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/time-of-flight (TOF) 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 at 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 efficiency of the respective systems.

Methods

**Single Quad Instrument (RGA)**

- MS: QMS 422 (Inficon, Bad Ragaz, Switzerland) with 20 cm rod length and equipped with both Faraday cup and off-axis SE detector with El-422 amplifiers
- Ion Source: SPM ion source with Tungsten filament.
- Chemicals: Hydrogen 5.0 (Messer Industriegas 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

**Single Quad Instrument**

- MS: Tofwerk EI-TOF (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 VACOM11VM-16CF-M5-S valve (VACOM Vakuum Komponenten & Messtechnik GmbH, Germany).

Results

**Observed baseline shift**

The baseline increases by about 3 orders of magnitude for 2500 V 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 is naturally 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 1–10 Torr mbar pressure inside the quadrupole and 2–10 mbar Hydrogen pressure at the SPM ion source entrance.

**Ion breakthrough**

By increasing the amount of ions and neutral molecules in the quadrupole region the ion/ion and ion/neutrals 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.

**Secondary electron emission**

When positive ions are fitted 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 secondary electrons 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.

Figure 6: Bremsstrahlung mechanism from ions to soft-X-rays at a quadrupole instrument.

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 anode 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 to what extent the effect of the baseline shifts in that a 90° angle with respect to the quadrupole axis and hence only reflected radiation can reach the SEM.

**ADC induced baseline shift**

The amplifier/ADC used in the instrumental setup may influence the levels of baseline if there is one 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 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 emission currents are gradually changed. This is attainable by varying the SEM voltage step by step to increase the signal with a defined anode flow and filament emission. The experiments have shown that an increase of the SEM voltage from 1450 V to 2500 V 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 shift. 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 change the anode 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 determine the extent of the phenomenon that 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.
    - Using a different amplifier/ADC/acquisition system could solve the amplifier/ADC issue.
    - Placing all detectors and using a two way deflection unit that reflects as less radiation as possible could solve or at least reduce the effect with bremsstrahlung in single stage quadrupole instruments.
    - Using an additional quadrupole operated in RF only
  - Photon 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)

**ACKNOWLEDGEMENT**

Generous support from Carl Zeiss SMT, Oberkochen, Germany, is gratefully acknowledged.