Characterization of Quadrupole Mass Filters regarding elevated entrance ion currents

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Introduction

- A pronounced baseline shift was observed when single Quadrupole systems are exposed to elevated entrance ion currents. The effect spans three orders of magnitude when using an SEM detector. A similar effect has been observed in a hybrid quadrupole/TOF instrument
- Three hypotheses have been proposed to explain this behavior:
- **Ion breakthrough**
  Ions in the Quadrupole shield each other from the electric field. This would lead to the baseline shift because ions reach (unfiltered) the SEM.
- **Photon interaction**
  Secondary electrons, emanating upon ion impact ions, lead to soft X-ray radiation emission reaching the SEM.[1]
- **Secondary ionization**
  Said secondary electrons or emitted X-ray photons ionize neutral gas molecules present in the quadrupole region, which subsequently reach (unfiltered) the detector.
- Experiments to investigate these hypotheses have been conducted/ are planned in order to modify existing quadrupole systems to reduce the effects responsible for the elevated baseline and thus increase the sensitivity/dynamic range of these systems.

Methods

Single Quad instrument (RGA)

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

Ion Source: SPM source with Tungsten filament.
Chemicals: Hydrogen 7.0 (Vici DBS NM Plus).
Sampling: Gas flows controlled by mass flow controllers (MKS Instruments, Berlin, Germany) and mixed with a custom mixing manifold.

Quadrupole/TOF

MS: Tofwerk EI-CTOF (Tofwerk AG, Thun, Switzerland), equipped wit an RF-only transfer quadrupole.
Ion Source: Crossbeam ion source with Rhenium filament
Chemicals: Laboratory air and a gas mixture of 10 ppm decane in nitrogen (Linde Gas, Pullach, Germany)
Sampling: Gas flows controlled by mass flow controllers (MKS instruments, Berlin, Germany). Gas flow into the MS was regulated manually with a VACOM11LVM-16CF-MS-S valve (VACOM Vakuum Komponenten & Messtechnik GmbH, Germany).

Ion Breakthrough

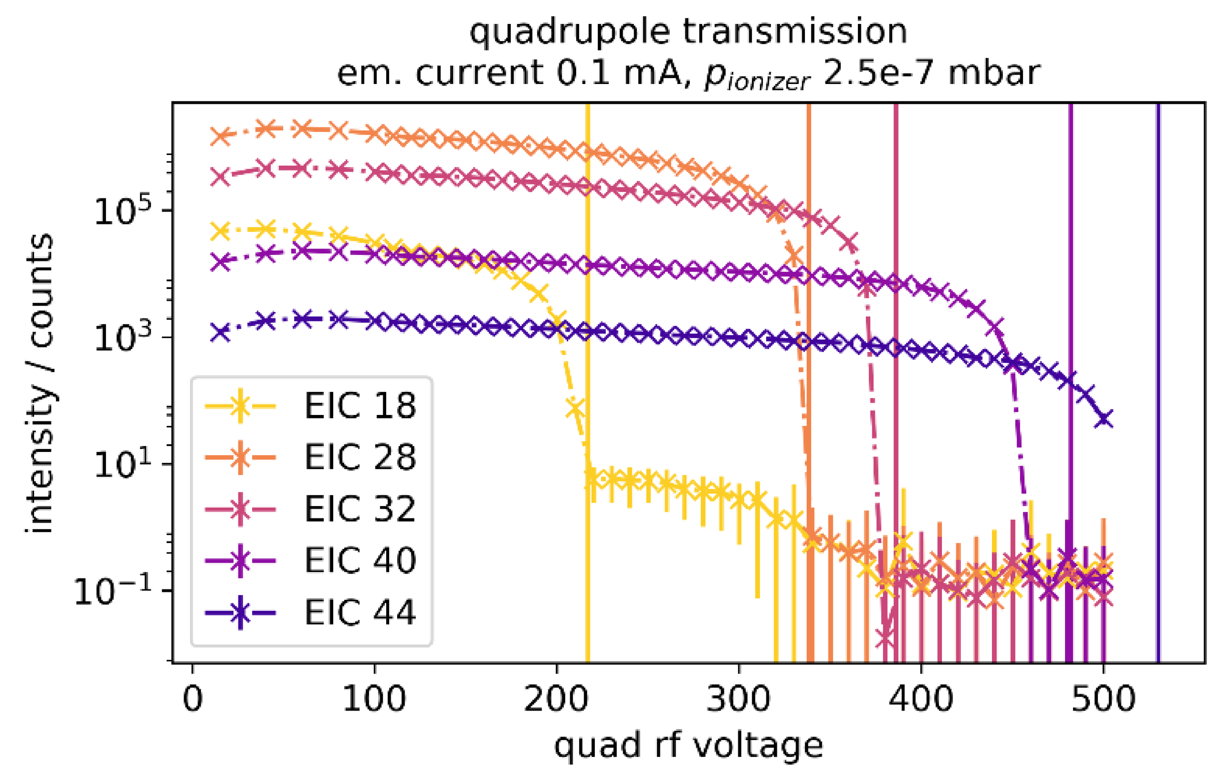

Fig. 1: Ions are successfully filtered out at their cut off voltage.

***Figure 1**, top*: At low ionizing chamber pressure in the EI-CTOF instrument, the transfer quadrupole filters ions at their respective cut-off voltage. The cut off for low mass ions is rather sharp at the respective RF voltage, while for heavier ions the signals start to decline below their theoretical cut-off voltage.

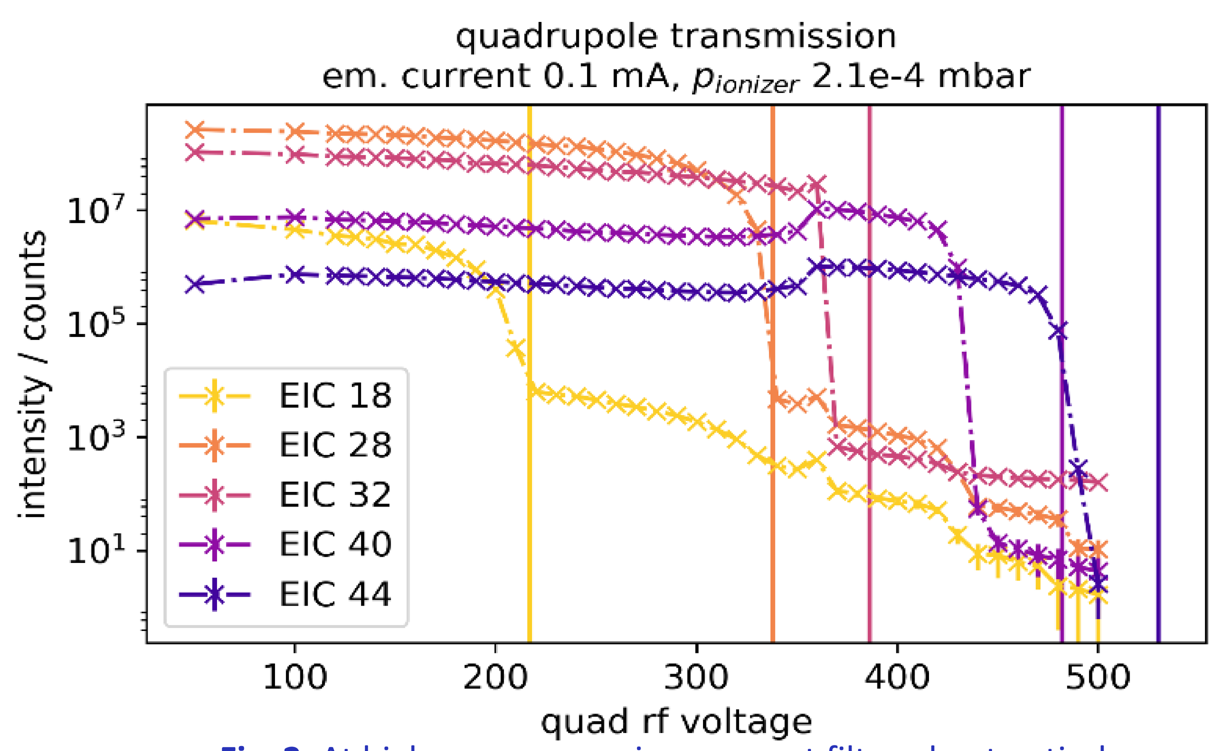

Fig. 2: At higher pressures, ions are not filtered out entirely.

***Figure 2**, center*: At elevated pressure levels the ions "break through" the quadrupole and reach the TOF even though the respective cut-off voltage is higher. At maximum RF voltage not every ion species is filtered out. Remaining ion species cause an increase in signal due to the previous saturation of the detector.

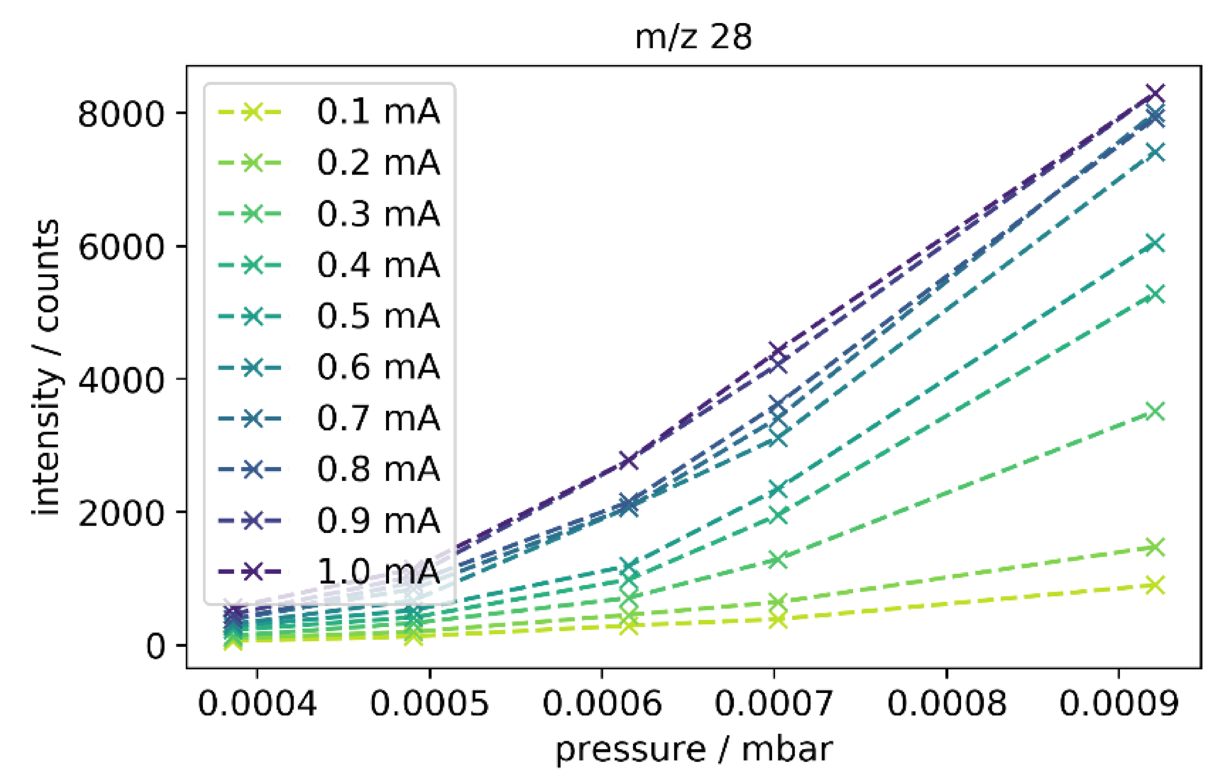

Fig. 3: Nitrogen signal goes up at higher pressures even though it should be cut off.

***Figure 3**, bottom*: In a dodecane/N_2 mixture, nitrogen ions show a different behavior than dodecane ion signals. Even though the quadrupole is set to the maximum RF voltage (cut-off at m/z 42) the N_2^+ intensity increases with pressure, indicating ion breakthrough due to high ion currents in the quadrupole region.

Secondary Ions & Photons

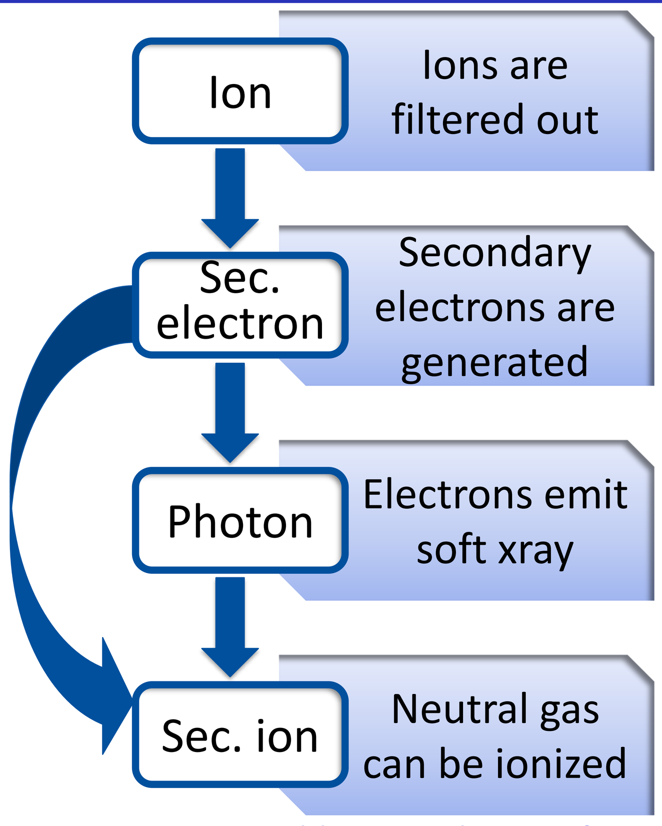

Fig. 4: Bremsstrahlung mechanism from ions to secondary ions.

Figure 4: When positively charged ions are filtered in the quadrupole, they are collected on the (transiently) negatively based metal rods. The impact of the ions can lead to the ejection of electrons from the metal rod [1], which are then accelerated onto the adjacent positively biased rods. The maximum acceleration voltage is twice the RF voltage [2]. The electron impact leads to soft X-ray emission (Bremsstrahlung). The intensity depends on the ion current in the quadrupole [3].

When these photons reach the SEM, the baseline will rise due to the X-ray radiation. However, the SEM is installed perpendicularly to the main quadrupole axis, so only photons reflected off the metal deflection unit can reach the SEM. Furthermore, secondary electrons as well as radiation can ionize neutral gas molecules present in the quadrupole. These ions are generated over the entire length of the quadrupole and can thus reach the deflection unit and the SEM. All ions generated in this way show up on every m/z and in turn raise the instrument baseline.

Baseline shift

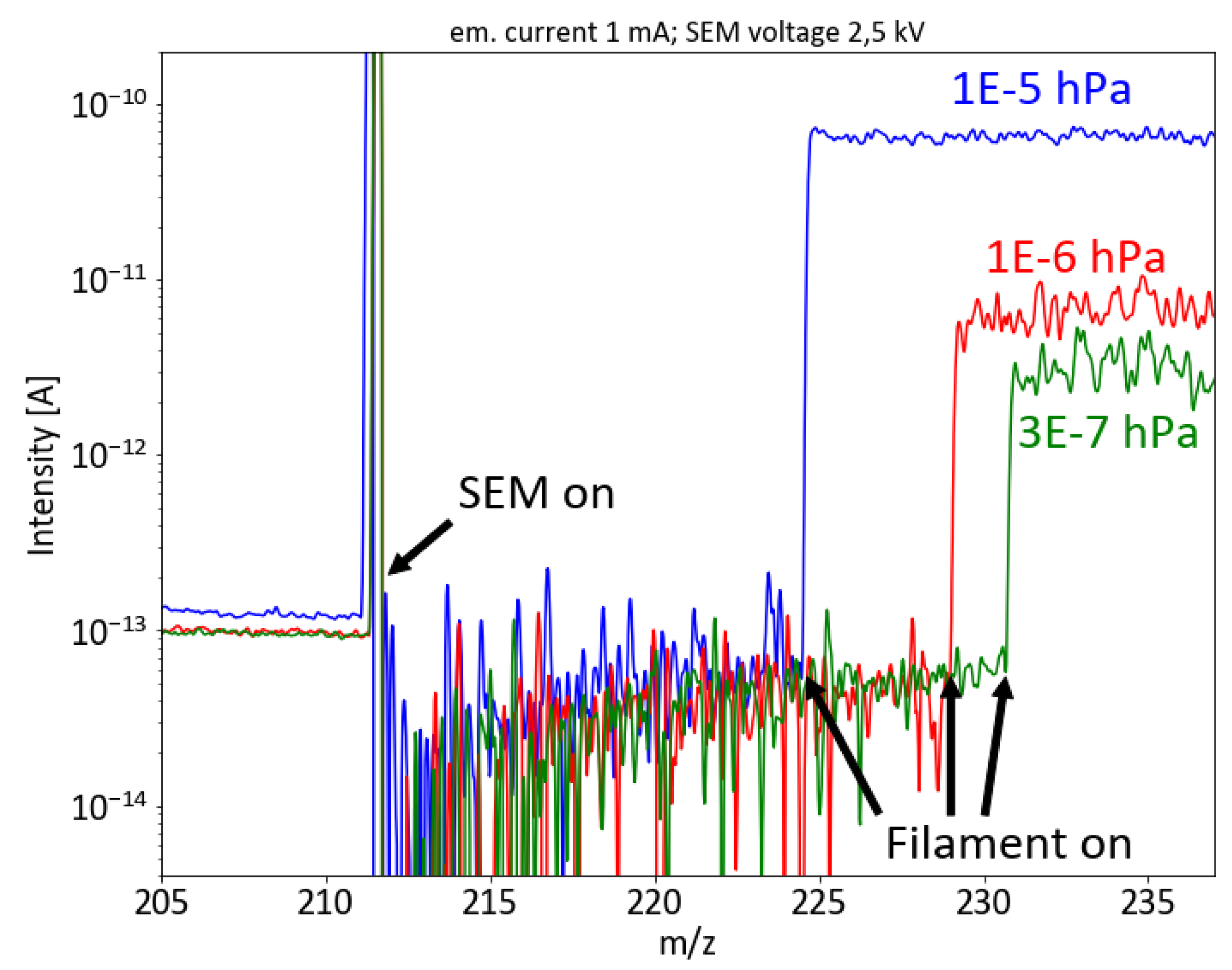

Fig. 5: The observed shift of the baseline at different pressure levels of air in the quadrupole region.

Figure 5: Without SEM and filament turned on, a smooth baseline around 1E-13 A is observed. When the SEM is turned on to a voltage of 2500 V there are discernible spikes in the mass spectrum. The baseline shows an increase in random spikes, representing the dark count rate of the SEM at that voltage. As soon as the filament is turned on as well, the baseline jumps several orders of magnitude, depending on the pressure in the ion source/quadrupole region and accordingly on the ion current through the analyzer. At the highest tolerated quadrupole pressure (1E-5 hPa) the baseline rises by about three orders of magnitude and any spikes disappear entirely. The magnitude of the shift increases with increasing SEM voltages. At < 1700 V there is no shift at all. Small signals are entirely masked by the rising baseline up to the point where they are not discernible anymore.

Conclusion & Outlook

Conclusions

- Three hypotheses have been proposed to rationalize the observed orders-of-magnitude shift of the baseline of a quadrupole mass spectrometer upon exposure to high ion currents.
- Ion breakthrough in single quadrupoles was observed in a quadrupole/TOF system in two different scenarios. The baseline shift originating from ion breakthrough plays no role in hybrid quadrupole/TOF instruments. The abundantly excess ions were mass resolved in the TOF mass spectrum at 500 V RF voltage.

Outlook

- After the main reason for the baseline shift in single quadrupole instruments has been identified, means of reducing that effect are evaluated.
- A dual stage quadrupole instrument (RF only quadrupole/filter quadrupole) potentially adds orders of magnitude of sensitivity by reducing ion currents in the filter quadrupole.
- The X-ray/VUV route is investigated further by placing a LiF window in front of the SEM. This eliminates interaction between ions and the SEM detector.

Literature

[1] *Über einen die Erzeugung und Verwandlung des Lichtes betreffenden heuristischen Gesichtspunkts*, A. Einstein, Annalen der Physik, *322*(6), 132–148, 1905
[2] *Quadrupole Mass Spectrometry and its applications*, Peter H. Dawson, Elsevier Scientific Publishing Company, Amsterdam-Oxford-New York, 1976.
[3] *Gerthsen Physik*, H. Vogel, 20th edition, Springer Verlag, Berlin-Heidelberg-New York, 1999.

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