Application of single photon ionization time-of-flight mass spectrometry (SPI-TOFMS) with an electron beam pumped excimer lamp for the detection of trace compounds in combustion processes

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Introduction

Single-photon ionization (SPI) with vacuum-ultraviolet (VUV) light allows an efficient and soft ionization of organic compounds yielding mass spectra with no or only few fragment peaks. Selectivity is provided via the ionization potential (IP), as only compounds with an IP lower than the photon energy can be ionized. New compact and robust, mobile SPI-MS instruments based on a novel VUV-lamp technology have been developed for on-line analysis of trace compounds (ppb concentration level). Such systems exhibit several advantages over laser based instruments such as a more compact, less expensive and easier to handle setup. Recently, this was successfully demonstrated by applying a compact and mobile quadrupole mass spectrometer (QMS) system with a continuous working Argon VUV-lamp[1; 2], which can be used for on-line monitoring of trace compounds such as monochlorobenzene (MCB) or aliphatic and aromatic hydrocarbons. Controlling such trace compounds is often an effective way to reduce toxic compounds such as polychlorinated dibenzo-p-dioxins and furans (PCDD/PCDF) in flue gases.

This concept is now expanded by combining a gateable VUV lamp with a time-of-flight mass spectrometer (TOFMS), which is described in the following.

Methods and Materials

An electron gun generates a 13 keV electron beam, which is sent into a rare gas cell. The rare gas volume (p ~2 bar) is separated from the vacuum, in which the electrons are produced, by means of a 0,7x0,7 mm^2, 300 nm thick silicone nitride (SiN_x) foil. In the dense rare gas the energetic electrons are stopped, leading to ionization and excitation of the gas atoms. In successive gas kinetic steps diatomic rare gas excited molecules (excimers) are formed. The radiative decay of these excimers provides intense and brilliant VUV radiation. This novel “electron-beam pumped rare-gas excimer VUV-lamp” technique[3] generates relatively monochromatic VUV-radiation[3; 4]. By choosing various rare gases or rare gas mixtures in the lamp, different wavelengths can be generated (e.g. Ar – 126 nm, Ne/H_2 – 121.57 nm, Kr – 147 nm) leading to an adjustable selectivity according to the different ionization potentials of analyte compounds.

The VUV-excimer lamp (TuiLaser, Germering, Germany) is coupled to a compact, mobile time-of-flight mass spectrometer (Kaesdorf, Munich, Germany) by a special interface consisting of two equal spherical MgF_2-lenses forming a 1:1 imaging system which collects several percent of the isotropically emitted VUV-light, which is subsequently focused into the centre of the ion source.

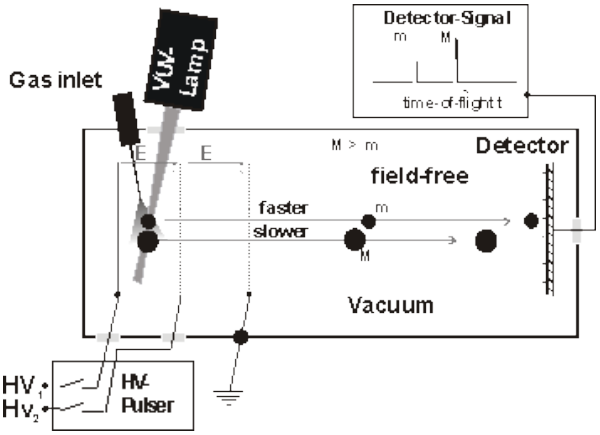

Figure 1: Schematic drawing of the electron-pumped rare gas excimer VUV-lamp-TOFMS system.

Figure 1 shows a schematic drawing of the experimental setup. Matching the operating conditions of the TOFMS the VUV-lamp was operated with a HV-Pulser producing VUV-pulses with a frequency of 50 Hz and a pulse width of 1 µs. Average pulse energy was 6 mW yielding a number of approximately $4*10^9$ VUV-photons/pulse. The TOFMS system operated in reflectron mode accordingly with an ion extraction frequency of 50 Hz. For this first demonstration, 500 single spectra were averaged to reduce the signal to noise ratio resulting in a time resolution of ten seconds. However, it will be feasible to extend the pulse frequency to 1 kHz, thus reducing the time resolution considerably to 0.5 s.

Limits of detection (LOD) down to 50 ppb for benzene, toluene and m-xylene (BTX) were achieved with this prototype, using a 13keV electron beam. For acetone and MCB, respectively, even lower values could be attained (34 and 28 ppb), which for the letter may be due to their higher photo ionization cross-section[5].

Results and Discussion

One of the most important features of single photon ionization with VUV-light is the fragmentation free ionization of organic compounds[6]. This is demonstrated exemplarily in Figure 2 by a SPI-TOFMS spectrum of a gas standard containing 10 ppm MCB recorded with an electron beam pumped argon excimer VUV lamp emitting 126 nm pulses.

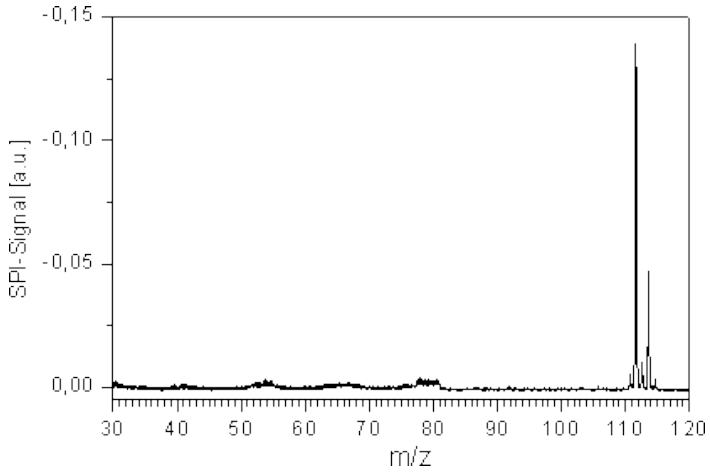

Figure 2: SPI-TOFMS spectrum of MCB utilizing a pulsed argon excimer lamp providing VUV photons with a

wavelength of 126 nm

Figure 3 depicts a first application of the new conceived SPI-TOFMS system presenting an on-line recorded mass spectrum of cigarette main stream smoke. Several compounds such as propene (m/z 42), butadiene (m/z 54), cyclopentadiene (m/z 66), isoprene/furane (m/z 68), several furane derivatives (m/z 82, 96), and xylenes (m/z 106) could clearly be distinguished. Furthermore, nicotine (m/z 162) was detected. The fast mass spectrum acquisition also allows continuous monitoring, well suited for industrial (process control, pollutant monitoring) and scientific research applications.

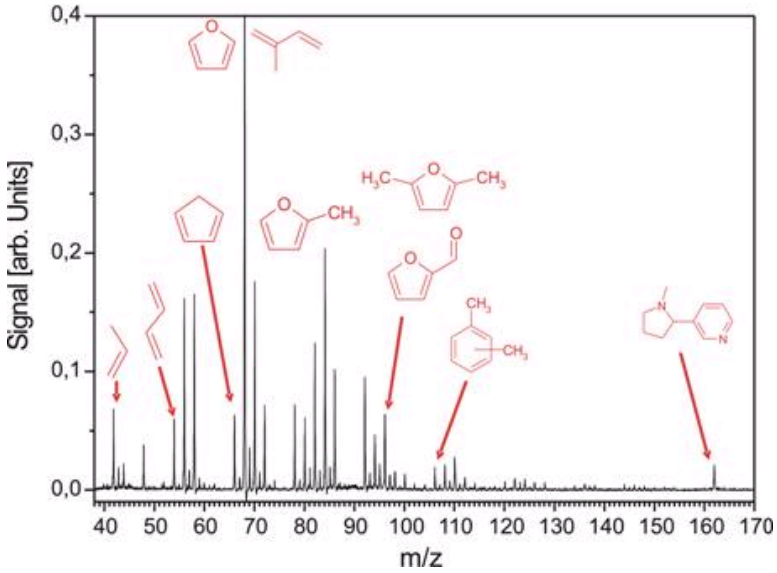

Figure 3: VUV-lamp SPI-TOFMS on-line, real-time analysis of cigarette main stream smoke.

Acknowledgements

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References

[1]Mühlberger, F., Wieser, J., Ulrich, A. , and Zimmermann, R. (2004) *OrganohalogenCompounds* 66: 795-799.

[2]Mühlberger, F., Wieser, J., Morozov, A., Ulrich, A. , and Zimmermann , R. (2005) *Anal. Chem.* 77(7): 2218-2226.

[3]Wieser, J., Murnick, D. E., Ulrich, A., Huggins, H. A., Liddle, A. , and Brown, W. L. (1997) *Rev. Sci. Instrum.* 68(3): 1360-1364.

[4]Wieser, J., Salvermoser, M., Shaw, L. H., Ulrich, A., Murick, D. E. , and Dahi, H. (1998) *J. Phys. B* 31: 4589-4597.

[5]Tonokura, K., Nakamura, T. , and Koshi, M. (2003) *Anal. Sci.* 19(8): 1109-1113.

[6]Butcher, D. J. (1999) *Microchem. J.* 62: 354-362.