Organohalogen Compounds, Volume 60, Pages 513-516 (2003)

COMPREHENSIVE ON-LINE FLUE GAS ANALYSIS, USING A NOVEL TIME-OF-FLIGHT MASS SPECTROMETER UTILIZING THREE IONISATION METHODS OF DIFFERENT SELECTIVITY IN PARALLEL

F.Mühlberger[1], K.Hafner[1], R.Zimmermann[1,2,3*]

1 GSF Forschungszentrum Umwelt und Gesundheit GmbH, Institut für Ökologische Chemie, Ingolstädter Landstraße. 1, D-86764 Neuherberg, Germany
2 Universität Augsburg, Institut für Festkörperchemie, Professur für 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
* Corrosponding author e-mail: ralf.zimmermann@gsf.de

Introduction

Waste incineration flue gases are complex mixtures of -partly toxic- inorganic and organic combustion-by products in a nitrogen, water, oxygen vapour and carbon dioxide matrix. The toxic combustion by-products from waste incineration processes represent a severe environmental problem. In order to minimize the direct stack emission of the toxic compounds, such as chlorinated dibenzo-p-dioxins-/furans (PCCD/F), polycyclic aromatic hydrocarbons (PAH), heavy metals, carbon monoxide, sulphur dioxide or nitrogen oxides, modern waste incineration plants are equipped with large flue gas cleaning devices (secondary measures). However, persistent pollutants, such as PCDD/F, PAH or heavy metals are transferred into the waste incineration residue streams (fly ashes, flue gas cleaning residues, slag etc.) by the flue gas cleaning processes. Thus, the residue streams bear a high toxic potential and need to be treated (e.g. fly ash smelting) or deposited as hazardous waste. Recent research addresses the investigation of potential primary measures (i.e. combustion process integrated measures) for minimization of toxic compound formation. 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, 2,, 3), (ii) Single photon ionisation with VUV photons (SPI) (4-6), (iii) Chemical ionisation (CI) (7-9) and (iv) Electron impact (EI) ionisation with low kinetic energy (LKE) electrons (LKE-EI) (10). The ionisation techniques address different compounds/compound classes. The laser based REMPI technique is highly selective (down to ppt-region) and sensitive (depending on the UV laser wavelength) but is restricted mostly to soft ionisation of aromatic species. The also 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 achieve sensitivities in the ppb-regions. EI address 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 approach towards understanding of pollutant formation requires an comprehensive knowledge of the flue gas composition. This is particularly true for understanding of the formation of ultra trace compounds such as the PCDD/F. A recent study investigated potential surrogates in the flue gas for prediction of the PCDD/F content in waste incineration residues. The study exhibited that the gas phase concentration of small inorganic compounds, e.g. carbon monoxide or hydrogen chloride as well as large polycyclic aromatic hydrocarbons can be used in a multivariate correlation model for prediction of the PCDD/F content in fly ashes. This demonstrates that a more comprehensive analysis of the flue gases might help considerably in better understanding pollutant formation processes. In this work a newly developed Time-Of-Flight mass spectrometer (TOFMS) for process analytical studies is presented that applies the three ionisation methods REMPI, SPI and LKE-EI in parallel and thus allows a rather comprehensive on-line flue gas analysis in a single TOFMS-instrument.

Methods and Materials

In this work we present a novel mass spectrometer (TOFMS) that 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 ionisation 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 (i.e. monochlorobenzene) (11, 12) 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 (4-6). 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). The ions are analysed in the TOFMS within 20 µs after the laser pulse and the MS are recorded via a transient recorder. Between the laser pulses, however, the TOFMS is not used for 99.98 msec. 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). Figure 1 shows the ion source of the new instrument with gas inlet and the geometry of the different ionisation laser and electron beams (view is towards the direction of the ion exctraction). The instrument is designed as a mobile device. The OPO laser 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.

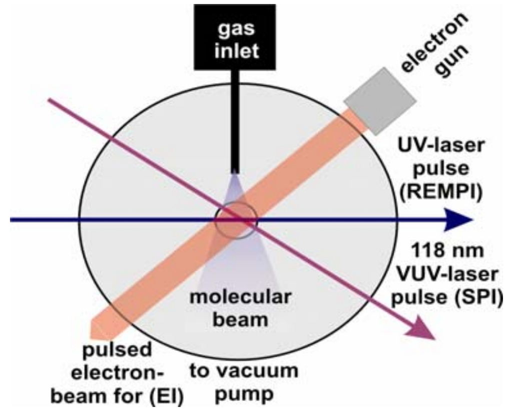

Figure 1: Ionisation region of the new mass spectrometer: The molecular beam can be alternatively ionise by an UV- (REMPI) or VUV-laser beam (SPI) or by an electron beam (EI)

Results and Discussion

The new instrument was tested in a 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 and directly quenches the sampled gases to temperature of about 300 °C. Figure 2 shows the measurement set-up at the waste incineration plant. The instrument was able to detect a large variety of compounds. Figure 3 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 toxic aromatic PAH (ppb level). At specific wavelengths, nitrogen-containing compounds (important for NOx-formation, not shown in figure 3) such as aniline or carbazole were detectable. The SPI method (middle trace in figure 3) shows NH_3, some aliphatic compounds, benzene, phenol, cyanobenzene and some further significant smaller aromatics at ppb or ppm levels. With the EI method the major compounds, such as O_2, CO_2 or H_2O are also detectable. Furthermore minor compounds such as HCN, SO_2, acetylene and HCl were measured in the higher ppm-range by EI-TOFMS (lower trace in figure 3). The important improvement is that the spectra are recorded in parallel, i.e. 5 SPI- and 5 REMPI-mass spectra as well as one EI mass spectrum (19990 sweeps) are recorded every second. In Figure 4 time-to intensity profiles (partly quantified) of ammonia (SPI), hydrogen cyanide (EI), hydrogen chloride (EI), toluene (SPI), cyanobenzene (SPI), naphthalene (REMPI), methylbiphenyl (REMPI), cyanonaphthalene (REMPI) and pyrene (REMPI) are depicted.

Figure 3: The instrument at the measurement place in a waste incineration plant.

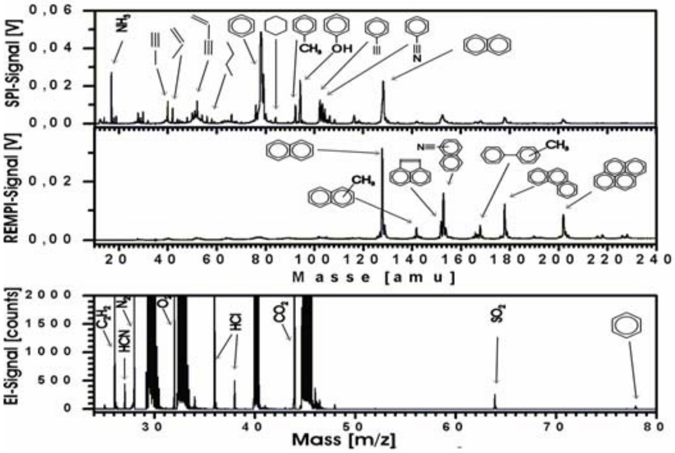

Figure 2: Waste incineration flue gas mass spectra obtained with the new instrument. For detail see text

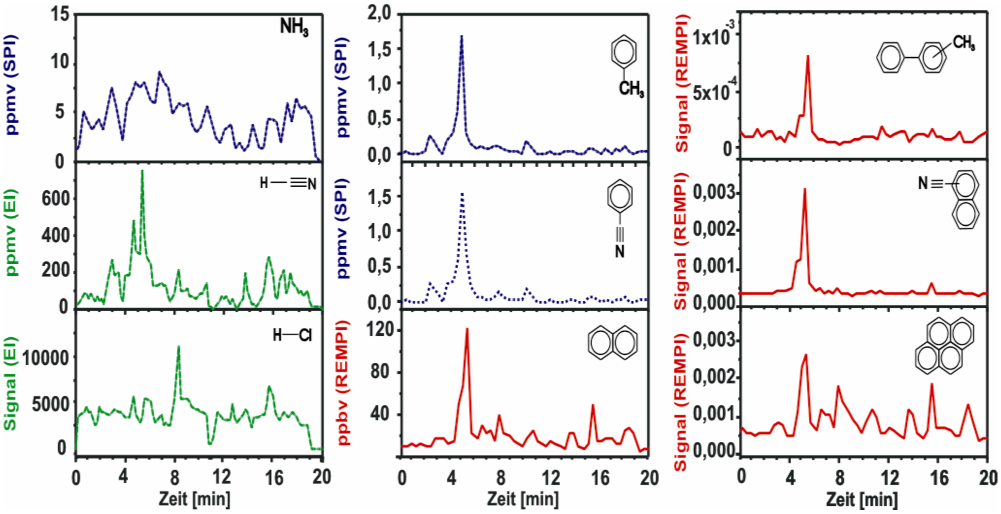

Figure 4: Time-to intensity profiles of different compounds in the flue gas of the waste incineration plant

In summary the developed mass spectrometer is useful for a comprehensive on-line characterization of flue gases. The correlation between different chemical species, e.g. between known PCDD/F surrogates and compounds which potentially are involved in PCDD/F formation mechanisms, may help to reveal the complex chemical reaction taking place in the flue gas channel.

Acknowledgements

Funding of the research by the *Deutsche Bundesstiftung Umwelt* (projects AZ 04778 and AZ 12447) and the German *Federal Ministry of Education and Research* (BMBF) gratefully acknowledged.

References

(1) Zimmermann, R.; Heger, H. J.; Kettrup, A.; Boesl, U. *Rapid Communications in Mass Spectrometry* **1997,** *11*, 1095-1102.
(2) Thanner, R.; Oser, H.; Grotheer, H.-H. *European Mass Spectrometry* **1998,** *4*, 215-222.
(3) Heger, H. J.; Zimmermann, R.; Dorfner, R.; Beckmann, M.; Griebel, H.; Kettrup, A.; Boesl, U. *Analytical Chemistry* **1999,** *71*, 46-57.
(4) Mühlberger, F.; Zimmermann, R.; Kettrup, A. *Analytical Chemistry* **2001,** *73*, 3590-3604.
(5) Mühlberger, F.; Wieser, J.; Ulrich, A.; Zimmermann, R. *Analytical Chemistry* **2002,** *74*, 3790-3801.
(6) Butcher, D. J.; Goeringer, D. E.; Hurst, G. B. *Analytical Chemistry* **1999,** *71*, 489-496.
(7) Yamada, M.; Hashimoto, Y.; Suga, M.; Waki, I.; Sakairi, M.; Hori, Y.; Sakamoto, M. *Organohalogen Compounds* **2001,** *54*, 380-383.
(8) Hishimoto, Y.; Suga, M.; Yamada, M.; Takada, Y.; Waki, I.; Sakairi, M. *Organohalogen Compounds* **2001,** *20*, 221-224.
(9) Zimmermann, R. Habilitation-Thesis, Technische Universität München, 2000.
(10) Mühlberger, F. Ph.D.-Thesis, Technische Universität München, München, submitted, 2003.
(11) Zimmermann, R.; Heger, H. J.; Blumenstock, M.; Dorfner, R.; Schramm, K.-W.; Boesl, U.; Kettrup, A. *Rapid Communications in Mass Spectrometry* **1999,** *13*, 307-314.
(12) Grotheer, H.-H.; Nomayo, M.; Pokorny, H.; Thanner, R.; Gullett, B. K. *Trends in Applied Spectroscopy* **2001,** *3*, 181-206.