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

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Introduction

Challenge: The active zone of a low temperature plasma provides a lucrative environment for reasonable ionization and mass analysis. However, the interplay between the plasma, the sample volume and the ion optical elements of the subsequent mass spectrometer make the challenges in terms of the analytical requirements (i) stability, (ii) reproducibility and (iii) exploitation of the mass spectrometric information.

Approach:
- A Helmholtz metastable enriched efficient of a primary DC discharge driven 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
- Investigations on the performance and operational parameters were carried out.
- Stable plasma modes
- Distances and offsets of auxiliary electrodes
- Buffer gas pressure (1 - 10 mbar)
- Sampling gas pressure (500 to 1000 mbar)
- Sheath gas: He for charge transfer (CT) and alternatively, N2 for proton transfer (PT).
- Pulsed sampling vs. continuous sampling
- Total ion current
- Visual observations

Experimental Setup

Ionization stage:
- Integrated into the first differentiavng stage of a TOF/TOF spectrometer 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:
- Consistently designed inlet allows addition of sheath gas for plasma stabilization
- Fast switching three-channel valve enables pulsed sampling as well as continuous sampling.

Influence of the Sheath Gas
- The coastal 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 plasma gas in the TOF is mitigated.
- 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

Analytical Performance:
- S/N: measurements were carried out with toluene in nitrogen as analyte in CT as well as PT mode.
- The lower detection limit of 5 pptV was measured at 200 ms.
- Limit of quantification: 3 pptV.
- Analysed gas: helium.

Continous Analyte Sampling
- In continuous analyte sampling mode with a sampling of 200 mbar numerous measurements were carried out to optimize operational parameters.
- The minimal sampling pressure was determined to 25 mbar.
- We expect the flow throughput of the skimmer to be choked if the sample pressure is above 100 mbar.

Analytical Performance – LOD:
- Measurements were carried out with toluene as nitrogen in 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 (90% acquisition time).

Pulsed Analyte Sampling
- With N2 the limit of detection was determined to 60 pptV in CT mode (n=10 as basic signal) and to 300 pptV (n=9) in base peak in a pulsed width of 500 ns and sample pressures of 600 mbar were applied.
- Better detection limits: 20-30 pptV.
- The signal intensity was enhanced of the helium containing pulsed current between sample pulses increased up to 20x.

Variation of the background pressure in the ionization chamber:
- In the range of 5 and 10 mbar for different helium pressures in the PT.
- The signal intensity when 250 pSV toluene in nitrogen was present was evaluated.
- Optimum background pressure is 1 to 3 mbar independent of the helium pressure in the PSI.
- 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.
- Further lateral movements 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.

Variation of the sheath gas flow:
- AT the given configuration, helium is added to the helium gas flow in the range of 50 to 300 pptV.
- In case of 100 pptV the ion current is increased by a factor of 30.

Conclusions

Instrumentation:
- A plasma based ion source was developed for implementation in the first differentiavng stage of a TOF/TOF STOF-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: 200-400 pptV in CT mode.
- Pulsed sampling: 100-200 pptV (CT) and 200 ppb (PT).
- Total ion current: In N2, matrix up to 5 nA.
- In N2, matrix up to 20 nA.

Outlook:
- Stabilization of Seeded Plasma Mode

Literature

Seeded Plasma
- 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 plasma volume is stabilized between skimmer and inlet electrode (Fig. 1 and Fig. 2. a). What is the advantage of this setup?
- 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.
- 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.

Acknowledgement
Carl Zeiss SMT GmbH, Oberkochen, Germany, is acknowledged for supplying the instruments and financial support.
ZEISS plasma applications consulting GmbH & Co. KG for support and construction of the ionization source.

Figure 1: Schematic setup.