Absolute Calibration of Mass Spectrometric Ion Signals Using a Custom Electron Ionization Source

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Introduction

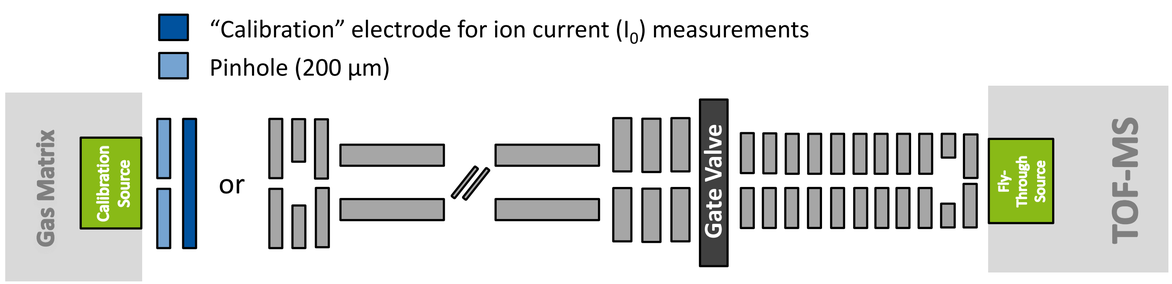
This work presents the concept of a "calibration" source which is used for comprehensive determination of ion transport efficiencies throughout the mass spectrometer as well as ion density measurements. The used MS system includes a 170 cm hexapole transfer stage, enabling long-distance ion sampling. A key application for such a system is in-situ ultra-trace element plasma analysis in hydrogen matrices as occurring in semiconductor manufacturing environments.

The present work introduces a custom, separately evacuated electron ionization (EI) source as such calibration source. The EI-based approach provides well-defined and controllable ionization conditions, enabling stable ion flux generation suitable for absolute ion counting and quantitative ion transport efficiency studies.

As a potential downside, filament burn-out may occur, particularly when operating the matrix gas containing chamber at elevated pressure.

Concept

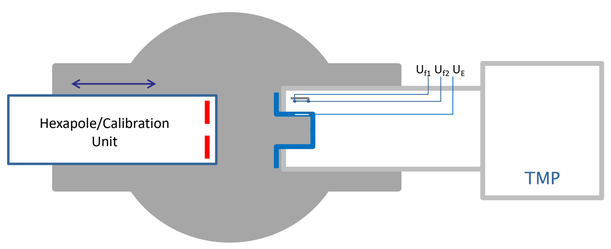
- Ion current (I_0) per time and area is measured at the "calibration" electrode with defined geometry and similar properties as the MS inlet stage.
- Due to the same geometry of the first transfer stage lens and the first calibration optic lens, the number of ions entering the MS-system through the transfer stage can be deduced.
- The total ion count emitted by the calibration source is also measured at the detector.
  - Mass resolved ion current per area and time provides insights in transport efficiencies through transfer and vacuum stages as well as plasma ion densities.
- Simultaneous measurement with the calibration unit and MS is not possible.



Schematical illustration of the calibration source concept including the transfer stage or calibration unit.

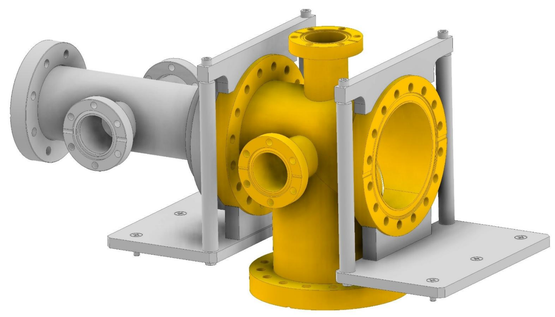
Instrumentation

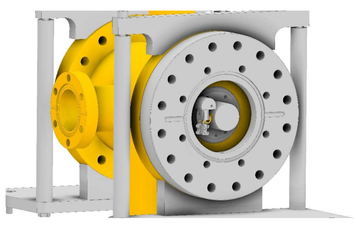
- A separately evacuated electron ionization source is developed to generate ions under well-defined and reproducible matrix gas conditions.
  - Source delivers a stable ion flux on the calibration electrode and into the MS.
- This approach should enable the quantification of total and species-specific ion losses across transfer stages and vacuum interfaces.



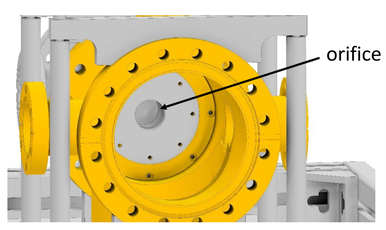
Schematic illustration of the EI-based calibration approach including a custom designed pumped EI-source.

3D-ISO view of the low-pressure (~10^{-6} mbar) area including the filament (gray) and the high-pressure (~10^{-2} mbar) area (yellow).





Rear view of the calibration source from the low-pressure side, with filament and cup electrode in view.



Front view in gas volume and cup electrode from the detector perspective.

Results

- Highly focused and narrow electron beam through orifice in cup electrode.
- Ions are produced in and around the electron beam.
  - Argon radicals are visible in blue/purple.
- Signal drop can be observed when the detector orifice is misaligned with the ion beam.

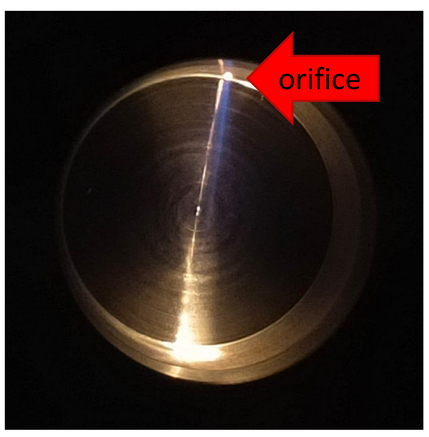
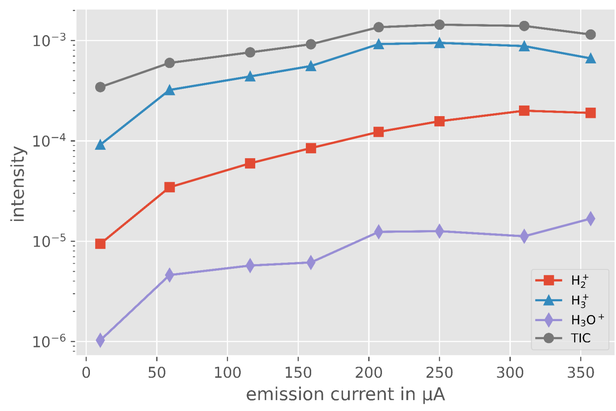


Image of the electron beam in argon matrix (~6 Pa), viewed from above at the bottom of the cup.

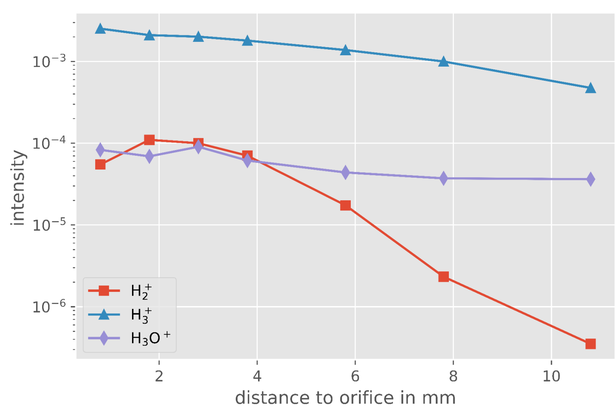
Variation of emission current

- Higher emission currents increase the abundance of all ionic species.
- H_2^+ scales linearly with the emission current, better visible on a linear scale.
- No cup voltage, space charge only in this experiment.

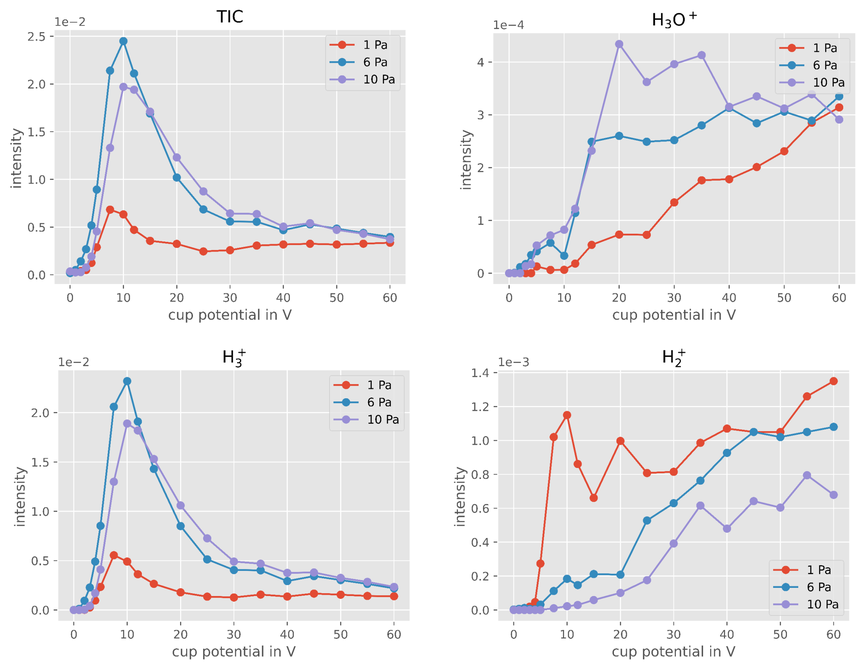


Distance variation: Ion source – Detector Inlet

- Linear decrease of the H_3^+ ion signal with increasing distance between the detector and ion source.
- Decrease in the H_2^+ signal with increasing distance due to the longer flight path and thus increased collision probability.



Cup potential variation at different H_2 pressures



- Higher cup voltages increase the abundance of H_2^+ and H_3O^+.
- Total ion count is drastically dominated by the H_3^+ ion signal.
- H_3^+ exhibits a maximum at an acceleration voltage of 10 V.
- Higher H_2^+ abundance is observed at lower pressures due to the reduced collision probability.

Conclusion & Open Questions

Motivation for an EI-based Approach:

- Determination of absolute ion fluxes through the MS system.
  - EI provides well-characterized and reproducible fragmentation patterns with established reference libraries.
- Enables quantitative benchmarking of ion yield and detector response.
- Facilitates separation of ion production physics from current measurement artifacts.
- Provides an energy-defined reference to interpret kinetic and transport phenomena observed in a plasma source in future studies.

Open Questions and Outlook:

- Precise calibration of mass-resolved ion signals for different species over an extended mass range.
- Quantification of the number of ions contributing to each spectral peak.
- Determination of uncertainty limits of the calibration source and their impact on the determination of absolute ion fluxes.
- Modification of the calibration unit detector to better replicate the MS system.
  - Adding a pumping stage.
  - Adapting the inlet geometry.
- Modeling of the calibration system under varying conditions (gas species, pressure, etc.).

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