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Analysis of Charged Droplets from ESI in a Vacuum System by Displacement Current Measurements

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Introduction

Electrospray ionization (ESI) is the most important ionization techniques in atmospheric pressure ionization mass spectrometry (API-MS). An analyte solution is sprayed into an electric field between the ESI needle (4 kV) and the mass spectrometer entrance, resulting in the formation of highly charged droplets containing the analyte. A Nebulizer Gas flow is injected at the sprayer tip to assist the spray process. Experimental observations [1,2] show that a significant portion of these highly charged droplets generated by ESI can pass through the MS inlet into the vacuum system of the instrument due to their long lifetime.

This leads to the conclusion that the droplets not only impact analytical performance but also result in contamination of the mass spectrometer.

Simulations Provide more Information

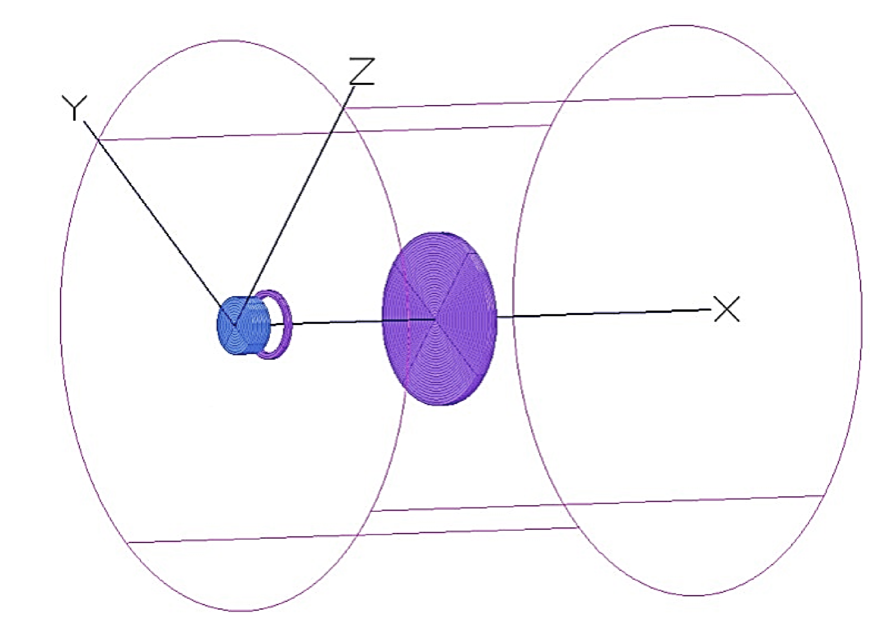

Fig. 2: Simulation vacuum chamber

The findings were interpreted, with additional insights from numerical simulations using SIMION. Information of the expected signal pulse in dependence on speed and charge of the droplets can be derived from the simulation.

Thus, these results together offer an initial estimation of the actual charge carried by the measured particles.

Droplet Charge Measurement Setup

Measurements of displacement current were conducted to directly determine the absolute charge of individual aspirated droplets. Charged droplets are created by electrospray ionization at atmospheric pressure and are subsequently transported into a vacuum chamber. This chamber is designed to replicate the conditions of a typical first vacuum stage in a mass spectrometer.

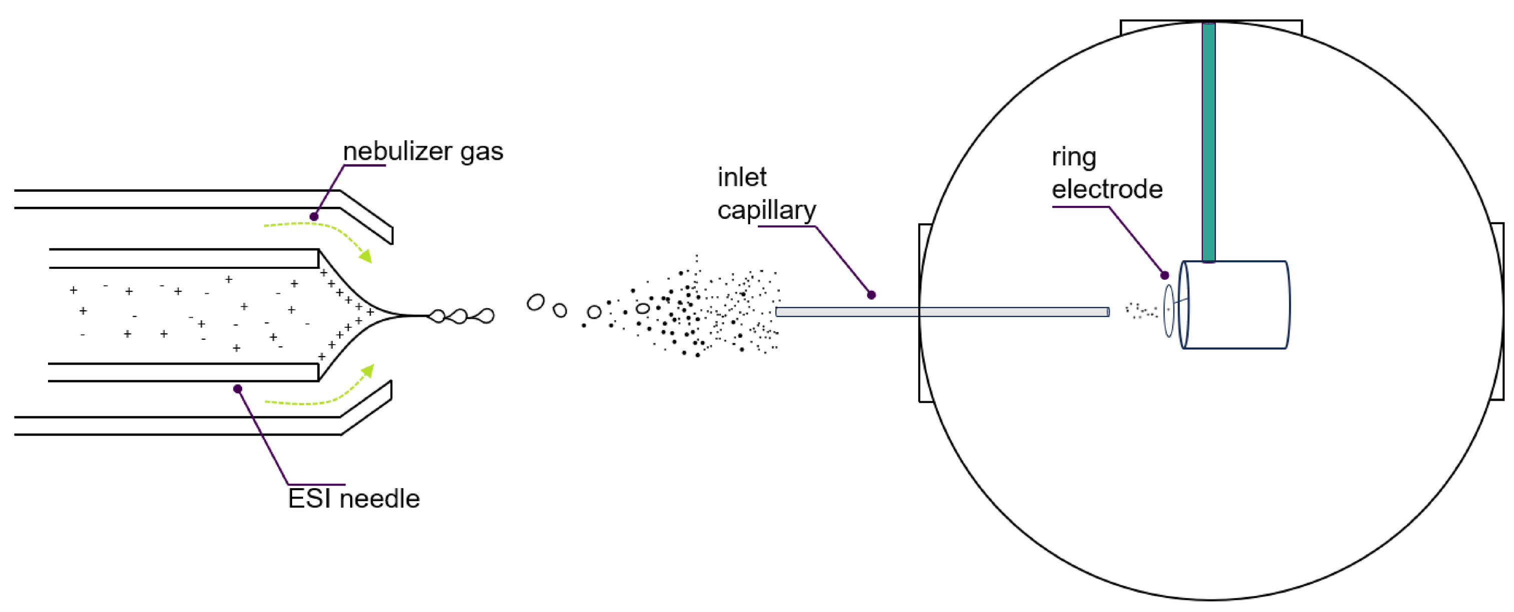

Fig. 1: Scheme of the experimental setup

The charged droplets pass through a wire ring in the vacuum region, which serves as a detection electrode. The displacement current generated by the passing charged droplets on the measuring electrode is amplified using a sensitive amplifier before being recorded by an oscilloscope. The predominant observation with the described experimental setup was the occurrence of strong signal pulses at highly regular intervals.

Droplet Signal Simulation Results

The simulation of the displacement current signal of charged droplets passing the detection electrode shows a very distinct pulse shape. This peak results from the droplet approaching and leaving the detection electrode (ring electrode).

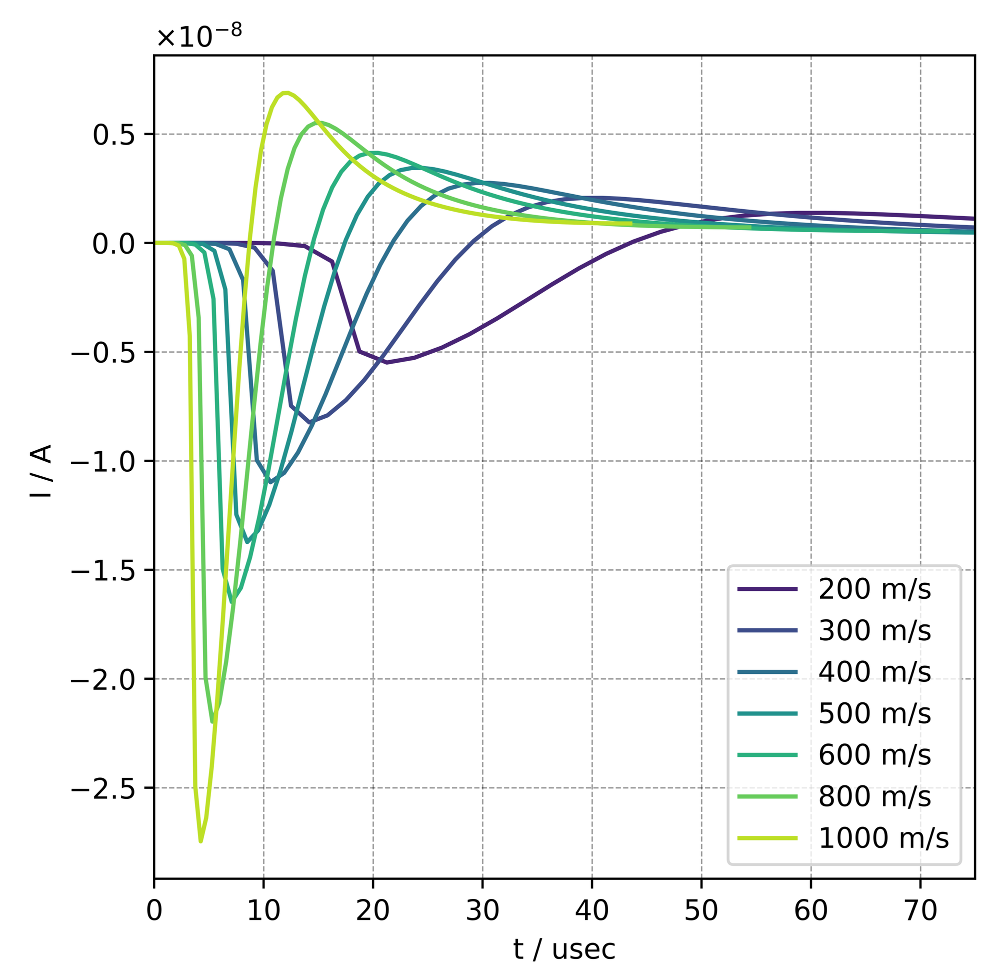

Fig. 3: Simulated pulses with droplets of 1×10^6 elementary charges

- The signals in Fig. 3 illustrate particles with varying speeds and 1×10^6 elementary charges
- The current pulses become narrower as the speed increases
- A particle with 1×10^6 elementary charges at $10^3\ \mathrm{m\,s^{-1}}$ generates a simulated peak signal of 2×10^{-8} A.

Droplet Charge Approximation

- The observed displacement current is the result of charged particles moving through the measuring electrode ring.
- Experimental measurements were amplified by a factor of $10^8\ \mathrm{V\,A^{-1}}$ using a transimpedance amplifier.
- The observed current corresponds to the *displaced charge* and not to the charge of the droplets directly.
- Therefore, it is necessary to determine a factor from the simulations to establish the sensitivity of the detection arrangement to the charged particles.

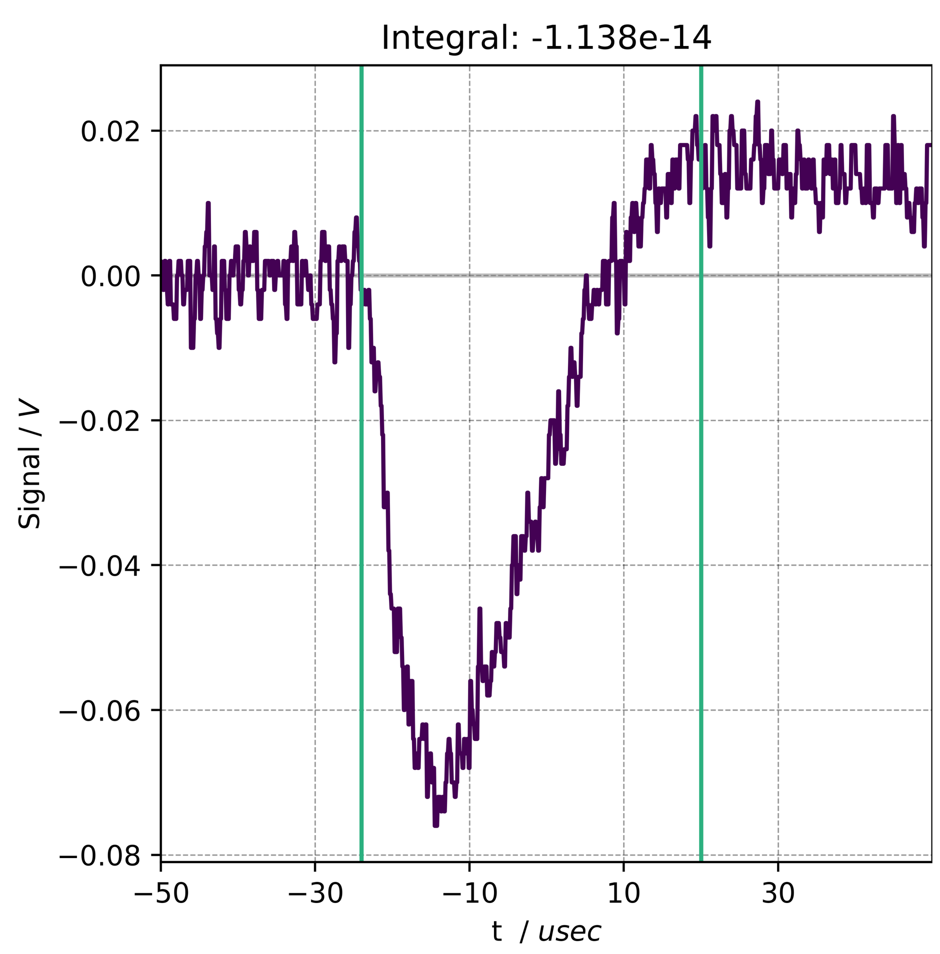

Fig. 4: Displacement current measurement with a solution of of reserpine in acetonitrile and Water

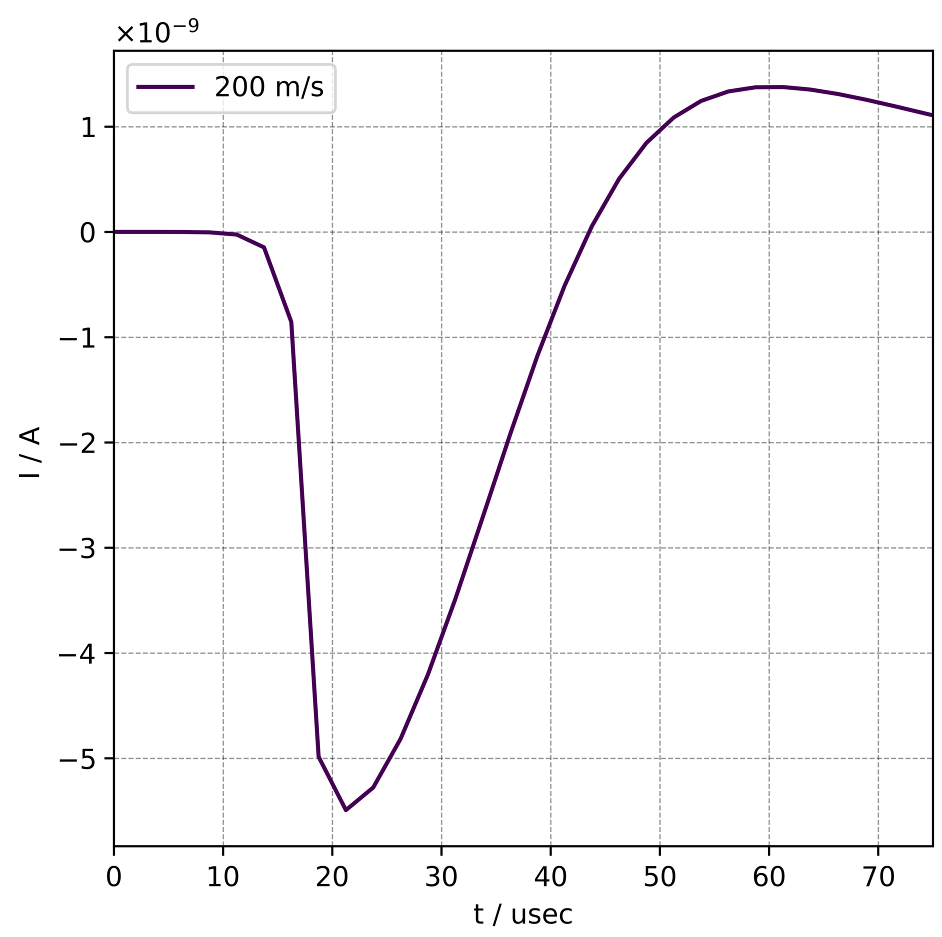

Fig. 5: Simulated displacement current from a droplet with 1×10^6 elementary charges and $1 \times 10^2\ \mathrm{m\,s^{-1}}$

Result

- Comparison between simulation and experiment shows: The particle in Fig. 4 moves through the measuring electrode at approximately $1 \times 10^2\ \mathrm{m\,s^{-1}}$
- indicating an elementary charge of 1×10^5.

Outlook

- The experiment will be extended to include an ion source that closely resembles a commercial ESI source.
- Space resolved measurements using another electrode.

References

[1] Markert, C.; Thinius, M.; Lehmann, L.; and 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*, **2021**, *10.1007/s00216-021-03452-y*

[2] Kang, Yang and Schneider, Bradley B. and Covey, Thomas R.*On the Nature of Mass Spectrometer Analyzer Contamination*, **2017**, *10.1007/s13361-017-1747-3*