

Introduction

An electrospray (ES) ion source can be described as an electrochemical cell. In ESI, the application of an electric field between the electrodes leads to electrophoretic charge separation in the solution. As a result, ions of one polarity accumulate at the capillary tip, which leads to the formation of charged droplets. In order to maintain the formation of the charged droplets, charge balance takes place through electrochemical reactions at the electrodes. [1] Small quantities of electrolyte (e.g. formic acid) are generally added to the analyte solution to ensure charge separation.

The electrochemical reactions at the emitter electrode can change the analyte solution composition and therefore may influence the formed gas phase ions. A better understanding of the electrochemistry and the effect of various parameters of an ESI device, is expected to lead to an improvement of ESI-performance. [2]

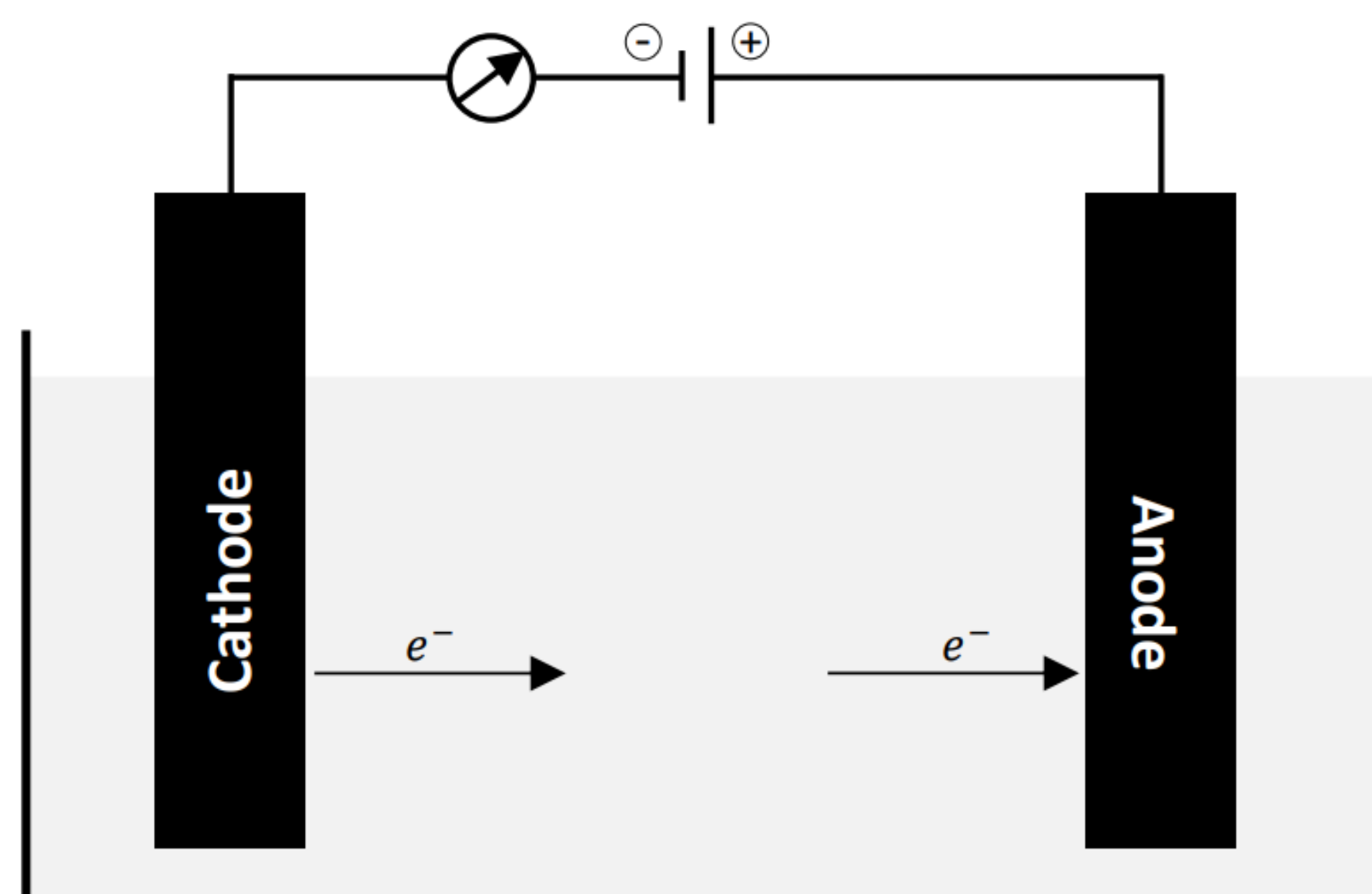


Fig. 1: Schem of an electrolytic cell

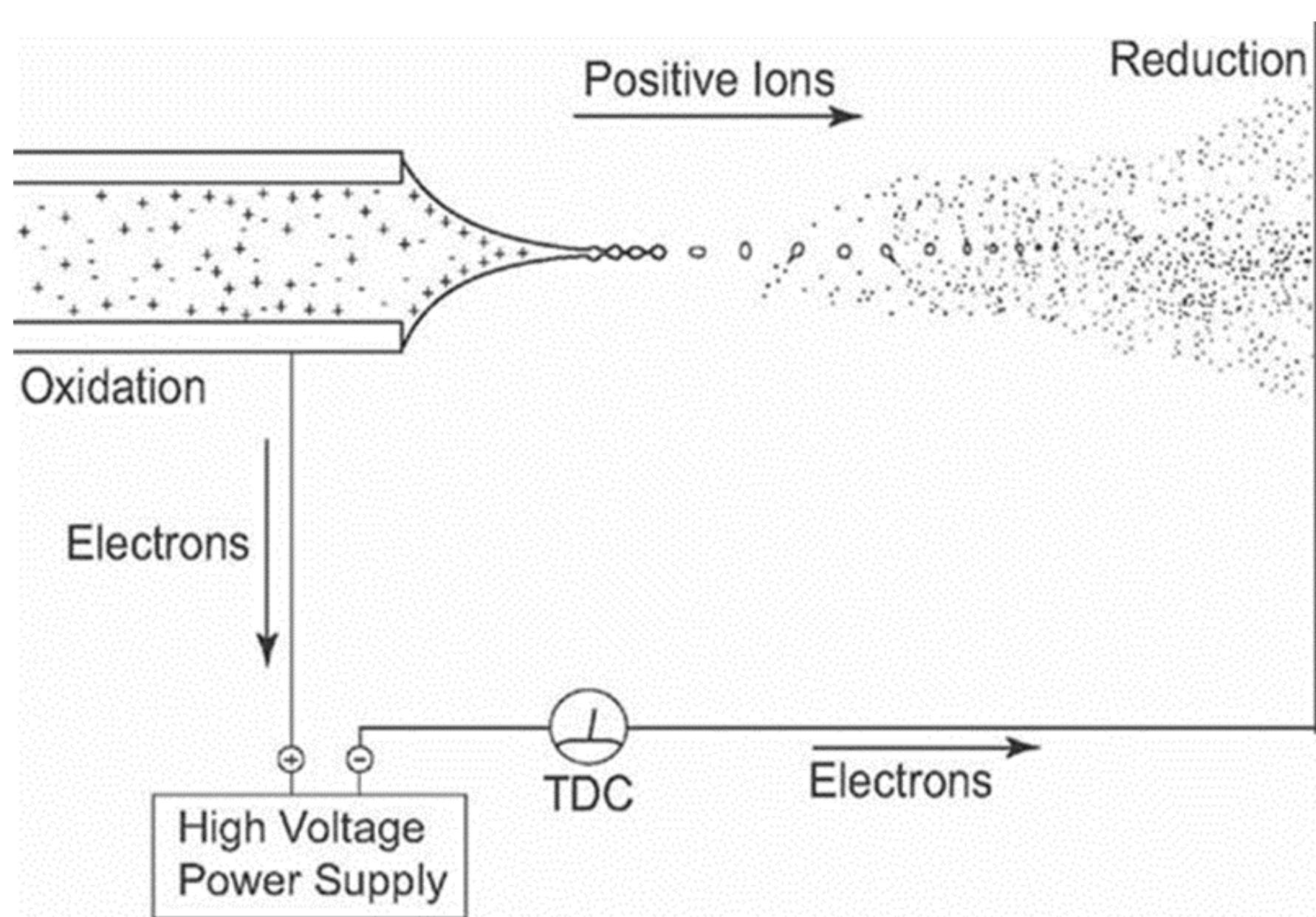
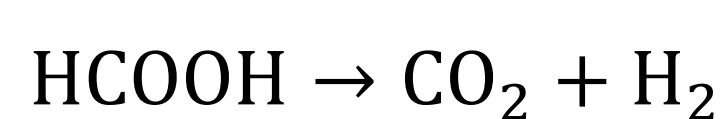


Fig. 2: Schem of an ES ion source [2]

Aim and Approach

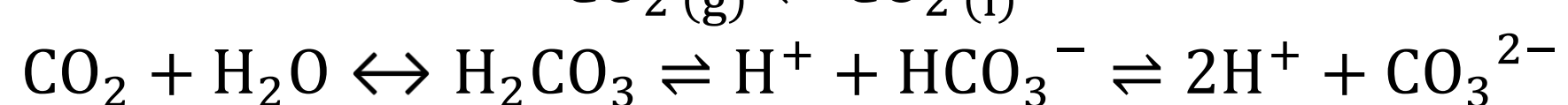
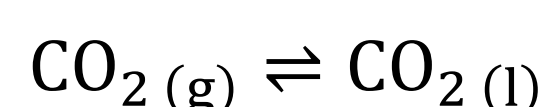
Aim of this work was the investigation of the electrochemical processes in an ESI ion source. Therefore, a solution with small quantities of formic acid was used. During the ESI process, the oxidation and reduction reactions at the electrodes lead to the electrolysis products of formic acid, CO₂ and H₂.



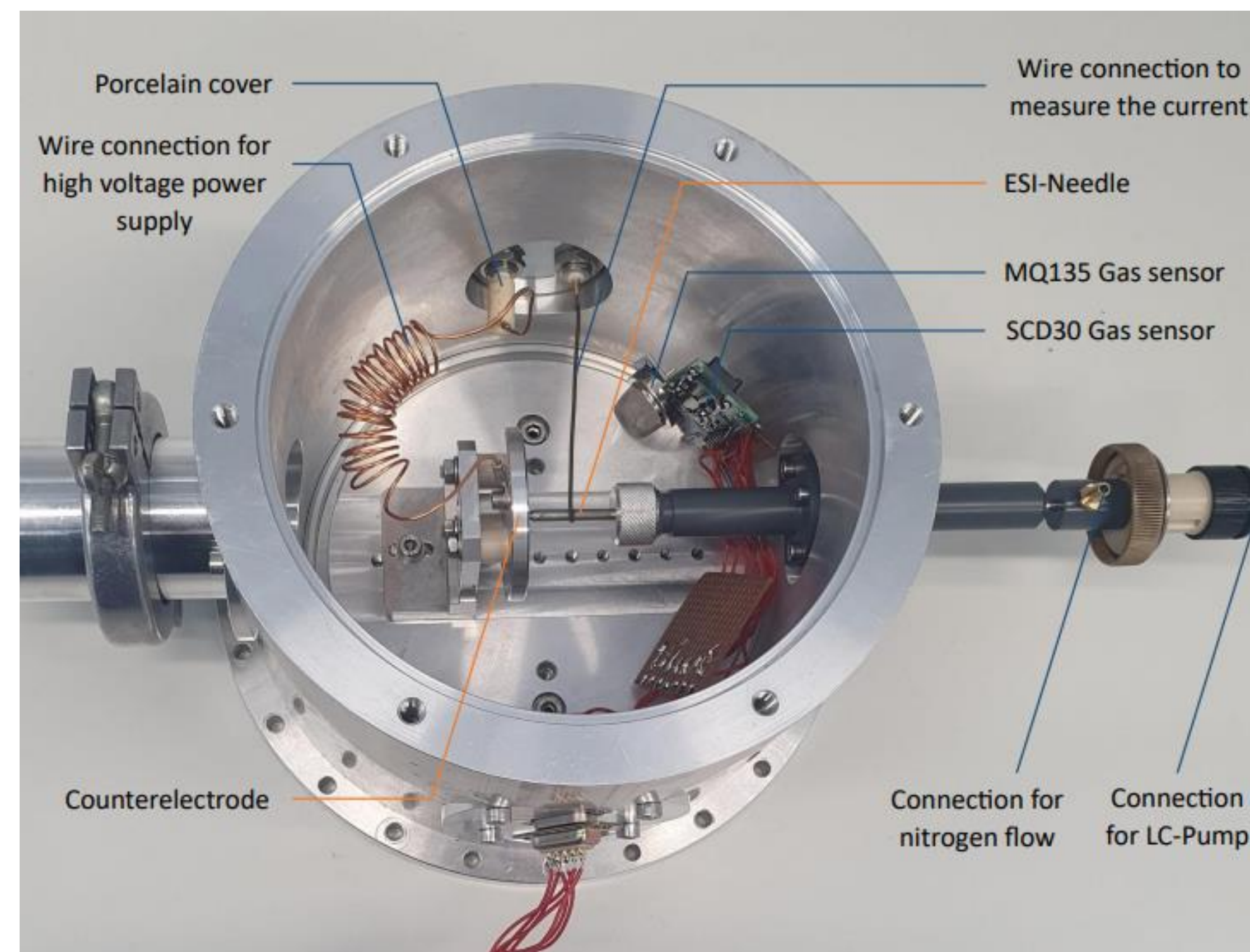
To investigate the electrochemical processes in ESI, the electrolysis products were observed in the gasphase under various different parameters.

Conclusion

- › The measurements show a clear increase in the electrolysis products of formic acid (CO₂ and H₂) at the start of the ESI process.
- › Electrode polarity switching shows no significant impact on the measured CO₂ mixing ratios.
- › Besides the electrochemical processes, the solvent, particularly water and the solubility of water, seem to have a considerable effect on the measured CO₂ mixing ratios.

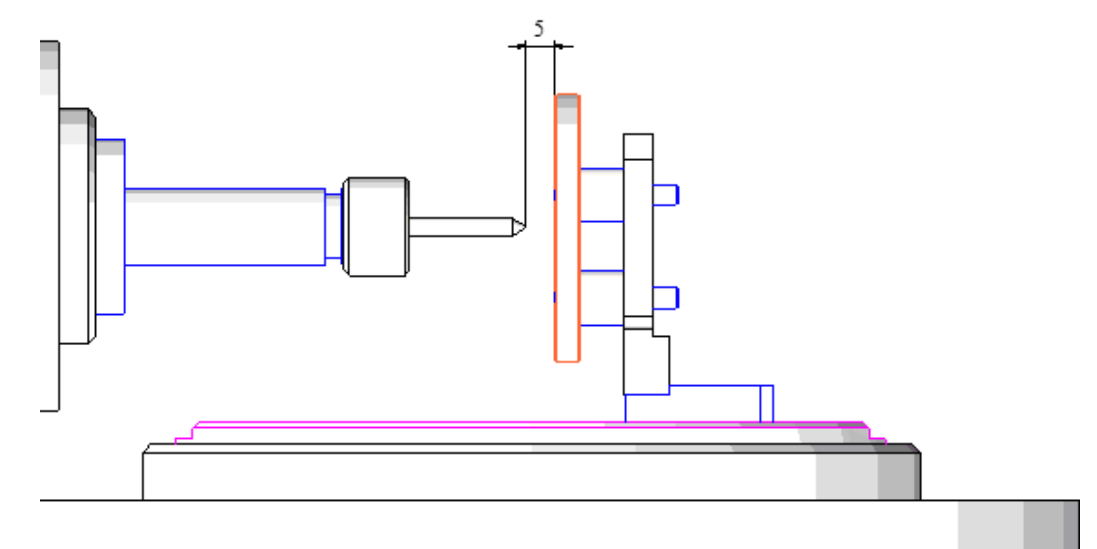


Experimental Setup



- › Emitter-Electrode: Spray probe of an Sciex6500
- › Counter-Electrode: Plate of stainless steel
- › The electrodes were operated at a distance of 5 mm in the grounded emitter system
- › Addition of solution: Merck Hitachi L7200 LC-pump
- › Solution: 50 V% water, 50 V% acetonitril, 0,1 V% formic acid
- › Analytics: CO₂: MQ135-, SCD30- gas sensor
H₂: MQ8-, MiCS4541- gas sensor
Current: VC870 digital multimeter

Fig. 3: Arrangement of the electrodes in the experimental Setup with a distance of 5 mm.



Results

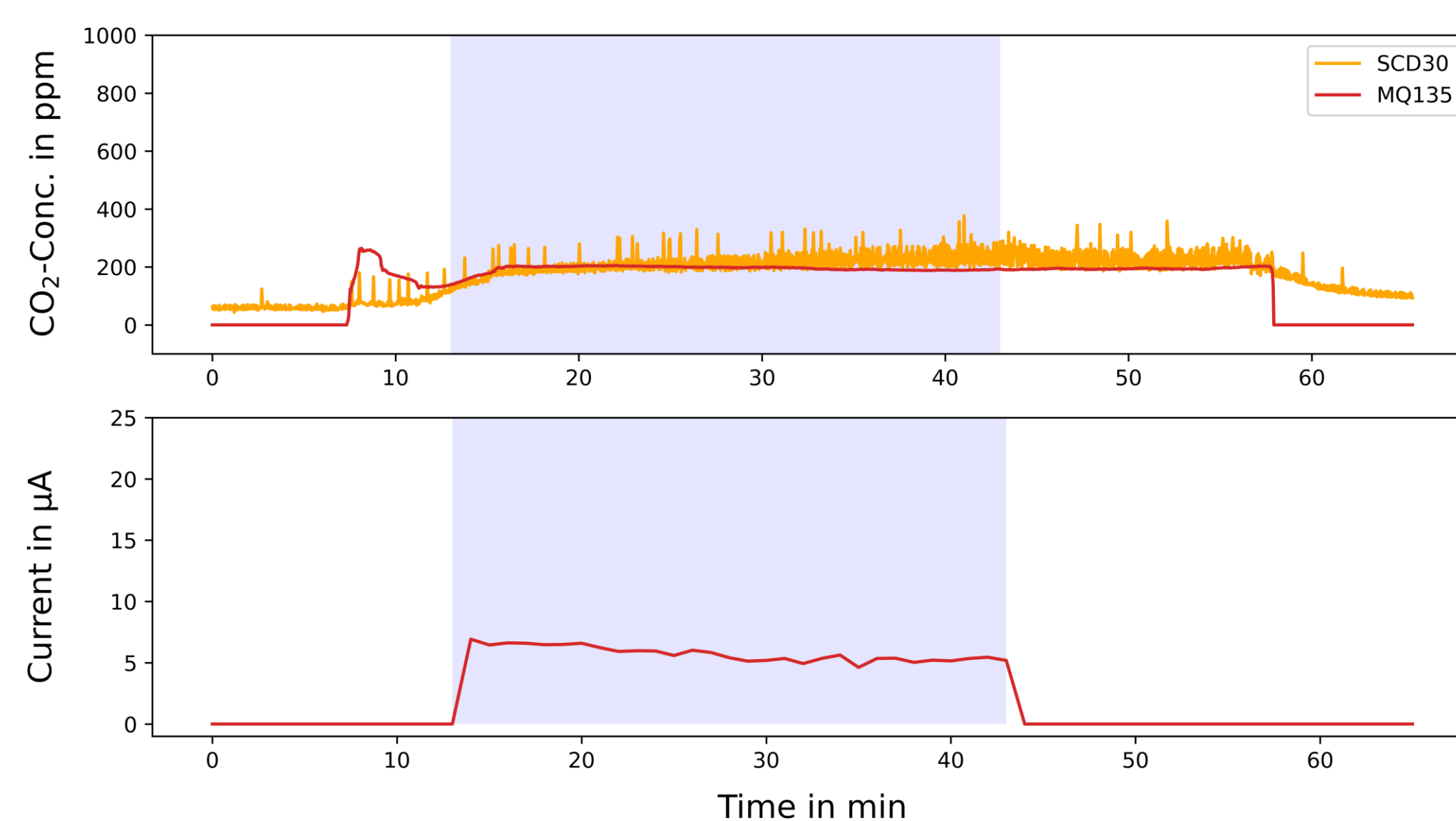


Fig. 4: 700 mbar, 3 kV, 25 µL/min, negative ion mode: CO₂ mixing ratios from both CO₂ gas sensors and needle current. CO₂ mixing ratio increases at the beginning of the ESI process (applying of voltage and addition of solution)

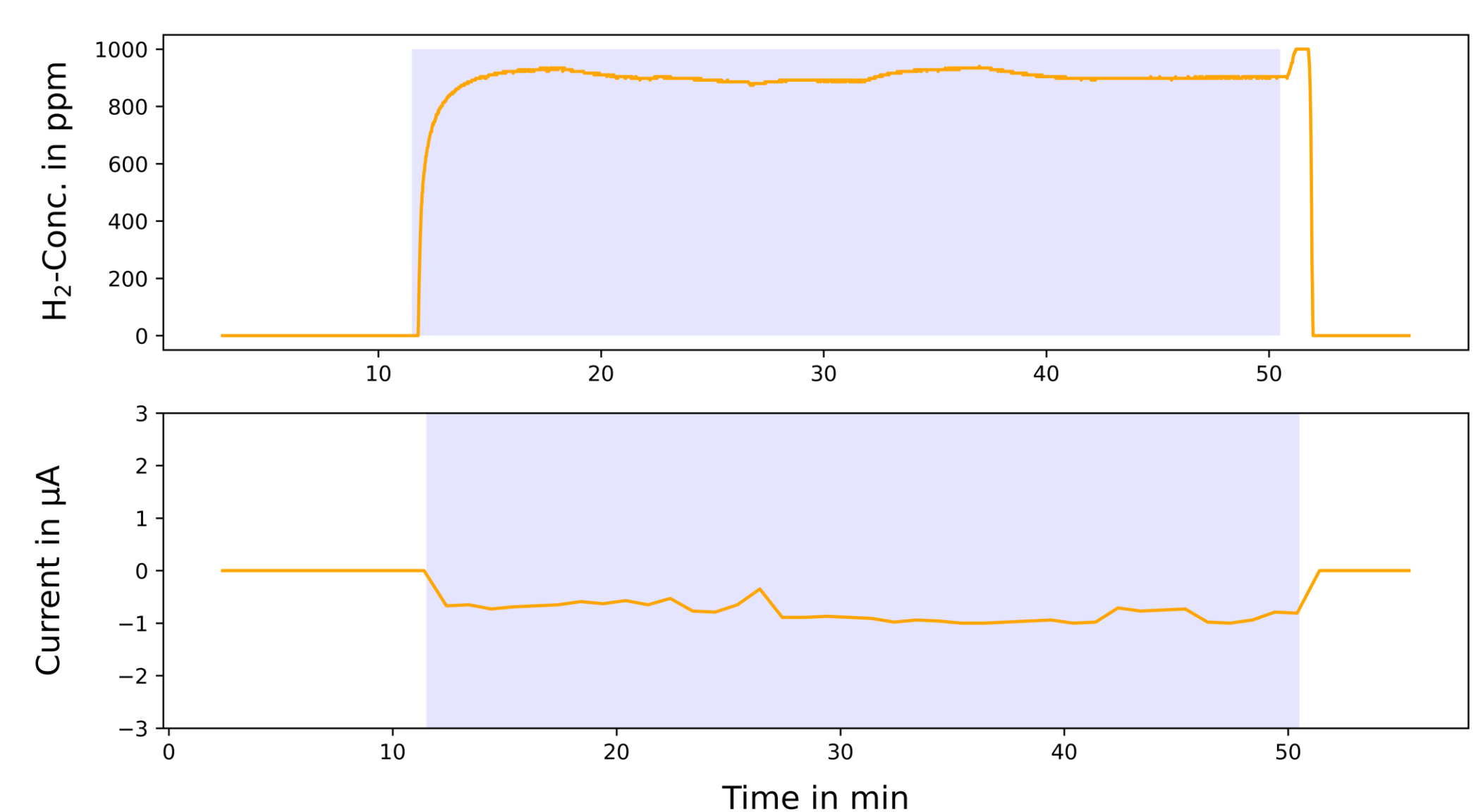


Fig. 5: 700 mbar, 3 kV, 1 µL/min, positive ion mode: H₂ mixing ratios and current measured with the MiCS4541 gas sensors. H₂ mixing ratio shows a strong increase at the beginning of the ESI-process.

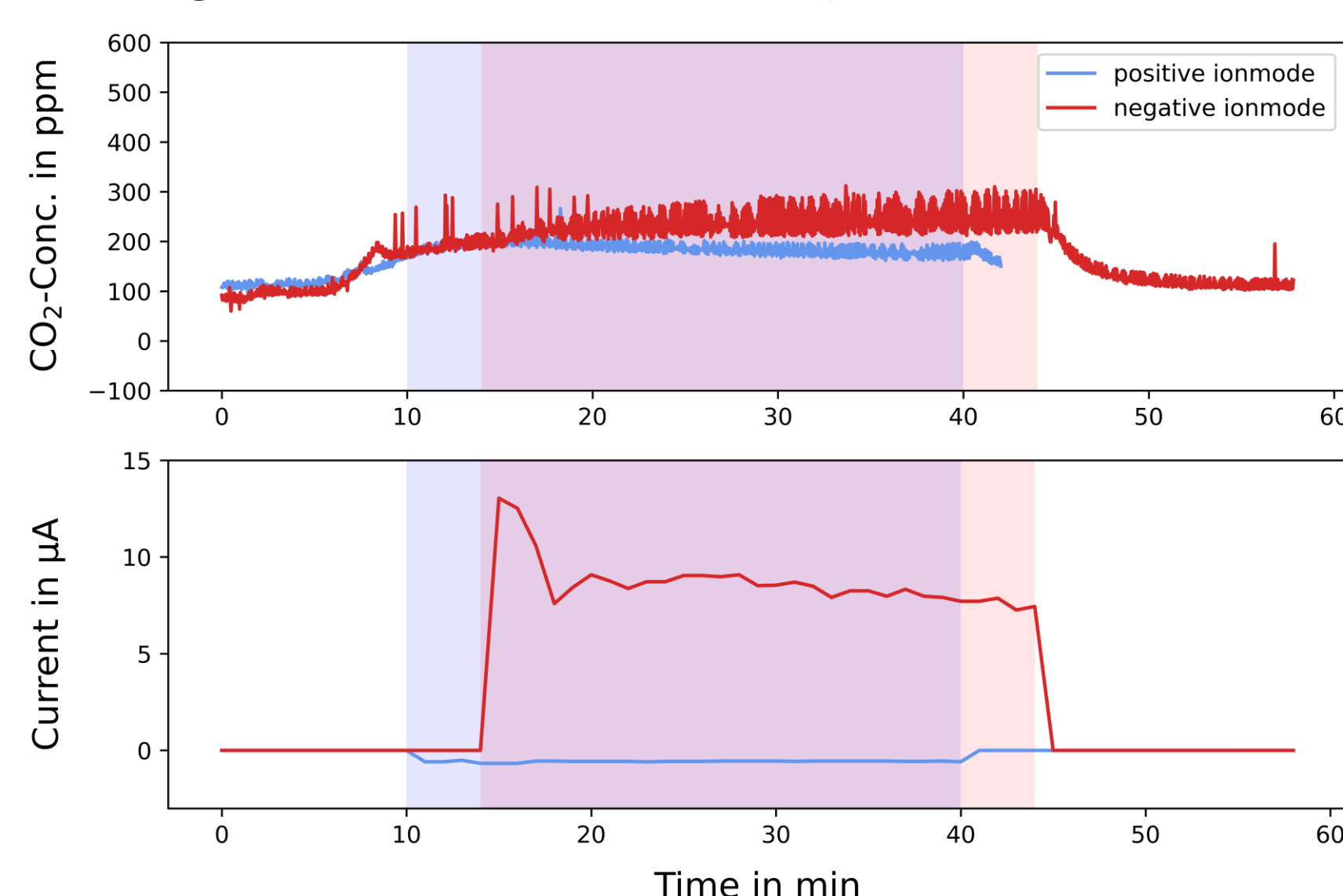


Fig. 6: 700 mbar, 3 kV, 25 µL/min, negative ion mode: CO₂ mixing ratios with a positive and a negative potential at the counter electrode. A comparison between the ion modes show no significant difference in the measured CO₂ mixing ratios.

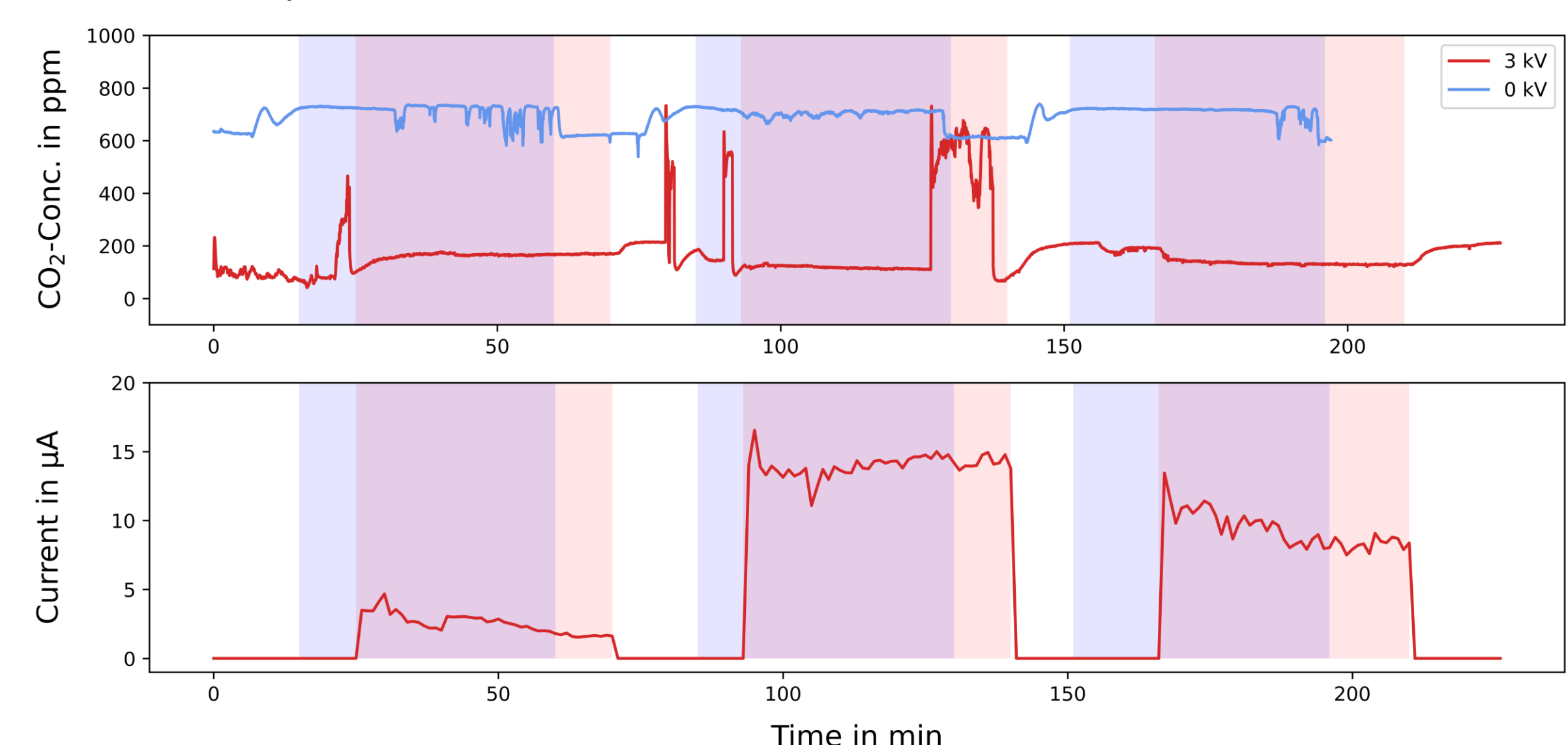


Fig. 7: 700 mbar, 25 µL/min, negative ion mode: Three measurements of the CO₂ mixing ratios with an applied voltage of 3 kV and without an applied voltage at the counter electrode. CO₂ mixing ratios show much higher values in the measurements without voltage than in those with an applied voltage of 3 kV.

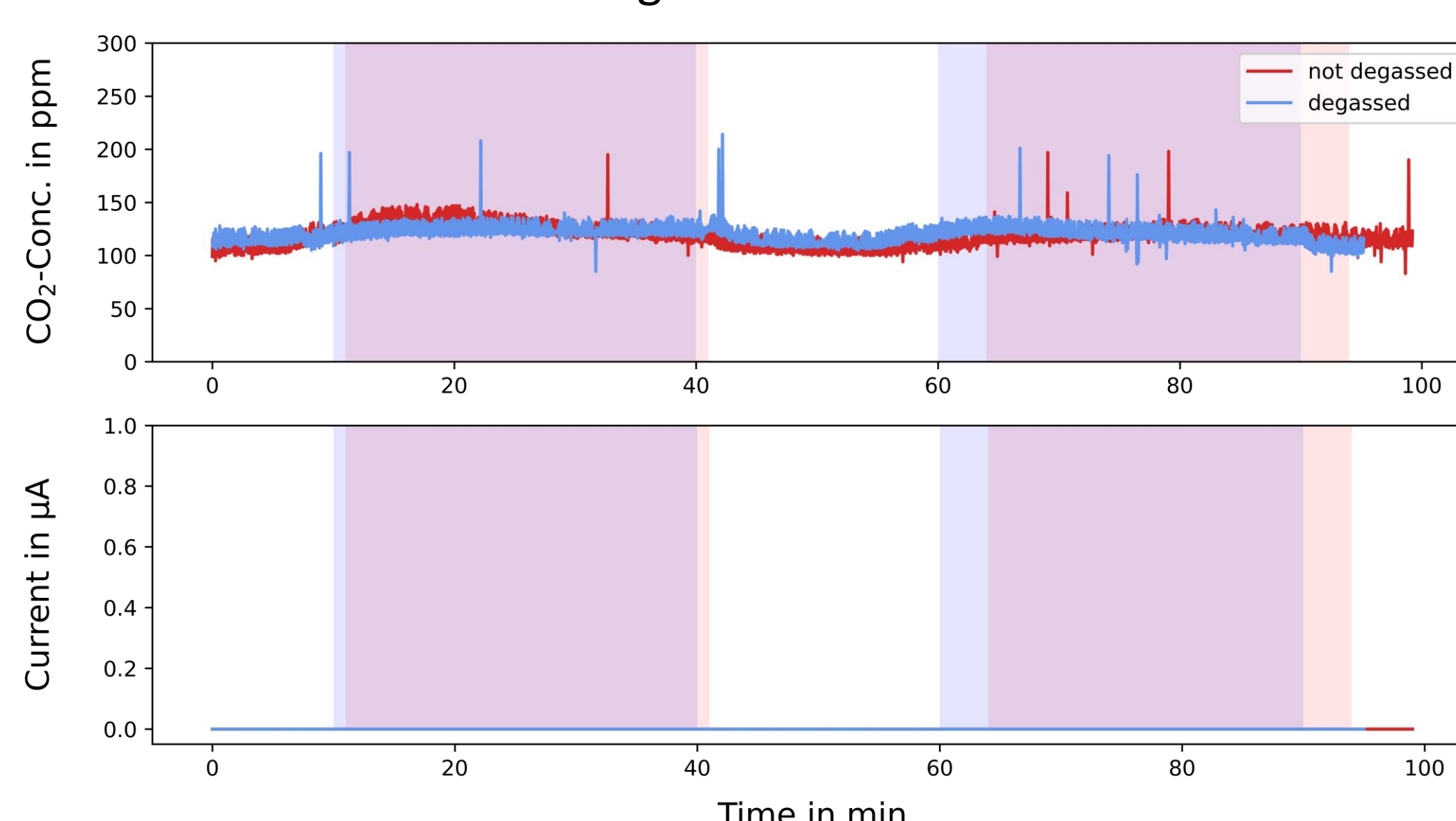


Fig. 8: 700 mbar, 3 kV/0 kV, 25 µL/min, negative ion mode: CO₂ mixing ratios of degassed and not degassed acetonitrile with (left) and without (right) applied voltage. The CO₂ mixing ratios show similar behavior for the degassed and the not degassed acetonitrile. Due to the low conductivity of acetonitrile, no current was measured.

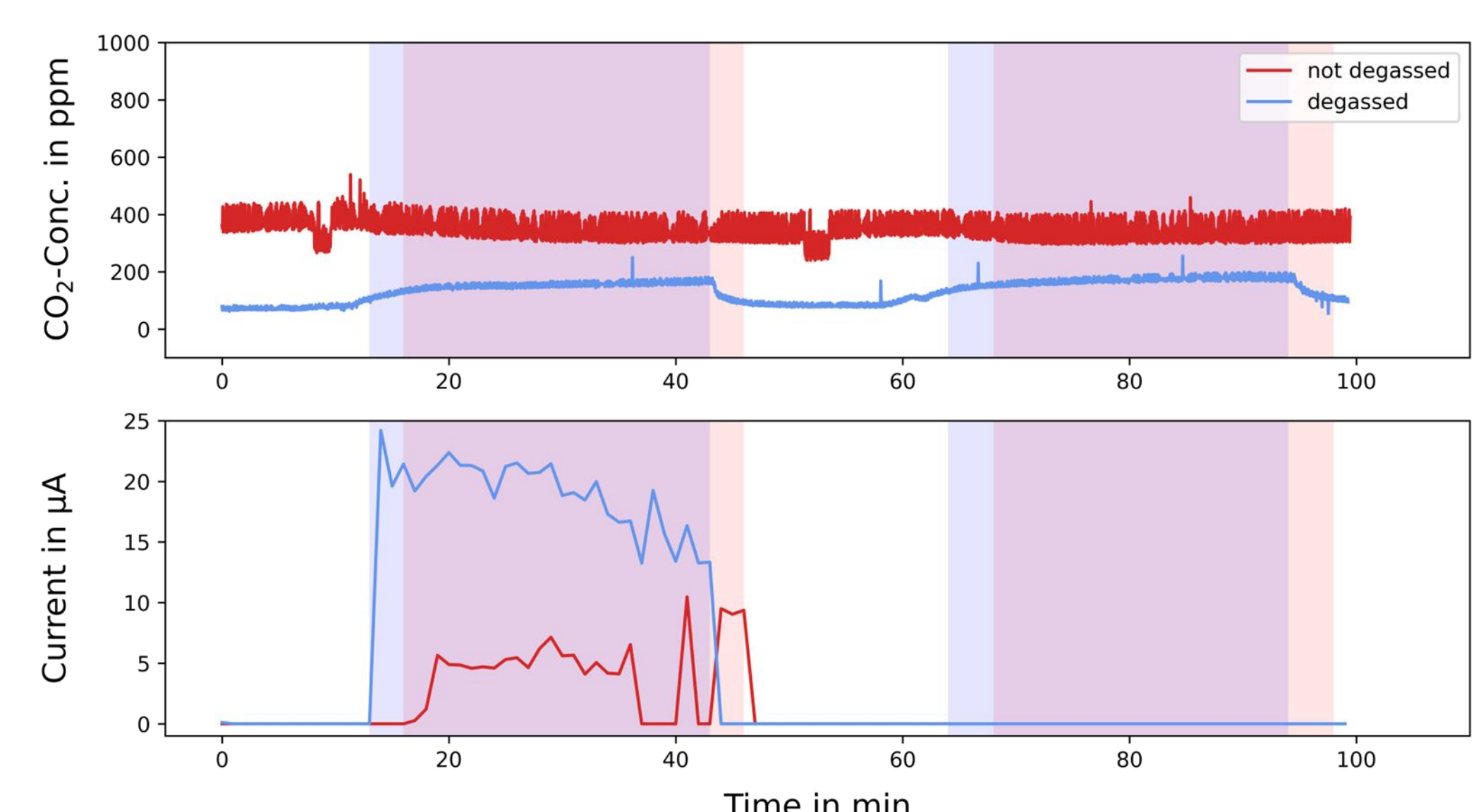


Fig. 9: 700 mbar, 3 kV/0 kV, 25 µL/min, negative ion mode: CO₂ mixing ratios of degassed and non degassed water with (left) and without (right) applied voltage. Considerably higher CO₂ mixing ratios can be observed with the addition of not degassed water.

References

- [1] G. J. Van Berkel und Feimeng. Zhou, „Characterization of an Electrospray Ion Source as a Controlled-Current Electrolytic Cell“, Anal. Chem., Bd. 67, Nr. 17, S. 2916–2923, Sep. 1995, doi: 10.1021/ac00113a028
- [2] R. B. Cole, Electrospray and MALDI Mass Spectrometry Fundamentals, Instrumentation, Practicalities, and Biological Applications, 2. Auflage. John Wiley & Sons, 2010