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Laser Ionisation Mass Spectrometry for On-Line Characterization of Combustion Processes

R. ZIMMERMANN[1,2,3], F. MÜHLBERGER[1] and K.HAFNER[1]

1 GSF-Forschungszentrum Umwelt und Gesundheit GmbH, Institut für Ökologische Chemie, Ingolstädter Landstr. 1, D-86764 Neuherberg, Germany, e-mail: ralf.zimmermann@gsf.de

2 Universität Augsburg, Institut für Physik, Analytische Chemie, Universitätsstraße 1, D-86159 Augsburg, Germany

3 BIfA-Bayerisches Institut für Umweltforschung und -technik, Abteilung Umwelt und Prozesschemie, Am Mittleren Moos 46, D-86167 Augsburg, Germany

* coresspondence: ralf.zimmermann@gsf.deFirst LAST, First M. LAST

Abstract - **A comprehensive view on the complexity of environmental pollution is required in order to develop new scientific approaches for minimization its impact on mankind. In this paper two innovative instrumental analytical concepts for a more comprehensive description of air pollution are presented and discussed. The first concept (A) deals with comprehensive on-line emission monitoring (e.g. from waste incineration plants) of inorganic and organic compounds by combining three different ionisation methods (two laser ionisation methods and electron impact ionisation) for process gas mass spectrometry. The second concept (B) deals with a comprehensive detection of the organic inventory of urban particulate matter (PM2.5) by two-dimensional comprehensive gas chromatography –time of-flight mass spectrometry (off-line immission monitoring).**

A) Comprehensive on-line emission monitoring: Analysis of organic and inorganic pollutants in flue gases from industrial processes by a novel mass spectrometer with multiple ionisation techniques

Flue gases form combustion processes are complex mixtures of inorganic and organic combustion-by products in a nitrogen, water vapour, oxygen and carbon dioxide matrix. Toxic products of incomplete combustion as well as inhalable particles from emissions originated from combustion processes are considered to be responsible for severe health effects. In order to minimize the stack emission of pollutants, such as chlorinated dibenzo-p-dioxins-/furans (PCCD/F), polycyclic aromatic hydrocarbons (PAH), heavy metals, carbon monoxide, sulphur dioxide or nitrogen oxides, modern incineration plants are equipped with large flue gas cleaning devices (secondary measures). However, during non-stationary combustion episodes, pollutants can pass the flue gas cleaning devices. Recent research addresses the investigation of potential primary measures (i.e. combustion process integrated measures) for minimization of the formation of toxic compounds. Prerequisites for this research task are process monitoring devices which allow the on-line measurement of the relevant chemical species in the flue gas. In the last decade experimental process gas monitors based on mass spectrometry (MS) with soft (i.e. fragmentation free) ionisation techniques have been developed. The applied ionisation techniques were: (i) Resonance Enhanced MultiPhoton Ionisation (REMPI, [1-3]), Single Photon Ionisation with VUV photons (SPI, [2, 4, 5], (iii) Chemical Ionisation (CI, [6-8] and (iv) Electron Impact (EI) ionisation with low kinetic energy (LKE) electrons (LKE-EI). The respective ionisation techniques address different compounds/compound classes.

The laser based REMPI technique is highly selective (depending on the UV-laser wavelength) and sensitive (down to ppt-region) but is restricted mostly to soft ionisation of aromatic species.

The laser based SPI technique is less sensitive (down to ppb-region) but allows soft ionisation of nearly all organic compounds. Small aliphatic compounds as well as many inorganic species are not detectable by SPI-MS. The CI methods exhibit different selectivities (depending on the used reagent

gases) and can reach sensitivities in the ppb-regions.

EI ionises small inorganic and aliphatic analytes at moderate sensitivities (down to ppm-region). Each individual ionisation method addresses only a selected part of the compounds present in the flue gases. However, a comprehensive knowledge of the flue gas composition is required for studying pollutant formation processes. In this work, a newly developed Time-of-Flight mass spectrometer (TOFMS) for process analytical studies is presented. The mass spectrometer applies the three ionisation methods REMPI, SPI and LKE-EI in parallel and thus allows a comprehensive on-line flue gas analysis within a single, mobile TOFMS-instrument.

The novel mass spectrometer (TOFMS) is equipped with the three different ionisation techniques REMPI, SPI and LKE-EI. The ionisation methods can be operated quasi-simultaneously in order to achieve a comprehensive characterization of complex substance mixtures (i.e. due to the different ionisation selectivity profiles). REMPI is powerful to ionise aromatic organic molecules such as benzene or polycyclic aromatic hydrocarbons (PAH). Ionisation is performed by a two-photon absorption. Prerequisites for a laser ionisation by REMPI are: a) the energy of the two photons must exceed the ionisation potential and b) the one photon energy must be in resonance with an excitable electronic molecular state. In combination with TOFMS (REMPI-TOFMS) the REMPI method was successfully applied for on-line monitoring of e.g. PAH and PCDD/F-surrogates (e.g. monochlorobenzene, [9, 10] at waste incineration plants. The SPI method uses VUV-photons for ionisation (typical 118 nm laser generated photons). SPI is applied for ionisation of aliphatic compounds, such as alkanes, amines or aldehydes [2, 4, 5]. The spectrometer is equipped with a novel, mobile, Nd:YAG-laser pumped, tunable (220-340 nm) OPO-Laser for REMPI. The Nd:YAG laser also generates 355 nm laser pulses, which are frequency tripled in a rare gas cell to 118 nm (10.5 eV) for SPI. The Nd:YAG laser is operated with 10 Hz. The pulses are separated into 5 UV laser shots (REMPI) and 5 VUV 118 nm laser shots (SPI) every second.. The ions formed by REMPI or SPI are analysed in the TOFMS within 20 μs after the laser pulse. The mass spectra are acquired via a 8 bit 250 MHz transient recorder PC-card. Between the laser pulses, however, the TOFMS is not used for 99.98 msec., respectively. During this time, 1999 EI-TOFMS spectra are recorded at a sweep rate of 20 kHz. The ion extraction is gated for all ionisation methods (i.e. ionisation occurs under field free conditions). The instrument is designed as a mobile device. The wavelength tuneable OPO laser (OPO type II, 200 – 340 nm) is mounted in a special temperature controlled housing on top of the instrument. The data acquisition is performed by a home written software program. A special EI-geometry has been designed for the instrument. EI spectra are recorded at a sweep rate of 20 kHz by a single ion counting PC-card. The new instrument was tested in a field measurement campaign at a municipal waste incineration plant. The sampling probe was positioned in the flame zone of the incinerator. A special home-built sampling probe was used. The probe could resist temperatures up to 1200°C. The sampled flue gas is quenched to temperatures of about 300 °C within 100 msec. The instrument is able to detect a large variety of compounds. Figure 1 shows flue gas mass spectra obtained with the new instrument. The upper trace depicts the SPI-mass spectrum (118 nm), the middle trace the REMPI-mass spectrum (224 nm) and the lower trace the EI-mass spectrum (LKE-EI: 23 eV).The REMPI method (middle trace) selectively shows some aromatic PAH (ppb level). At specific wavelengths, nitrogen-containing compounds such as aniline or carbazole were detected (not shown in figure 1). The SPI method (upper trace in figure 1) shows NH3, some aliphatic compounds, benzene, phenol, cyanobenzene and other aromatics at ppb or ppm levels. With the EI method, the major compounds, such as O2, CO2 or H2O are detectable. Furthermore minor compounds such as HCN, SO2, acetylene CH4 and HCl were measurable in the higher ppm-range by EI-TOFMS (lower trace in figure 1). The important improvement is that the spectra shown in figure 1 were recorded in parallel, i.e. 5 SPI- and 5 REMPI-mass spectra as well as one EI mass spectrum (19990 sweeps) were recorded every second. Thus a direct, continuous on-line monitoring of the species shown in figure 1 is possible. In summary, the developed mass spectrometer can be used for a comprehensive on-line characterization of complex gas mixtures, such as combustion flue gases. The instrument well suited to investigate the correlations between the occurrence of different individual molecular chemical species, e.g. PCDD/F-surrogates and combustion conditions.
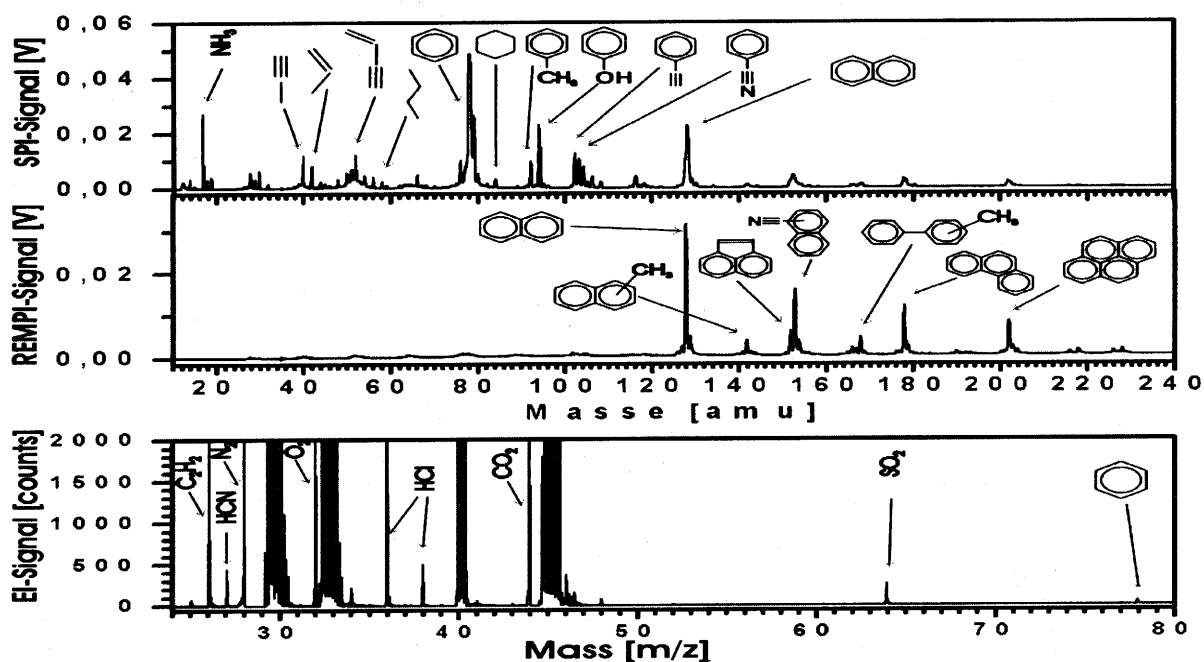
Fig. 1. Waste incineration flue gas mass spectra obtained with the new instrument. For details see text.

B) Comprehensive on-line emission monitoring: Analysis of organic and inorganic pollutants in flue gases from industrial processes by a novel mass spectrometer with multiple ionisation techniques

The characterization of the semi-volatile organic compounds (SVOC) from ambient particulate matter (PM) represents an actual topic in current environmental research. Information on the organic composition of ambient PM is important for source appointment as well as for studying acute or chronic health impacts of ambient PM. Several studies address the organic composition of ambient PM, using gas chromatography-mass spectrometry (GC-MS) for separation and identification of SVOC. GC-MS is a well-established technique for the separation and analysis of complex mixtures. However, GC cannot provide sufficient chromatographic resolution for the separation of the large numbers of organic compounds present in ambient PM. Thus the majority of the organic compounds present in ambient PM is not identified yet. Typical gas chromatograms of SVOC from PM exhibit broad unresolved bands ("unresolved carbonaceous matter", UCM), including the majority of the SVOC compounds. Novel analytical techniques with increased resolving power are required in order to increase the chemical knowledge about the UCM bands. Comprehensive two-dimensional gas chromatography (GCxGC) is a new technique to enhance the GC resolution [11-13]. A promising technique for analysis of organics in PM is GCxGC hyphenated to fast time-of-flight mass spectrometry (TOFMS) [14, 15]. The two-dimensional comprehensive gas chromatograph (GCxGC) consists of two connected separation columns, a long first-dimension column (typically with a non-polar stationary phase) and the much shorter, second-dimension column (typically with a polar stationary phase). A thermal modulation unit (TM) is located between the two separation columns. On the first column, a conventional high resolution gas chromatographic separation takes place. In the TM the analytes are enriched and cryo-focussed for e.g. 6 sec. and then released into the second, short polar column. This enriched fraction is then separated within 6 sec. in a fast-GC run on the second
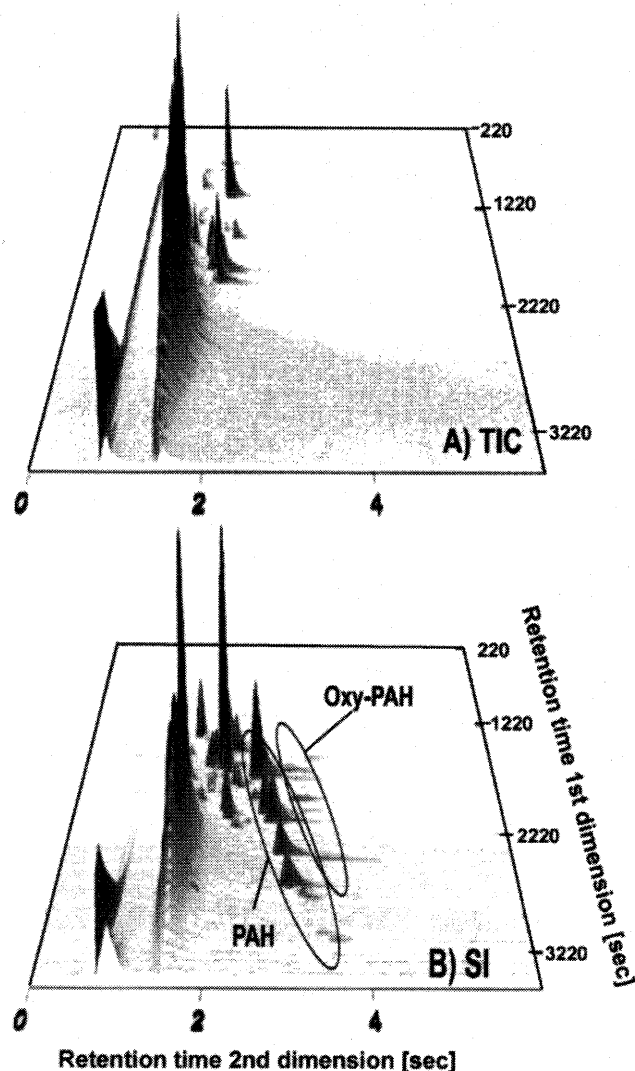
Figure 2: Two-dimensional GCxGC-TOFMS chromatogram of a Augsburg PM2.5 sample in 3D landscape-plot: left) total TOFMS ion current (TIC); right) selected ion (SI) representation for PAH masses (178, 202, 228, 252, 276 m/z m/z) and oxy-PAH masses (180, 194, 204, 230 m/z).

column, providing a different separation characteristics. The detector is placed at the end of the second column. After 6 sec. this cycle is repeated. The resulting chromatogram corresponds to the first-dimension chromatogram (typ. duration 4000 sec.), repetitively modulated by second dimension chromatograms (typ. duration 4-6 sec.). When the second dimension chromatograms are displayed in a staggered ordering, one obtains a 3D plot with the axes first-dimension retention time, second-dimension retention time and peak intensity. Note, that each individual point on the 2D-chromatogram surface corresponds to a full TOF mass spectrum. The 2D-chromatogram can be displayed for the total ion current (TIC) or for selected ions (SI). Analytical GCxGC-TOFMS parameters (instrumentation: LECO Ltd, MI, USA) were as follows. Injection: 1µl splitless, 60s purge, 280°C; Columns: 1st D.-column - DB-5, 30m, 0.32mm i.d., 0.25mm film thickness, 2nd D.-column-DB-17MS, 2.5m, 0.18mm i.d., 0.2mm film thickness, Flow: 1.5 ml/min helium, Oven parameters: primary oven (1st D.) 50°C (5 min hold) to 300°C (4 min hold) at 10°C/min; secondary oven (2md D.) 55°C (5 min hold) to 300°C (4 min hold) at 10°C/min; Modulation frequency: 0.166 Hz. The TOFMS was operated with a data acquisition frequency of 125 Hz. PM2.5 samples were

collected in Augsburg, Germany from ambient air glass fibre filters. An aliquot of 120 m³ air was extracted with dichloromethane. The extract was concentrated to 100 µl. In the investigated samples (SRM 1649a, "urban dust" and PM2.5 Augsburg samples) several thousand peaks were found in the 2D-chromatogram using an automated peak identification routine based on deconvolution methods. Among various others compound classes, alkanes, long chain carboxylic acids and esters, substituted aromatics, PAH, oxy-PAH and heterocyclic aromatic compounds were identified. An interesting feature is the ordered appearance of chemically related compounds in the 2D chromatogram. This is due to the physico-chemical similarities within compounds classes and the gradual changes of these properties with increasing molecular sizes/chain length. The ordered appearance helps to classify unknown substances. In Figure 2, two 2D-chromatograms of an Augsburg PM2.5 sample are shown as 3D plots. The upper 3D plot is due to the total ion current (TIC, Figure 2A). The chromatogram is dominated by non-polar hydrocarbons (e.g. alkanes), which are representing the bulk of the SVOC. These compounds are only weakly separated on the second chromatographic axis with the chosen column parameters. However, many compounds which are suspect to be health relevant are occurring in rather low concentrations and are more polar than the alkanes. In order to visualize these compounds, characteristic selected ions are chosen (SI) for generating the 3D-plot. The lower 3D-plot (Figure 2B) is based on the typical ions for polycyclic aromatic hydrocarbons (PAH, e.g. phenanthrene, pyrene, chrysene, benzpyrenes) and oxygenated PAH (oxy-PAH, e.g. 9H-fluren-9-one, 9,10-anthracenedione). The observed groups of PAK- and oxy-PAK-peaks are marked by circles in Figure 1B. The ordered appearance of the chemically related peaks in GCxGC is clearly visible. Pattern recognition techniques, using the 2D-retention-time information as well as mass spectral data can be applied to find chemical differences in PM2.5 samples or to classify peaks according to their substance class [15].

Acknowledgements

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