Physical & Theoretical Chemistry
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Metastables as a source for baselineshift in Quadrupole Mass Analyzers

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Introduction

- Single stage quadrupole instruments show a strong elevation of their baseline by several orders of magnitude at elevated inlet pressures, depending on device parameters
- This behaviour was reconstructed with a custom mock-up system
- Hitherto conducted experiments eliminated ions directly emitted from the ion source as a possible cause
- Current objectives of this study are the impact of metastable atoms and photons and their interactions with detector systems to induce a signal

Baselineshift

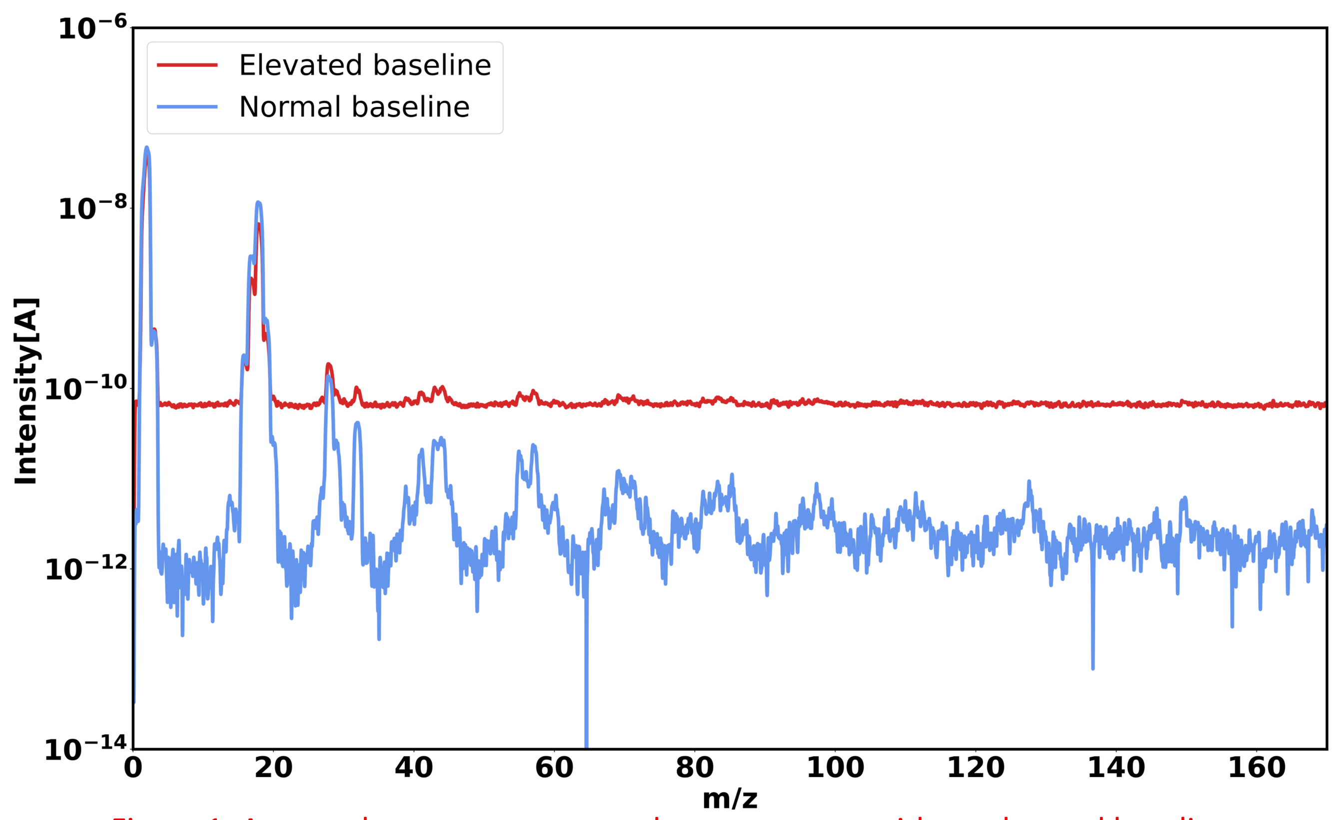

Figure 1: A normal spectrum compared to a spectrum with an elevated baseline

A shift of the baseline in any analytical instrument is inevitably accompanied by a loss of information. Figure 1 illustrates said loss using the dataset acquired with the investigated RGA system using hydrogen as carrier gas. The shown behaviour is expected from a detector that senses electrical current throughout the entire scan of the instrument. Every piece of information received from the mass scan is technically still in the spectrum, added onto the baseline, but the signal to noise ratio is severely reduced. Notably, the intensity of high peaks is not affected by the baseline, since these are orders of magnitude larger compared to the baseline. Previous experiments have shown that the level of the baseline is affected by the emission current of the ion source, thus the source for the effect originates from there. Additionally the pressure in the source has a major impact, giving further evidence that the ion source parameters are of critical importance. The pressure downstream of the ion source, within the analyzer/detector regions, does not have any influence on the baseline level. There is also a dependency on the type of gas used, as hydrogen and noble gases lead to a more pronounced shift than nitrogen.

Methods

Chemicals: Argon 5.0 (Messer SE & Co. KGaA, Krefeld, Germany), Hydrogen 7.0 (Vici DBS NM Plus)

Single Quad instrument (RGA)

MS: QMG 422 (Inficon, Bad Ragaz, Switzerland) with 20cm rod length and both Faraday Cup and off-axis SEM 217

Ion Source: SPM source with tungsten filament

Mock-up system

Ion Source: Open Crossbeam source (Pfeiffer Vacuum Technology AG, Aßlar, Germany) with tungsten filament

Separation: Custom electrodes to filter out ions downstream of the ion source

Sampling: Gas flows controlled by mass flow controllers (MKS Instruments, Berlin, Germany)

Detection: Custom built Faraday-Cup and off-axis SEM 217 (Inficon, Bad Ragaz, Switzerland)

RGA System

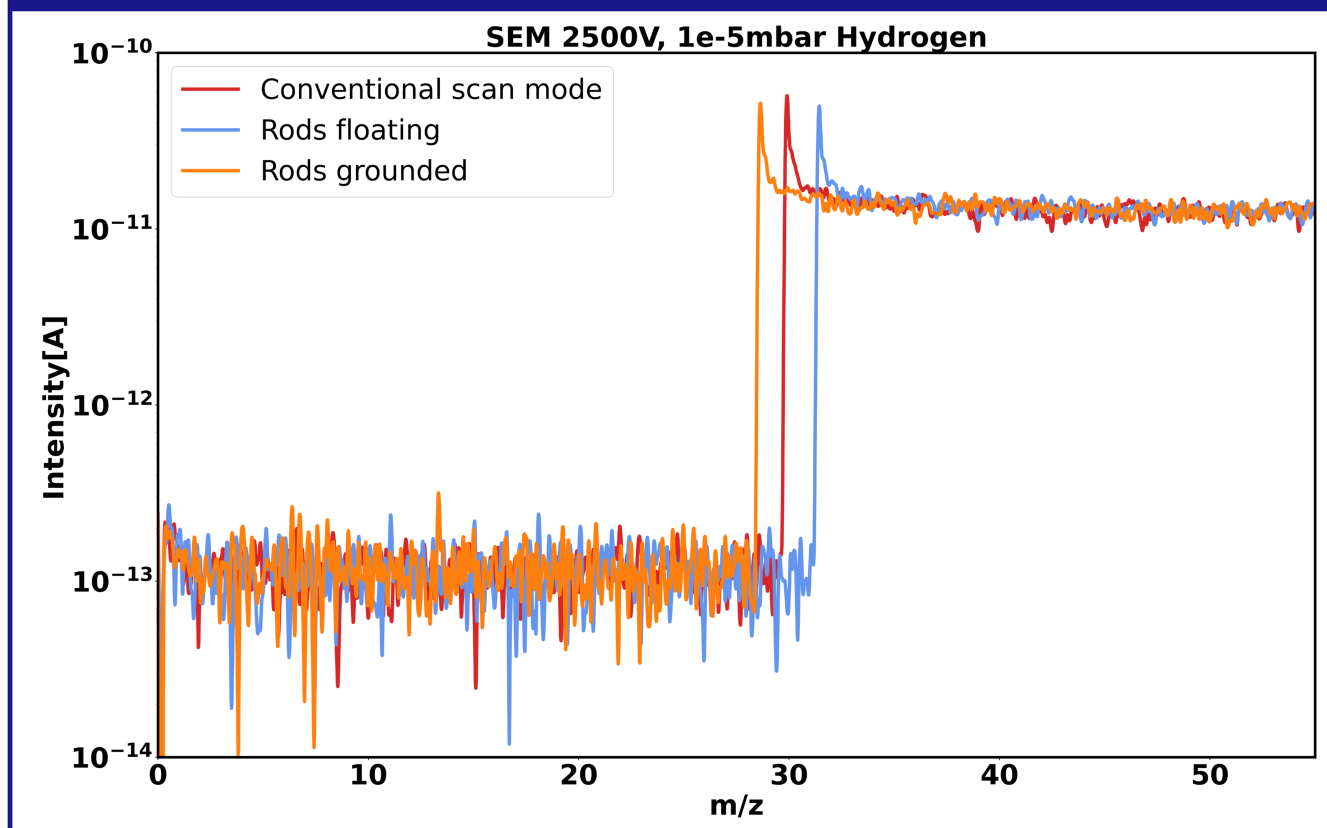

Figure 2: Baseline recorded with several operating modes of the quadrupole

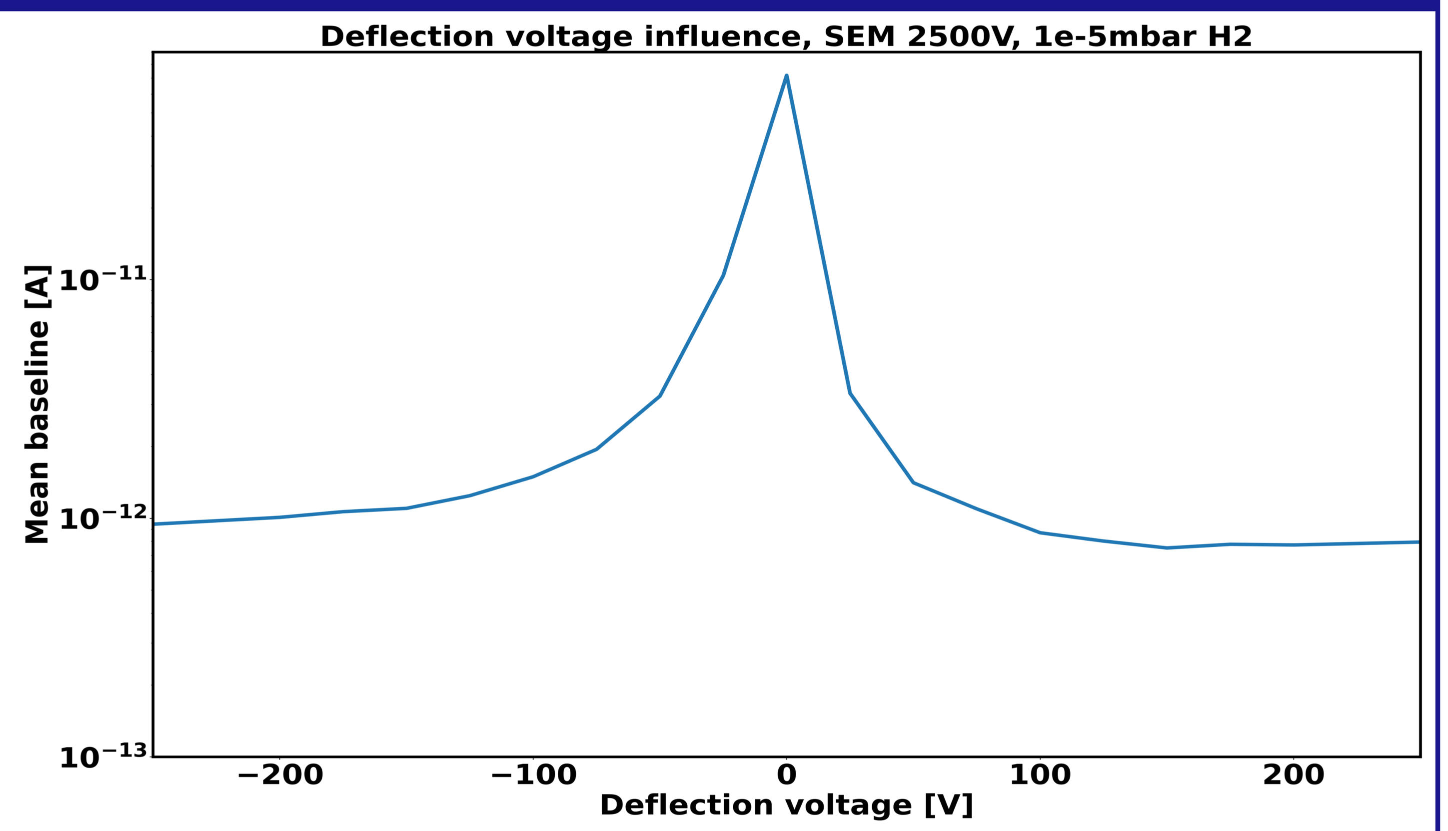

Figure 3: Influence of potentials applied downstream of the rod system on the baseline

Figure 2 illustrates that the shift of the baseline is entirely independent on the mode of the quadrupole filter. If the rods are grounded, ions are not guided towards the detector. If the quadrupole is operating as intented the amount of ions leaving the rod system towards the detector is proportional to the ratio of ions with a stable m/z ratio so at high m/z no ions should be transfered through the device, yet the baseline remains at a constant elevated level. This leads to the conclusion that whatever is determining the level of the baseline cannot be ionic when it is passing through the rod system. On the other hand figure 3 shows a direct impact of applied potentials to the elctrode usually used to bend ion trajectories towards the SEM, indicating ionic species being present in that part of the device. These two experiments combined only leave one deduction: Whatever is causing the signal is not ionic between ion source and detector but subsequently is ionized between the end of the rod system and the SEM. A possible route for this might be resonant ionization on the surface of the Faraday Cup[1,2], photoionization[3] or Penning ionization downstream of the rod system.

Mock-up System

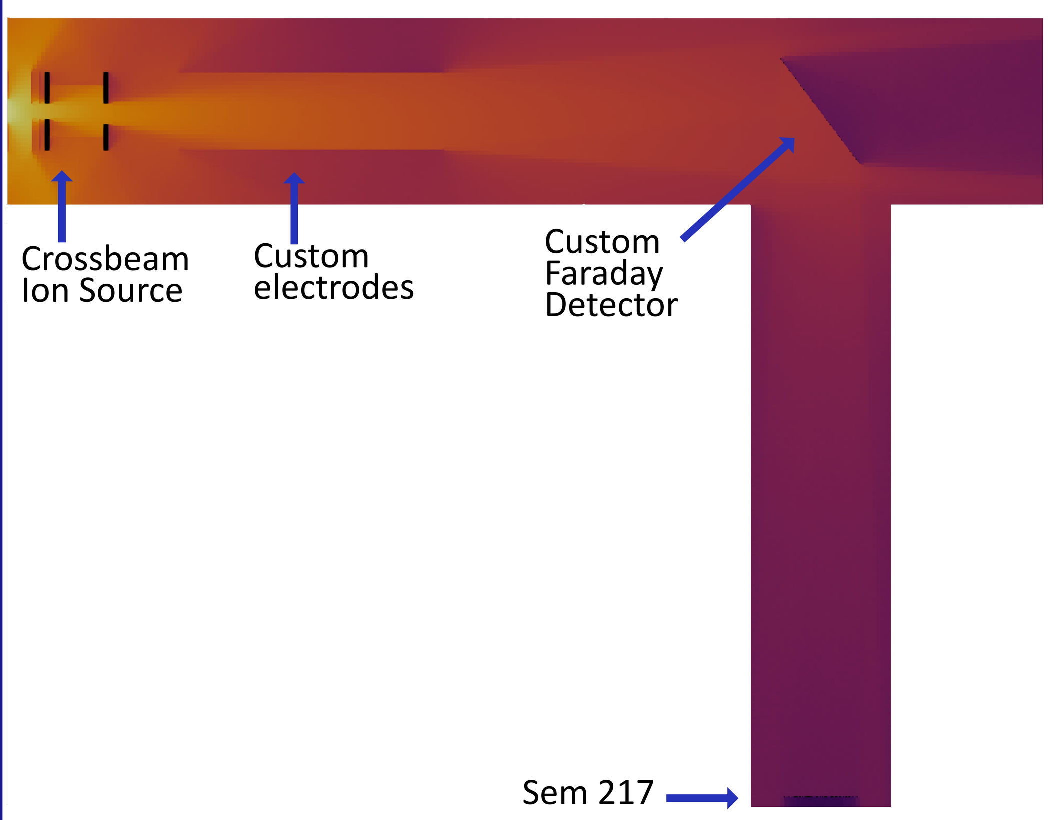

Figure 4: SPARTA simulation of particle density of metastable atoms in the mock-up sytem

Additional experiments were performed with an LiF window in front of the detector to further investigate the phenomenon (Figure 5). These revealed that photons play a significant role in this setup while the influence of applied potentials after the first surface the metastables could interact with is negligible. Contrary to that, in the case where no Faraday Cup, i.e. specular surface, is present there is still a discrepancy between the signals detected with and without LiF window. These studies show that most likely several factors are responsible for the false positive signal on the detectors and their weighting factors depend on the exact experimental setup. In the mock-up system (Fgure 4) the Faraday cup is a reflective stainless steel surface while it is a grid in the original RGA system, which explains the prevalence of photons on the detector. If resonant ionization takes place, the surface should be of utmost importance to determine the ratio for this reaction compared to Auger deexcitation[4], leading to neutral argon and an electron. The surfaces used in both setups are not identical and minor differences could have a big impact on the ratios of the concurring reactions. The orientation of the Faraday cup has surprisingly little contribution to the baseline.

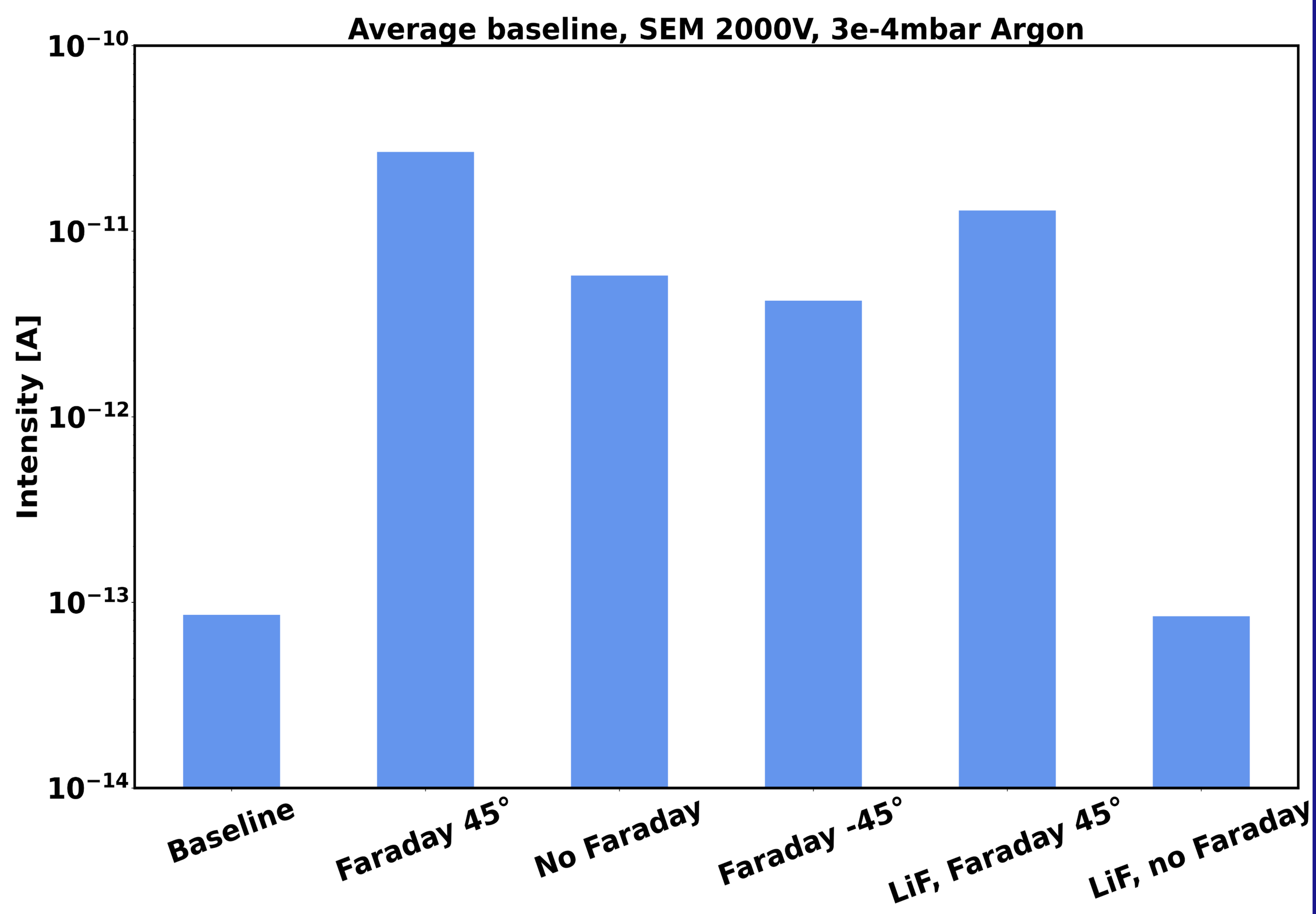

Figure 5: Influence of different faraday orientations on the signal

Conclusion and Outlook

Conclusion

- Ions ejected from the Ion Source have been eliminated as a source for the baselineshift
- Metastable atoms still remain a reasonable source for the current on the detector system
- Photons may play a significant role in the false positive signals on the faraday cup and SEM
- The complete mechanism entirely explaining the experimental observations remains unclear
- The mock-up system and the examined RGA device are not fully comparable but remain vital for future research
- Most likely several superimposed mechanisms are at work

Outlook

- Time of flight experiments are planned to seperate the effects of photons and metastables
- Experiments with other chemicals, and thus other energy levels and cross sections, will give insight into a deeper understanding of the mechanisms
- It is planned to determine the energy of incoming ions onto the detectors to gather evidence of their origin
- Further studies regarding resonant ionization and its plausibility will either rule out this mechanism entirely or lead to a new path of data interpretation.

Literature

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