Displacement Current Measurements to Analyse Charged Droplets Generated by Electrospray Ionization in a Vacuum System

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Introduction

Electrospray ionization (ESI) is the most important ionization technique 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.

The aspirated droplets not only potentially impact analytical performance but also result in contamination of the mass spectrometer.

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.

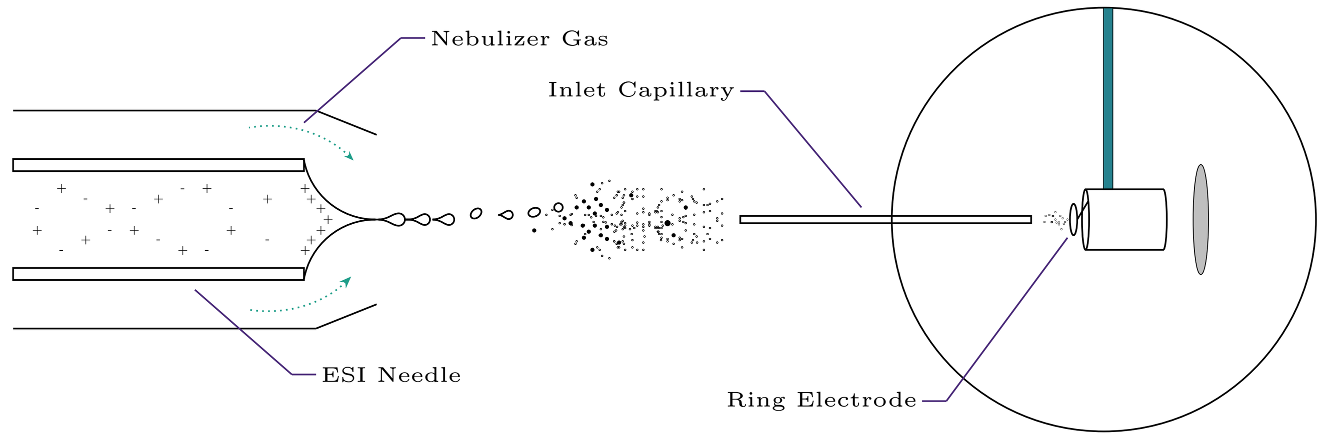

Fig. 1: Scheme of the experimental setup

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.

Simulations Provide more Information

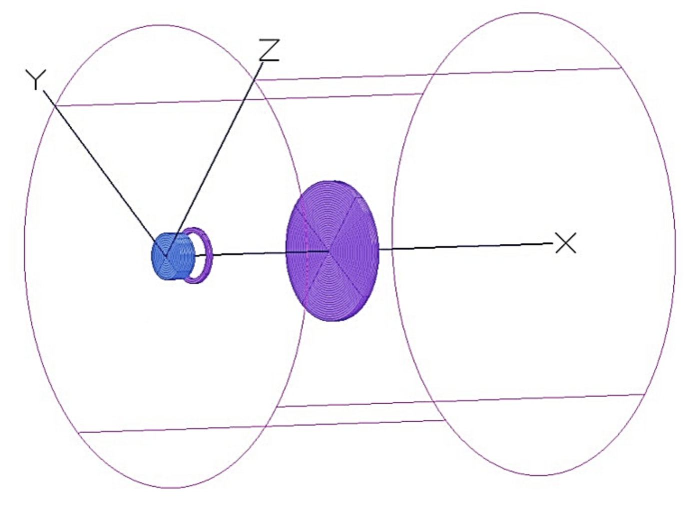

Fig. 2: Simulation vacuum chamber

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.

In combination with experiments, these results offer an initial estimation of the actual charge carried by the measured particles.

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).

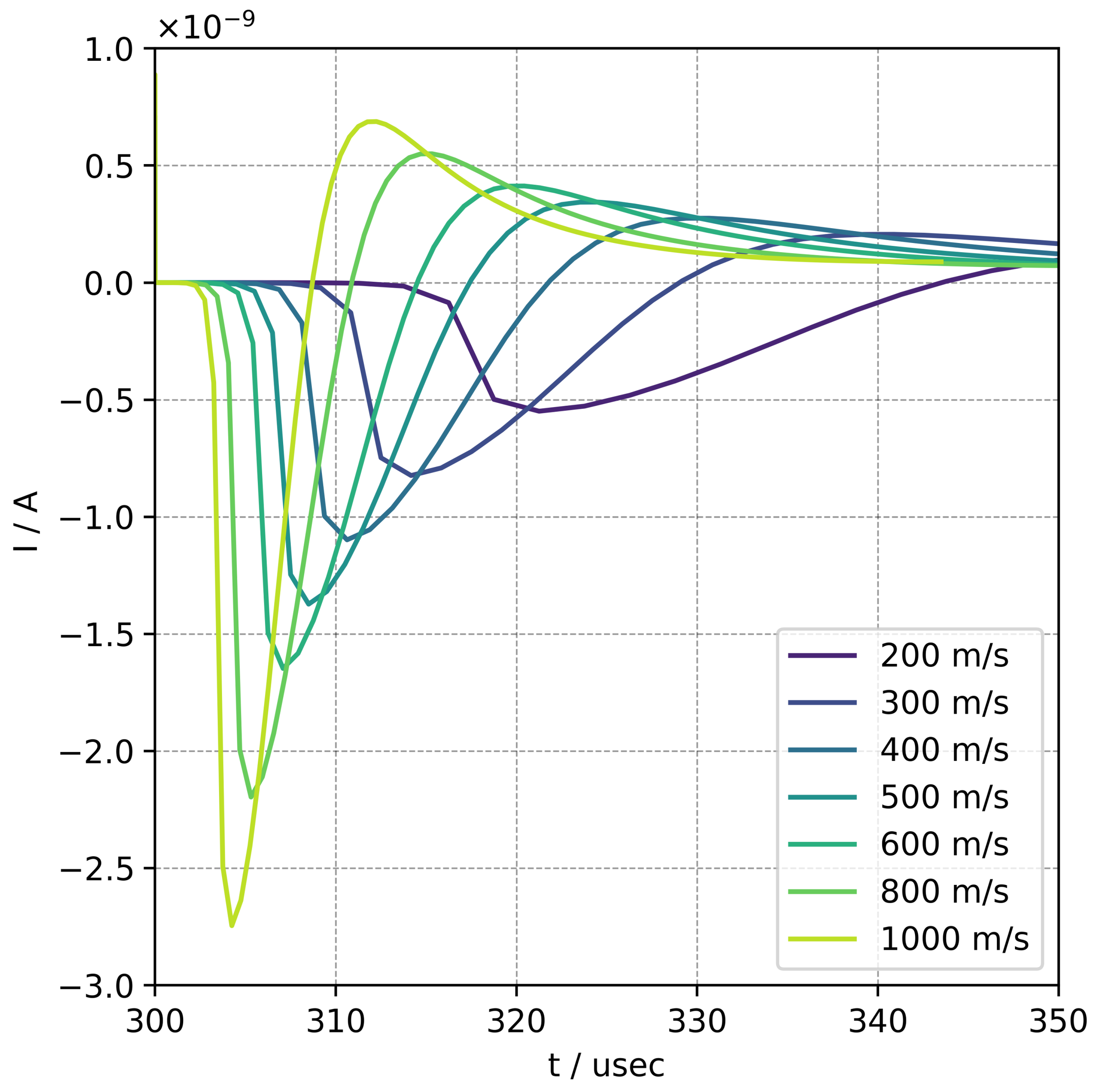

Fig. 3: Simulated pulses with droplets of 1×10^5 elementary charges

- ➡ The signals in Figure 3 illustrate particles with varying speeds and 1×10^5 elementary charges
- ➡ The current pulses become narrower as the speed increases
- ➡ A particle with 1×10^5 elementary charges at 10^3 m s^{-1} generates a simulated peak signal of 3×10^{-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 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.

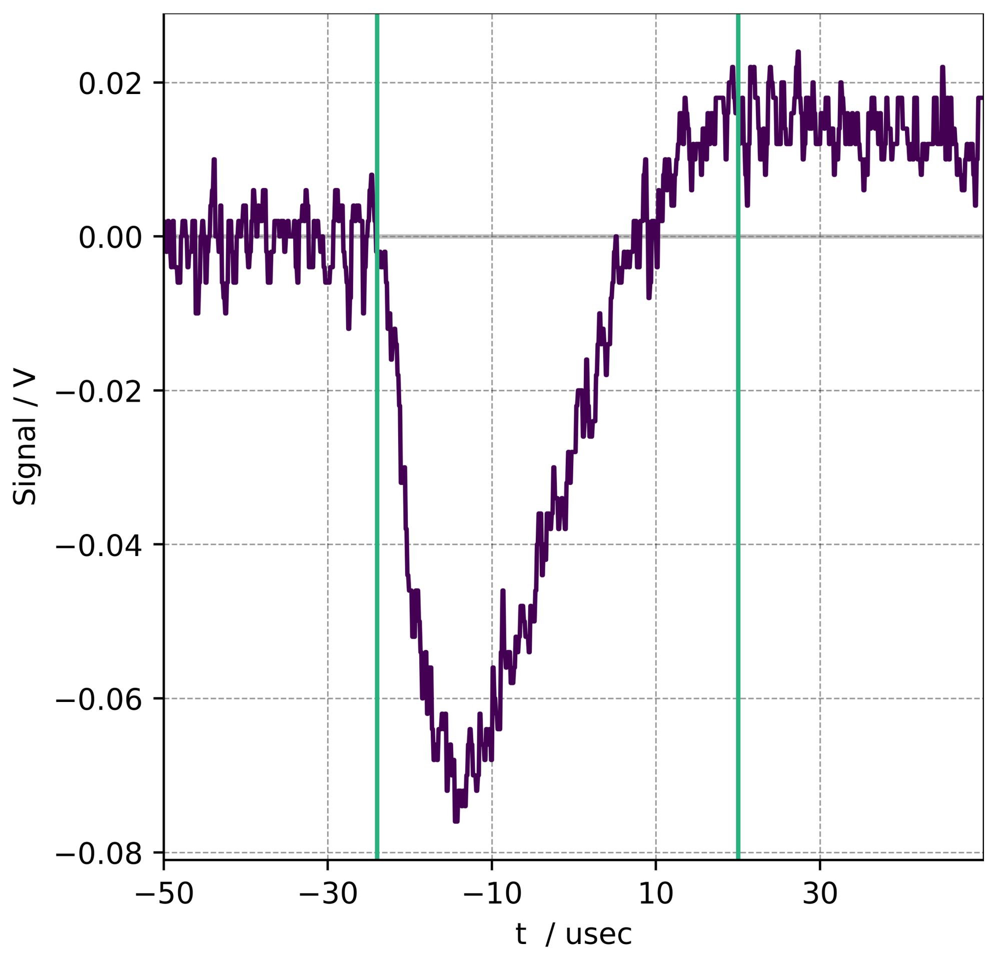

Fig. 4: Displacement current measurement with a solution of reserpine in acetonitrile and water

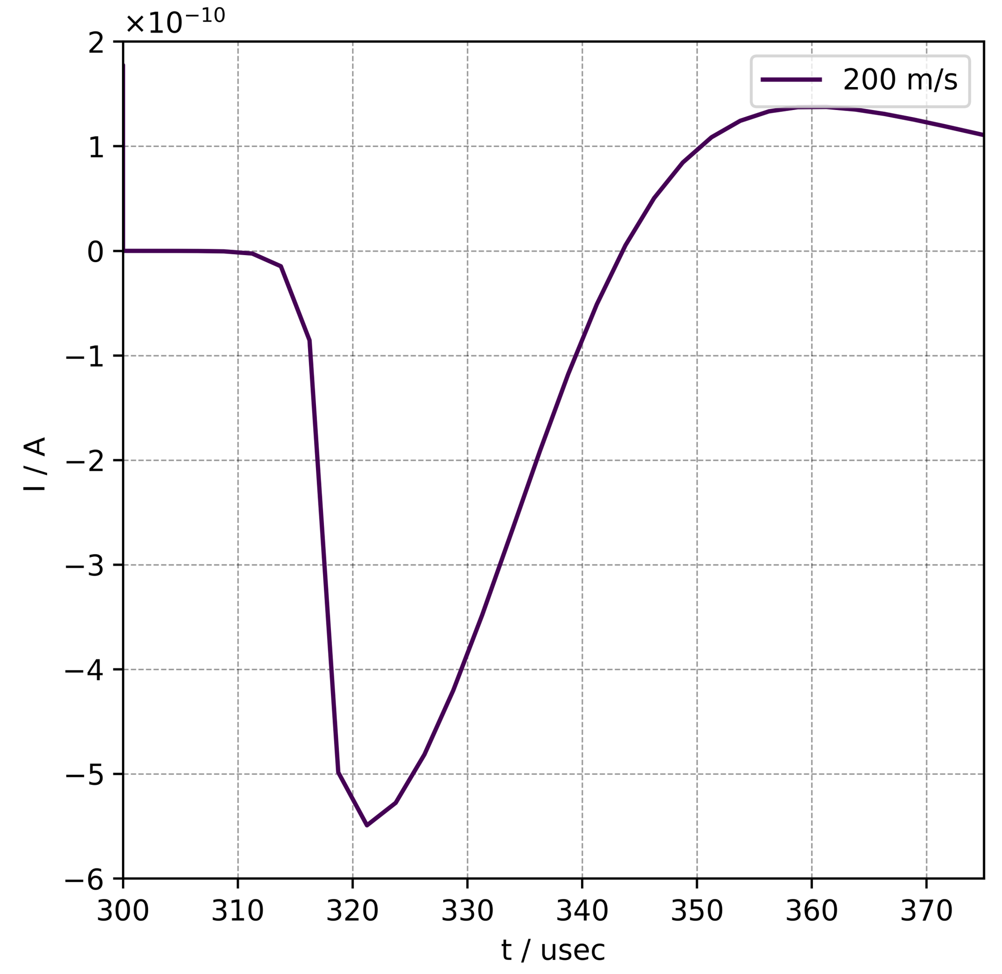

Fig. 5: Simulated displacement current from a droplet with 1×10^6 elementary charges and 1×10^2 m s^{-1}

Results

- ➡ Figure 4 shows the peak of a droplet recorded with an oscilloscope. A simulated droplet passing the ring electrode is shown in Figure 5.
- ➡ Comparison between simulation and experiment shows: The particle in Figure 4 moves through the measuring electrode at approximately 1×10^2 m s^{-1}.
- ➡ The observed droplet indicating an elementary charge of 1×10^5.

Outlook

Experimental Setup and Simulations

- ➡ An additional ring electrode will be installed to extend the experiment. A first simulation of this is shown in Figure 6.
- ➡ The distances between the electrodes will be varied.
- ➡ This allows spatially resolved measurements, e.g. to determine particle velocity from the experiment.

Ion source

- ➡ The experiment will be extended to include an ion source that closely resembles a commercial ESI source.
- ➡ The dependence of the solvent on the droplet charge will be the subject of investigation.
- ➡ In addition, the concentrations of the solvents and the analytes are varied in order to investigate their influence on the particle charge.

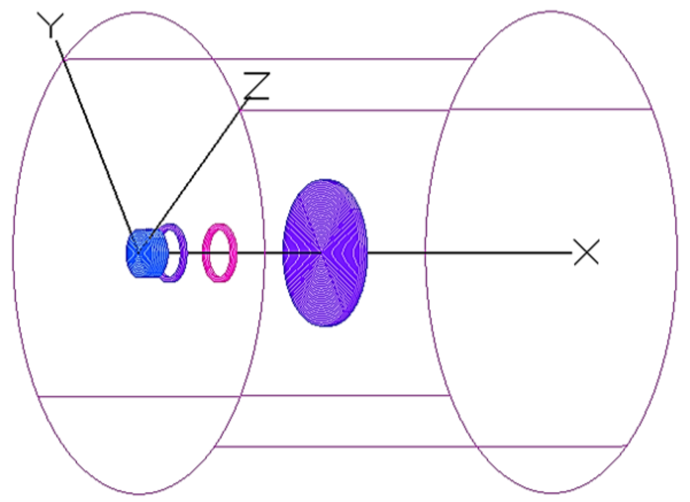

Fig. 6: 3D simulation of vacuum chamber with a second ring electrode

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 Schneider; Bradley B.; Covey, Thomas R.*On the Nature of Mass Spectrometer Analyzer Contamination*, **2017**, *10.1007/s13361-017-1747-3*

The authors declare no competing financial interest.