Elevation of the Baseline in Quadrupole Mass Spectrometers: Mechanism and Solution

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Introduction

- A pronounced baseline shift has been observed in single stage quadrupole devices
- This baseline shift reduces the limit of detection and dynamic range significantly
- Experiments and simulations were conducted to investigate the mechanism of the false positive signal and propose a solution.

Methods

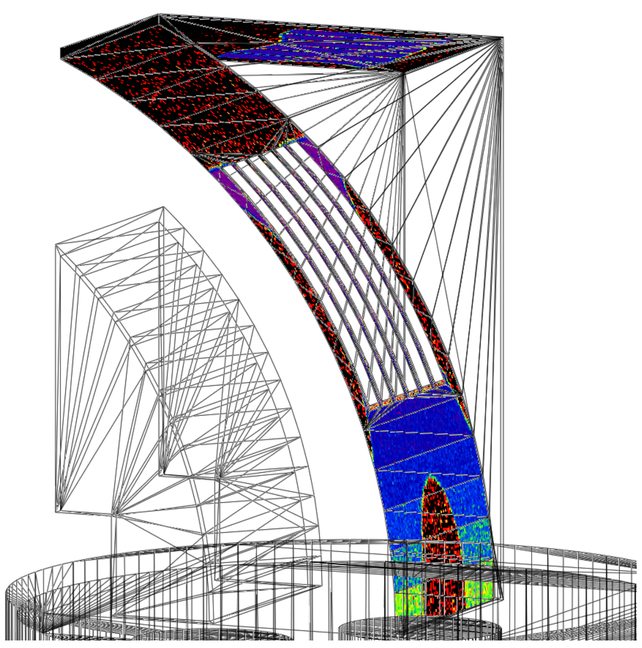
MS: QMG 422 (Inficon, Bad Ragaz, Switzerland) with 20 cm rod length and equipped with both Faraday cup and off-axis SEM detector and EP 422 pre-amplifiers

Ion Source: SPM source

Chemicals: Hydrogen 7.0 (Vici DBS NM Plus) argon 5.0 (Messer Industriegase GmbH, Bad Soden, Germany)

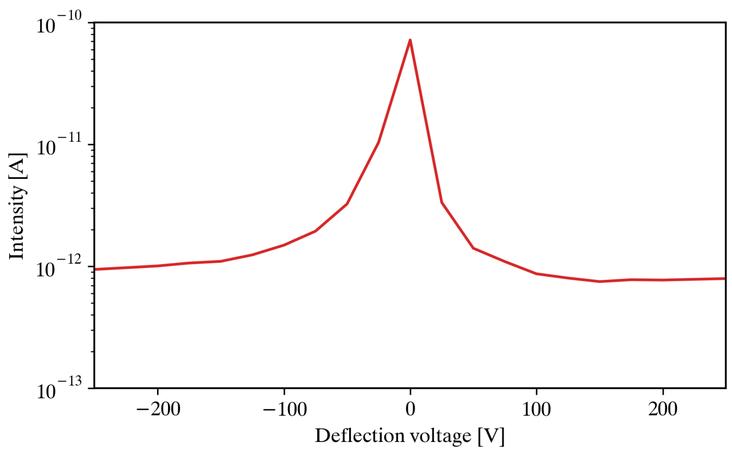
Sampling: Gas flows controlled with mass flow controllers (MKS Instruments, Berlin, Germany) and mixed with a custom gas mixing manifold.

The deflection unit



- MOLFLOW simulations of the deflection unit exhibit particle impact on the surfaces of this component.
- 0.1% of *neutral* particles leaving the ion source reach the deflection unit
- If metastable species undergo ionization on these surfaces, they might be collected by the SEM,
- especially in the lower area, close to the rod system

Deflection potential



- The level of the baseline as a function of the potential applied to the deflection plate
- 0V leads to the highest baseline
  - Drops sharply as any potential is applied
- Upstream of this part of the device no potentials lead to a variation of the baseline
- Ions that make out the baseline are generated in this part of the mass spectrometer and are slower compared to ions from the ion source

Acknowledgment

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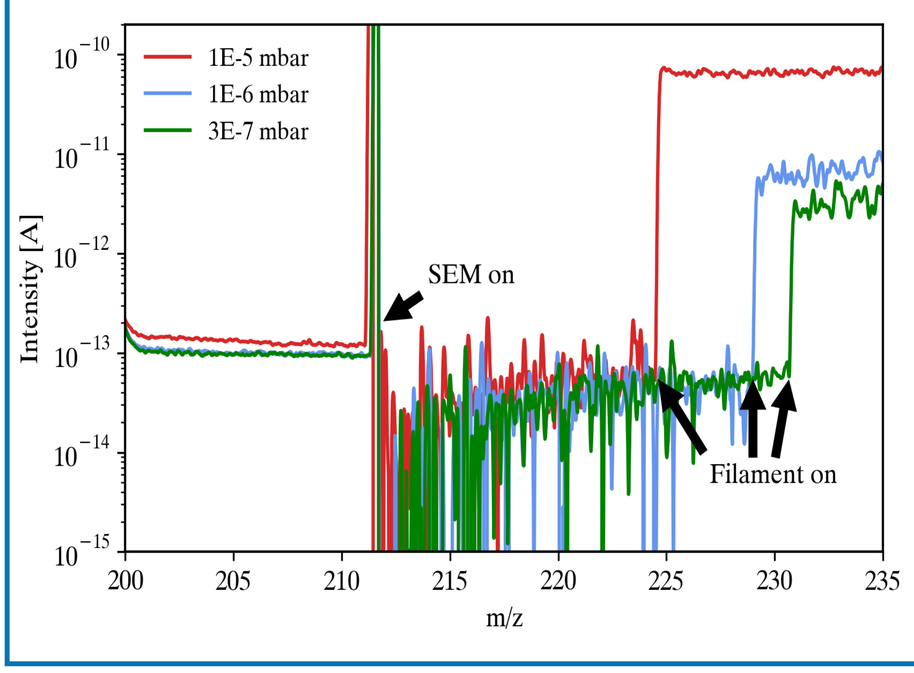
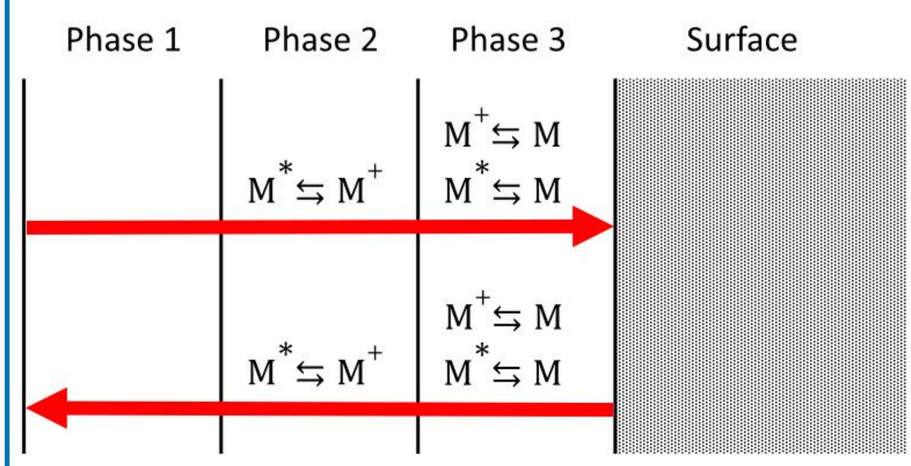
The baseline shift



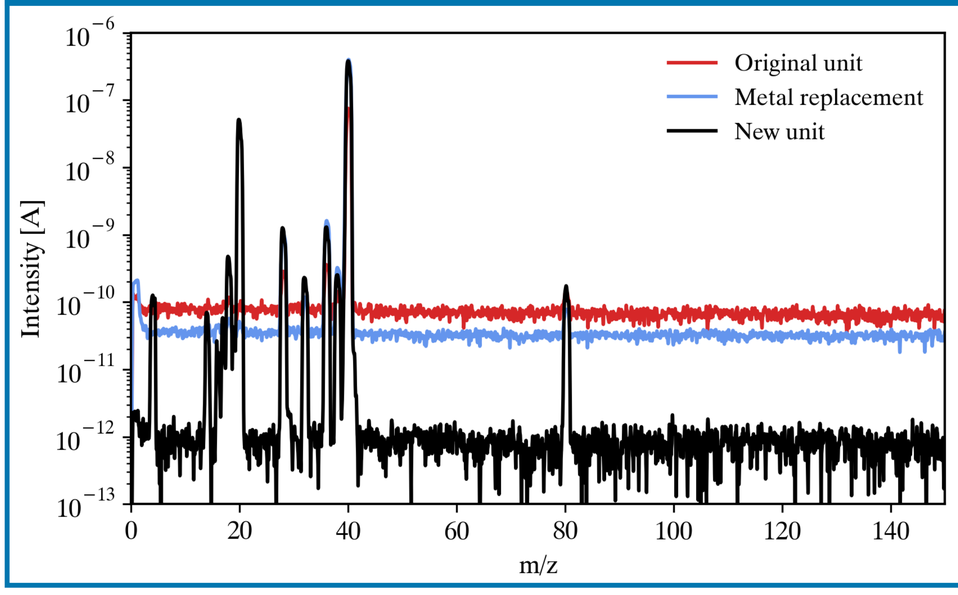
- The baseline is at electronic noise level and smooth when both SEM and filament are turned off
- The jitter of the signal becomes visible when high voltage is applied to the SEM
- The baseline increases (“shifts”) up to three orders of magnitude as the filament is switched on and the pressure is sufficiently high (p > 1E-7mbar)
- The shift is mass-independent and is not affected by the progression of the mass scan of the quadrupole
- Potentials applied to the lens system of the ion source do not influence the level of the baseline at all
- Downstream of the quadrupole rod system the baseline is affected by electric fields
- The voltage of the conversion dynode plays a major role in the mechanism leading to the effect

Resonant Ionization



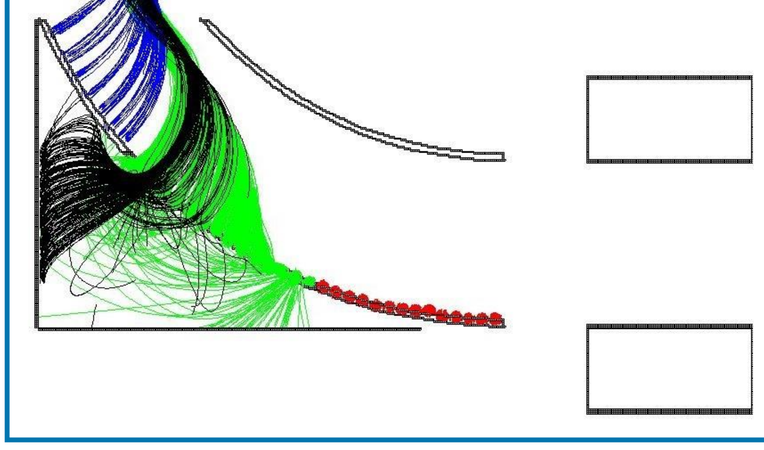
- As a particle approaches a surface, its electrons start to interact with the surface
- This reduces the effective ionization of an excited species due to electrostatic repulsion of electrons[1]
- As a result the potential curves for the ion and the excited levels can overlap[2]
- If a particle in a metastable state undergoes ionization when approaching the surface, it may neutralize again in close vicinity to the surface[3]
- However, such a particle may not undergo ionization when approaching/colliding with the surface but on its way back from the surface [2]

Comparison of different surfaces



- Prior investigations demonstrated that the deflection unit, situated between the rod system and the detector, affects the position of the base line strongly
- Experiments with a) the original deflection unit, b) a metal replacement surface oriented perpendicularly to the ion beam and c) with the new unit were conducted
- A flat metal surface, replacing the original unit, decreases the elevation slightly (b)
- There is still a shift of one order of magnitude with the new unit installed (c)
- Results demonstrate clearly the necessity of a surface present at this location for the baseline shift to occur

Simulations of the deflection unit



- Ions of m/z2 are generated at different positions of the original deflection unit
  - Red: Close to the rod system
  - Green: On the grid part
  - Blue: Close to the detector
  - Black: Through the grid system at the edge of the unit
- Results are very similar to experiments with varying deflection potentials
  - Most cations reach the SEM at 0V deflection potential
  - Sharp decrease as either positive or negative potential is applied
- These simulations[5] support the possibility of ionizing reactions on the surface of the deflection unit

Conclusion

- A mechanism is proposed for the hitherto unexplained baseline shift in single-stage quadrupole mass spectrometers
- Experiments demonstrate the ionic nature of the elevation downstream of the rod system
- However potentials upstream of the deflection unit do not interfere with the effect at all
- The mechanism involves resonant ionization of metastable species upon interaction with metal surfaces
- An alternative deflection unit was designed to eliminate the effect nearly quantitatively
- A minor shift is still visible, which is probably caused by photons or ionizing reactions in the gas-phase

Literature

[1] W. Sesselmann et al. “*Interaction of metastable noble-gas atoms with transition-metal surfaces: Resonance ionization and Auger neutralization*”; doi: n10.1103/PhysRevB.35.1547
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[4] R. Kersevan Ady“*Recent developments of Monte-Carlo codes MolFlow+ and SynRad+M.“; doi: 10.18429/JACoW-IPAC2019-TUPMP037*
[5] D. A. Dahl. “*Simion for the Personal Computer in Reflection”;* doi: 10.1016/S1387-3806(00)00305-5