Characterization of Quadrupole Mass Filters regarding elevated entrance ion currents

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Introduction

A pronounced baseline shift has been observed when single quadrupole systems are exposed to elevated entrance ion currents. The effect spans up-to three orders of magnitude when using a SEM detector. A similar effect has been observed in a quadrupole/TOF (qTOF) instrument

Three hypotheses have been developed 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 the broken through molecules show up on every mass.
- **Photon interaction**
  Generation of secondary electrons from filtered out ions impacting on the rods leading to soft X-ray radiation that reaches the detector.[1]
- **Acquisition system issues**
  The amplifier/ADC system shifts the baseline to keep the highest/lowest signal ratio within its dynamic range.

Experiments to test these hypotheses have been conducted or are planned in order to modify existing Quadrupole systems to reduce the effects responsible for the elevated baseline and thus increase effectivity of the respective 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 ion source with Tungsten filament.

Chemicals: Hydrogen 5.0 (Messer Industriegase GmbH, Krefeld, Germany).

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

Quadrupole/TOF

MS: Tofwerk EI-CTOF (Tofwerk AG, Switzerland), equipped with an RF-only quadrupole.

Ion Source: Starbeam ion source with Rhenium filament

Chemicals: Lab 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

By increasing the amount of ions and neutral molecules in the quadrupole region the ion/ion and ion/neutral interactions naturally increase as well. Space charge effects and collisions between ions and molecules change the trajectories dictated by the RF voltage and thus the separation efficiency is adversely affected.

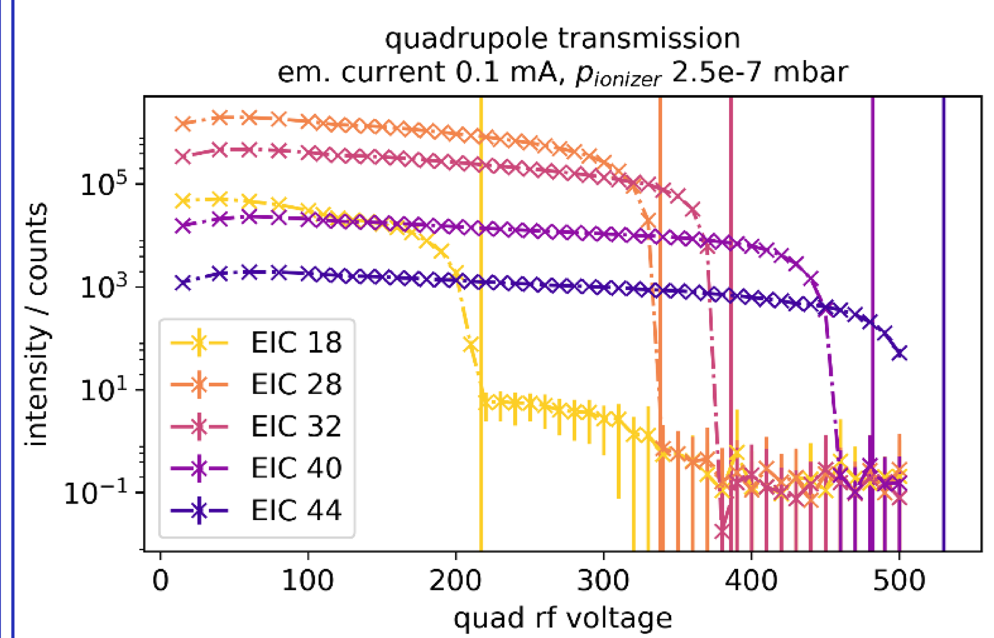

Fig. 1: Ions are successfully filtered out at their cut off voltage

Figure 1, Left: At low pressure inside the ionizing chamber of a quadrupole/Tof instrument the quadrupole filters out all the generated ions at their respective cut off voltage. The cut off for smaller molecules is rather sharp at the respective RF voltage while for heavier ions the signals begin to decline below their theoretical cut-off voltage.

Figure 3, Right: Decane shows an intensity peak at a certain pressure and then starts to decline as the pressure further increases. This behavior is representative for all the decane fragments in the MS. The maximum position shifts to lower pressures for higher m/z. This effect most likely originates from space charge effects in the quadrupole region which lead to unstable trajectories and ultimately collision with the metal rods.

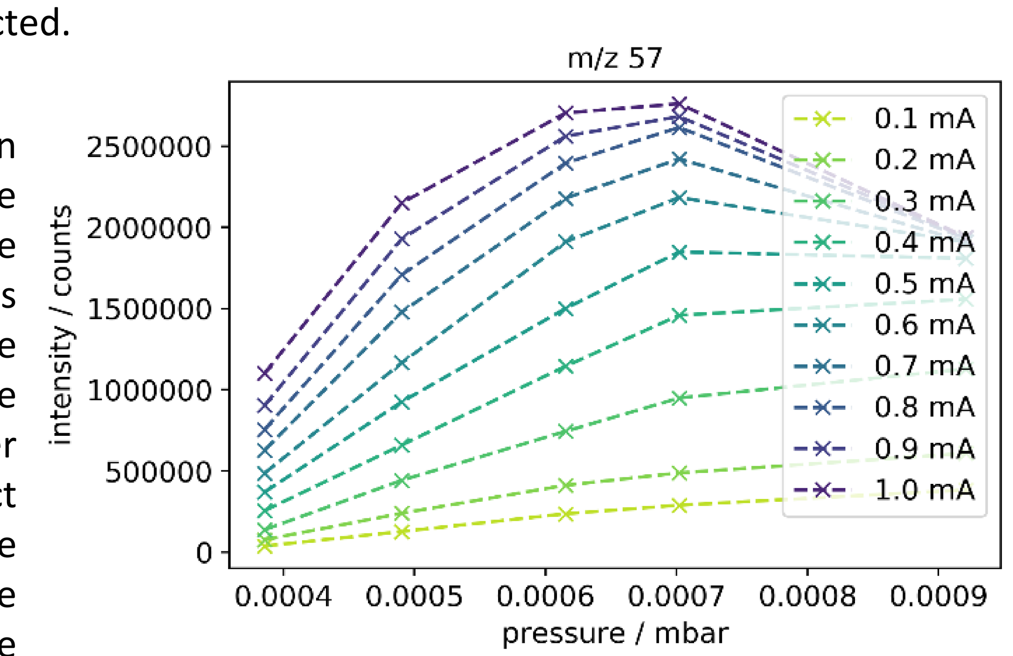

Fig. 3: Decane signals run through a maximum before declining again

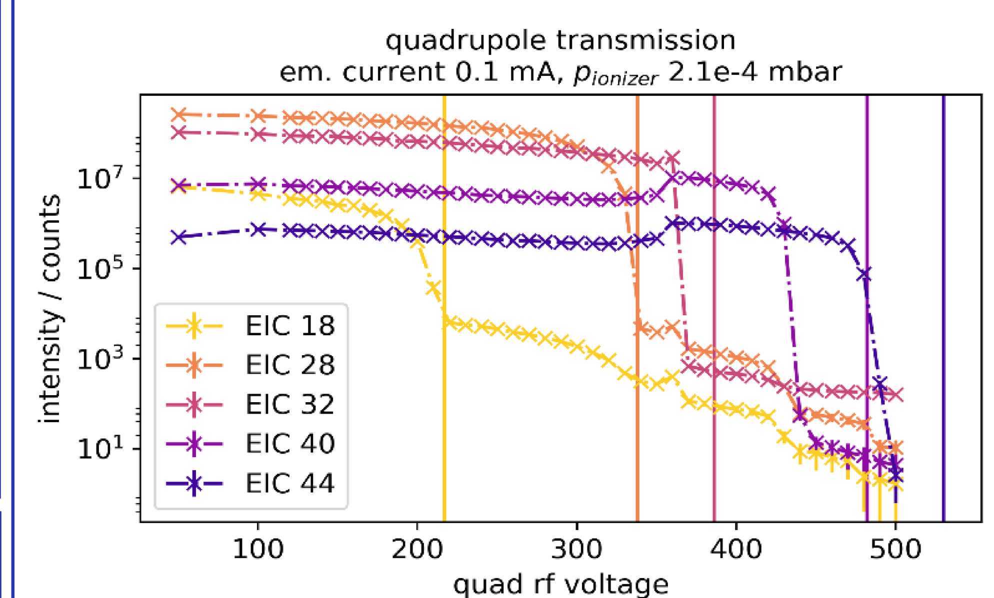

Fig. 2: At higher pressures the ions are not filtered out entirely

Figure 2, Left: At elevated pressure levels the ions "break through" the quadrupole and reach the TOF even after their respective cut off voltage was reached. Even at maximum RF voltage not every species is filtered out. Remaining species show an increase in signal due to the previous saturation of the detector.

Figure 4, Right: The most abundant species, Nitrogen, shows a different behavior. Even though the quadrupole is operated at the maximum RF voltage (with a cut off at m/z42) it shows an increase in intensity as the pressure rises, indicating ion "breakthrough" due to high ion currents in the quadrupole region. The peak at m/z28 is again visible in the spectrum.

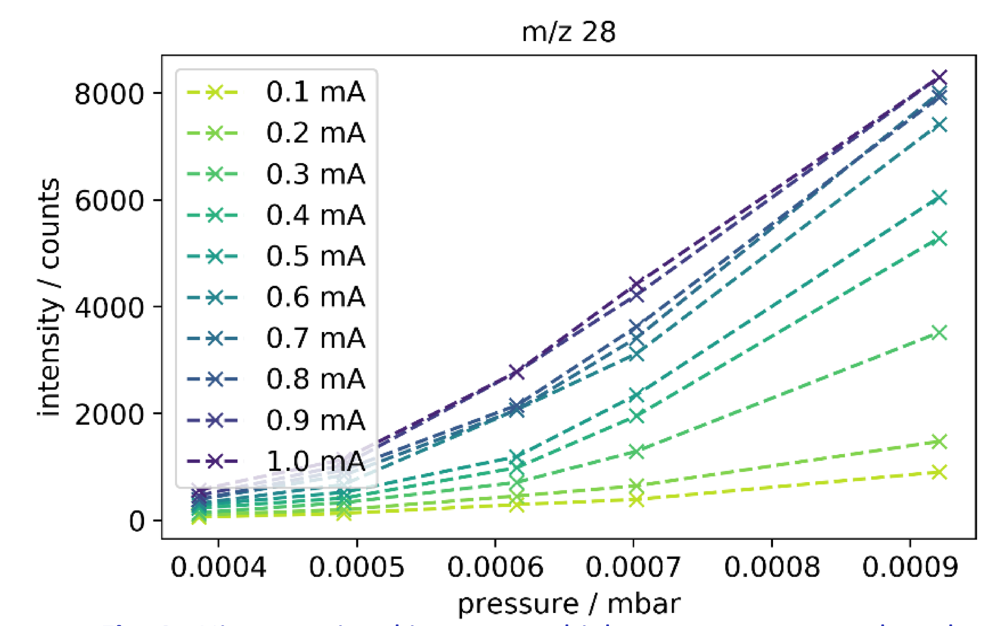

Fig. 4: Nitrogen signal increase at higher pressures even though it should be filtered out

Observed baseline shift

The baseline increases by about 3 orders of magnitude for 2500V SEM voltage in a single stage quadrupole instrument when the filament is turned on. The spikes in the baseline disappear because the signal is far above the dark count rate of the SEM. The effect naturally is lower for lower SEM voltages but cannot be attributed to enhanced jitter at higher voltages as the magnitude of the effect is too large. Measurements were taken at $1 \cdot 10^{-5}$ mbar pressure inside the quadrupole and $2 \cdot 10^{-2}$ mbar Hydrogen pressure at the SPM ion source entrance.

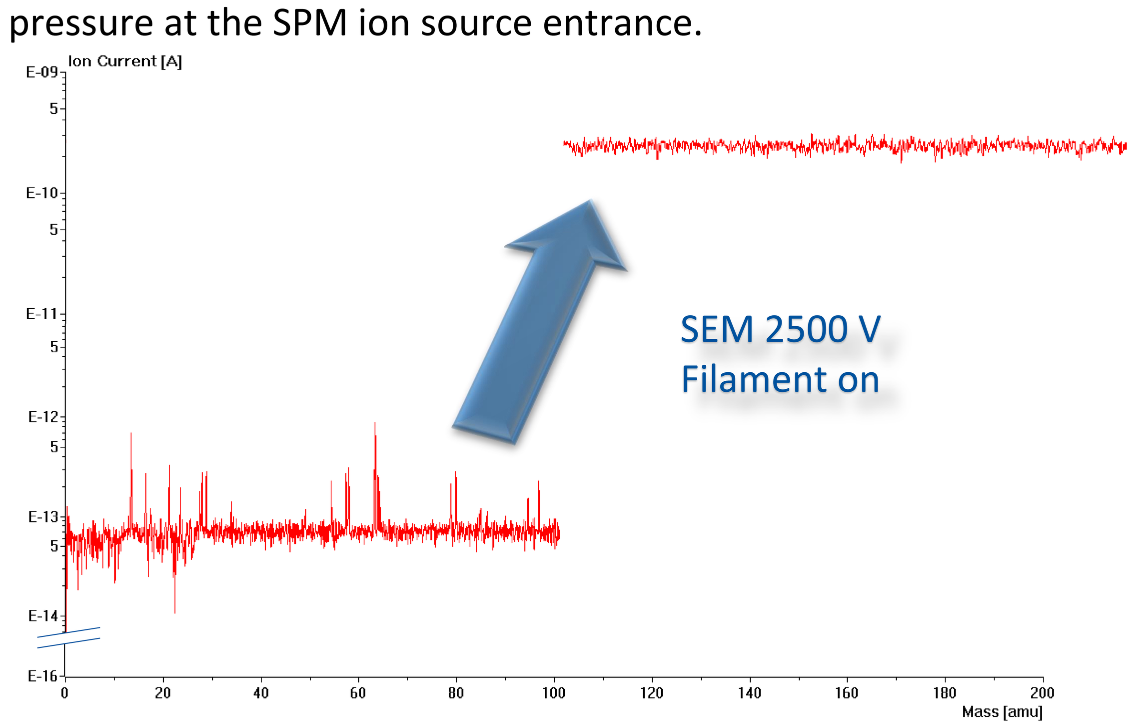

Fig. 5: The baseline goes up by 3 orders of magnitude when the filament is turned on; $2 \cdot 10^{-2}$ mbar SPM source and $1 \cdot 10^{-5}$ mbar analyzer pressure

Secondary electron emission

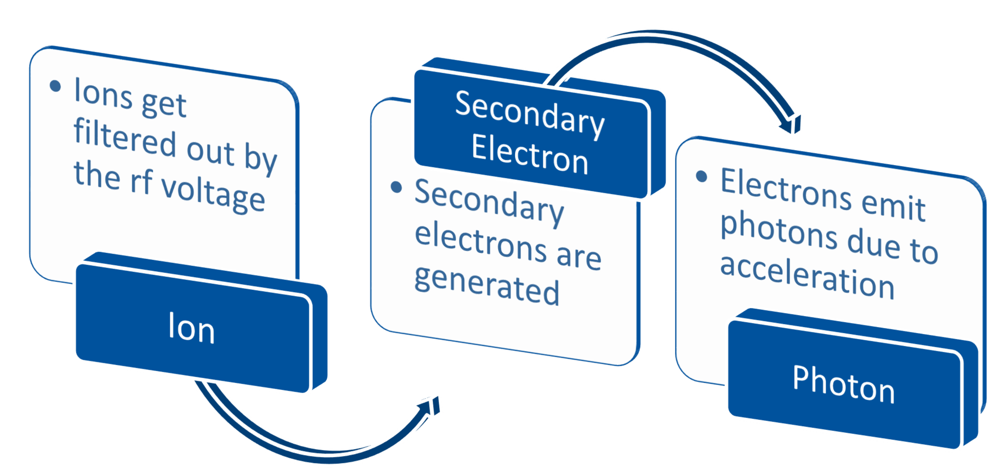

Fig. 6: Bremsstrahlung mechanism from ions to soft X-rays in a quadrupole instrument

When positive ions are filtered out in the quadrupole region they are collected on the negatively charged metal rods. The impact of the ion can lead to the ejection of an electron from the metal rod which is then accelerated onto the adjacent positively charged rod. The impact of the electron may lead to the emission of bremsstrahlung, whose extent depends on ion current through the quadrupole and potential applied to the rods. This can lead to false signals when the detector is not mounted off-axis to the quadrupole region. The radiation may also be reflected by metal surfaces in the deflection unit of some devices.

To determine the extent of this effect it is planned to measure the signal intensity compared to the level of the baseline with different emission currents and stable analyte flow. This way the pressure in the quadrupole region stays the same while ion current rises gradually, possibly inducing higher levels of bremsstrahlung and an increase in the false positive signal at the detector. Additionally comparisons between the Faraday cup and the SEM may show the extent of this effect since the SEM is positioned at a 90° angle with respect to the quadrupole axis and hence only reflected radiation can reach the SEM.

Acknowledgement

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Literature

(1) Quadrupole Mass Spectrometry and its applications, Peter H. Dawson, Elsevier Scientific Publishing Company, Amsterdam-Oxford-New York, 1976, p. 290

ADC induced baseline shift

The amplifier/ADC used in the instrumental setup may influence the level of the baseline if there is one dominant peak in the mass spectrum. If the ratio between the highest and lowest signal in the spectrum is higher than the dynamic range of the amplifier/ADC it is possible that the system recalibrates to match its dynamic range. To test this effect the highest peak needs to stay at the same intensity, while other parameters (pressure, ion current) are gradually changed. This is attainable by varying the SEM voltage step by step to increase the signal with a defined analyte flow and filament emission current. Experiments have shown that an increase of the SEM voltage from 1450V to 2500V with turned on filaments led to an increase of the baseline by one order of magnitude. This factor is known and can be accounted for in the interpretation of those experiments.

Conclusion & Outlook

Conclusion

- Three hypotheses were established that could explain the observed baseline increase.
- **Ion breakthrough** in single quadrupoles was observed in a quadrupole/TOF system in two different experiments. The baseline shift caused by ion breakthrough plays no role in TOF instruments but Nitrogen ions were clearly detectable in the TOF spectrum at 500 V RF voltage, i.e. at amplitudes far above the theoretical cut off voltage.

Outlook

- Experiments to determine the effect of **secondary electron emission** in the quadrupole region on the baseline are planned. The basic idea is to gradually vary the emission current to increase the ion current.
- The influence of the used **amplifier/ADC** will be examined in future experiments. It will be tested by changing the SEM voltage to shift the analyte signal to higher levels.
- It is possible that the observed effect is caused by a mixture of all discussed phenomena. The first goal is to find out what phenomenon has the biggest impact on the observed baseline shift.
- After the main reason for the baseline shift has been identified means of reducing that effect will be evaluated.
  - Usage of a different amplifier/ADC/acquisition system could solve the amplifier/ADC issue.
  - Placing all detectors off-axis and using a two way deflection unit that reflects as less radiation as possible could solve or at least reduce the issue with bremsstrahlung in single stage quadrupole instruments.
  - Usage of an additional quadrupole operated in RF only + Notch filter mode in front of the filtering quadrupole could lead to a dynamic range, which is orders of magnitude higher than that of a single stage quadrupole system. (see Miller, P.E.; Investigations of the RF-only quadrupole mass analyzer; Dissertation; University of Arizona, AZ, USA, 1985)