Signatures of Liquid Droplets from Electrospray in the Mass Analyzer Region of a Commercial ESI-TOF-MS

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Introduction

Electrospray Ionization (ESI) is one of the most frequently used atmospheric pressure ionization (API) techniques in mass spectrometry (MS). An analyte-solution is sprayed in a strong electric field leading to the generation of charged droplets. It is a common assumption that the droplets fully evaporate within the ion source chamber bearing bare ions. However, a series of experiments[1] shows that a significant quantity of large, charged droplets from the electrospray reaches the high vacuum region of an ESI-MS. Droplets penetrating deeply into the vacuum system potentially lead to a diminished analytical performance. Thus, it is crucial to understand the mechanisms leading to aspiration of large droplets into an ESI-MS to improve the quality of received mass spectra and lower the maintenance effort.

Methods and Setup

Charged droplet signatures are investigated in a Bruker microTOF with an auxiliary ion detector (secondary ion detector – SEM) located downstream the TOFs pulser region (cf. Fig. 1). By connecting the SEM output signal to an oscilloscope with appropriate input impedance, we were able to directly observe and analyze the appearance of charged droplet signatures in terms of intensive ion signal bursts (cf. Fig. 2). The acquired burst oscillograms were analyzed using a custom software. Furthermore, we recorded non-summed individual TOF spectra and analyzed them also with custom analysis programs. All measurements were done in dependance of ESI source parameters. As an analyte system we used a solution of 8 µmol·L^{-1} reserpine in a 1:1 mixture of water and acetonitrile.

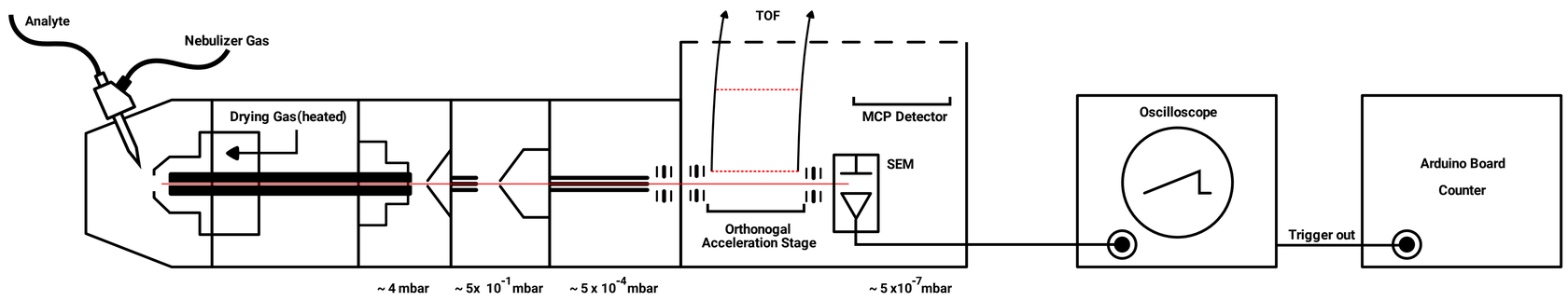

Fig. 1 *Schematic representation of the experimental setup with a Bruker micrOTOF and droplet signature detection*

Droplet Signature Appearance

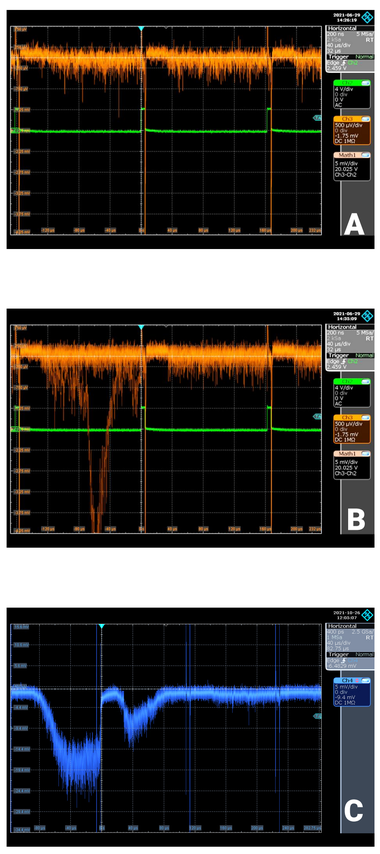

Fig. 2 *Screenshots of oscillograms. The orange channel shows the SEM signal, the green channel shows the TOF acceleration stage trigger signal and is pictured as reference.* ***(A)*** *pictures the regular ion current reaching the SEM. Right after the TOF-push at 0 µs, there is a region of approx. 30 µs where no ions hit the SEM ("cut-out" region) due to the acceleration of an ion package into the TOF flight tube.* ***(B)*** *shows one of the statistically appearing ion bursts. The signal is magnitudes higher than the regular ion current hitting the SEM.* ***(C)*** *shows another measurement, where the ion burst lasts longer than a TOF cycle and shows a cut-out area right after the push. This indicates that the observed signal burst originates from an actual highly correlated group of ions and not a compact single particle with high charge number.*

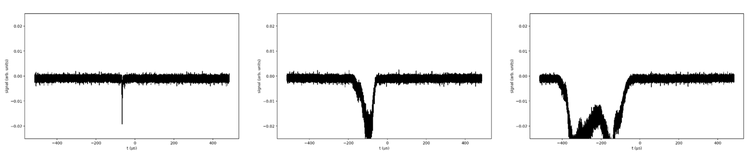

Fig. 3 *Three different oscillograms of droplet signatures, recorded with disabled pusher to prevent the "cut out".*

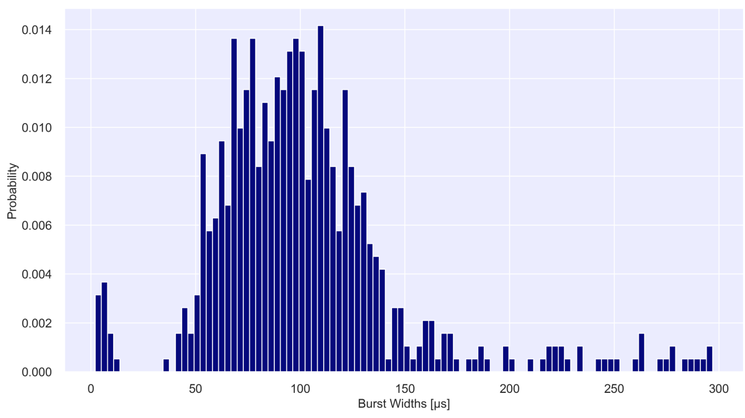

Fig. 4 *The histogram of all recorded burst widths during a long-time measurement show a distinct width distribution. We conclude that the burst widths probably depend on the location of the fragmentation of the initial compact droplet. If this fragmentation appears further down the ion stream, the burst signal becomes narrower. An earlier fragmentation and thus longer spreading occurs in a wider signal.*

Long-Term

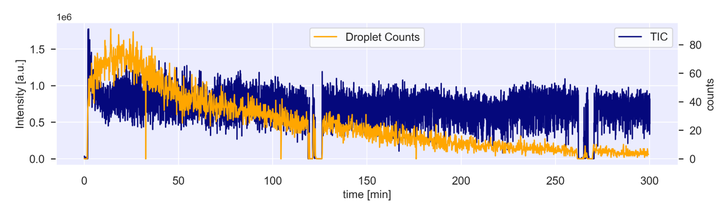

Fig. 5 *Long-term measurement of an electrospray with focus on the droplet signature count and the TIC, recorded at the microTOF MCP detector. The zero-signal at approx. 5500 seconds is reasoned by a syringe switch. The droplet count is decreasing over the time.*

Source Parameter Variation

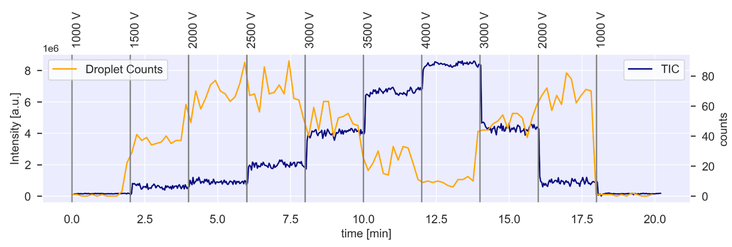

Fig. 6 *Observed dependences between droplet signature count, TIC and the variation of the capillary voltage. Other parameters suggest also a dependence of observed droplets. All parameters which are crucial for the spray generation show the highest impact on the droplet count.*

Non-Summed Time-of-Flight Spectra

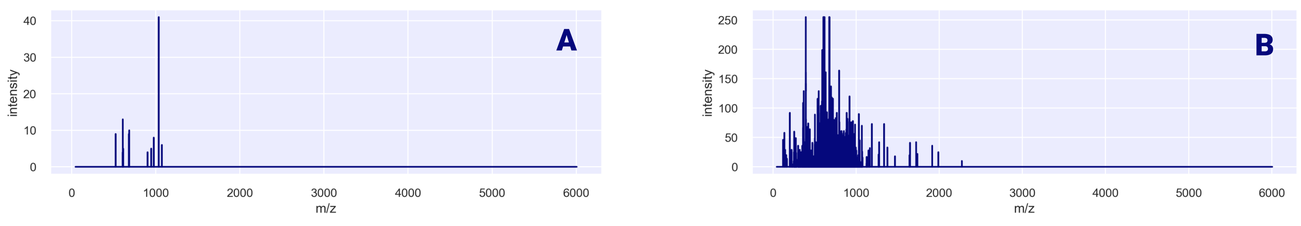

Fig. 7 *Non-summed mass spectra from the same measurement.* ***(A)*** *Regular spectrum with a low total sum of registered ions (550).* ***(B)*** *Example spectrum with a total ion count magnitudes over the regular spectrums case (~13000) which are comparably rare.*

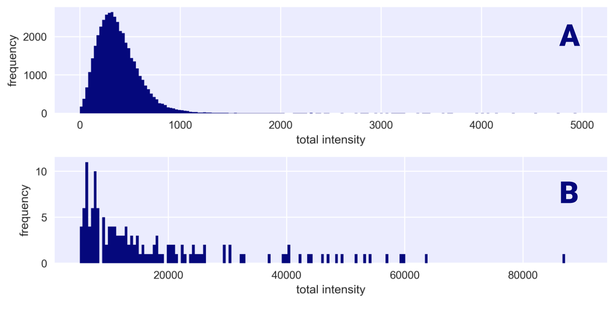

Fig. 8 (A) *shows the distribution of total intensities of all recorded single non-summed mass spectra.* ***(B)*** *heightens the area from 5000 to 90000.*

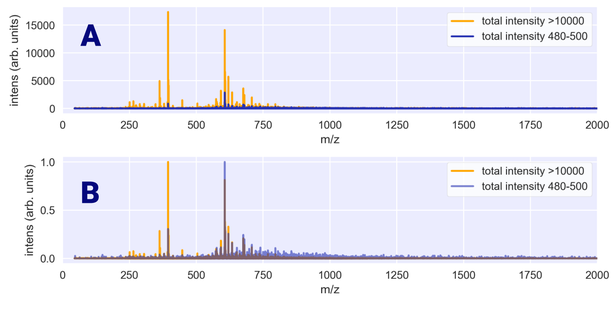

Fig. 9 *All single spectra with a total intensity between 480 and 500 (blue plot, spectra in total) and over 10000 (orange plot, 94 spectra in total) were summated.* ***(A)*** *absolute intensities* ***(B)*** *normalized intensities.*

Conclusion

- Demonstration of the existence of highly charged, large conglomerates in the high vacuum region
- Cut-out area in SEM oscillogram indicates that droplets are fragmented to "ion bursts"
- Different ion burst signal widths suggest that the droplet fragmentation occurs in variable distances before the TOF acceleration stage
- Long-term measurements show a decreasing droplet count within several hours
- Variation of source parameters show dependence on droplet count
- Ion bursts are even visible in TOF single (non-summated) spectra as very intense spectra
- Reassembled mass spectra from intense and „normal" spectra show different peak intensities and peak distribution
- Less summated high intensity spectra lead to a more intense mass spectra than more summated low intensity spectra

Literature

[1] 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.