

Single Photon Ionization Mass Spectrometry with a Novel Electron-Pumped Excimer Lamp for Detection of Trace Compounds from Thermal Processes

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Introduction

A combination of soft and selective photo-ionization methods, like the single photon ionization (SPI) using vacuum ultraviolet (VUV) light with mass spectrometry (MS), provides powerful analytical instrumentation for real-time on-line-monitoring of trace substances in complex process gases. New compact and robust, mobile SPI-MS instruments have been developed for on-line analysis of trace compounds (ppb concentrations). It is based on a novel VUV-lamp technology for efficient SPI ionization. With the VUV-lamp technology the development of rugged photo-ionization mass spectrometer systems seems feasible. These instruments can be used for continuous on-line monitoring of trace compounds, such as monochlorobenzene (MCB). Chlorobenzene, known as a surrogate for the emissions of dibenzo-p-dioxins (PCDD) and dibenzofurans (PCDF), was used to predict the emitted toxicity of PCDD/F (I-TEQ)¹. Controlling such trace compounds is therefore an effective way to reduce toxic compounds in flue gases.

A short description of the new SPI-MS is given. The combination of the new VUV-light source with a quadropole-MS is described briefly, and first results are presented.

Methods and Materials

Single photon ionization with VUV-light allows an efficient and soft (fragmentation free) ionization of organic compounds. Ultraviolet laser light can be used for that purpose for research and development. Industrial monitoring, however, suffers from the fact that laser based SPI requires expensive and sophisticated laser system. In principle, single photon ionisation mass spectrometry can also be performed using VUV-lamps, e.g. deuterium lamps, as photon source. Their power density, however, is weak in the required spectral range. Thus it is difficult to use conventional VUV-lamps for fast on-line analysis of trace compounds. In this work a new incoherent VUV-photon source, in the form of an electron beam pumped rare gas excimer lamp was applied as a single photon ionisation (SPI) source for a quadruple mass spectrometer (QMS).

The main innovation of this novel VUV-excimer lamp is a $0,7 \times 0,7 \text{ mm}^2$, 300 nm thick silicone nitride (SiN_x) foil, which separates a rare gas volume ($p \sim 1 \text{ bar}$) from a vacuum chamber containing an electron gun (EG). The EG² generates a 13 keV electron beam which is sent into a rare gas through the 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. The novel “electron-beam pumped rare-gas excimer VUV-lamp” technique² (VUV-excimer lamp) represents an ideal alternative to laser light sources for SPI-MS³, as it also generates relatively monochromatic VUV-radiation^{2, 4}. By choosing various rare gases or rare gas mixtures in the lamp, different wavelengths can be generated (e.g. Ar – 126 nm, Ne/H₂ – 121,57 nm, Kr – 147 nm).

A special interface has been developed for combining a VUV-excimer lamp from TuiLaser (Germering, Germany) with a compact, mobile quadrupole mass spectrometer (QMS 200, Pfeiffer, Germany).

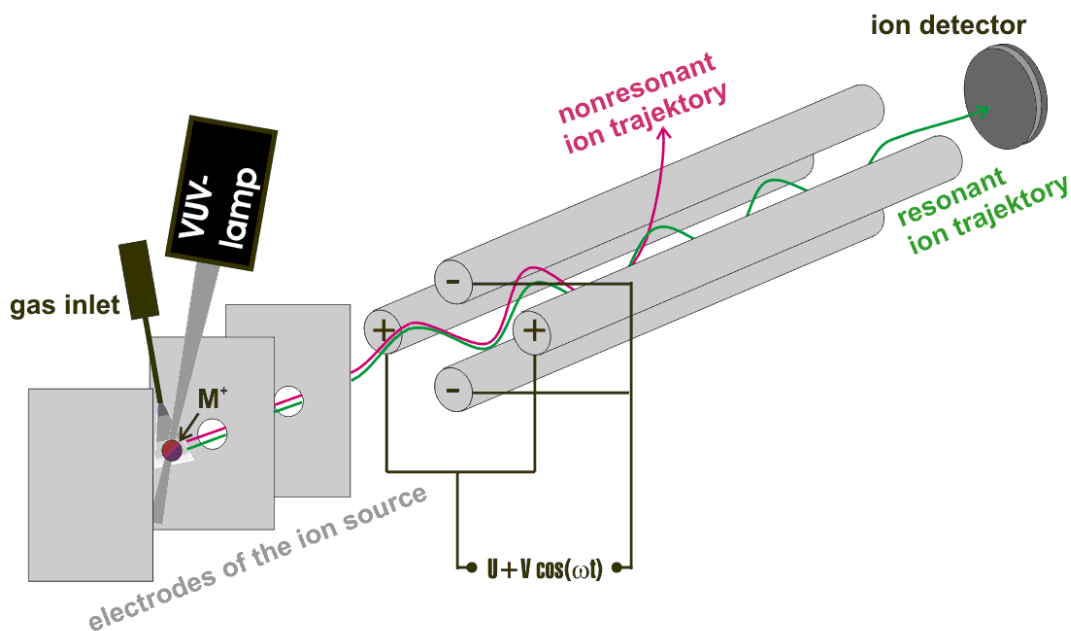


Figure 1: Schematic drawing of the electron-pumped rare gas excimer VUV-lamp-QMS system.

The interface consists of two equal spherical MgF_2 -lenses forming a 1:1 imaging system which collects several percent of the isotropically emitted VUV-light. The light is focused into the centre of the ion source. Using a sodium salicylate fluorescent screen the diameter of the VUV-beam could be measured at the centre point of the ion source. Measurement showed that 80% of the collected light could be focused to the focal point within a diameter of 3 mm.

According the operating conditions of the QMS the VUV-light was generated continuously. For other applications the light source may also be pulsed³. A first prototype (Figure 1) of a VUV-excimer lamp-QMS instrument was built and tested in the laboratory.

Detection limits (DL) down to 50 ppb for benzene, toluene and m-xylene (BTX) were achieved (scan speed 1s/amu) with the prototype, using a 10 μ A, 13keV electron beam. Using a QMS with a 8 mm rod system should give DL's in the low ppb or even in the upper ppt region.

Results and Discussion

Fragmentation free ionisation of fragile aliphatic compounds was demonstrated. The ionisation selectivity can be adjusted to the species which has to be detected due to the variability in the VUV wavelength which is achieved by exchanging the gas filling in the lamp (i.e.)^{2,4}. Figure 2 shows a SPI-QMS spectrum of MCB recorded with an electron beam pumped argon excimer VUV lamp emitting 126 nm. MCB has an ionisation potential of 9,07 eV and has a relatively high photoionization cross-section for VUV-light⁵. No gas standard with MCB in ppb or ppm concentrations was on-hand during the measurement for figure 2 and therefore the DL for MCB can only be estimated. Tonokura⁵ measured the photoionization cross-section of MCB and Benzene. He found that MCB has a 3,25 times larger photoionization cross-section than benzene at 121.6 nm. Regarding his results and assuming a larger cross-section for MCB compared with benzene also at 126nm the DL of the new system should be in the low ppb range for MCB.

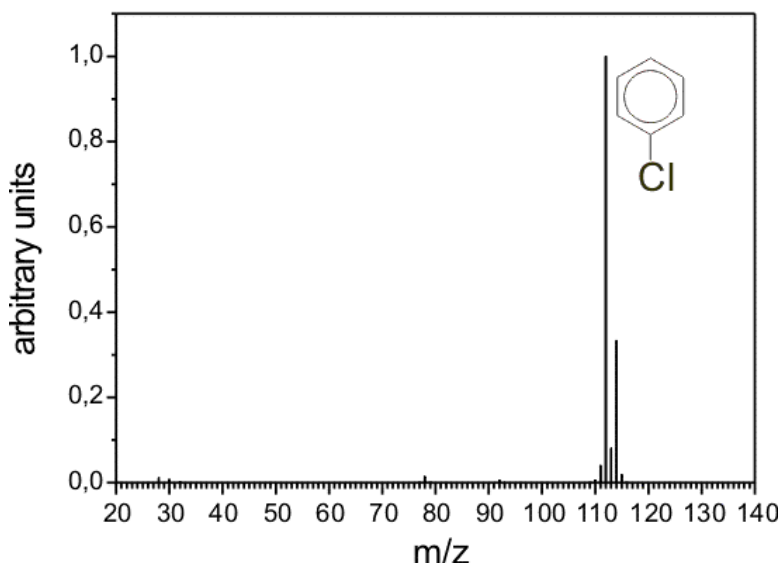


Figure 2: SPI mass spectrum of MCB recorded with a 126 nm VUV argon excimer lamp used as the ionization source

Furthermore first on-line real-time application results were obtained with the VUV-lamp SPI-QMS technique. The exhaust gas of an automobile with petrol engine was analysed in detail. Several compounds like nitric oxide (m/z 30, IP 9,26 eV), butadiene (m/z 54, IP 9,07), butenes (m/z 56, IP 9,13 – 9,55 eV) crotonaldehyde (m/z 70, IP 9,73 eV), benzene (m/z 78, IP 9,24 eV), toluene (m/z 92, IP 8,82 eV), xylenes (m/z 106, IP 8,44 – 8,56 eV) and trimethylbenzenes (m/z 120, IP 8,27 – 8,41 eV)^{6,7} were detected and partly quantified. The time history of the concentrations of

these compounds during a cold engine start and three acceleration cycles (rapidly increased engine revolution without load) are shown in Figure 3.

Besides these already very promising results of the VUV-excimer lamp-QMS prototype, significant potential for further optimisation was identified. The new system is in principle perfectly suited for industrial process monitoring applications. The lamp is very robust and the overall system can be placed in a 1 m high 19" cabinet. Due to the stability and the expected lifetime of the light source this technique has the potential to become a continuously running system e.g. for monitoring MCB as surrogate for dibenzo-p-dioxins (PCDD) and dibenzofurans (PCDF). Several other possible applications can be projected for the VUV-lamp SPI-QMS approach for example in the chemical, minearil-oil producing and food processing industry, as well as in scientific research.

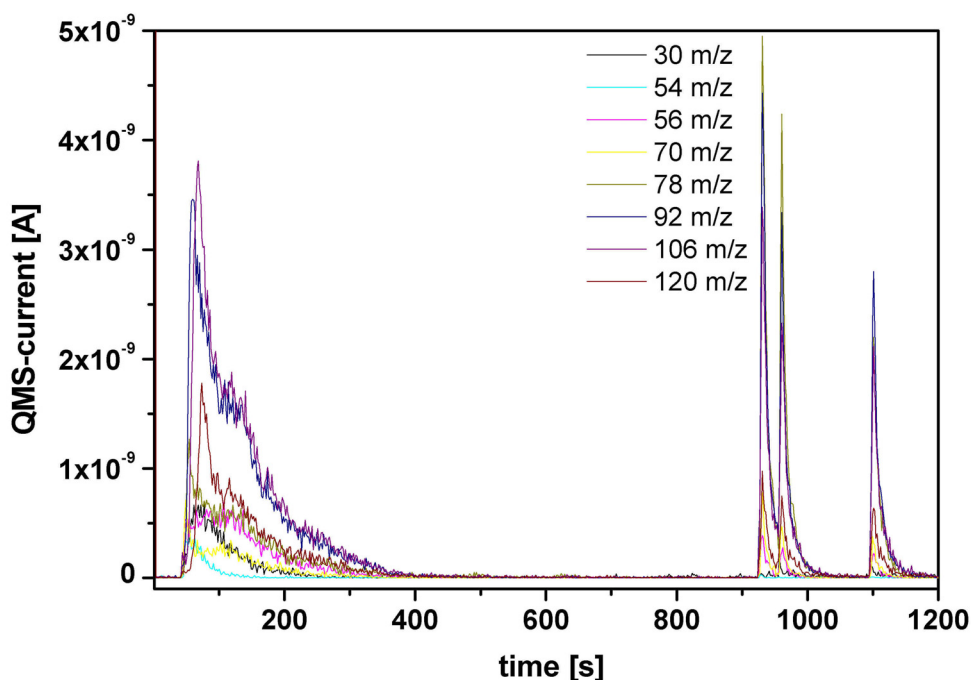


Figure 3: VUV-lamp SPI-QMS on-line, real-time gas analysis of automobile exhaust gas. The concentration changes of several compounds listed in the text are shown for a cold engine start and three additional acceleration cycles at $t = 920, 950$ and 1000 s during which the engine revolution was transiently increased without load.

Acknowledgements

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References

- 1 Blumenstock, M., Zimmermann, R., Schramm, K.-W., Kaune, A., Nikolai, U., Lenoir, D., Kettrup, A. (1999) *Journal of Analytical and Applied Pyrolysis*, 49, 179-190.
- 2 Wieser, J., Murnick, D. E., Ulrich, A., Huggins, H. A., Liddle, A., Brown, W. L. (1997) *Review of Scientific Instruments*, 68, 1360-1364.
- 3 Mühlberger, F., Wieser, J., Ulrich, A., Zimmermann, R. (2002) *Analytical Chemistry*, 74, 3790-3801.
- 4 Wieser, J., Salvermoser, M., Shaw, L. H., Ulrich, A., Murick, D. E., Dahi, H. (1998) *Journal of Physics B*, 31, 4589-4597.
- 5 Tonokura, K., Nakamura, T., Koshi, M. (2003) *Analytical Chemistry*, 19, 1109-1113.
- 6 Butcher, D. J., Goeringer, D. E., Hurst, G. B. (1999) *Analytical Chemistry*, 71, 489-496.
- 7 Schmiedel, H.-P., German Society for Petroleum and Coal, Science and Technology: Hamburg, 2003, pp 81.