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Introduction

Electrospray ionization (ESI) has become the most important atmospheric pressure ionization (API) method in analytical applications, partly due to its characteristic of soft ionization [1]. However, the dynamics of the spray and ionization process is not yet fully understood. Several experiments have demonstrated that that initially formed charged droplets do not completely evaporate in the ion source. Contrary to common assumption, significant fraction of charged droplets and / their fragments are aspirated into the mass spectrometer's (MS) inletsystem and pass through the individual vacuum stages, causing a variety of adverse consequences [2,3]. Intense bursts of ion signal have been detected in the intensity distribution of non-summed mass spectra. These bursts are limited to ESI: Further experiments with other API methods, without the transfer from the liquid phase, do not yield comparable results. A detailed investigation of recorded individual spectra on various commercially available mass spectrometry devices which considers the impact of different solvent systems provides more information about the underlying mechanism.



(A) Bruker micrOTOF

(B) Bruker amaZon ETD

Fig. 1 Schematic layout of the utilized mass spectrometers

Methods

Ion Trap (Bruker amaZon) and TOF (Bruker micrOTOF) instruments (Fig. 1) in combination with a binary pump system (L-7200, Merck Hitachi) for direct injection of the sample solution.

Reserpine is used as the analyte at a concentration of 8 μ M. The mobile phase is a mixture of aqueous and organic solvents (B = ACN; MeOH) with the addition of 0.1% formic acid (FA). The variation of B allows a comparison of the effect based on the chemical properties of the solvent system, the solvent composition being varied in isocratic elutions (B = 10; 50; 60%).

The effect on the intensity distribution is studied using the manufacturer's own APCI and ESI sources.

References

[1] Cole, R. B. (2010) Electrospray and MALDI Mass Spectrometry. Fundamentals, Instrumentation, Practicalities, and Biological Applications, 2nd ed.; John Wiley & Sons Incorporated: Hoboken

[2] Markert, C.; Thinius, M.; Lehmann, L.; 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, Analytical and bioanalytical chemistry. 2021, 413, pp. 5587–5600 [3] Kang, Y.; Schneider, B. B.; Covey, T. R. On the Nature of Mass Spectrometer Analyzer Contamination, Journal of the American Society for Mass Spectrometr • Intense spectra which are related to the ion bursts can be detected in various MS-systems 2017, 28, pp. 2384–2392

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Statistical Analysis of Aspirated Charged Droplet Signatures in Non-summed Mass Spectra from various **commercial LC-ESI-MS Systems**

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- Inlet-parameters such as the nebulizer pressure and the solvent mixture have noticeable impact
- Intensity distribution changes with solvent mixture (solvent types and organic ratio) (Fig. 2 3)
- Distribution shifts to an approximate normal function by Increasing the nebulizer pressure (**Fig.6**)
- Reduction of the number of empty spectra and high intensity mass spectra

Solvent Dependency with micrOTOF



intensity of the analyte decreases with the higher nebulizer pressure. ESI exhibits a significantly higher amount of very intensive spectra than APCI.

Conclusion

- intensity (**Fig. 4 5**)
- bursts can only be observed with ESI

flow significantly changes the intensity distribution.

• In some experiments, the summation of single spectra with a high intensity yields a very different mass spectrum than those with low total

• Comparison of the intensity distribution of non-summed mass spectra (Fig. 7) from different API methods showed that intense ion signal

• Fig. 7 indicates that a distinctive amount of the total ion signal could stem from the aspirated droplet fragments