPI at 248 nm on-line monitoring of PAHs. Here, naphthalene and phenanthrene (lower traces) are on two different time scales: the whole process (upper picture) and a 2-min sequence with flickering of naphthalene (lower picture). The time resolution of the CO monitoring and the REMPI PAH monitoring is 60 s and 200 ms, respectively. The CO sensor is installed far from the plant, and the time difference of 2 min between sampling and registration has been corrected for this comparison.

observed that are not resolvable by the conventional flue gas analysis. The depicted measurement represents a time resolution of 200 ms.

This unexpected diversity in behaviors of PAHs shows that, with on-line REMPI-TOFMS measurements, an interesting new field of combustion research is opened up in addition to its application for emission monitoring.

DISCUSSION AND OUTLOOK

On-line real-time detection of PAHs with REMPI-TOFMS is a powerful tool for fundamental and applied combustion research. Real-time observation of the formation of PAHs is possible by direct flame sampling methods^{16–18} and now by probing the flue gas at different points in an incineration plant or in a flow reactor. With advanced data acquisition and analysis, the whole mass spectrometric information can be provided at one glance using 3D contour plots, as shown in Figure 8. The data from the previous experiments (Figures 5 and 6) are used to build up contour plots with the dimensions time and molecular mass. Both plots show the process conversion from combustion to gasification.

In Figure 8a, the REMPI at 248 nm contour plot is depicted (equivalent to the concentration profiles in Figure 6). At 900 s, the attenuation setting of the transient recorder has been changed, with the consequences already discussed above. The dynamic phase between 700 and 800 s is characterized by the broad emission peaks of benzene (78 amu) and naphthalene (128 amu). Figure 8b shows the REMPI at 266 nm measurement as a contour plot. The dynamic phase here is represented by four short emission maxima of benzene, naphthalene, and various other PAHs. The differences in the depicted relative benzene intensities are a consequence of the different laser wavelengths; with KrF benzene is ionized very efficiently, while with Nd:YAG at 266 nm the benzene intensity is poor.

While the precursors of benzene (e.g., acetylene, butadiene)³⁶ are not accessible with the laser wavelengths used, the intermediates in the growing of PAHs after benzene is formed can be observed. PAHs are grown by acetylene addition^{37,38} and furthermore can grow by addition of two PAHs.^{39,40} Examples of typical intermediates are phenylacetylene (102 amu) and indene (116 amu), both observed in the REMPI-TOFMS measurements. In general, the aromatic compounds from benzene (78 amu) to naphthalene (128 amu) are the first occurring at nonoptimum combustion conditions. The variety of substances between naphthalene and phenanthrene (178 amu) follows with notably different individual time behaviors. Despite the different process dynamic in Figure 8a and 8b, phenanthrene in both measurements shows a delayed and nonstructured broad concentration maximum. The second contour plot (REMPI at 266 nm) further shows that the PAHs larger than 178 amu can exhibit again fast concentration changes similar to naphthalene but additionally can show individual behavior in the following, e.g., the peaks of pyrene (202 amu) around 800 s and the broad maximum of the 252 amu PAHs between 700 and 900 s.

Both observed conversions of the combustion process can be divided into two phases: a dynamic phase in the beginning, showing highly individual transient emission peaks of a variety of PAHs and substituted PAHs from benzene to 276 amu (e.g., benzo[ghi]perylene, see also Figure 4b), and a postdynamic phase, with PAHs showing broad, unstructured emission maxima. The postdynamic phase starts with phenanthrene and continues with methylphenanthrene followed by pyrene. In this phase, there are no aromatic compounds smaller than phenanthrene observed, with an exception in the Nd:YAG contour plot around 900s, where another dynamic process can be seen. This indicates that there is a kind of memory effect in the plant. This is possibly due to adsorption and/or reactions on surfaces with subsequent desorption in broad emission peaks. This behavior should be determined by the gas dynamics in the plant and might be a property of the individual plant. It is important to emphasize that the fast dynamics observed up to 276 amu exclude that memory effects

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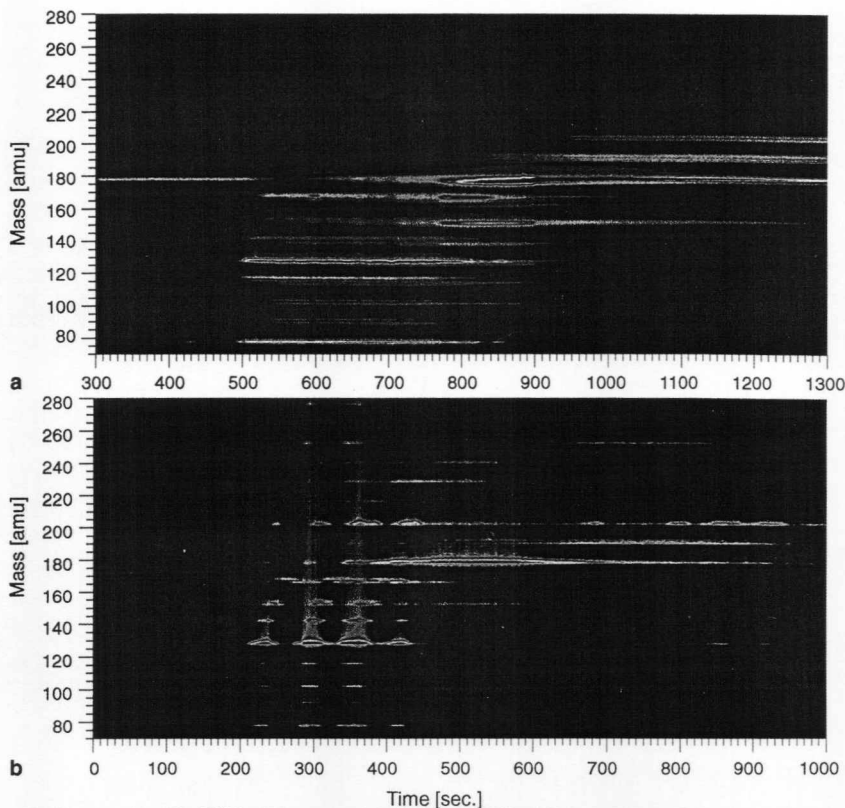


Figure 8. 3D contour plots of the REMPI at 248 nm mass spectra (a) and the REMPI at 266 nm mass spectra (b). The color map is made with logarithmic scaling. The upper plot shows a dynamic phase with concentration peaks from benzene (78 amu) to dibenzobenzofuran (168 amu) (see also Figure 6), which is followed by a phase with broad peaks of phenanthrene (178 amu) and pyrene (202 amu). In the lower plot, the dynamic phase shows three or four peaks for benzene (78 amu) up to 276 amu (e.g. benzo[*ghi*]perylene) with individual time behavior (see also Figure 5), again followed by a broad phenanthrene peak (178 amu).

in the sampling system of the REMPI-TOFMS device exist, which might falsify the measurement.

Obviously, a pattern of typical PAH time-concentration profiles can be found, and further studies will investigate the differences in dynamic processes and the postdynamic phenomena observed. With on-line measurement of PAH kinetics under well-defined conditions, information on the detailed reactions is accessible. In combination with methods for modeling the gas dynamics, temperature, and CO concentration in an incineration plant, on-line measurements of PAHs can contribute to the development of advanced incineration technology. These contour plots can be constructed in real time during the on-line measurement using the data analysis tools implemented in the LabVIEW programming language, and patterns can be compared with a library of different malfunctions using pattern recognition. The fast and subtly differentiated response and the possibility to record the important

PAHs directly predestine the REMPI-TOFMS device for use as a sensor for feedback control of combustion processes. Parameters might be found that will be useful for active control of combustion parameters such as air supply or flue gas recirculation.

In this work, PAHs have been observed selectively as a substance class. This is best suited for a supervision of the combustion dynamics and for process control. Another application of on-line REMPI-TOFMS is the on-line emission monitoring of selected target substances. For detailed observation of a single PAH species, isomer-selective ionization is required. An application would be the monitoring of benzo[*a*]pyrene, which is used as an indicator for PAH-related toxicity. The selective detection of benzo[*a*]pyrene requires separation from the isomer benzo[*e*]pyrene, perylene, and benzo[*fluoranthene*]. The REMPI spectra, of e.g., perylene and benzo[*a*]pyrene⁴¹ demonstrate that this separation is possible. As outlined before, for isomer-selective

resonant ionization, a supersonic beam inlet system is required. Furthermore, due to the low energy of the S_1 of PAHs, the isomer-selective ionization of the PAHs, in general, requires a two-color REMPI scheme.⁴² It is still a challenge to run a two-color laser system in an industrial environment. However, with recent and upcoming developments in laser technology, e.g., encapsulated, tunable, all-solid-state lasers, a sufficiently robust two-laser setup may be possible, and the isomer-selective on-line monitoring of benzo[a]pyrene might justify the effort.

Other prominent toxic combustion byproducts are polychlorinated dioxins and furans (PCDD/F). The PCDD/F have ppqv concentrations in the flue gas of modern incineration plants and thus are far beyond today's detection limits for on-line REMPI-TOFMS. The concentration of toxic PCDD/F congeners, e.g., in a flue gas sample, is expressed in the International Toxicity Equivalence value (I-TEQ). The I-TEQ value is based on toxicological data and gives the equivalent amount of 2,3,7,8-TCDD (the most toxic congener) representing the toxicity of all present PCDD/F congeners. Numerous studies have proposed and established so-called indicator parameter relations of chlorinated aromatic molecules, e.g., pentachlorobenzene and the I-TEQ value.^{43,44} These indicator substances have a flue gas concentration that is orders of magnitudes higher than the dioxin concentration and could be analyzed by REMPI-TOFMS.

The application of REMPI for on-line monitoring of chlorinated aromatics was proposed a decade ago,⁴⁵ but for spectroscopic reasons, e.g., short lifetime of the intermediate state due to fast intersystem crossing (ISC), a sophisticated two-color REMPI setup is required for all higher chlorinated aromatic molecules. The spectroscopic aspects of an application of REMPI for on-line monitoring of chlorinated aromatic hydrocarbons as indicator compounds have been examined in detail.³⁴ Only the low chlorinated aromatic molecules are accessible with a one-color REMPI arrangement. Recent investigations point out that 1,2-dichlorobenzene and also monochlorobenzene concentrations are good indicator parameters for the PCDD/F concentration in the flue gas (i.e. the I-TEQ -value).⁴⁶ This compounds can be easily detected using a one-color REMPI scheme with a tunable laser. Recently we succeeded in detecting monochlorobenzene (MCB) on-line in the flue gas of a German industrial hazardous waste incinerator (22 MW thermal power) in the 100 pptv concentration range with a mobile REMPI-TOFMS device (REMPI at 269.8 nm). The MCB concentration in the flue gas, measured on-line by REMPI-TOFMS prior to the dust precipitator of the plant, shows variations in time due to changes of the combustion conditions.⁴⁷ Together with the indicator parameter relation between PCDD/F and MCB,⁴⁶ thus an indirect on-line measurement of the PCDD/F

formation and emission in the flue gas of, e.g., waste incinerators is possible.⁴⁷

In addition to monitoring combustion flue gas, numerous applications for on-line REMPI-TOFMS measurements are possible. Monitoring of technical processing in food technology, like roasting of coffee,²⁰ is another application already realized.

With the use of recently developed small Nd:YAG lasers, optical filters for beam direction, and a small and simple TOFMS, the development of a robust and compact REMPI-based PAH sensor is possible.

CONCLUSION

REMPI-TOFMS is suitable for on-line measurements of PAHs and PCDD/F indicators in the flue gas of waste incinerators. The mobile device was designed and constructed to work reliably in the dusty and hot atmosphere and on the vibrating floor of an industrial plant. A sampling and inlet system for direct probing of the untreated flue gas has been constructed. The system allows sampling of PAHs up to 280 amu without retention or memory effects. The combination of effusive inlet and fixed-frequency laser (either KrF excimer at 248 nm or fourth harmonic Nd:YAG at 266 nm) allows a compound class-selective ionization of PAHs with sufficient sensitivity. Variations in the 100 pptv concentration region for naphthalene, for instance, have been detected. Quantification has been performed using external dynamic gas standards. The observed PAH concentration profiles show a variety of different time behaviors for the different substances during transient processes. It has been shown that, even in large-scale incinerators, fast and short emission peaks occur (e.g., fwhm 4 s for pyrene). The CO concentration turned out to have little correlation to the concentration of larger PAHs such as phenanthrene. The PAH concentrations show a variety of different time behaviors, ranging from similar but slightly shifted dynamics to completely individual emission maxima. It is possible to define qualitatively different phases during a malfunction, the dynamic phase with PAHs showing fast transient concentration changes and the postdynamic phase with broad emission maxima of larger PAHs and the absence of benzene and small PAHs. The acquisition of the total TOFMS mass spectrometric information allows the creation of concentration-to-time profiles and contour plots of the combustion dynamic. The use of these parameters may lead to improvement of the combustion plant design as well as a feedback control of the combustion process itself as a primary measure for reducing pollutants.

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