BERGISCHE UNIVERSITÄT WUPPERTAL

Physical & Theoretical Chemistry

University of Wuppertal

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

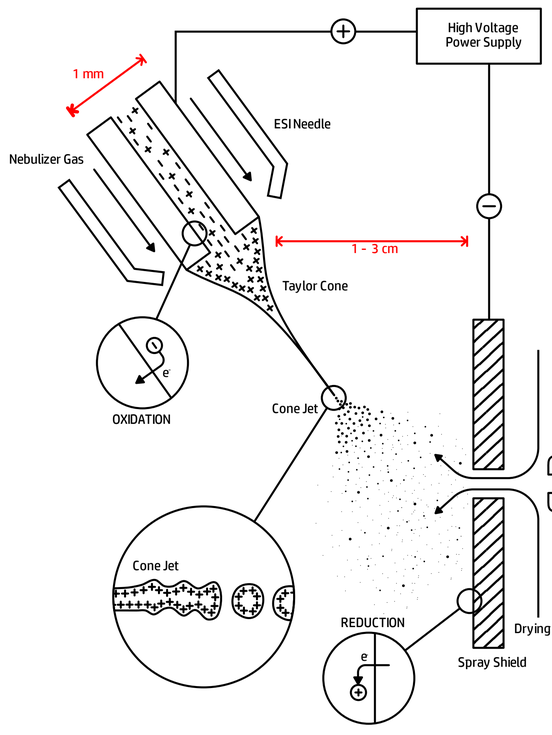


Fig. 2 *Scheme of the general mechanism leading to the spray generation*

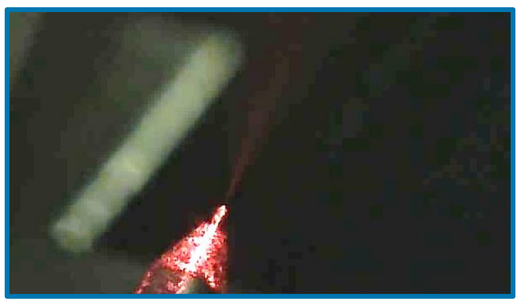
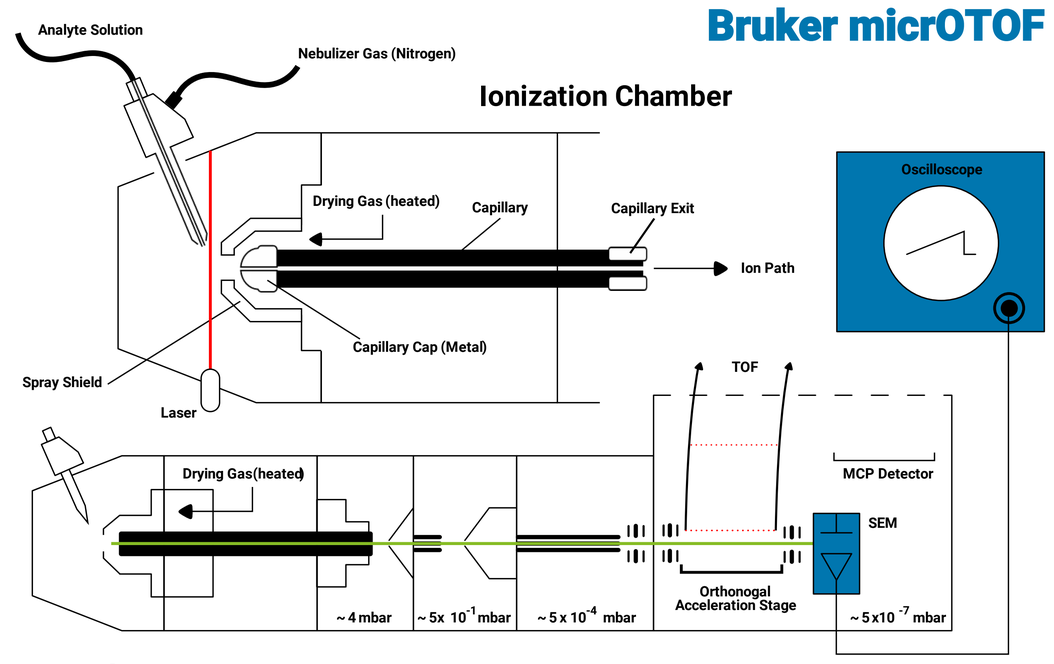


Fig. 1 *Photography of the used electrospray during a measurement*

AREA OF INTEREST
Oberservation of droplets in the transfer and analyzing region

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

Setup



General Setup

Fig. 3 *Schematic scheme of the used setup with an oscilloscope connected to an auxiliary SEM detector and Arduino microcontroller*

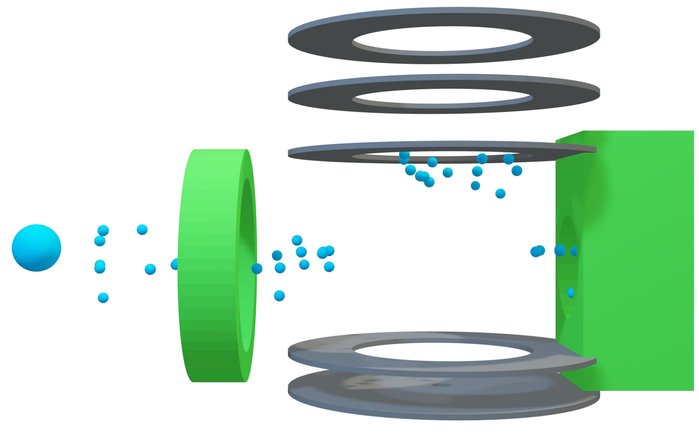


Fig. 4 *Schematic 3D-rendering of the orthogonal acceleration stage with auxiliary SEM detector in the moment of a TOF push*

Observing Droplet Signatures in the High Vacuum Region

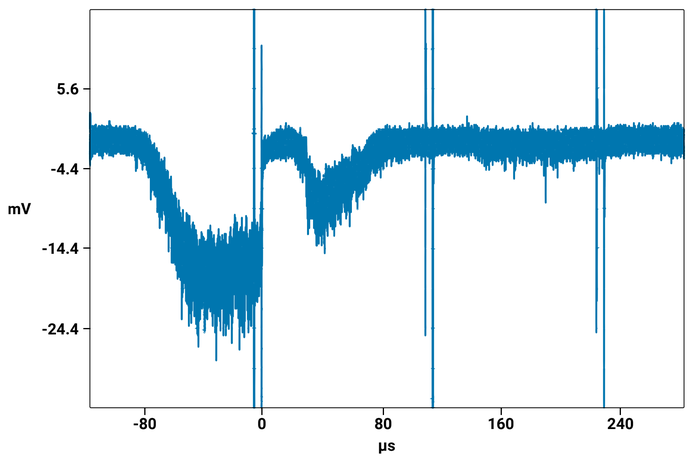


Fig. 5 *Recorded oscillogram of three TOF measurement cycles*

- Ion current hitting the auxiliary SEM detector
- Interrupted by pusher as shown in Fig. 4 (sharp peaks)
- Only with ESI: super intense ion bursts occur with few Hz frequency
- Bursts of fragmented droplets (bursts be split by a push)

Method of Optical Spray Observation

USB microscope camera module was installed to monitor the spray condition

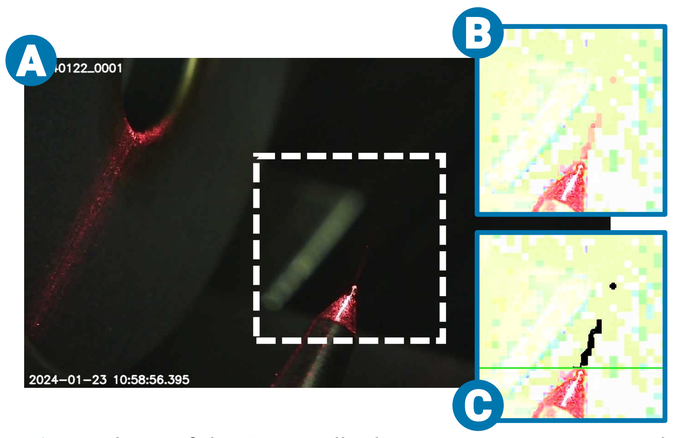


Fig. 6 *Photo of the ESI needle during a measurement and edited versions to calculate the spray area*

- Automated script crops and edits the image (A)
- Inside a manually chosen box all red pixels representing the spray were counted (marked as black pixels in Fig. 6C)
- Ratio of spray pixels to all other pixels is calculated

Results of Optical Spray Observation during long-term Measurements

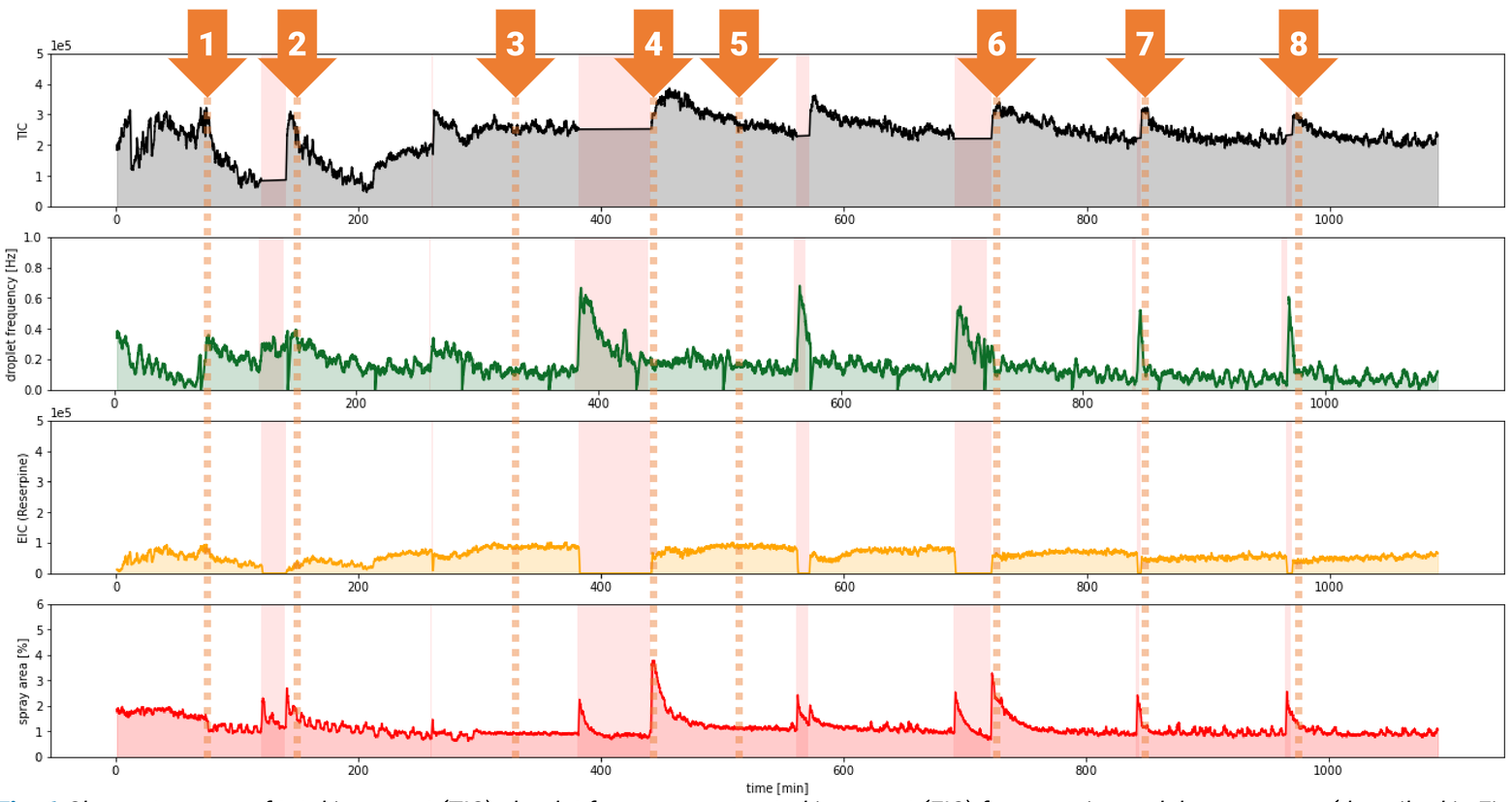


Fig. 6 *Chromatograms of total ion count (TIC), droplet frequency, extracted ion count (EIC) for reserpine and the spray area (described in Fig. 5). Red areas mark periods of negative ESI mode.*

- **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 the other way), which seems to cause a **higher droplet signature occurrence frequency**
- But: Not every increased spray area causes an increase in the droplet frequency (see 4)
- Even with a **stable spray**, there are droplets signatures in the high vacuum region observable (see 3)
- **Correlation** between **spray area and TIC** (see 1-8)

References

[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