Investigation of Intensity Distributions of Aspirated Charged Droplets and Their Fragments Generated by ESI and Comparison with nanoESI and APCI

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Introduction

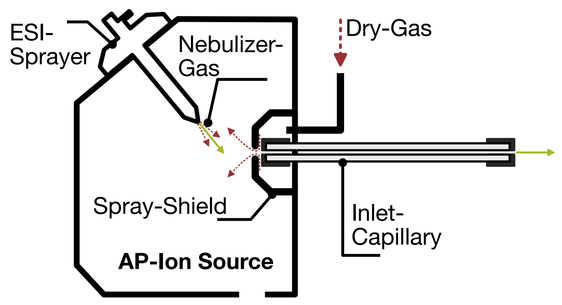
Electrospray ionization (ESI) is one of the most widely used atmospheric-pressure ionization techniques. Recent studies have shown that incompletely desolvated charged droplets can survive the atmospheric interface and enter the mass spectrometer, causing transient high-intensity signals that are hidden in averaged spectra [1, 2, 3].

Single (non-summed / non-averaged) spectra dynamics allow to observe the temporal dynamics of the ion current entering the instrument.

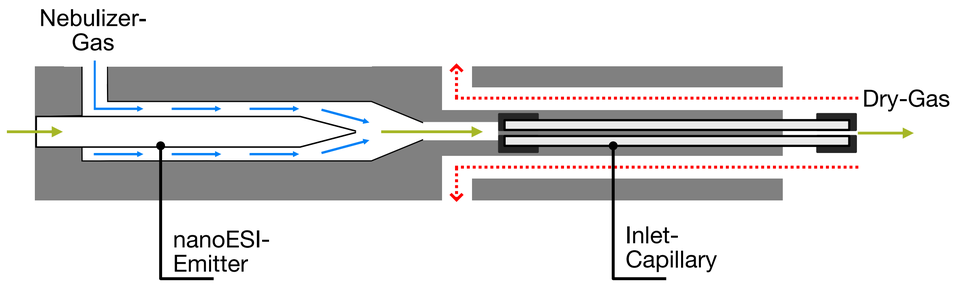
This work investigates scan-to-scan TIC intensity distributions to study droplet-related events and compares ESI with nanoESI and APCI.

Methods

ESI / APCI Source:

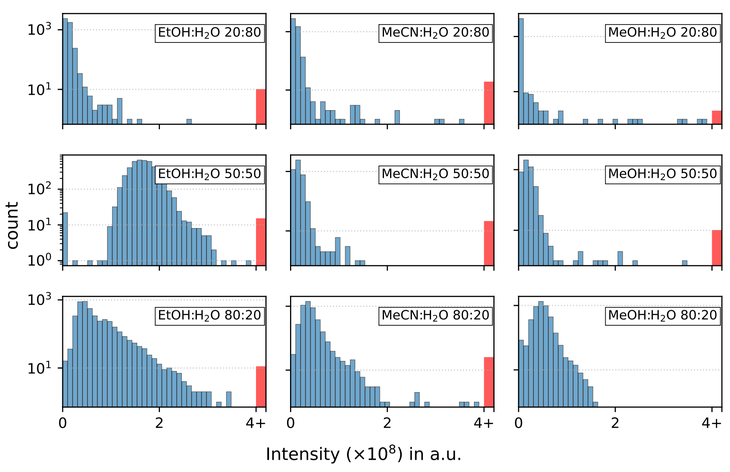


nanoESI Source:



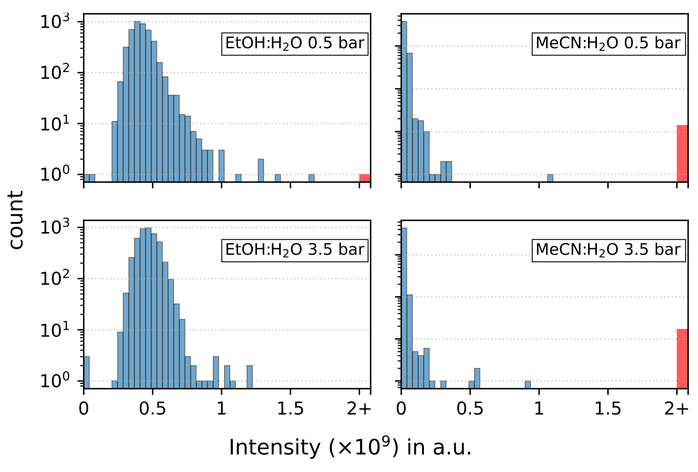
- Single (non-summed) mass spectra with a Bruker amaZon ETD Quadrupole Ion Trap (QIT-MS)
- Ion sources:
  - ESI / APCI (Bruker Apollo Source)
  - nanoESI (Bruker Captive Spray 1 Source)
- Analyte: Reserpine
- Analysis of different solvent systems (ethanol, methanol, acetonitrile / water mixtures)
- Statistical analysis of single spectrum intensity distribution: Determination of temporal ion current dynamics

ESI: Solvent / Ion Source Parameters



Effect of Solvent:

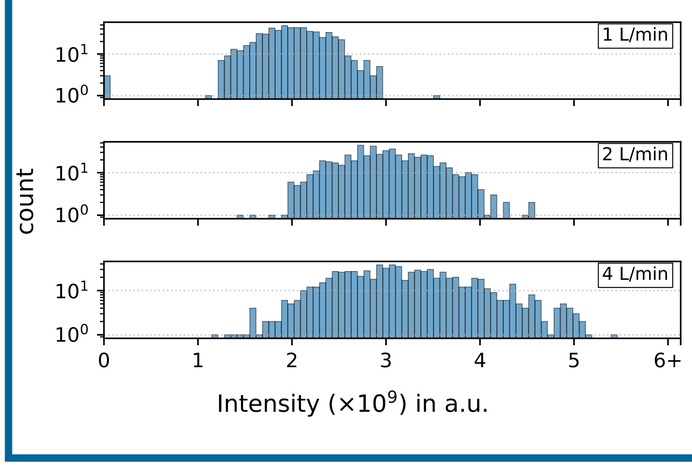
- Strong effect of solvent type and solvent ratio
- $EtOH:H_2O$: Very strong shift of intensity distribution center
- Abundance of very intense events (red bins in histograms) strongly dependent on solvent



Effect of Nebulizer Pressure:

- Remarkably: Only minor effect of nebulizing gas pressure
- In contrast: Strong effect of dry gas temperature on transient signal behavior

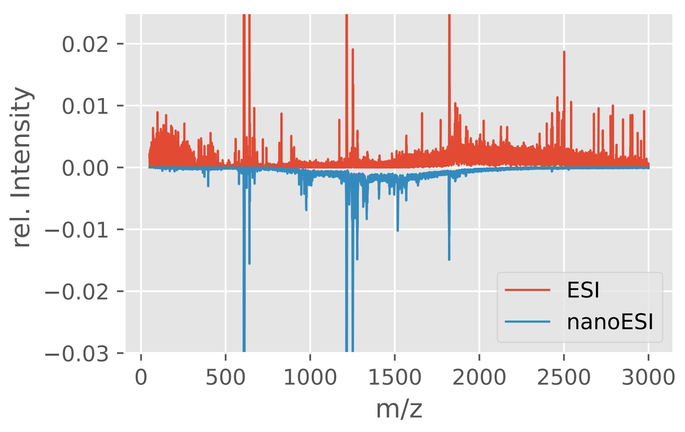
nanoESI: Ion Source Parameters



Effect of Dry Gas Flow:

- Higher dry gas flow shifts the intensity distribution towards higher intensities
- Higher dry gas flow broadens the intensity distribution

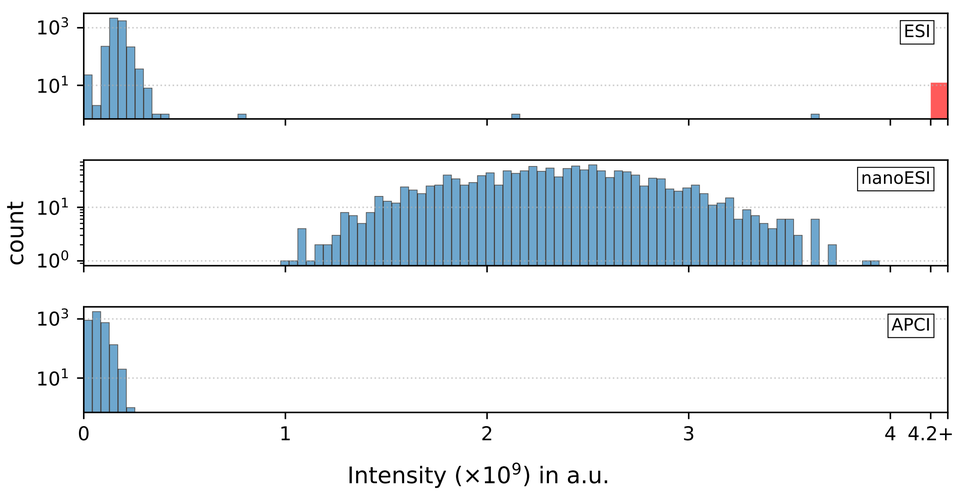
nanoESI vs. ESI: Droplet Signatures in Mass Spectra



Droplet Debris signals in Mass Spectra:

- Broad continuous signal regions for both ESI and nanoESI, shifted in m/z
- ESI shows low m/z fragments ($m/z < 500$) associated with droplet fragments [2, 3]

ESI vs. nanoESI vs. APCI



- ESI exhibits a pronounced high-intensity tail (red bin in histogram)
- nanoESI shows a broad, continuous distribution shifted to higher intensities
- APCI exhibits a narrow distribution at comparatively low intensities

Conclusions

- ESI exhibits heterogeneous intensity distributions with pronounced high-intensity tailing
- Solvent composition strongly affects ESI intensity distributions and the occurrence of high intensity events
- nanoESI and APCI show more continuous intensity distributions without pronounced high-intensity tailing
- Droplet related signals are observed for both ESI and nanoESI

References

[1] Heintz, C., Schnödewind, L. et al., *J. Am. Soc. Mass Spectrom.* 2024, 35, 508—517

[2] Heintz, C. Kersten, H. et al., *J. Am. Soc. Mass Spectrom.* 2025, 36, 839–849

[3] Markert, C., Thinius, M., et al., *J. Am. Soc. Mass Spectrom.* 2021, 413, 5587—5600

Conflict of Interest

The authors declare no conflicts of interest.