

Introduction

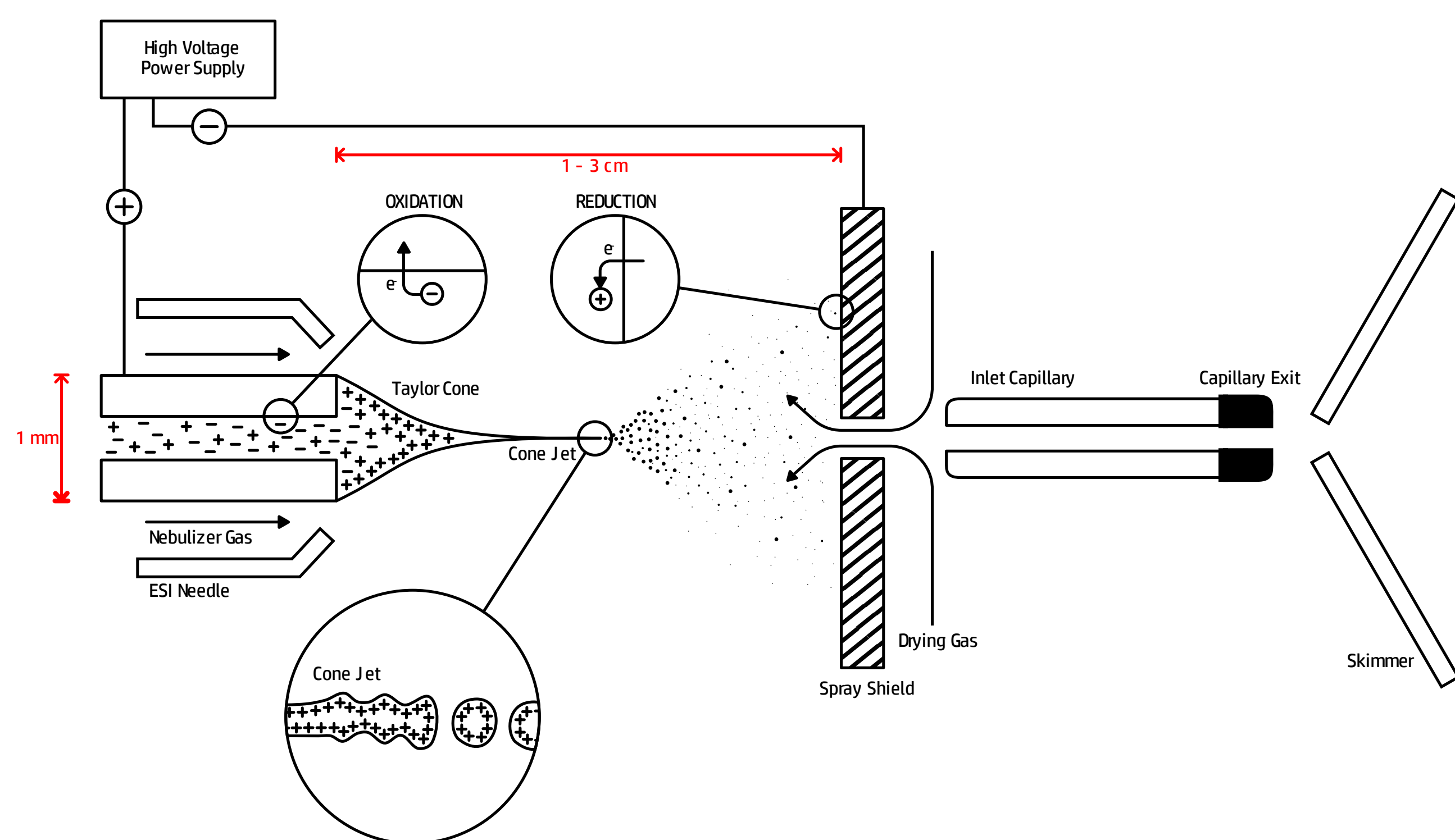
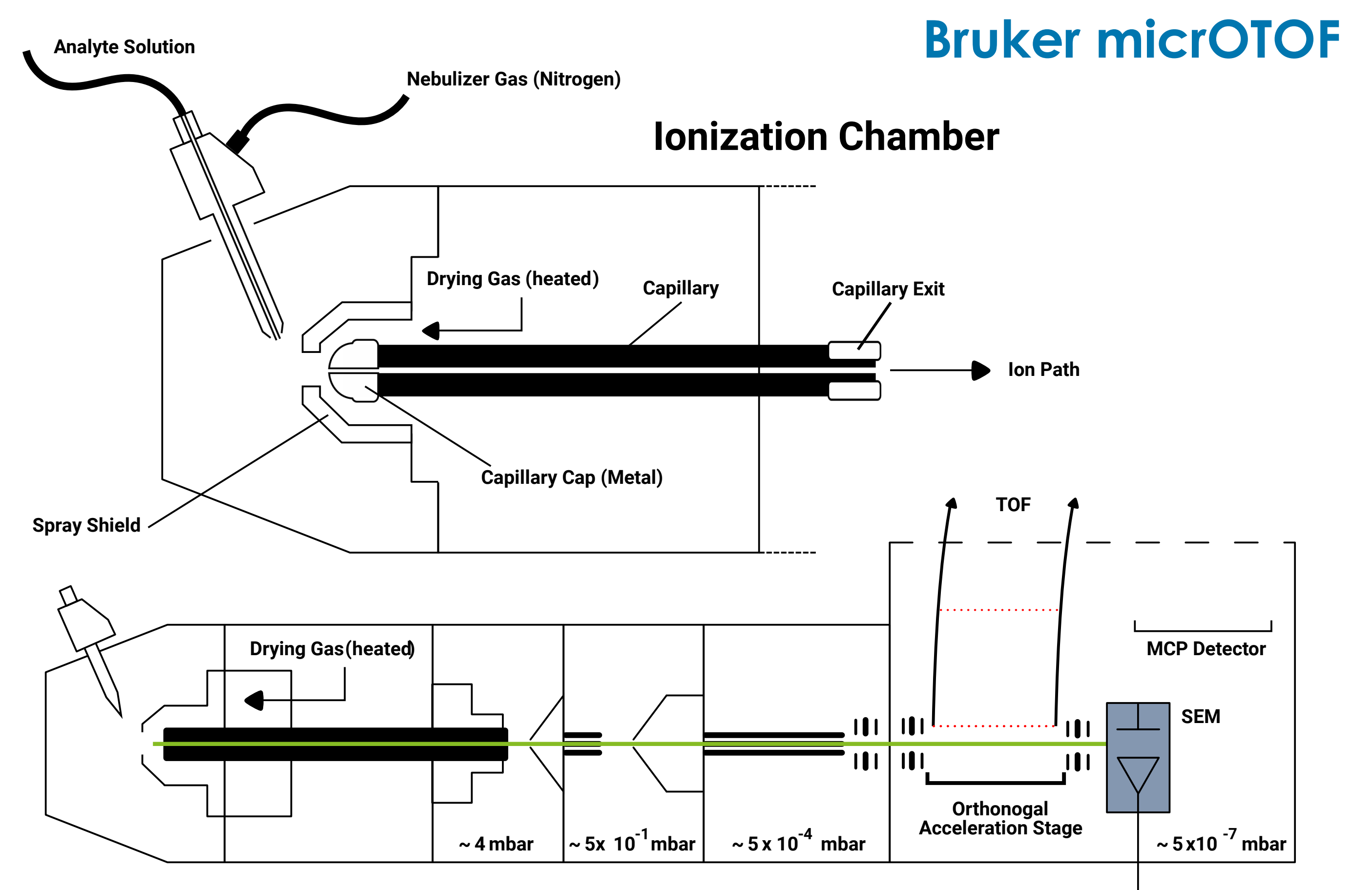


Fig. 1 Scheme of the general mechanism leading to the spray generation

- ▶ Electrospray ionization (ESI) is one of the most used techniques in the field of atmospheric pressure ionization
- ▶ Small analyte ions containing droplets are generated by spraying a liquid solution into a strong electrical field supported by a nitrogen gas flow (nebulizer gas)
- ▶ Textbooks and literature suggest that droplets undergo a temporal shrinkage mechanism toward naked ions within the ionization chamber
- ▶ Recent experiments prove the existence of droplets far behind the ionization chamber throughout the whole instrument

Setup



General Setup

- ▶ Oscilloscope connected to auxiliary SEM detector

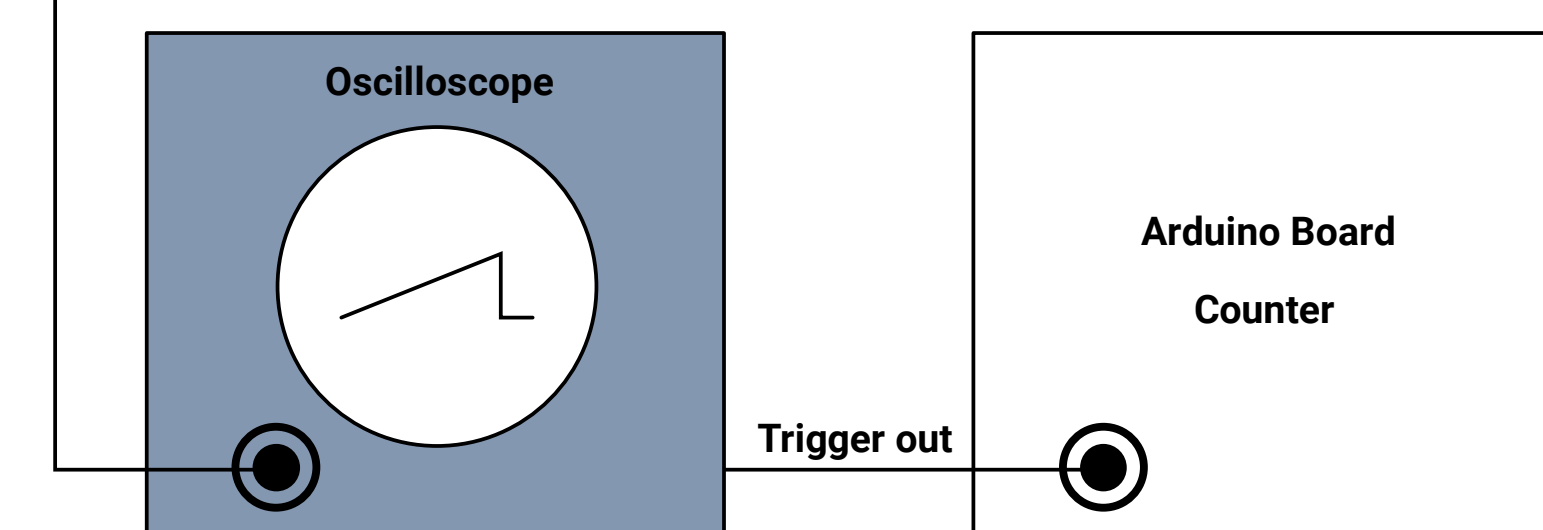


Fig. 2 Schematic scheme of the used setup with connected oscilloscope to an auxiliary SEM detector and Arduino microcontroller

Observing Droplet Signatures in the High Vacuum Region

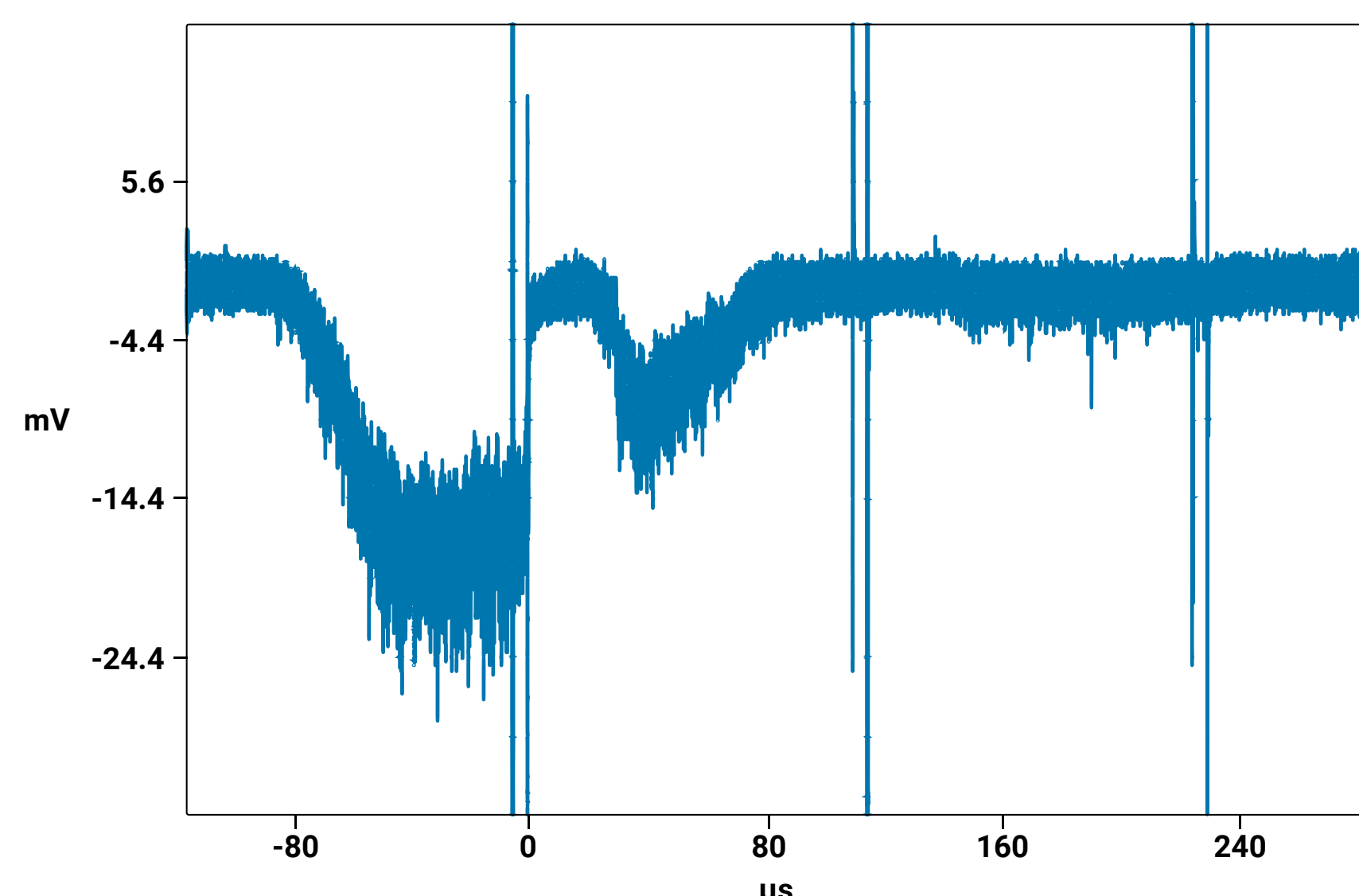


Fig. 3 Recorded oscillogram of three TOF measurement cycles

- ▶ Connecting an oscilloscope to the SEM allows a direct observation of the ion beam between the TOF pulses (every pulse is visible as pair of two very intense peaks)
- ▶ While ESI ionization large ion burst signals appears which are interrupted by the TOF pulses
- ▶ Comparing measurements with APCI and APPI show no highly intense ion burst signals, which suggest that the intensive ion bursts are originating from highly charged particles aspirated from the ESI source
- ▶ The ion burst contains a very high number of elementary charges since the ion burst signals differs significantly from an ordinary measurement cycle (e.g., between 120 and 220 μ s)
- ▶ When the TOF pulses within the appearance of an ion burst, much more ions are reflected into the flight tube and a significantly more intense mass spectrum is recorded, which leads to a lower signal stability in contrast to APCI and APPI

Long-term Measurements

Long-term behavior of ESI signals

- ▶ Analyte signal shows a significant instability within the first 30 minutes, often reported as warm-up time by the manufacturer
- ▶ Applying a rolling mean to the chromatogram reveals a highly regularly oscillating signal intensity after 2 hours of measuring
- ▶ Ion burst frequency remains constant at 0.2 Hz after 1 hour. However, switching the polarity recovers the signal (Fig. 5)

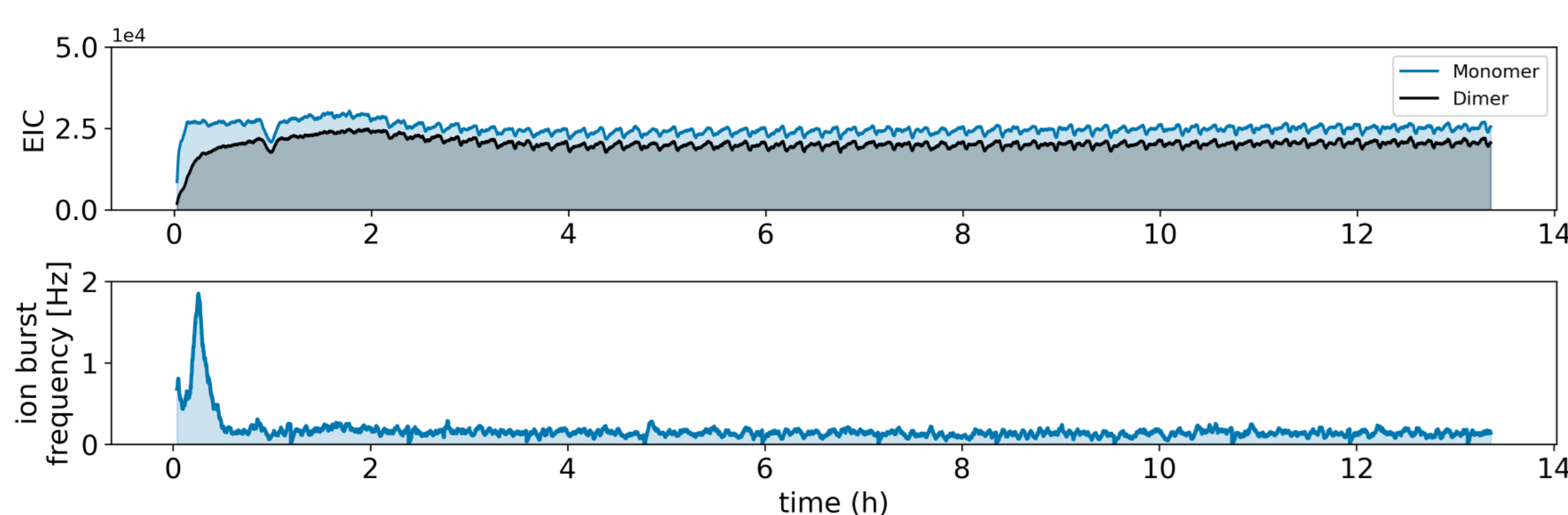


Fig. 4 Long-term measurement with recorded signal stability and ion burst frequency

Recovering Signal after Switching Polarity

- ▶ Droplet signature signals remains high for a short time after switching back to positive ion mode
- ▶ The longer the period of negative ion mode the longer the following abundance of droplet signatures

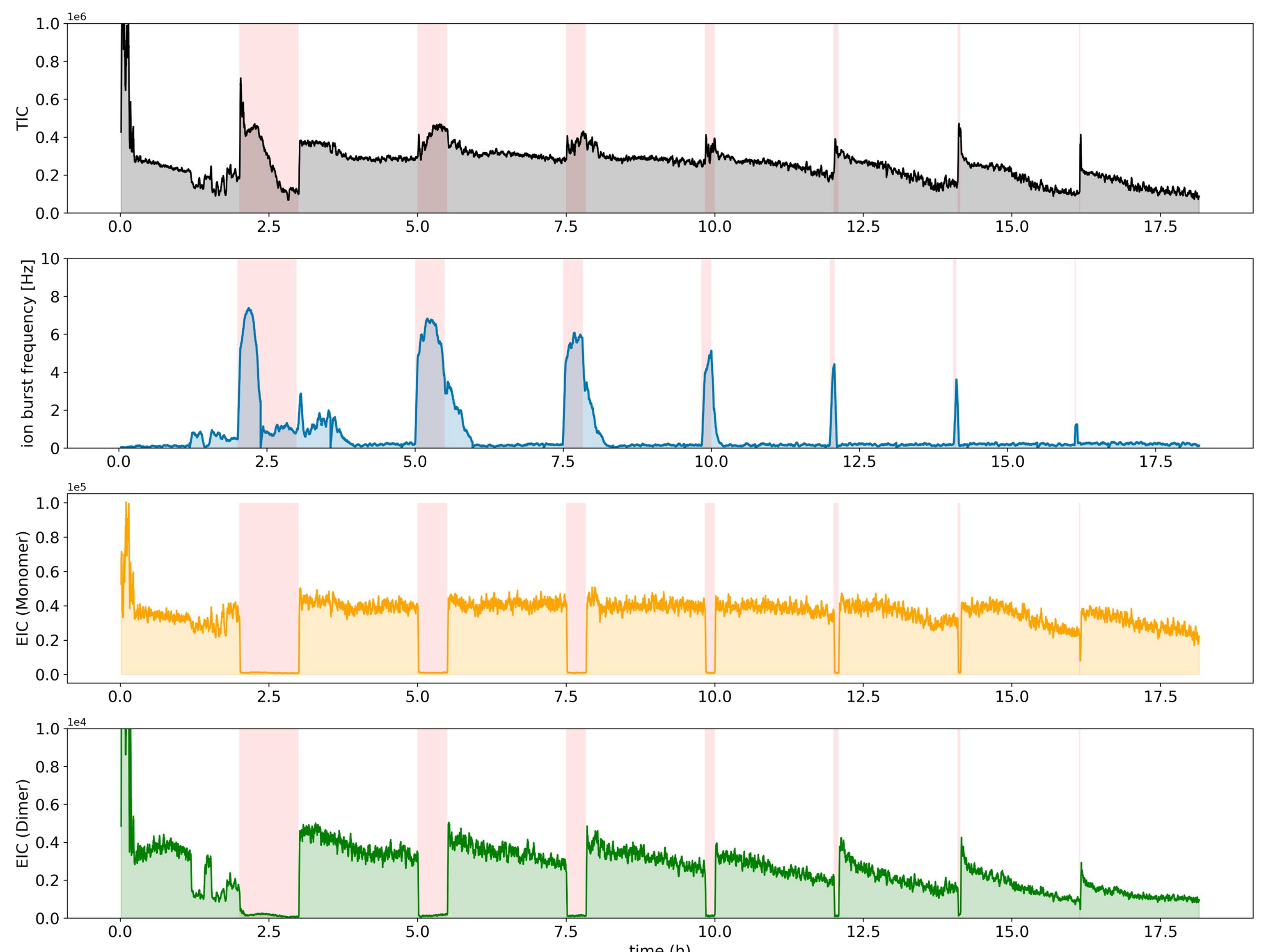


Fig. 5 Long-term ESI measurement of reserpine with periodically switching of polarity of alternating duration. Negative ion mode is depicted as light-red background. Plotted are the total ion count (TIC) the number of registered droplet signatures within 5 seconds, the extracted ion chromatogram for reserpine and reserpine dimer and the ratio between monomer and dimer.