Observation of charged ESI droplets aspirated in a Linear Ion Trap (LIT)

BERGISCHE UNIVERSITÄT WUPPERTAL

Physical & Theoretical Chemistry
University of Wuppertal

Adem Bulut*, David Coenen, Walter Wissdorf, Thorsten Benter
*adem.bulut@uni-wuppertal.de

Abstract

Electrospray Ionization (ESI) is one of the most common ionization methods in mass spectrometry (MS). One of the specific characteristics of ESI is the generation of highly charged droplets, which contain the analyte. Previous experiments show that these highly charged droplets can pass through the different vacuum and ion guiding stages of a mass spectrometer and even reach the mass analyzer region. As these droplets do affect the analytical performance of the instrument it is important to understand which parameters influence the aspirated droplet ensemble. An ion trap is used to investigate these parameters, as it is particularly well suited for this task, due to its ability to isolate and fragment different mass ranges.

Methods

- MS: Thermo Fisher linear ion Trap (LIT) XL and Velos Pro
- Analyte: Reserpine in ACN/H_2O (1:1) with 0.1% formic acid

Variation of isolation window

Fig. 1: Mass spectra of reserpine for different isolation windows (highlighted in grey) with an isolation width of m/z = 100

- Different isolation windows with a width of m/z = 100 were isolated.
- In all spectra reserpine as analyte is detected as a fragment signal from isolated species.
- Therefore, reserpine was captured in the isolated species and is released from them in the trap.
- Additional signals with m/z values above the isolation window are observed, especially with an isolation window of m/z = 1150-1250.
- A possible explanation for those signals is charge loss of the droplets, resulting in higher m/z values.

Variation of Activation Time

- *Activation time*: Time between end of ion injection and the mass analysis (ion ejection).
- Comparison of 10 ms, 1000 ms, 5000 ms activation time
- In all spectra reserpine was investigated after the isolation of the mass ranges m/z = 1000 ± 50.
- In the first spectrum only signals in the isolated range was detected without any further signals. In spectrum 2 and 3 also a bare reserpine signal appears
- Spectra show: No analyte signal with 10 ms Activation time. With increasing activation time, the intensity of the analyte also increases. Reserpine was captured in the isolated species and is released from them in the trap.

Fig. 2: Isolation mass spectra of reserpine solution with three different activation times. In all spectra the mass ranges m/z = 1000 ± 50 was isolated.

Fig. 3: Left spectrum: Isolation at m/z = 550 ± 25. Right spectrum: Isolation at m/z = 550 ± 50. The spectra in the insets show the mass range from m/z = 850 - 1000. Both spectra have an Activation time of 60000 ms.

- In this measurements the mass range m/z = 550 ± 25 (left spectrum) and m/z = 550 ± 50 (right spectrum) was isolated
- Additional signals with m/z values above the isolation window are observed in both spectra.
- Comparison of both spectra shows that the width of the additional signals correlate with the isolated mass range width.
- This indicates that both signals are directly related. A possible explanation is a m/z shift due to charge loss, resulting in higher m/z values.

Variation of Helium pressure

- Helium gas is used to collisionally cool the arriving ions in the ion trap. Additionally, it is used as a collision gas in the trap during the activation and fragmentation process.

Fig. 3: The mass spectrum of reserpine with different Helium supply pressures is shown. In all spectra the mass ranges m/z = 1400 ± 50 was isolated.

- the signals are not effected by a decreasing Helium supply pressure from 2.8 bar to 1.1 bar. With 0.8 bar the reserpine and his dimer signal disappear completely and the isolated signal changes its shape significantly.

Fig. 5: Measurement of Reserpine with an isolation at m/z = 750 ± 0.1. Helium pressure was turned off.

- In this measurement the Helium pressure was turned off.
- Isolated main signal at m/z = 700 is clearly observed. Additionally there is a second, smaller peak around m/z = 760. This signal structure, a clear peak and a smaller peak next to it, was also observed at m/z = 1100, but with lower intensity.
- The surprising signal similarity could indicate that both signal groups belongs to the same ion, but with different charge states.

Variation of capillary temperature

Isolation window m/z = 850-950
Isolation window m/z = 750-850

Fig. 6: Variation of the capillary temperature for the the mass range m/z = 850-950 and *750-850*.

- Two different mass ranges was isolated, so no further signals should be observed. The capillary temperature was varied for both isolation windows.
- All spectra show signals in the isolated mass range. With lower capillary temperature under 250°C there are additionally signals of reserpine (m/z=609) and the dimer (m/z=1217) observed.
- At higher temperature no further signals are detected, which indicated a correlation between the capillary temperature and the release of reserpine from the isolated species.

Summary and outlook

- The experiments show that charged droplets or at least their fragments reach the mass analyzer region of the Linear Ion Trap.
- The intensity of the bare analyte signal depends strongly on the activation time and the capillary temperature.
- The analyte signal shows strong dependency on the Helium pressure. Mass and charge loss of the initially isolated species was observed.

References

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