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Mobile resonance enhanced multiphoton ionisation–time-of-flight mass spectrometer with a novel hybrid laser desorption/molecular beam ion source for rapid detection of aromatic trace compounds from gas phase and solid samples

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Abstract

A mobile, field applicable resonance enhanced multiphoton ionisation–time-of-flight mass spectrometer (REMPI–TOFMS) for direct-inlet gas-phase analysis as well as for characterisation of solid samples, has been developed. For solid-sample analysis, laser desorption (LD) with IR-laser pulses is used for volatilisation of the neutral analytes from a target in the ion source prior to REMPI–TOFMS analysis. For direct inlet gas-phase analysis, a needle gas inlet is used and the formed molecular beam is REMPI-ionised directly in the ion source. A special ion source was developed, which can be rapidly interchanged between the REMPI–TOFMS and the LD–REMPI–TOFMS modes. The system is equipped with a tuneable optical parametrical oscillator (OPO)-laser system. The analytical properties are characterised for both modes of operations. In both cases, analytical performance is similar to that achieved with instruments specifically designed for either gas-phase or solid-phase characterisation. Results from field measurements of a wood combustion flue gas of a 174 kW bio mass furnace are given. Gas-phase analysis was applied for time-resolved on-line REMPI–TOFMS of the semi-volatile aromatic flue gas constituents. The low-volatile aromatic compounds, which were precipitated with the particulate matter in the filtering unit of the sampling train, were characterised by direct LD–REMPI–TOFMS of the glass fibre filter material. By combining the gas-phase and particulate results a rather comprehensive characterisation of the aromatic species present in the flue gas (i.e. aerosol – gas phase plus particulate matter) was achieved.
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1. Introduction

In the last decades, some analytical methods based on laser ionisation mass spectrometry were developed and found an increasing application field in analytical chemistry. Most prominent technique in this context is the matrix-assisted laser desorption/ionisation mass spectrometry (MALDI–MS) [1] predominantly used for analysis of large molecular weight bio molecules such as proteins. However, several other laser-based mass spectrometry techniques including laser desorption (LD) approaches have been established.

The resonance-enhanced multiphoton ionisation (REMPI) [2–6] is a soft gas-phase ionisation method. As the technique is based on pulsed lasers it preferably is coupled to time-of-flight mass spectrometry (TOFMS). The REMPI–TOFMS technique is established as an analytical method for on-line monitoring of traces of aromatic species – such as polycyclic aromatic hydrocarbons (PAH) – in complex gas mixtures. The gas sample can be directly introduced into the ion source

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of the mass spectrometer via a thin tubing or capillary, allowing fast on-line analysis with down to sub-second time resolution. Mobile REMPI–TOFMS instruments were developed for on-site real-time process analysis at e.g. automotive engine test facilities [4], coffee roasting facilities [7], incineration or pyrolysis test reactors [8,9], bio mass/wood combustion plants [5] or municipal and hazardous waste incineration plants [6,10,11]. A similar straight-forward analysis of solid samples by REMPI–TOFMS, however, is not possible. Prior to the ionisation step the chemical compounds of interest need to be volatilised. An appropriate volatilisation technique for pulsed laser ionisation (REMPI or single photon ionisation (SPI)) mass spectrometry is laser desorption [12–22].

In LD, a laser pulse is slightly focused onto the surface of the sample target and induces prompt evaporation of the neutral analyte molecules. With higher desorption laser intensities ($\sim 10^7$–10^{10} W/cm^2), however, also ionisation of elements and molecular fragments occur (laser desorption/ionisation (LDI)). Early laser desorption mass spectrometric experiments generally utilised the LDI process for ion generation [23]. The LDI approach is often used for microprobe analysis [23–26] and recently got new attention in the field of single particle mass spectrometry [27,28]. One drawback of LDI–MS are matrix effects, although successful applications for qualitatively or semi-quantitatively detection of several elements and some inorganic species are reported [26]. Furthermore a soft LDI of the rather stable polycyclic aromatic hydrocarbons from carbonaceous matrices (i.e. soot) is possible [29–32]. In the LDI process, however, usually only a minor fraction of the desorbed species is ionised. Furthermore the ionisation yield of one specific compound strongly depends on the chemical composition of the desorption plume and the total number of formed ions. Consequently several laser desorption–postionisation experiments were developed, where the laser desorption process (i.e. the volatilisation of the neutral analytes) is timely and spatially separated from the ion formation process. In principle both processes – desorption and ionisation – can be optimised independently and thus matrix effects can be minimised. Two general experimental strategies for combination of laser desorption with resonance enhanced multiphoton (post)ionisation (LD–REMPI) have been realised.

In the first, rather complicated strategy, the laser-desorbed analytes are injected either into a supersonic jet (SSJ) gas pulse [12–14,20,22] or into a thermalisation gas pulse [33]. The hot laser desorbed molecules are cooled by in-coupling into the SSJ. This set-up has been realised by several research groups in slightly different variations. By this approach, rotational temperatures of laser desorbed molecules of 3 K and below are achievable. Supersonic jet cooled molecules often exhibit highly resolved, well-structured UV-spectra, which can be used for selective REMPI ionisation [22]. However, the pulses SSJ set-up is rather sophisticated. Recently a simplified set-up using not a supersonic beam

but a pulsed thermalisation gas pulse was reported and successfully applied for spectroscopic and analytical purposes [33].

The second, considerably less complicated strategy does not use any gas inlet. The REMPI post-ionisation is performed in the direct vicinity of the desorption spot within the ion source. Some microseconds after the impact of the desorption laser the UV-laser pulse for REMPI post-ionisation is fired and ionises the desorbed species [16–18,21,34,35]. Usually the laser desorption sample target also functions as repeller electrode for the mass spectrometer. This approach is named LD–REMPI–TOFMS. Recently, this approach was also realised for single-particle laser mass spectrometry [36].

In this paper, a newly developed laser mass spectrometer is described, which can perform on-line REMPI–TOFMS analysis of gas-phase compounds (Fig. 1A) and analysis of low-volatile aromatic species from solid samples by LD–REMPI post-ionisation of the desorbed neutral molecules (LD–REMPI–MS; Fig. 1B). The new mobile laser mass spectrometer allows fast on-site analysis of e.g. gaseous and solid-phase combustion products (aerosol particles, fly and boiler ashes, slag). Key part of the laser mass spectrometer is a novel ion source, which can be rapidly interchanged between the gas-phase REMPI–TOFMS und the solid-phase LD–REMPI–TOFMS modes (Fig. 1C).

2. Experimental

The instrument described here is designed as mobile analytical device, suited for laboratory use as well as for field measurements. The mobile instrument is equipped with a custom made time-of-flight mass spectrometer (S. Kaesdorf, Geräte für Forschung und Industrie, Munich, Germany) and can be used in linear or reflectron mode. When used in reflectron mode, the field-free drift region is 801 mm long and a mass resolution ($R_{50\%}$) of 1100 at 78 m/z (gas-phase ionisation) is achievable. The laser system is based on an Nd:YAG-laser (Quanta Ray INDI 50-10, Spectra Physics, Mountain View, CA, USA), which includes devices for generation of the third and fourth harmonic frequencies (i.e. 355 and 266 nm). The 266 nm pulses can be used directly for REMPI ionisation. With the 355 nm pulses an optical parametrical oscillator (OPO with second harmonic generation unit, custom made by GWU-Lasertechnik, Erftstadt, Germany) is pumped for generation of tuneable coherent pulses in the wavelengths range 220–350 nm with output pulse energies between 0.5 and 2.5 mJ/pulse. The output pulse bandwidth is nearly constant ($\sim$5 cm^{-1}) in the whole tuning range (phase matching type II OPO-process). The OPO-system is mounted in a thermally isolated box on top of the instrument cabinet, which is kept on a constant temperature by a heat exchanger system. The heat exchanger system is connected to the thermalised cooling circuit of the YAG-laser (air/water cooler) to allow stable conditions even for field measurements under rough environmental conditions (e.g. at
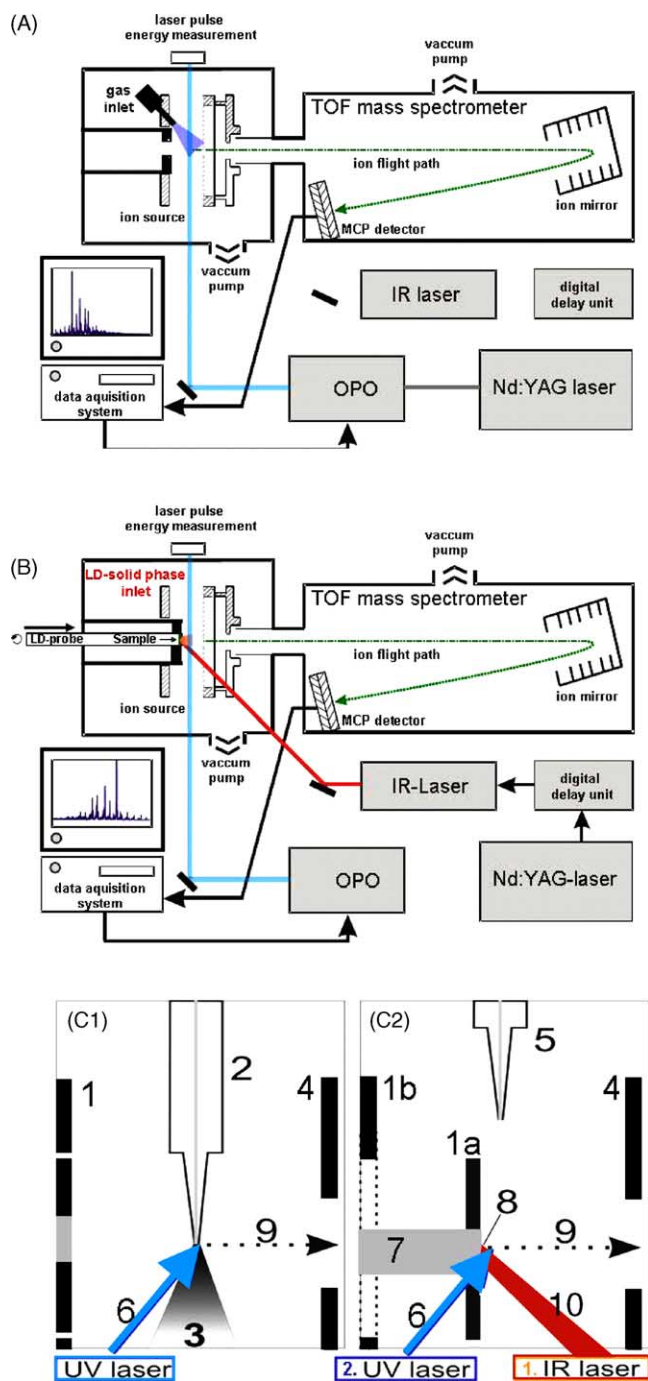
Fig. 1. (A) Instrumental scheme, REMPI–TOFMS (gas phase) mode; (B) instrumental scheme, LD–REMPI–TOFMS (solid phase) mode; (C) schematic representation of the two ion source modes: C1: gas-phase measurement (REMPI–TOFMS) and C2: laser desorption measurement (LD–REMPI–TOFMS). Assignment: **1** repeller electrode (gas-phase mode), **1a** shifted movable inner part of the repeller electrode (LD-mode), **1b** outer part of the repeller electrode, **2** heated gas-phase inlet needle with fused silica capillary for sample transfer for gas-phase mode (with straight opening for effusive molecular beam or restriction nozzle for supersonic molecular beam), **3** effusive or supersonic molecular beam, **4** first extraction electrode, **5** withdrawn gas-phase inlet needle (LD-mode), **6** UV-laser for REMPI (gas-phase mode and LD-mode), **7** probe for laser desorption target (LD-mode), **8** laser desorption target (LD-mode), **9** ion trajectory to TOFMS, **10** IR-laser for laser desorption (LD-mode).

industrial combustion plants). The OPO output wavelength is constantly controlled by a wave meter (λ-meter LRL-005, ATOS GmbH, Germany). Furthermore a small CO_2-laser (μ-TEA, Laser Science Inc., MA, USA) for laser desorption is integrated. The CO_2-laser generates 10.6 μm IR pulses of 15 mJ pulse energy with ca. 100 ns pulse width. The energy of the desorption laser can be adjusted by a variable focal aperture (iris) located directly in front of the focusing optics. In addition to the laser systems and the TOF mass spectrometer, all the required periphery is integrated in a single dust shielded rack of the dimensions 130 cm $\times$ 70 cm $\times$ 157 cm. This includes the instrument steering electronics the data acquisition system as well the as vacuum control units. The data acquisition is based on an 8-bit PC transient recorder card (DP110, Acqiris, Switzerland) and can be performed with an acquisition rate of up 1 GS/s (250 MHz bandwidth). Data acquisition, treatment and handling are done with a home written, LabView (National Instruments, USA) based software package [5]. A diffusion-/permeation-cell calibration gas generator for quantification of the gas-phase measurements is also included in the system [5,37,38].

The novel key part of the new system is a Whiley McLaren-type [39] TOFMS-ion source, which can be switched within seconds from the on-line REMPI gas-phase measurement mode to the LD–REMPI post-ionisation measurement mode for analysis of solid samples. Similar as in preceding instruments, the gas-phase inlet system is based on a needle type inlet for generation of either a continuous effusive molecular beam [5,11] or a supersonic jet [40]. The heated inlet needle reaches in the centre of the ion source and is on electrical ground potential. The REMPI ionisation occurs directly underneath (1–2 mm) the needle tip [5]. For a rapid change between gas-phase REMPI–TOFMS and laser desorption REMPI–TOFMS analysis it is important not to change the position of the ionisation laser (OPO or 266 nm Nd:YAG pulses) as the laser adjustment procedure is critical and time consuming. Therefore, a special adjustable ion source allows rapid change between REMPI (gas phase) and LD–REMPI mode without changing the parameters of the ionisation laser. When the system is changed from gas-phase mode to laser desorption mode, the laser desorption target disk (ϕ = 6 mm), which is mounted on the tip of a sampling probe, is inserted via an air-lock from behind the repeller electrode. The spherical repeller electrode (ϕ = 68 mm) consists of a movable inner part (ϕ = 6 mm) and a fixed concentric outer part. The movable core of the repeller electrode exhibits a central opening (ϕ = 6 mm) for supplying the desorption target into the ion source. This part of the repeller can be moved towards the centre of the ion source. In order to operate the instrument in the LD–REMPI mode, the gas-phase inlet needle needs to be withdrawn from the ion source. For this purpose, the inlet flange is mounted on a bellows whereby the height of inlet flange position can be adjusted and fixed by an external mounting. The inner part of the repeller electrode is subsequently moved towards the centre of the ion source and

the LD-probe is inserted through the air lock (see Fig. 1C). The movable inner part of the repeller electrode is connected via gliding contacts with the high voltage supply. Due to the shift of the central part of the repeller electrode, the whole geometry of the ion source is changed. Therefore, a different set of voltage settings is required for gas-phase and solid-phase mode. For LD–REMPI, IR-laser pulses (CO_2-laser, 10.6 μm, 1 mJ) are focused on the desorption target surface (φ = 500 μm) for soft desorption of chemical compounds corresponding to a power density of 5×10^6 W/cm². An important variable for the optimisation of the LD–REMPI scheme is the delay t_D between the IR desorption laser pulse and the UV-laser pulse. The optimal t_D time for the current experiments was 15 μs. For triggering, the internal clock of the Nd:YAG-laser was used as 10 Hz master trigger. The data acquisition as well as a digital delay unit for controlling t_D is triggered by the synchronised output TTL-pulse signal of the YAG-laser. The digital delay unit then triggers the IR-laser of the respective following cycle after 100 ms t_D. The LD-probe is rotated by a small stepper motor in order to subsequently refresh the LD-target surface during the measurement.

In Fig. 1A and B, the beam paths for the laser(s) and position of ion source and inlet needle schematically are given for the gas-phase and laser desorption modes. Please note that in case of LD–REMPI measurements it is not necessary to block the inlet flow trough the gas-phase inlet capillary. The inlet flow, however, causes a slightly reduced LD–REMPI signal (approximately by a factor of two), most likely due to disturbance of the desorption plume by the increased ion source pressure.

3. Results

3.1. Direct gas inlet mode for gas-phase characterisation

In the gas-phase mode, the geometry of the ion source is equivalent to similar REMPI–TOFMS instruments, which were designed exclusively for gas-phase measurements [5,11,40]. Expectantly, similar gas-phase analytical properties (i.e. limits of detection (LOD)) were obtained. For example, with REMPI–TOFMS at a wavelength of 275 nm (OPO) and a pulse energy of 300 μJ (OPO spot size: 0.025 mm², power density: 1.5×10^7 W/cm²), the following limits of detection were determined for 100 averaged spectra (10 s measurement time, analytes were supplied by permeation/diffusion tube-based standard gas generator [5]) at a signal to noise level of two (S/N = 2): naphthalene, 80 ppt; guaiacol, 210 ppt; furfural, 5 ppb; phenol, 3 ppt; toluene, 16 ppb. A more detailed characterisation of the gas-phase measurement capabilities of the instrument is not given here as the analytical gas-phase REMPI–TOFMS properties of a comparable instrument (without LD-unit but with a similar OPO-laser system for generation of tuneable UV-laser radiation) are subject of a forthcoming publication.

3.2. Laser desorption mode for solid material characterisation

For the estimation of the LD–REMPI–TOFMS limits of detection a standard solution of perdeuterated polycyclic aromatic hydrocarbons (d-PAH), containing 10 mg/l of d_{10}-phenthrene (188 m/z), d_{10}-pyrene (212 m/z), d_{12}-chrysene (240 m/z), d_{12}-perylene (264 m/z) and d_{12}-coronene (312 m/z), respectively, in acetone as solvent was generated. Deuterated compounds were chosen because they can be used as internal standard for solid samples without interfering with the parent peak of the target compounds. A glass fibre filter of 6 mm diameter (28.3 mm² surface) was glued on the probe tip. Standard solution (5 μl of a 1/10 diluted) was applied on the filter, which corresponds to 5 ng of the deuterated PAH, respectively (180 pg/mm²).

During the measurement, which was performed with 10 Hz laser repetition rate, the probe tip was slowly rotated 360° by a stepper motor (20 s/rotation). The measurement was stopped after a full turn of the probe tip (i.e. after 200 laser shots). Due to the high repetition rate of 10 Hz overlapping of subsequent laser spots on the target occurs. However, apart from a decrease in signal intensity after the first laser shot this does not affect the ion signal from shot to shot. The LD- and REMPI-laser parameters were: wavelength, 275 nm; UV pulse energy, 150 μJ (spot size according to gas-phase measurements); IR pulse energy, 1 mJ. Please note that the rectangular OPO-output profile is focussed to a line in the ion source and therefore only a fraction of the irradiated UV photons can be utilised for the REMPI process.

The diameter of the IR-laser beam was ∼500 μm and hit the sample target 2.15 mm of axis. Therefore, a ring surface of 6.75 mm² was irradiated during the turn of the probe tip, which corresponds to 23.9% of the surface or 1.2 ng of the respective d_{10}-PAH compound. For determination of the limit of detection, the irradiated (IR desorption laser) surface is taken as basis. This allows the comparison of the performance of different instruments regardless the sampling probe geometry and surface. The 200 LD–REMPI–TOF mass spectra recorded for the measurement of a sample (i.e. full turn of probe) were added and the limit of detection for S/N = 2 was determined according to the formula: $\text{LOD}_{(S/N = 2)} = 2c\sigma/(p - m)$ [5] where c is the absolute amount of irradiated molecules (1.2 ng), σ the standard deviation of the noise, p the signal height and m is the base line level. The LOD are in the 100 pg range for the investigated compounds. In detail, the following LOD (S/N = 2) were determined: d_{10}-phenanthrene, 130 pg; d_{10}-pyrene, 180 pg; d_{12}-chrysene, 10 pg; d_{12}-perylene, 200 pg; d_{12}-coronene, 70 pg. The obtained LOD compare well with those reported from other LD–REMPI experiments. In the literature, for example, the following LD–REMPI–TOFMS limits of detection are given (REMPI at 266 nm, S/N = 2, 1.3 mm² desorbed surface, 72 laser shots): phenanthrene, 70 pg; pyrene, 40 pg; chrysene, 206 pg [41]. Please note that the differences in the relative ratio of the LOD is most

likely due to the different REMPI wavelength used in the experiments. The linearity of the LD–REMPI method was tested in a concentration range of three orders of magnitude by applying and analysing differently diluted d-PAH standard mixtures with the above-described procedure. For d_{12}-perylene and d_{12}-coronene a good linear behaviour was obtained. A mass resolution ($R_{50\%}$) of 530 was achieved in the LD–REMPI–TOFMS mode at 178 m/z.

The achieved gas-phase limits of detection as well as the LD–REMPI LOD are well comparable with the specifications obtained from instruments designed specifically for gas-phase REMPI or LD–REMPI application. Thus it can be stated that the newly developed hybrid-REMPI/LD–REMPI–TOFMS ion source does compromise the analytical performance of neither the gas-phase (REMPI–TOFMS) nor the solid-phase (LD–REMPI–TOFMS) approach. In the following, some LD–REMPI–TOFMS results on different sample types are given.

In Figs. 2 and 3, LD–REMPI–TOF mass spectra of different samples are shown. All investigated materials were available as fine powders. A disk ($\phi = 6$ mm) of double side adhesive tape was taped on the LD sample target and dipped into the powder. Loose powder was removed by blowing with nitrogen. IR-laser pulses of 1 mJ energy were used for desorption. Two hundred and seventy-five nanometres laser pulses of about 300 µJ energy were applied for REMPI post-ionisation. In Fig. 2A, the LD–REMPI–TOFMS spectrum of urban particulate matter (NIST Standard Reference material SRM 1648, National Institute of Standards and Technology, USA) is shown. Several polycyclic aromatic hydrocarbons species are detectable. These compounds are emitted from combustion processes, predominantly from automobile traffic. In Table 1, a tentative assignation of the peaks observed in the spectrum is given. LD–REMPI–TOFMS has recently been applied for highly sensitive, time-resolved measurement of PAH-species from ambient air samples [17,18]. Prior to
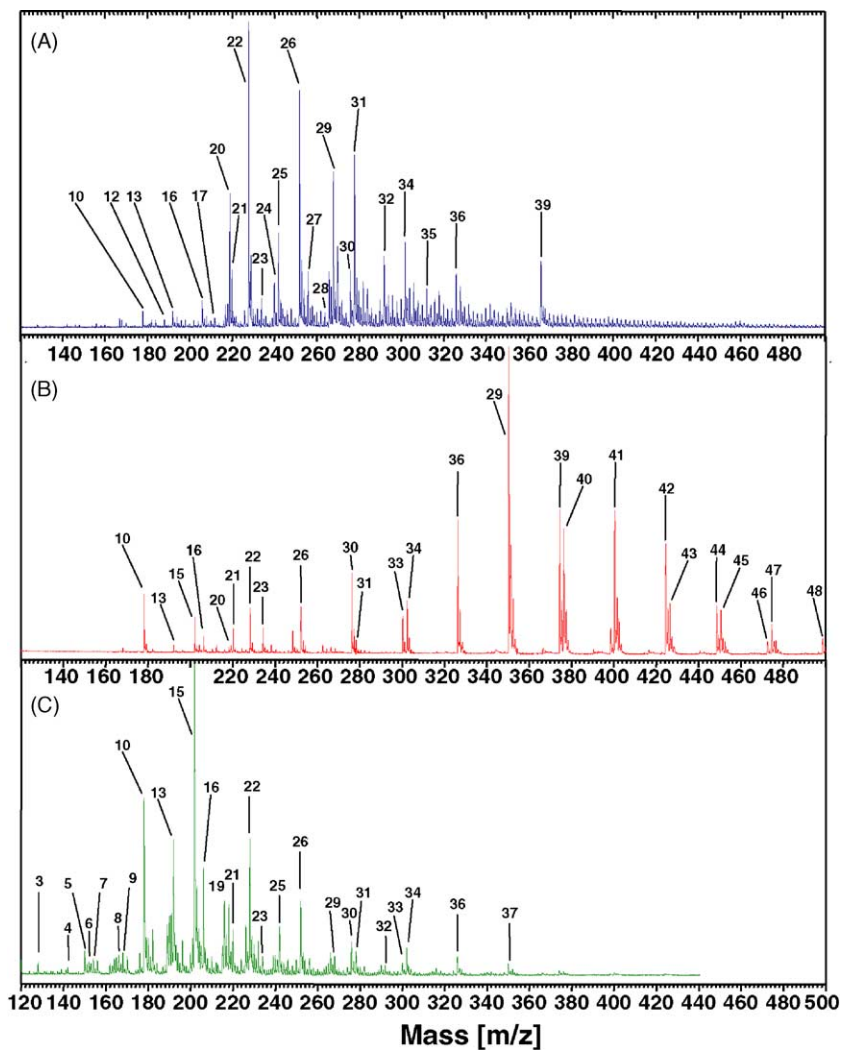

Fig. 2. LD–REMPI–TOF mass spectra of complex samples. Traces of PAH are detected in all samples. (A) LD–REMPI–TOF mass spectrum (275 nm) of an urban particulate matter sample (NIST SRM 1648); (B) LD–REMPI–TOF mass spectrum (275 nm) of soot from the combustion chamber of a wood incineration plant; (C) LD–REMPI–TOF mass spectrum (266 nm) of PAH contaminated river sediment.
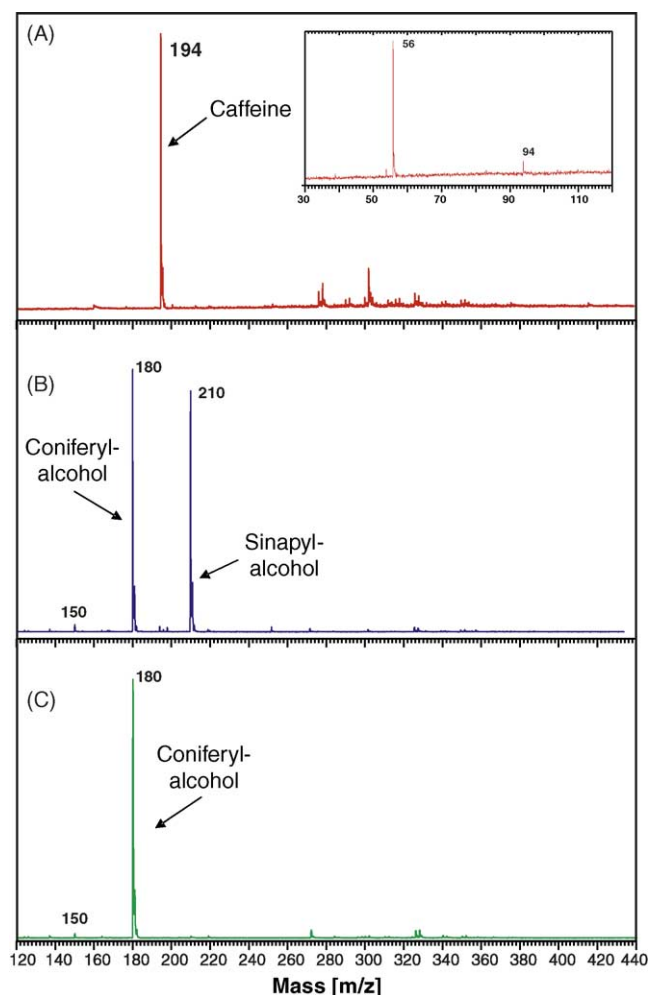
Fig. 3. LD–REMPI–TOFMS spectra of different plant material. (A) LD–REMPI–TOF mass spectrum (275 nm) of a green coffee sample (grinded); (B) LD–REMPI–TOF mass spectrum (275 nm) of a wood sample (beech-tree, hard wood); (C) LD–REMPI–TOF mass spectrum (275 nm) of a wood sample (spruce, soft wood).

analysis, 5 μl of the 1:10 diluted d-PAH standard solution (see above) was applied to the sample and standard peaks are assigned in the spectrum (peak #: 11, 17, 22, 26, 33). Many of the detected PAH carbon skeletons are accompanied by their alkylated homologues. The peak at 178 m/z, e.g. is dominated by the tricyclic PAH phenanthrene (the isomeric PAH anthracene plays only a minor role in combustion or environmental samples and furthermore exhibit weak REMPI cross-sections [5]). The peak series staring at 178 m/z with members 192, 206, 220 and 234 m/z is due to phenanthrene and its C_1–C_4 alkylated homologues. Other prominent PAH skeletons are visible at 228 m/z (four ring, e.g. chrysene), 252 m/z (five ring PAH, e.g. benz[a]pyrene) and 278 m/z (five ring PAH, e.g. dibenz[a,h]anthracene), partly also with alkylated homologues.

In Fig. 2B, the LD–REMPI–TOFMS spectrum of soot from the primary combustion chamber of a 0.7 MW wood incineration facility is shown (collected prior to secondary air supply at temperatures of ca. 950 °C). Here, predominantly PAH-species of higher masses are observed. Furthermore, alkylated derivatives are only observed for phenanthrene but not for the larger PAH skeletons. The spectrum thus appears considerably less complex if compared with the aerosol sample (Fig. 2A). This is typical for organic material from high temperature samples. At high temperatures, the formation of more stable, fully aromatic PAH skeletons are favoured. Alkylated and otherwise substituted PAH are predominately formed at either lower temperatures [9] or during non-stationary combustion conditions [5,42].

In Table 1, a tentative assignment of the detected peaks is given. The bottom trace in Fig. 2 shows a LD–REMPI–TOFMS spectrum of river sediment reference sample (Natural matrix certified reference material: "PAH contaminated Soil/Sediment" CRM104-100/lot: CR912 by RTC, distributed by Promochem, Wesel, Germany). For this sample, certified concentrations of PAH are available (Soxhlet extraction/GC–MS after US-EPA SW Methods 3540A and 8270A) and given in Table 2. The spectrum shows several compounds of higher volatility. Base peak is the mass 202 m/z (pyrene and fluoranthene). Higher masses are of relatively lower intensity. In Table 1, the tentative assignment of the detected peaks from the river sediment sample is given in Table 2. Furthermore, the achieved S/N levels for the respective PAH masses are given. This example shows that LD–REMPI–TOFMS is well suited for rapid detection of PAH from complex environmental samples such as sediments or soils.

By application of an internal deuterated PAH calibration standard, a rapid estimation of the PAH contamination of e.g. a soil sample is possible. As the measurement time per sample is very short (some minutes with preparation, sample insertion, measurement and sample removal) the LD–REMPI–TOFMS method is well suited for screening purposes e.g. for environmental remediation purposes. Please take into account that, however, for all here presented results on PAH no information on the isomeric composition of the detected PAH masses can be given (with exception of the masses: naphthalene, 128 m/z; acenaphthylene, 152 m/z; acenaphthene, 154 m/z and, with reservations, phenanthrene, 178 m/z). In Fig. 3, LD–REMPI–TOFMS spectra of plant material (coffee bean and wood samples) are shown. In contrast to the soot, urban particulate matter or polluted river sediment, PAH-species usually are not occurring in this type of samples. Furthermore, low-volatile aromatic structures are rare. An exception, however, are plants that contain aromatic alkaloids.

Coffee beans contain large quantities of caffeine. The LD–REMPI–TOFMS spectrum of green coffee is dominated by the caffeine peak at 194 m/z [7]. At higher masses, some non-assigned peaks are visible. In the lower mass range phenol ($m = 94 m/z$) and a peak at 56 m/z can be observed. As molecules with sufficient REMPI cross-section at 266 nm usually exhibit conjugated π-electron systems, acroleine could be a candidate for the peak at 56 m/z. In Fig. 3B

Table 1
Tentative peak assignation of LD–REMPI–TOFMS spectra from several samples types (Figs. 2 and 3)

Peak #	Mass peak (m/z)	Compounds name	Urban PM	Wood combustion Soot	River sediment	Green coffee (G), hard wood (H), soft wood, (S)
1	56	Acrolein (?)				G
2	94	Phenol				G
3	128	Naphthalene			+	
4	142	Methylnaphthalene			+	
5	150	Vinylguiacol, etc.				H, S
6	152	Acenaphthylene			+	
7	154	Acenaphthene, biphenyl			+	
8	166	Fluorene			+	
9	168	Dibenzofuran, methylbiphenyl			+	
10	178	Phenanthrene, anthracene	+	+	+	
11	180	Coniferyl–alcohol				H, S
12	188	d_{10}-Phenanthrene (*standard*)	+			
13	192	Methylphenanthrene	+	+	+	
14	194	Coffeine				G
15	202	Pyrene, fluoranthene		+	+	
16	206	C_2-phenanthrene	+	+	+	
17	210	Sinapyl–alcohol				H
18	212	d_{10}-Pyrene (*standard*)	+			
19	216	Methylpyrene, methylfluoranthene	+		+	
20	219	?	+			
21	220	C_3-phenanthrene, etc.	+	+	+	
22	228	Chrysene, etc.	+	+		
23	234	C_4-phenanthrene, etc.	+	+		
24	240	d_{12}-Chrysene (*standard*)	+			
25	242	Methylchrysene, etc.	+		+	
26	252	Benz[*a*]pyrene, perylene, benzofluoranthenes, etc.	+	+	+	
27	256	C_2-chrysene, etc.	+	+		
28	264	d_{12}-Benzpyrene (*standard*)	+			
29	268	?	+		+	
30	276	Benzoperylenes, anthanthrene, etc.		+	+	
31	278	Dibenzoanthracenes, etc.	+	+	+	
32	292	Methyldibenzoanthracenes, etc.	+	-		
33	300	Coronene		+	+	
34	302	Benzo[*b*]perylene, dibenzofluoranthenes, etc.	+	+	+	
35	312	d_{12}-Coronene (*standard*)	+			
36	326	Dibenzoperylenes, peropyrene, etc.		+	+	
37	350	Benzo[*a*]coronene, etc.		+	+	
38	366	?				
39	374	Dibenzocoronenes, etc.		+		
40	376	Dibenzantanthrene, etc.		+		
41	400	Naphthocoronene, periflanthene, etc.		+		
42	424	Benzonaphtocoronene, etc.		+		
43	426	Tetrabenzo[*a,cd,j,lm*]perylene, etc.		+		
44	448	Benzo[*a*]ovalene, etc.		+		
45	450	Decacyclene, tribenzo[*a,d,g*]coronene, etc.		+		
46	472	Dibenzo[*a,bc*]ovalene, etc.		+		
47	474	Dibenzodinaphthopentacene, etc.		+		
48	498	?		+		

and C, LD–REMPI–TOFMS spectra of two wood samples (hard and soft wood) are shown. The formed phenolic lignin subunits can be readily ionised by REMPI [34]. The spectrum of the hard wood sample (beech-tree, Fig. 3B) shows two phenolic units at 180 m/z (coniferyl–alcohol) and 210 m/z (sinapyl–alcohol). This is characteristic for hard wood samples [43]. The spectrum of the soft wood sample (spruce wood, Fig. 3C) in contrast only shows coniferyl–alcohol at 180 m/z.

3.3. Field measurement at wood fired furnace for heat generation

The primary motivation for construction of the investigated hybrid REMPI–TOFMS and LD–REMPI–TOFMS, however, was to facilitate the rapid change between REMPI–TOFMS and LD–REMPI–TOFMS measurements even under field measurement campaign conditions. This is important e.g. for on-line monitoring applications at in-

Table 2
Certified PAH concentrations in the river sediment sample (Fig. 2C and Table 1)

Compounds name	Molecular mass (m/z)	Certified concentration (ppm = mg/kg)	S/N in REMPI–TOFMS for PAH masses[a]
Naphthalene	128	0.77	110
Methylnaphthalene	142	Traces	80
Acenaphthylene	152	1.21	120
Acenaphthene	154	0.77	140
Fluorene	166	0.65	170
Dibenzofuran	168	0.66	190
Phenanthrene	178	5.79	1580
Anthracene	178	1.44	
Pyrene	202	15	2860
Fluoranthene	202	24.6	
Chrysene	228	8.6	1300
Benzo[a]anthracene	228	7.98	
Benz[a]pyrene	252	8.09	660
Benzo[b]fluoranthene	252	9.69	
Benzo[k]fluoranthene	252	5.1	
Benzo[1,2,3-cd]pyrene	276	4.46	290
Benzo[ghi]perylene		3.58	
Dibenzo[a,h]anthracene	278	1.55	210

[a] Noise is due to electronic noise (detector noise, i.e. noise determined from peak-free areas in spectrum).

dustrial combustion plants, if both the gas-phase part as well as the particulate matter part of the flue gas (i.e. combustion aerosol) should be analysed. Recently, several studies based on REMPI–TOFMS on-line measure-

ments at waste or wood combustion plants were performed [5,6,8,10,40,42,44,45]. Target compounds in these studies were indicator compounds for polychlorinated dibenzo-p-dioxins such as monochlorobenzene as well as the polycyclic aromatic hydrocarbons. In order to avoid particulate matter to clog the inlet system, a hot gas filtration unit needs to be implemented in the sampling train. Fine particulate matter from combustion processes, however, carries the higher molecular mass PAH-species [31,32]. These non-volatile PAH-species of larger molecular weight are particle bound even at elevated temperatures and thus are precipitated with the particles by the filtering unit. Under normal combustion conditions therefore PAH with masses higher than 252 m/z (chrysene and isomers) are invisible or considerably suppressed in REMPI–TOFMS flue gas measurements.

With the present sampling train a continuous, non-interrupted REMPI–TOFMS measurement sequence of e.g. PAH-species from the raw combustion flue gas can be performed for a time span of about less than one hour to a maximum of some hours. In dependence of the investigated combustion process and the chosen sampling point the filter then is overloaded and needs to be changed. The time consumption of the filter changing procedure is about 10 min. However, within this time span, a small piece of the loaded filter can be mounted on the sampling probe and a LD–REMPI measurement can be performed, showing the particle-bound PAH-species of the preceding sampling interval. Quantification in principle can be performed when the flue gas volume drawn through the filter surface is determined [17,18,46]. Thus, the hybrid gas-phase solid-phase laser mass spectrom-
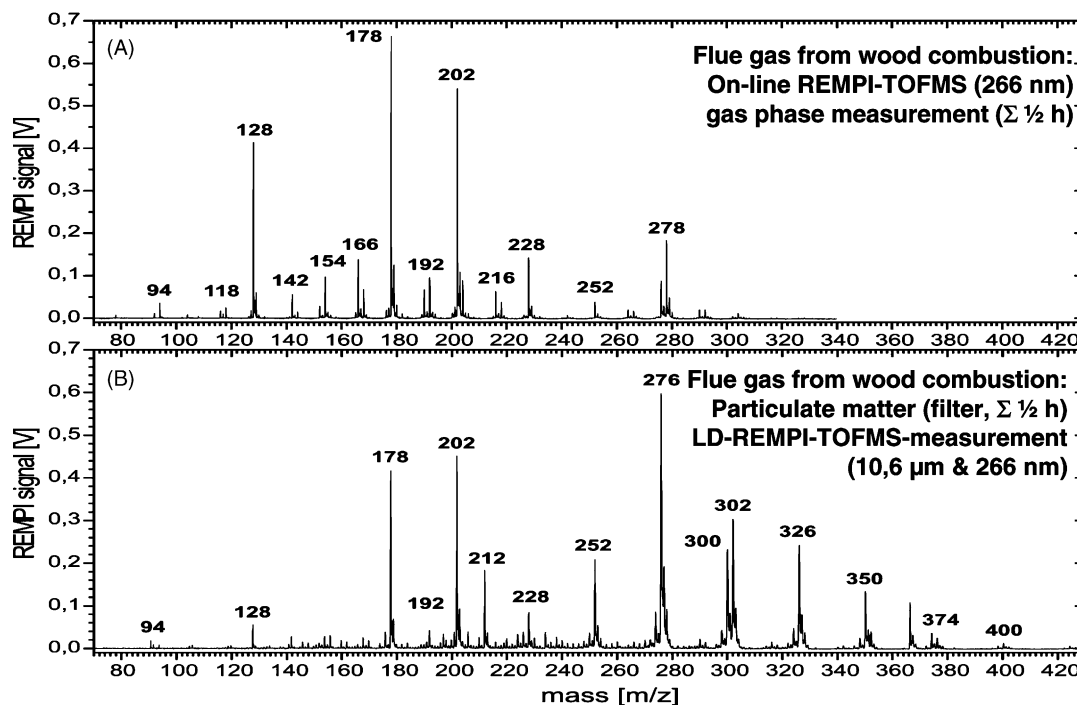

Fig. 4. (A) Gas-phase REMPI–TOF mass spectrum of wood combustion flue gas (summarised signal over the whole measurement sequence); (B) particle-phase LD–REMPI–TOF mass spectrum of wood combustion flue gas (particles collected parallel to the gas-phase measurement shown in Figs. 4A and 5).

eter allows a more comprehensive on-line analysis of flue or process gases.

In Fig. 4, a typical REMPI–TOFMS (top) and LD–REMPI–TOFMS (bottom) results for a flue gas measurement are shown. The laser wavelength of 266 nm was used for the online REMPI–TOFMS measurement as well as the LD–REMPI–TOFMS analysis of the collected particulate matter. Field measurement was performed at a 174 kW small-scale bio mass furnace for heat generation (furnace type: SR-EB 4, Bioflamm GmbH, Overath, Germany) at an agricultural company in South Bavaria, Germany. The furnace was operated with shredded spruce wood as feed. The shredded spruce wood is convoyed from the stock container via a tube and is fed discontinuously by a feeding plunger. The feeding rate is adjusted according to the boiler temperature (i.e. heat production). This discontinuous supply results in slightly non-stationary emission profiles. The sampling position was directly in the combustion chamber at approximately 800 °C. For the measurement, one feeding cycle was recorded (here: start of wood feeding at 25 s).

The REMPI–TOFMS spectrum shown in Fig. 4A represents an average spectrum over this combustion measurement (average over 3600 single mass spectra recorded at 10 Hz). Several gas-phase aromatic compounds are detected. The most prominent species in the gas-phase spectrum are naphthalene (128 m/z), phenanthrene (178 m/z) and pyrene/fluoranthene (202 m/z). For a list of tentatively assigned peaks, see Table 3. After the on-line measurement, sequence the filter was changed and a piece of the filter was used for the recording of the LD–REMPI–TOFMS spectrum. The LD–REMPI–TOFMS spectrum addresses the particles, which were precipitated during the 360 s measurement time of the gas-phase measurement at the fibre filter (filtration temperature ~200 °C). The filter was desorbed as described previously (one full rotation of the sampling probe, 200 laser shots). The LD–REMPI–TOFMS spectrum (averaged over all 200 laser shots) is shown in Fig. 4B. In the case of the precipitated particle sample, predominantly heavier PAH can be observed (i.e. the typical low-volatile PAH mass pattern [29,31,32] appears, see also Table 3). Note that for higher mass PAH peaks usually several isomeric species can contribute to the signal [29,31]. The signals of the PAH naphthalene (128 m/z), phenanthrene (178 m/z) and pyrene/fluoranthene (202 m/z) are higher than expected. Previous studies have shown that with the used sampling train at a filter temperature of 200 °C the latter mentioned compounds are not precipitated on the filter [5]. The reason for the comparable high signal of these compounds most likely lies in the filter changing procedure. For changing the filter, the heating cuffs need to be removed from the sampling train. Subsequently the filter housing is dissembled. However, prior the filter removal, the filter temperature is decreased considerably while flue gas is still in the sampling train. The relatively high concentrated PAH of higher volatility thus adsorb at the filter surface.

Table 3
Peak assignation (after [5,31,32]) of the REMPI–TOFMS (gas phase) and LD–REMPI–TOFMS (particulate phase on filter) spectra from the flue gas of a 174 kW wood fired boiler obtained during a field measurement camping (Fig. 4)

Mass peak (m/z)	Tentative peak assignation	Present in REMPI–TOFMS mass spectrum (gas phase)	Present in LD–REMPI–TOFMS mass spectrum (precipitated particulate matter)
94	Phenol	+	−
118	Indane, benzofurane	+	−
128	Naphthalene	+	(+)[a]
142	Methylnaphthalene	+	−
154	Acenaphthene, biphenyl	+	−
166	Fluorene	+	−
168	Dibenzofuran, methylbiphenyl	+	(+)[a]
178	Phenanthrene	+	(+)[a]
192	Methylphenanthrene	+	(+)[a]
202	Pyrene, fluoranthene	+	+
212	?	+	+
216	Methylpyrene, methylfluoranthene	+	+
228	Chrysene, etc.	+	+
252	Benz[a]pyrene, perylene, benzofluoranthenes, etc.	+	+
276	Benzoperylenes, anthanthrene, etc.	+	+
278	Dibenzoanthracenes, etc.	+	+
300	Coronene	−	+
302	Benzo[b]perylene, dibenzofluoranthenes, etc.	−	+
326	Dibenzoperylenes, peropyrene, etc.	−	+
350	Benzo[a]coronene, etc.	−	+
366	?	−	+
374	Dibenzocoronenes, etc.	−	+
376	Dibenzantanthrene, etc.		
400	Naphthocoronene, periflanthene, etc.	−	+

[a] Contamination from gas phase, probably condensed on during the filter change.

The important outcome, however, is that the low-volatile compounds – starting from coronene at 300 m/z – which cannot be detected by the REMPI–TOFMS on-line gas-phase measurement now are accessible by the LD–REMPI–TOFMS approach.

In Fig. 5A and B, the time evolvement of the REMPI–TOFMS gas-phase signals of the wood combustion flue gas measurement is shown (same measurement as shown in Fig. 4). The three-dimensional landscape plot (3D-Plot, Fig. 5A) shows the time evolvement of the REMPI–TOFMS signal during the measurement sequence. It is clearly visible
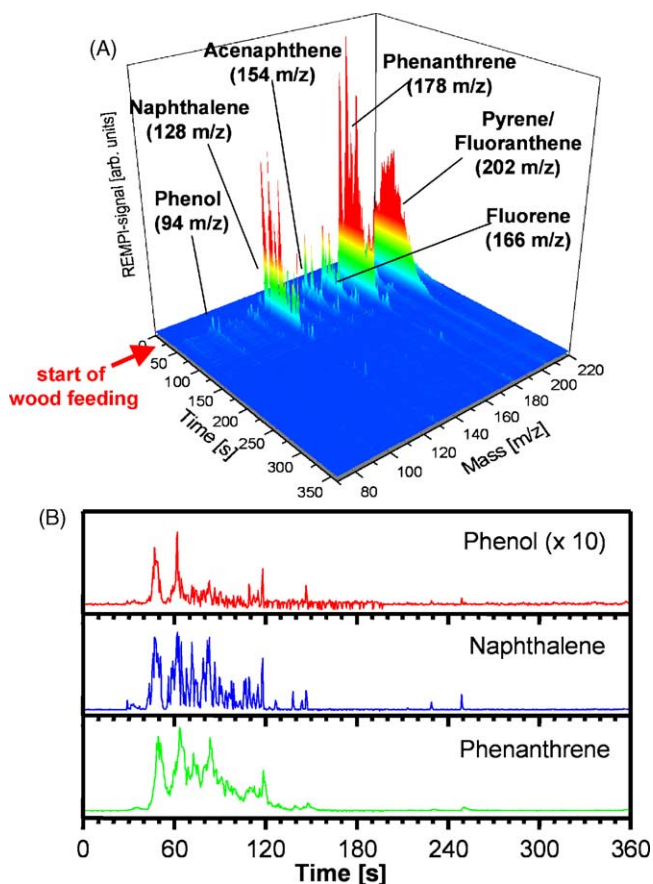
Fig. 5. (A) Three-dimensional plot of on-line REMPI–TOFMS wood combustion flue gas measurement sequence (gas phase, same measurement as in Fig. 4A; (B) time to intensity profiles of phenol, naphthalene and phenanthrene from the on-line REMPI–TOFMS wood combustion flue gas measurement sequence (gas phase, same measurement as in Fig. 4A).

that after about 25 s a steep increase of the concentration of several aromatic species can be observed, indicating the start of a phase with unstable and non-complete combustion conditions. About 100 s later, the concentrations of the aromatic compounds are again on the normal level. The observed incident is due to the operation of the feeding plunger. Fresh wood was supplied to the combustion chamber, leading to local air shortages in the furnace and therefore considerably increased formation of aromatic species and soot. In Fig. 5B, the time to intensity profiles for three masses/species are given. The relatively weak phenol signal ($m/z = 94$) is considered alongside with the more intense signals of the PAH's naphthalene and phenanthrene. While the relative courses of the PAH-species are relative similar to each other the phenol course shows some differences. After the second peak at approximately $t = 65$ s, the phenol signal shows relatively low intensities while naphthalene and phenanthrene still show increase relative signal intensities. This reflects, however, the different formation behaviour of different chemical compound classes in combustion processes.

4. Conclusions

A novel, mobile resonance enhanced multiphoton ionisation–time-of-flight mass spectrometer system is described, which can be operated either in a gas-phase or a laser desorption-mediated solid-phase analysis mode. The two operational methods are rapidly interchangeable because of the development of a novel adaptable ion source. By changing the ion source properties (i.e. electrode distances and potentials) upon interchange of the operational mode, the REMPI ionisation laser adjustment can be preserved. The instrument is designed for field applications. It is therefore possible to perform a comprehensive characterisation of e.g. process gases by addressing the gas phase (analytes that pass the sampling filter) and the solid phase (aerosol particles that are precipitated on the filter unit of the sampling probe).

In addition to the REMPI ionisation also laser-based single photon ionisation is of great interest for rapid characterisation or screening of the organic chemical composition of either gas [11,47] or solid [48] phase. Currently, an SPI unit, using 118 nm photons for comprehensive soft ionisation of organic compounds was successfully added to the instrument. SPI–TOFMS allows the detection of aliphatic compounds such as alkanes, alkenes, aldehydes or heterocyclic compounds in e.g. coffee roasting off-gas [7], mineral oil products headspace or combustion flues gases [11]. With LD–SPI–TOFMS, e.g. acetone and nicotine can be detected from cigarette smoke particulate matter collected on a glass fibre filter. Details on this method will be given in a forthcoming publication.

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