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 or 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 withTungsten 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 El-CTOF (Tofwerk AG, Thun, Switzerland), equipped with an RF-only transfer quadrupole.

Ion Source: Crossbeam ion source with Rhenium filament.

Chemicals: Laboratory air and a gas mixture of 10 ppm decaene 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 VACOM111VM-16CF-MS-S valve (VACOM Vakuum Komponenten & Messtechnik GmbH, Germany).

Ion Breakthrough

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<th>Transmission</th>
<th>em. current</th>
<th>0.1 mA</th>
<th>Eic 18</th>
<th>Eic 28</th>
<th>Eic 32</th>
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**Secondary Ions & Photons**

**Baseline shift**

**Conclusion & Outlook**

- 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.

**Ions are filtered out**

**Ions are successfully filtered out at their cut off voltage.**

**Neutral gas can be ionized**

**Ion**

**Secondary electrons**

**Electrons emit soft xray**

**Photon**

**Sec. ion**

**Figure 1:** At high ionizing chamber pressure in the El-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.

**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.

**Figure 3:** bottom: In a dodecan/N4 mixture, nitrogen ions show a different behavior than dodecan ion signals. Even though the quadrupole is set to the maximum RF voltage (cut-off at m/z 42) the N4+ intensity increases with pressure, indicating ion break-through due to high ion currents in the quadrupole region.

**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).

**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 the shift is not observed at all. Small signals are entirely masked by the rising baseline up to the point where they are not discernible anymore.

**Literature**