The effects of ion source and transfer parameters on charged droplets formed by ESI ionization

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Introduction and Experimental Setup

ESI Ion Source

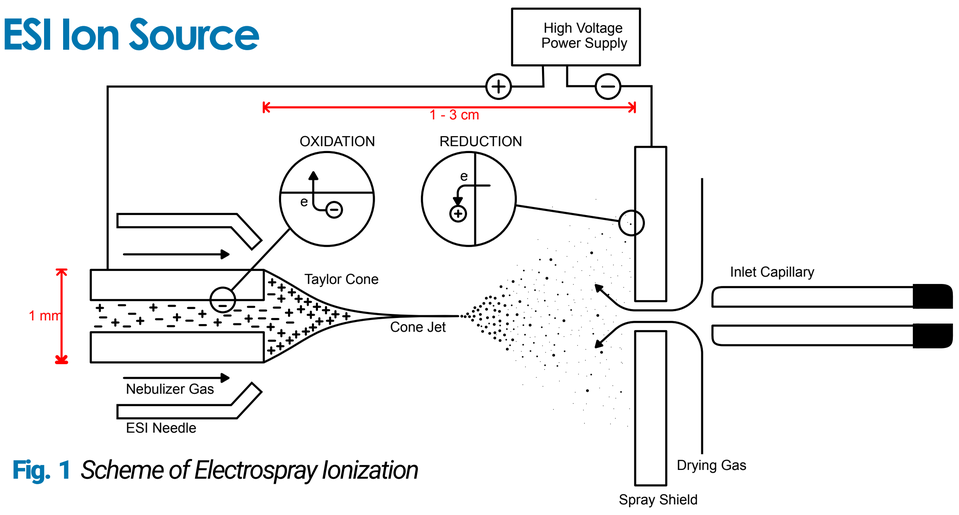


Fig. 1 *Scheme of Electrospray Ionization*

- Electrospray Ionization (ESI) generates highly charged liquid droplets
- Charged droplets are aspirated into the vacuum stages of modern API instruments [1, 2]
- Potential consequences: Instrument contamination, adverse ion / neutral chemistry, complex mass spectra

Droplet Observation on Bruker micrOTOF

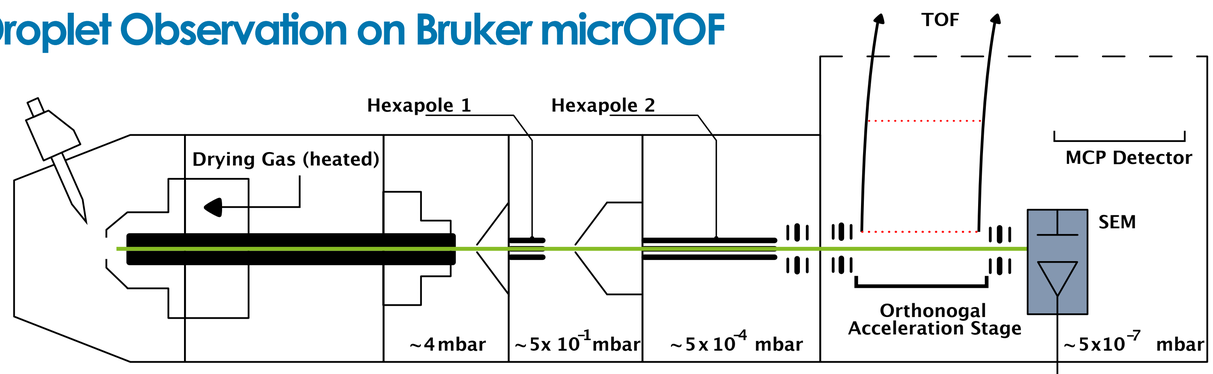
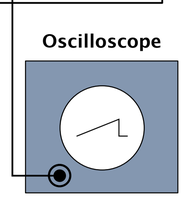


Fig. 2 *Scheme of micrOTOF Instrument*



- Direct observation of charged droplet signatures as intensive *ion signal bursts* with auxiliary detector
- Ion burst frequency can be observed parallel to mass spectra recording in dependence on ion source and transfer stage parameters
- Sprayed analyte solution: Reserpine (8 µmol/L) in 50:50 Acetonitrile / Water

Ion Burst Signal Shapes in Dependence of Hexapole RF Amplitude

Droplet Signature Observation

- Signatures of charged droplets directly visible as highly intensive ion bursts on auxiliary detector ("SEM" in Fig. 2)
- Bursts consist of very large number of individual charges (at least many thousands) but *not* monolithic large particles
- Proposed mechanism: Droplets are aspirated and fragment in the transfer stage, forming highly correlated *ion clouds* traversing the instrument

Hexapole RF Amplitude

- The micrOTOF has two transfer hexapoles
- Both hexapoles are connected to the same RF generator and have therefore the same RF amplitude

Dependence of Burst Signals on RF Amplitude

- Remarkably, the shape of the observed ion burst signals clearly depend on the hexapole RF amplitude
- The complex signal shape is highly reproducible for different RF amplitudes
- Direct connection between hexapole RF and signal shape strongly hints towards the hexapole region as an important droplet fragmentation location

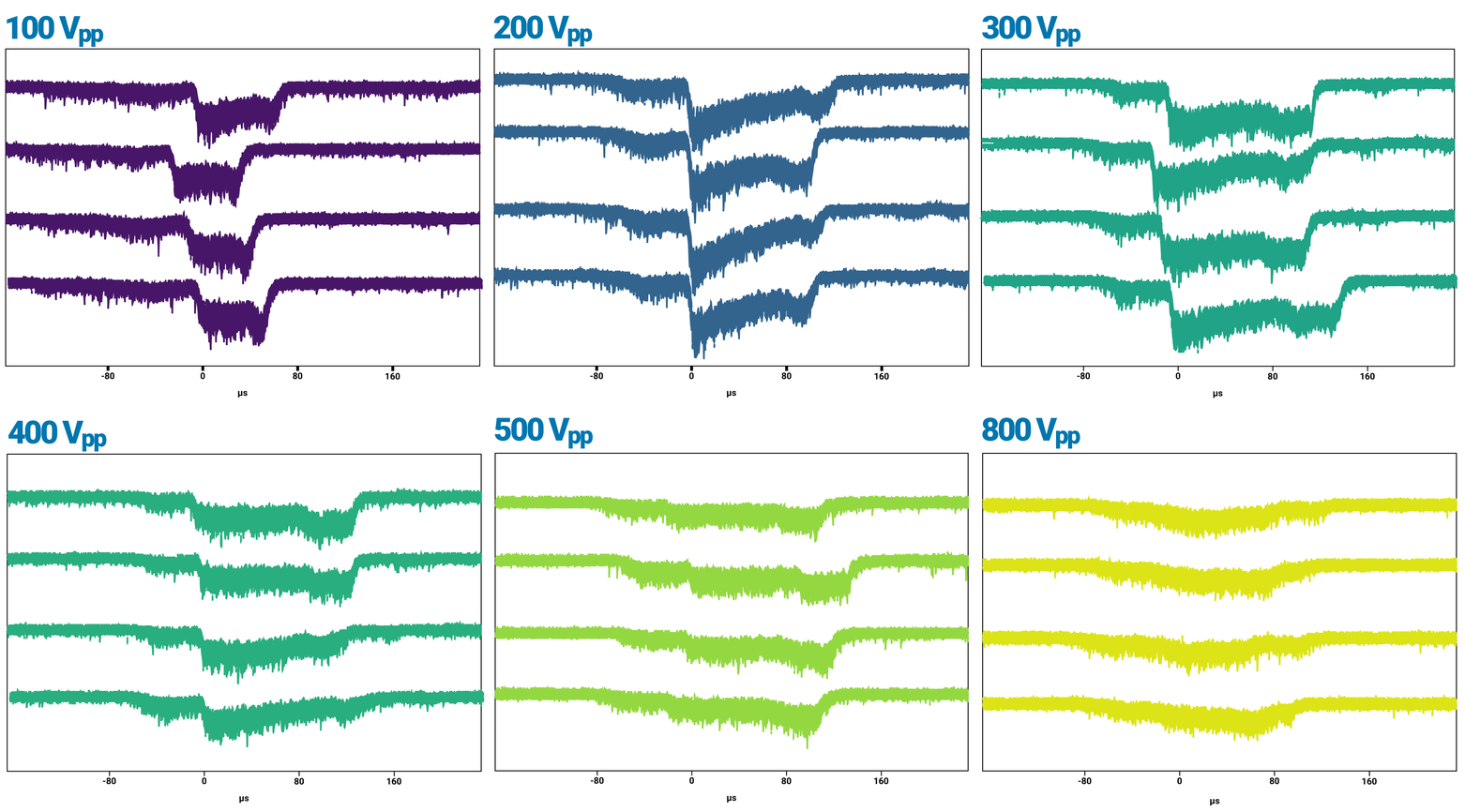
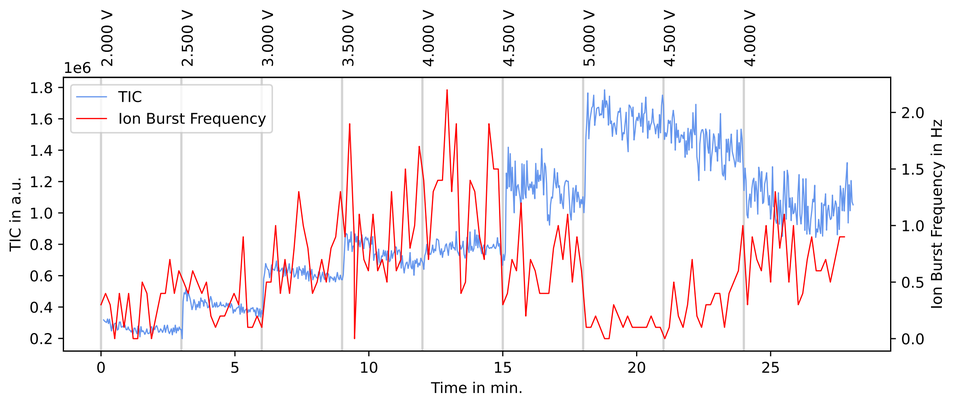


Fig. 3 *Examples of observed ion burst signals in dependence on the hexapole RF amplitude in an Bruker micrOTOF*

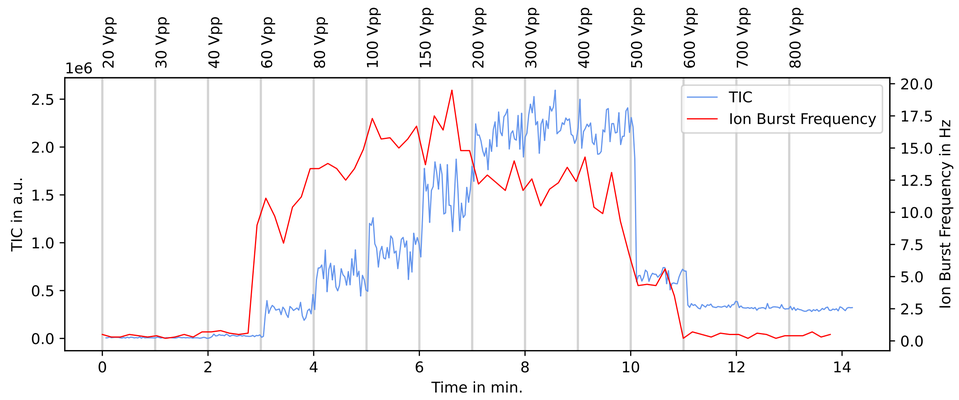
Burst Frequency and MS Signal: Polarity, Ion Source Parameters, Hexapole RF

Positive Ion Mode

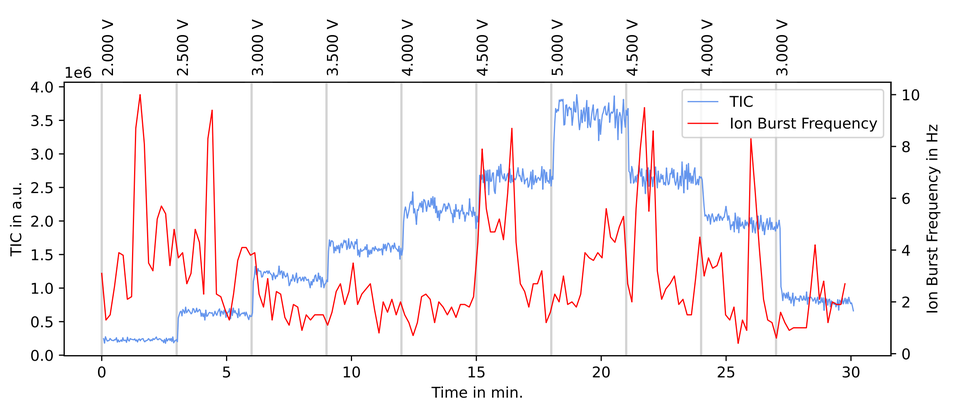
Capillary / ESI Voltage

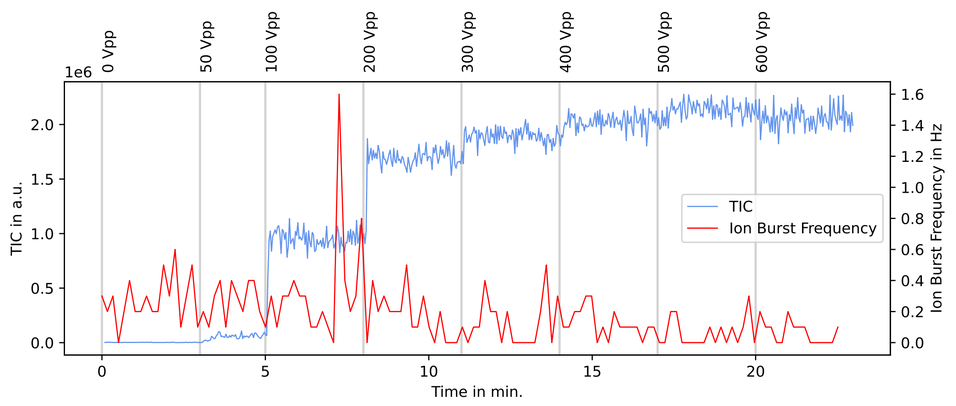


Hexapole RF Amplitude



Negative Ion Mode





- The frequency of detected ion bursts is recorded in parallel to the total ion current (TIC) visible with the TOF mass analyzer of the microTOF
- ESI / Capillary voltage strongly affects TIC in positive and negative ion mode
- Effect of capillary voltage on burst frequency is less clearly visible
- Positive and negative ion mode show different behavior for ion burst frequency and TIC for capillary voltage and hexapole RF amplitude
- Results show clearly: Transfer stage parameter and ion source parameter affect frequency and shape of observed ion burst signals

References:

(1) Markert, C.; Thinius, M.; Lehmann, L.; Heintz, C.; Stappert, F.; Wissdorf, W.; Kersten, H.; Benter, T.; Schneider, B. B.; Covey, T. R. Observation of Charged Droplets from Electrospray Ionization (ESI) Plumes in API Mass Spectrometers. Anal Bioanal Chem 2021. https://doi.org/10.1007/s00216-021-03452-y.

(2) Kang, Y.; Schneider, B. B.; Covey, T. R. On the Nature of Mass Spectrometer Analyzer Contamination. J. Am. Soc. Mass Spectrom. 2017, 28 (11), 2384–2392. https://doi.org/10.1007/s13361-017-1747-3.