A helium metastable seeded secondary plasma in the low mbar pressure regime – characterization and evaluation for mass spectrometric applications

Klaus Brockmann[1]; David Mueller[1]; Yessica Brachthaeuser[1]; Hendrik Kersten[1]; Thorsten Benter[1];
Achim von Keudell[2]; Thomas Kuschel[2]; Marc Boeke[2]; Joerg Winter[2];
Michel Aliman[3]; Gennady Fedosenko[3]; Ruediger Reuter[3]; Alexander Laue[3]; Valerie Derpmann[3]; Hin Yiu Chung[3]

1) Physical & Theoretical Chemistry
Wuppertal, Germany
Institute for Pure and Applied Mass Spectrometry

2) PAC - Plasma Application Consulting GmbH & Co. KG
Bochum, Germany

3) Carl Zeiss SMT GmbH
Oberkochen, Germany

Introduction

Challenge:

The active zone of a low temperature plasma provides a lucrative environment for reasonable ionization efficiencies. However, the interplay between the sample, the plasma volume and the ion optical elements of the subsequent mass spectrometer are quite challenging in terms of the analytical requirements (i) stability, (ii) reproducibility and (iii) simplicity of the mass spectrometric information.

Approach:

- A helium metastable enriched effluent of a primary DC discharge drives a secondary plasma in the lower mbar pressure range
- Different stable plasma modes, including a "seeded plasma", are established inside a cage of auxiliary electrodes
- A coaxial gas inlet allows separated buffer- and sampling gas introduction
  → minimized perturbation of the plasma
  → sampling from complex process gases

In depth – investigations on the performance and on operational parameters were carried out:

- Stable plasma modes
- Distances and voltages of auxiliary electrodes
- Buffer gas pressure (1 - 10 mbar)
- Sampling gas pressure (100 to 1000 mbar)
- Sheath gas: He for charge transfer (CT) or alternatively H_2 in He for proton transfer (PT)
- Pulsed sampling vs. continuous sampling
- Total ion current
- Visual observations

Methods

Detection

Mass Spectrometer [1]

- ➢ The plasma source (PS) is attached to a TOFWerk CTOF mass analyzer with custom ion transfer stage
- ➢ Narrow mass range filtering of reagent and carrier gas ions or other dominating ionic species allows efficient enhancement of the dynamic range of the TOF analyzer

Ion current

- ➢ Mesh electrode mounted in the ion transfer optics (between tube lens and filter orifice) [1]
- ➢ Acquisition of ion currents: Electrometer (6430 Sub-Femtoamp Remote SourceMeter®, Keithley)

Ionization

- ➢ The plasma source attached to the first differential pumping stage of the TOF analyzer (between sampler and skimmer)
- ➢ Orthogonal arrangement of analyte inlet, plasma source, and skimmer
- ➢ Plasma source is operated with Helium 5.0 (Messer Industriegase GmbH, Bad Soden, Germany) at reduced pressures
- ➢ Helium metastable enriched effluent is driving a secondary plasma
- ➢ For charge transfer helium as sheath gas and for proton transfer addition of H_2 in He

Experimental Setup

Ionization stage:

- Integrated into the first differential pumping stage of a TOFWerk CTOF with custom ion transfer optics [1]
- Plasma source (PS) is orthogonally attached with respect to the skimmer
- Established plasma is stabilized and spatially confined with an arrangement of auxiliary electrodes (inlet-electrode, face plate of PS, cage electrode)
- Background pressure is adjustable in the range of 1 to 10 mbar

Gas inlet:

- Coaxially designed inlet allows addition of sheath gas for plasma stabilization
- Fast switching three-channel-valve enables pulsed sampling as well as continuous sampling

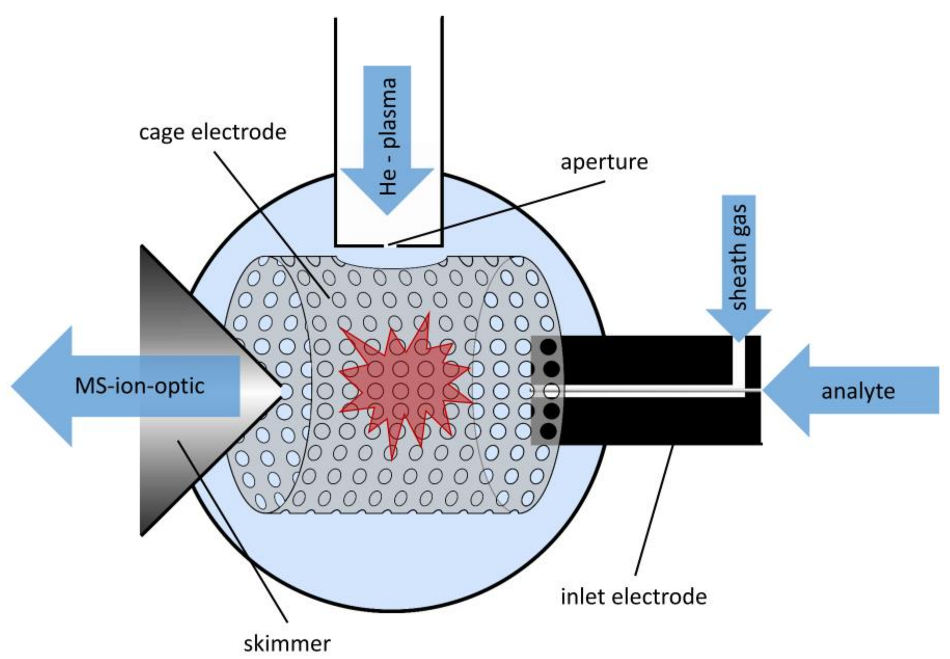


Fig. 1: Schematic setup

Influence of the Sheath Gas

- The coaxial design of the gas inlet allows for the addition of a sheath gas in the continuous as well as in the pulsed sampling mode
- The sheath gas is used to stabilize the plasma mode, thus perturbation of the plasma due to the presence of analyte and process gas is minimized
- However, the presence of additional sheath gas slightly decreases the analyte signal intensity, probably due to altered fluid dynamic properties
  - Measurements on the total ion current support this observation
  - Addition of small amounts of hydrogen to the helium sheath gas switches the ionization mode from CT to PT

$$He^M + H_2 \rightarrow HeH^+ / H_2^+ \rightarrow H_3^+$$

- For the detailed reaction cascade c.f. MP #63

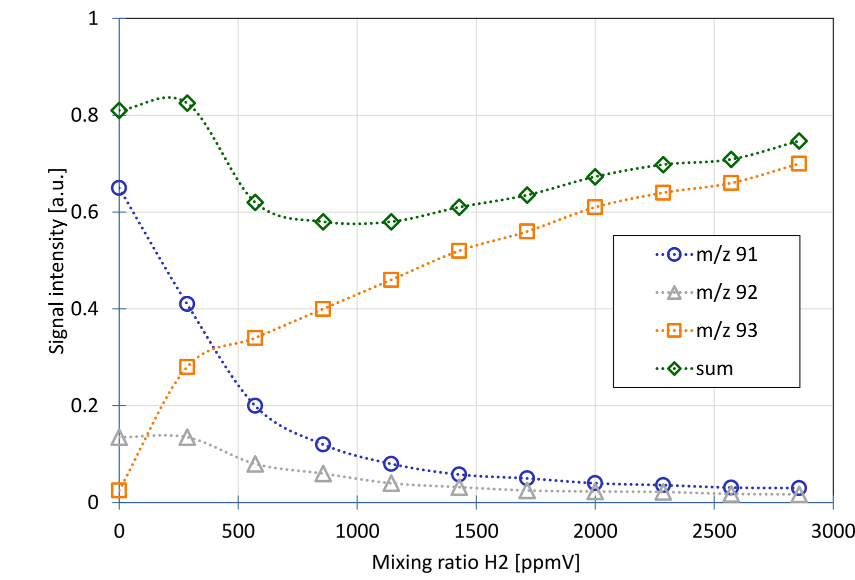


Fig. 5: Variation of the sheath gas composition. Hydrogen is added to the helium gas flow in the range of 300 ppmV to 2800 ppmV. Toluene as analyte is present at 100 pptV.

Continuous Analyte Sampling

- In continuous analyte sampling mode with a sampling pressure of 200 mbar numerous measurements were carried out to optimize operational parameters
- The minimal sampling pressure was determined to 15 mbar
- We expect the flow through the capillary to be choked if sample pressure is > 100 mbar [2]

Analytical Performance – LOD:

- Measurements were carried out with toluene in nitrogen as analyte in CT as well as PT mode
- Highly linear range observed down to 4 pptV
- The limit of detection was determined to be < 1 pptV in CT mode (60 s acquisition time)

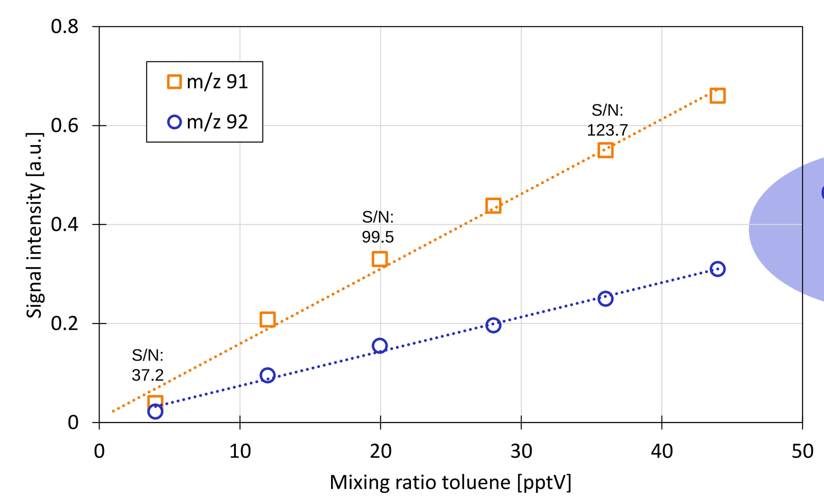
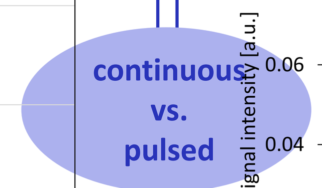


Fig. 2: Signal intensity of m/z 91 and 92 (CT mode) with toluene mixing ratio between 4 and 45 pptV; 1 min. acquisition time



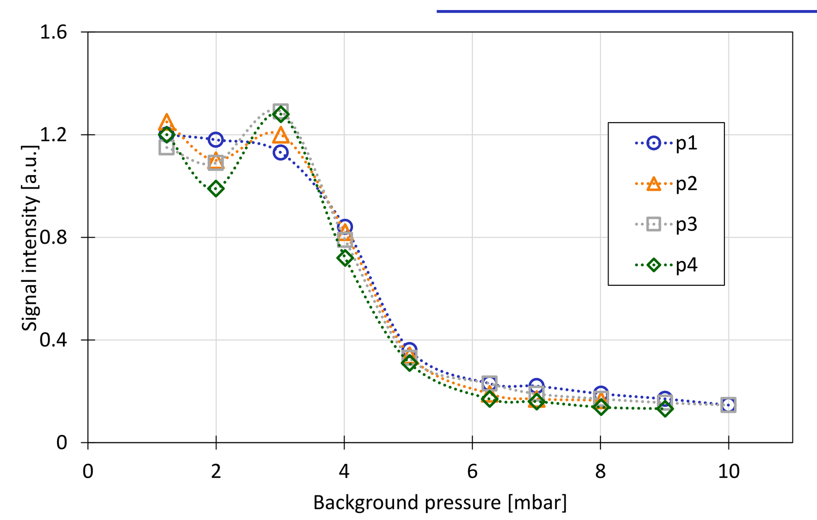


Fig. 3: Signal intensity of 250 pptV toluene in nitrogen (sum of m/z 91 and m/z 92) at different background pressure and different PS helium pressures ($p_1>p_2>p_3>p_4$).

Variation of the background pressure in the ionization chamber:

- Varied in the range of 1 and 10 mbar for different helium pressures in the PS
- Signal intensity when 250 pptV toluene in nitrogen were present was evaluated
  - ➢ Optimum background pressure is 1 to 3 mbar independent of the helium pressure in the PS
  - ➢ At higher background pressure the signal intensity is strongly decreasing

Variation of the inlet electrode distance:

- Skimmer-to-inlet-electrode distance was varied
- At position 1 the inlet-electrode is centered under the primary plasma source face plate orifice
  - ➢ Further lateral movement towards skimmer leads to signal decrease
- With increasing distance the signal intensity is constantly increasing
- Depending on the current design further increase of the electrode distances is not possible

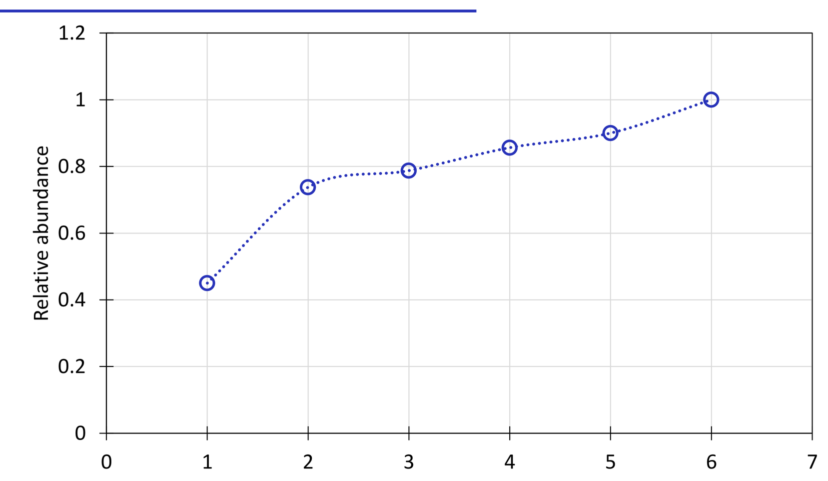


Fig. 4: Signal intensity of 250 pptV toluene in nitrogen with varying skimmer to inlet-electrode distance.

Pulsed Analyte Sampling

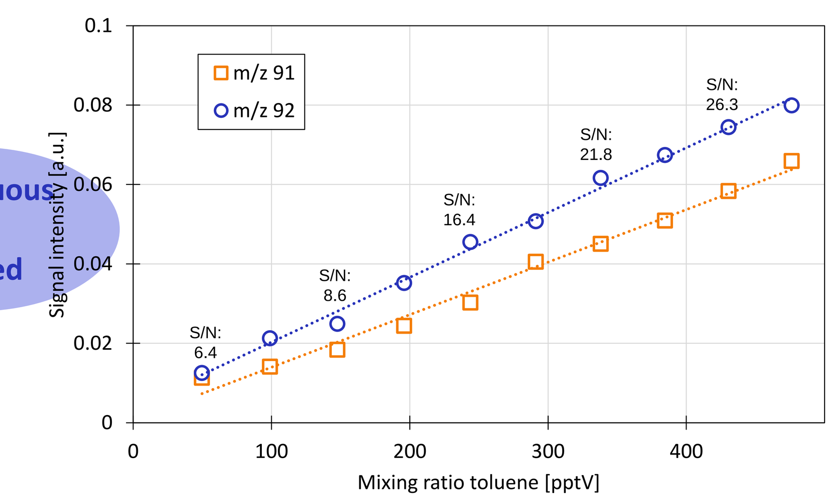


Fig. 6: Signal intensity of m/z 92 (CT mode) depending on the toluene mixing ratio between 50 and 480 pptV; 7 sec. acquisition time.

- With S/N = 6 the limit of detection was determined to 60 pptV in CT mode (m/z 92 as base signal) and to 200 pptV in PT mode (m/z 93 as base signal). Pulse widths of 500 ms and sample pressures of 600 mbar were applied.

What is the pursued advantage of pulsed analyte sampling?

- Significant perturbation of the plasma by the sampled analyte and/or process gas matrix is avoided in pulsed mode
- In continuous mode, perturbation of the plasma may lead to:
  - Instability of the plasma mode
  - Loss of analytical performance in terms of stability and reproducibility

Experimental procedure:

The sampling pressure was maintained at 600 mbar. A 3-way-valve switched between sample pulses and a continuous helium or nitrogen flow to maintain the background pressure in the ionization source.

Results:

Even with the analyte (in N_2 matrix) sampling pulse width set to the minimum value of 10 ms, the plasma changes instantly with the pulse (change in plasma glow)

→ In the present configuration the composition of the background pressure should be maintained by the process gas matrix

A constant ion current of approx. 5 nA was measured during, as well as between pulses with N_2 as the continuously added main gas. With helium as the main gas flow the ion current between sample pulses increased up to 20 nA.

Seeded Plasma [3]

Definition of seeded plasma mode

- A seeded plasma mode is stabilized only in combination with a primary plasma and the potential gradients within the electrode configuration of the secondary plasma
- In our current setup the visual plasma volume is stabilized between skimmer and inlet electrode (c.f. Fig. 1 and Fig. 7 c)

Why seeded plasma?

- Preliminary experiments revealed a significant, up to two orders of magnitude elevated ion current compared to the expansion mode with only the primary plasma being active (c.f. Fig. 7 b)
- Since the expansion mode in the actual setup leads to higher sensitivity than in the preliminary experiments it is expected that significantly enhanced sensitivities with the seeded plasma will result

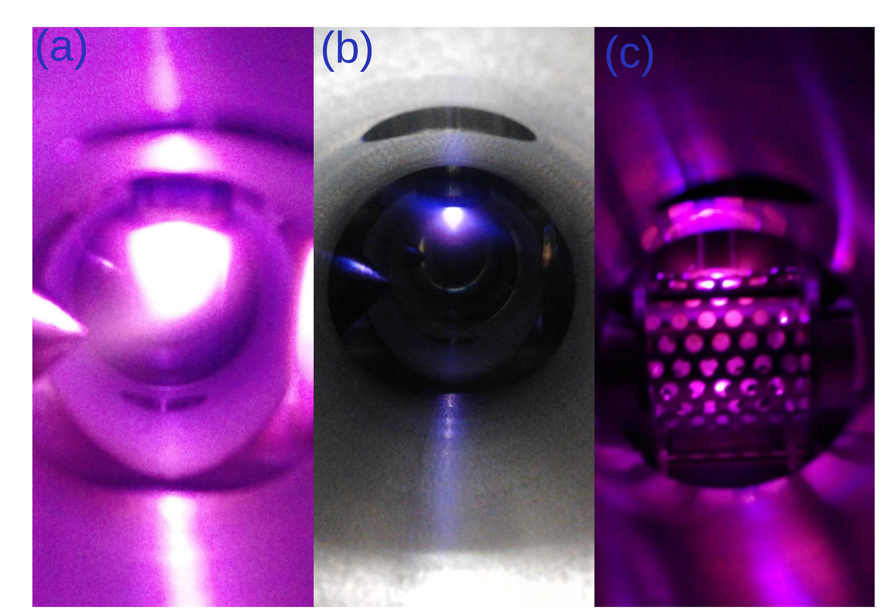


Fig. 7: Visual comparison of (a) seeded mode and (b) expansion mode of the preliminary tests. (c) Current setup.

Conclusions

Instrumentation:

- A plasma based ion source was developed for implementation in the first differential pumping stage of a TOFWerk CTOF-MS
- Minimum sampling pressure in this geometry, due to the capillary gas inlet is about 15 mbar
- Different plasma modes were established and investigated concerning stability and analytical performance
- With the most effective plasma mode further optimization measurements were carried out
  - The background pressure in the ionization chamber should be approx. 1 mbar
- The sheath gas helped to stabilize the plasma, although the signal intensity slightly decreased
- Addition of hydrogen to the helium sheath gas flow allows ionization via proton transfer
  → Simplification of mass spectra due to less fragmentation

Analytical Performance:

- Continuous sampling:
  - LOD: < 4 pptV in CT mode
- Pulsed sampling:
  - LOD: 60 pptV (CT) and 200 pptV (PT)
- Total ion current:
  - in N_2-matrix up to 5 nA
  - in He-matrix up to 20 nA

Outlook:

- Stabilization of Seeded Plasma Mode

Literature

[1] Brachthaeuser, Y.; Mueller, D.; Kersten, H.; Brockmann, K.; Benter, T. Development of a compact multiple-ionization-stage TOF mass analyzer system for trace component monitoring within chemically challenging process gas matrices, *62nd ASMS Conference on Mass Spectrometry and Allied Topics*, Baltimore, MD, USA (**2014**).
[2] Brockmann, K.; Wißdorf, W.; Hyzak L.; Kersten H.; Mueller, D.; Brachthaeuser, Y.; Benter, T.; Fundamental characterization of ion transfer capillaries used in Atmospheric Pressure Ionization sources; *58th ASMS Conference on Mass Spectrometry and Allied Topics*, Salt Lake City, UT, USA (**2010**)
[3] Patent application P21163DE of Carl Zeiss SMT GmbH, "Secondary Micro-Plasma"

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