BERGISCHE UNIVERSITÄT WUPPERTAL

Physical & Theoretical Chemistry
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Exploring the long-term Stability of Analyte Signals in Electrospray Mass Spectrometry through Ion Current Measurement and Optical Spray Monitoring

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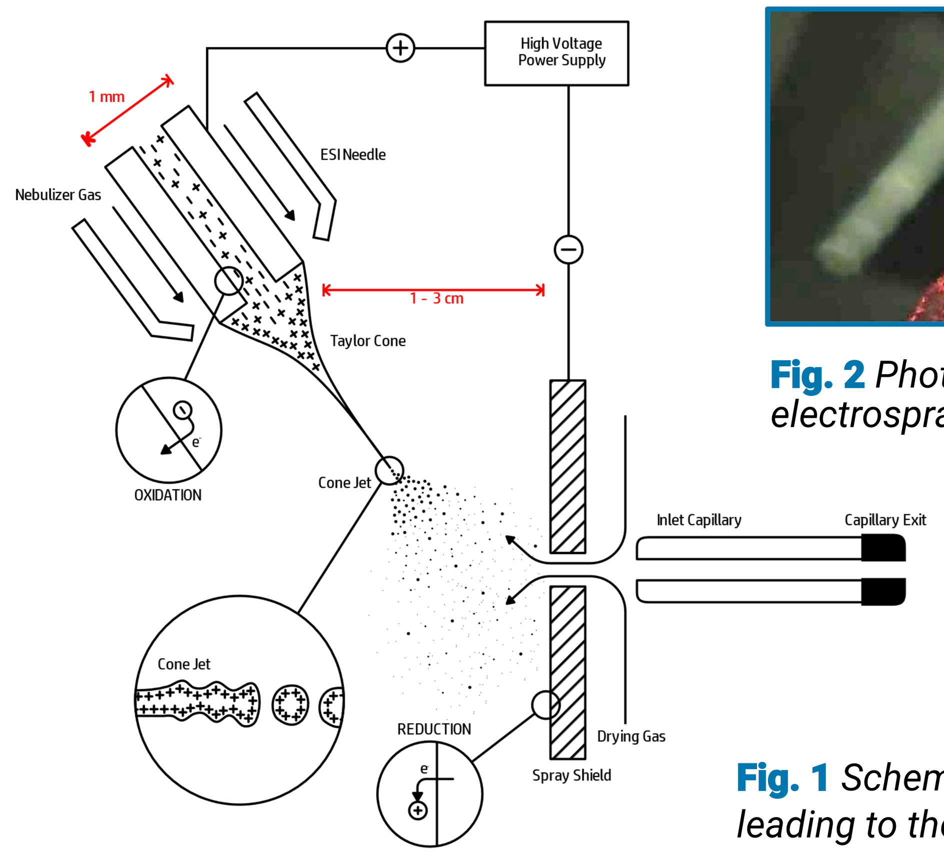
Introduction



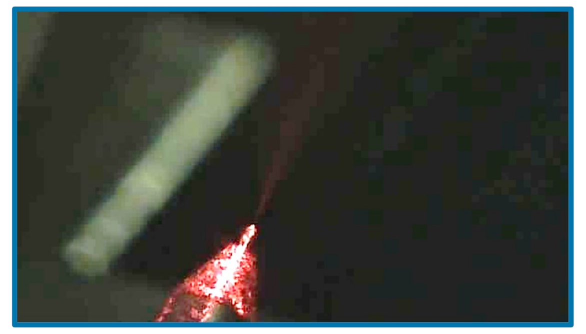


Fig. 2 *Photography of the used electrospray during a measurement*

AREA OF INTEREST
Observation of droplets in the transfer and analysing region

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

- Electrospray Ionization (ESI) is the most frequently used technique in atmospheric pressure ionization (API)
- Droplets containing small analyte ions are generated by spraying a liquid solution into a strong electrical field. The nebulization process is supported by a nitrogen gas flow (nebulizer gas)
- Recent experiments [1, 2, 3] prove the existence of droplets far behind the ionization chamber throughout the whole instrument, although textbooks suggest a release of bare ions solely inside the ionization chamber

References and COI

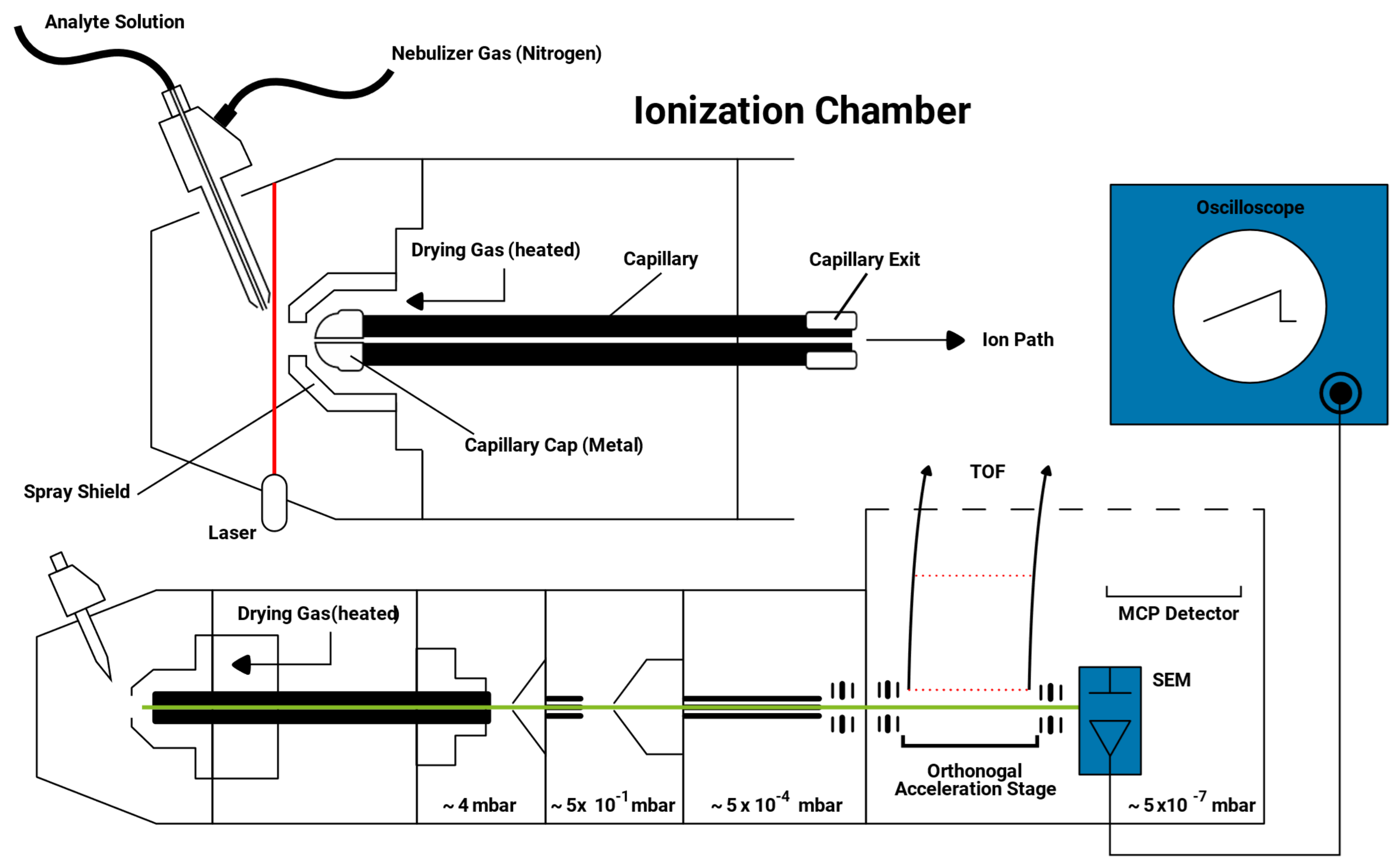
[1] Markert, C., Thinius, M., Lehmann, L., Heintz, C., Stappert, F., Wissdorf, W., Kersten, H., Benter, T., Schneider, B. B., & Covey, T. R. (2021). Observation of charged droplets from electrospray ionization (ESI) plumes in API mass spectrometers. *Analytical and Bioanalytical Chemistry*, *413*(22), 5587–5600. https://doi.org/10.1007/s00216-021-03452-y.

[2] Heintz, C., Schnödewind, L., Braubach, O., Kersten, H., Benter, T., & Wißdorf, W. (2024). Observation of Large, Charged Droplet Signatures within the High-Vacuum Region of a Commercial Electrospray TOF-MS. Journal of the American Society for Mass Spectrometry. https://doi.org/10.1021/jasms.3c00383.

[3] Heintz, C., Schnödewind, L., Braubach, O., Kersten, H., Benter, T., & Wißdorf, W. (2024). Influence of polarity mode switching and standby times on signal stability and detection of aspirated droplet signatures in electrospray mass spectrometry. International Journal of Mass Spectrometry, https://doi.org/10.1016/j.ijms.2024.117232.

The authors declare no competing financial interest.

Setup and Method of Optical Spray Observation



General Setup

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

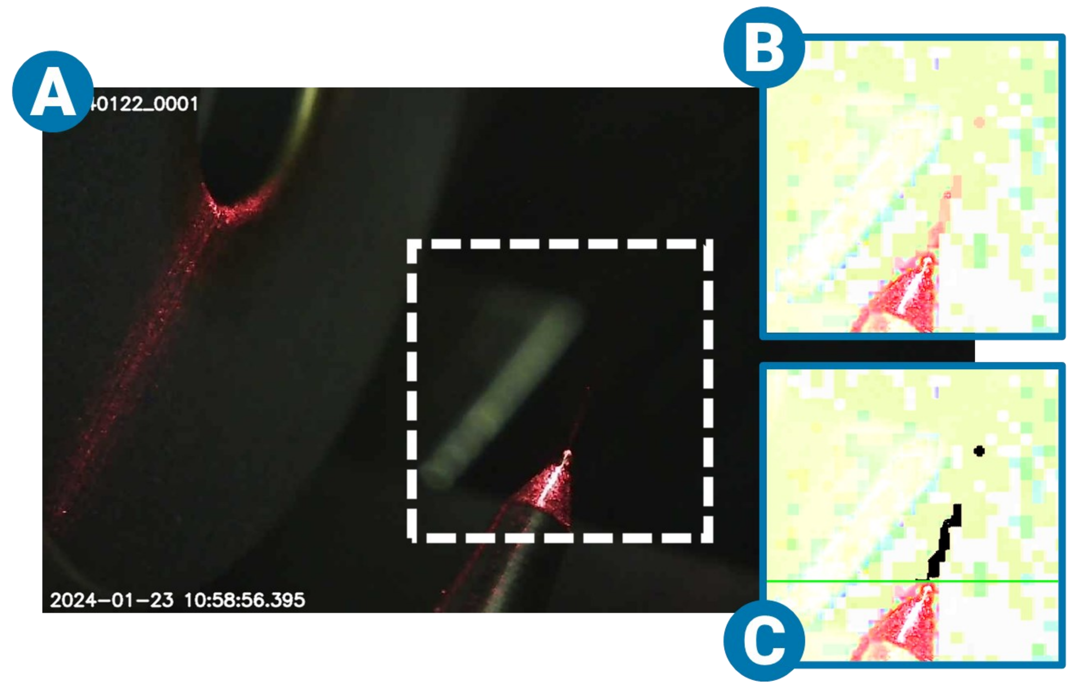


Fig. 3 *Photo of the ESI needle during a measurement and edited versions to calculate the spray area*

USB microscope camera module was installed to monitor the spray condition

- Laser module was placed inside the ionization chamber to illuminate the spray
- Automated script crops the image (A)
- Saturation and contrast is also automated adjusted by the script (B)
- Laser beam was send through a cylindrical glass lens to create a plane illuminating the spray cross-section (visible in B)
- Inside a manually chosen box all red pixels representing the spray were counted (marked as black pixels in C)
- Ratio of spray pixels to all other pixels is calculated

Results and Discussion

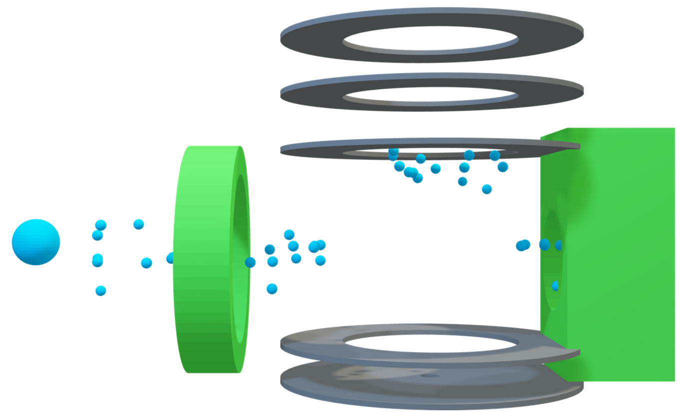


Fig. 4 *Schematic 3D-rendering of the orthogonal acceleration stage with auxiliary SEM detector in the moment of a TOF push*

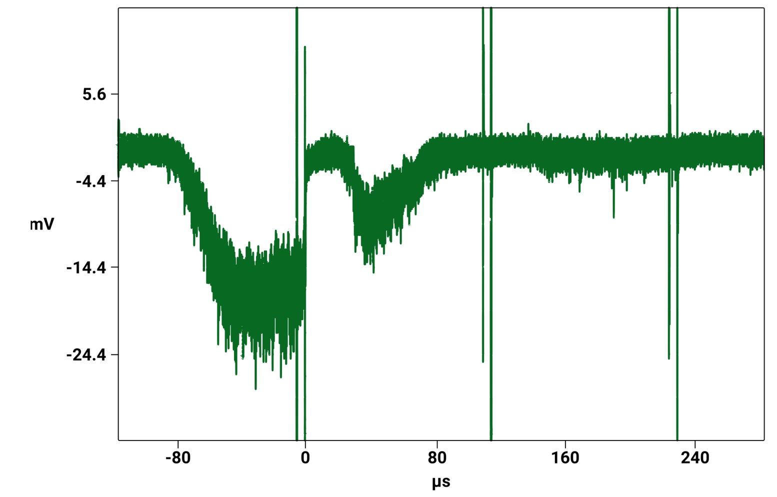
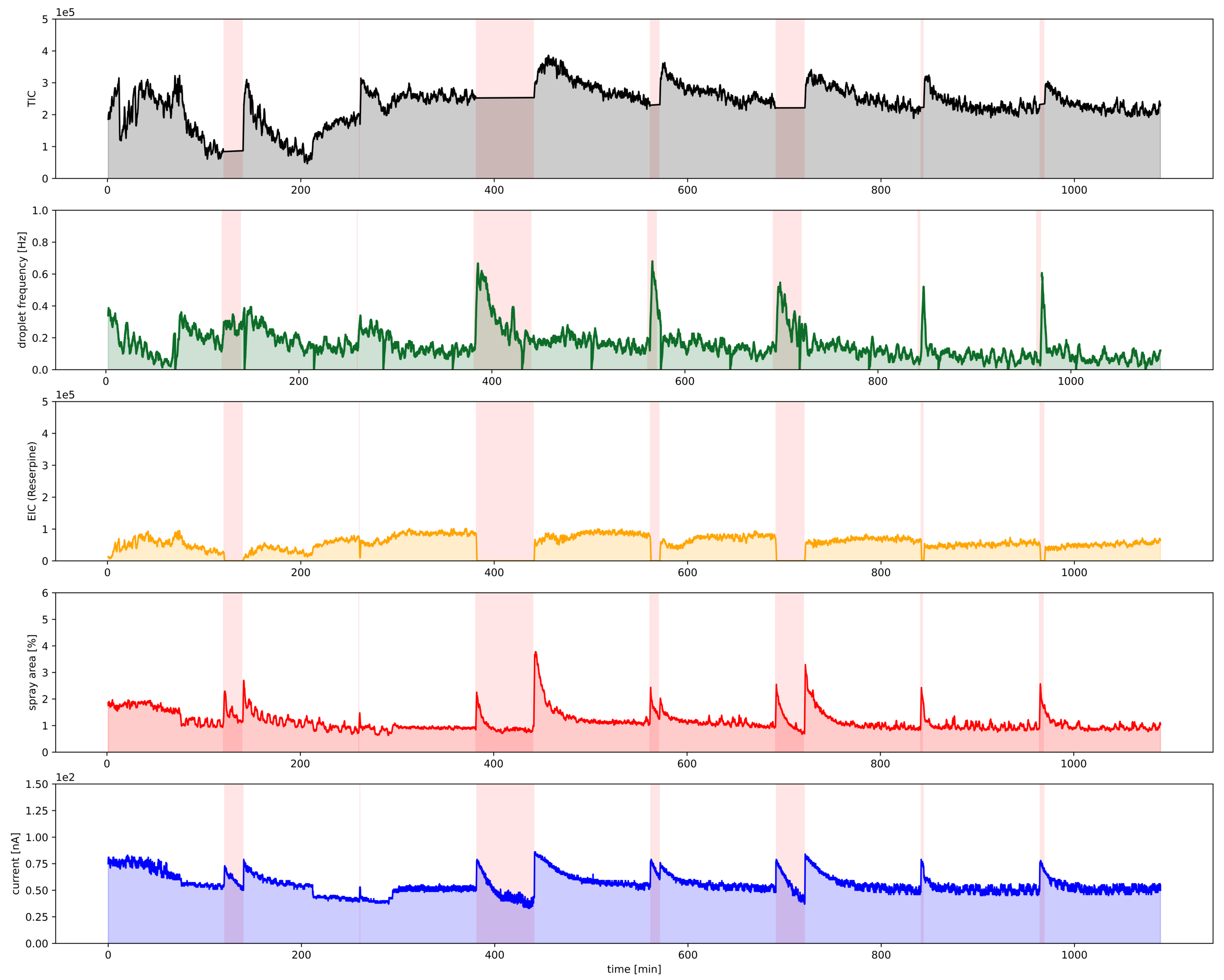
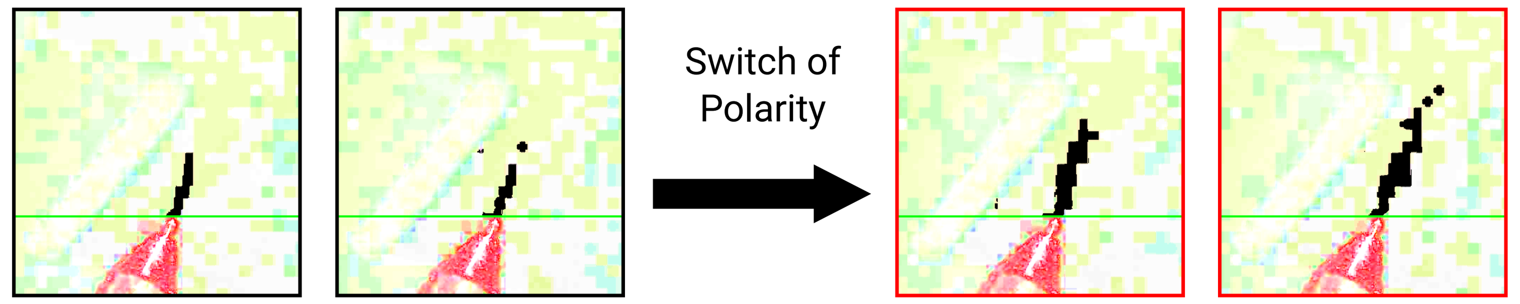


Fig. 5 *Recorded oscillogram of three TOF measurement cycles*



- **Droplet signature occurrence frequency increases** reproducibly when switching from positive in negative ESI mode
- Every polarity switch comes with an **increase of spray area** (from positive to negative smaller than vice verse), which seems cause a **higher droplet signature occurrence frequency**



- Even with a **stable spray**, there are droplets signatures in the high vacuum region observable
- **Correlation** between **spray area, TIC** and ion current (measured between ESI needle and spray shield)

Fig. 6 *Chromatograms of total ion count (TIC), droplet frequency, extracted ion count (EIC) for reserpine and the spray area (described in Fig. 3). Red areas mark periods of negative ESI mode.*