

Introduction

Electrospray ionization (ESI) is one of the most important ionization methods in mass spectrometry (MS). An analyte solution is sprayed into an electric field, resulting in the formation of highly charged droplets containing the analyte. Experimental observations [1,2] show that a significant portion of the charged droplets generated by the electrospray passes through the entrance into the vacuum system of the mass spectrometer. The generation of droplets and thus also the characteristics of aspirated droplets depend on the ion source conditions. Therefore, the operation parameters of the ion source also affect the charged liquid droplets observed in an ion trap mass analyzer.

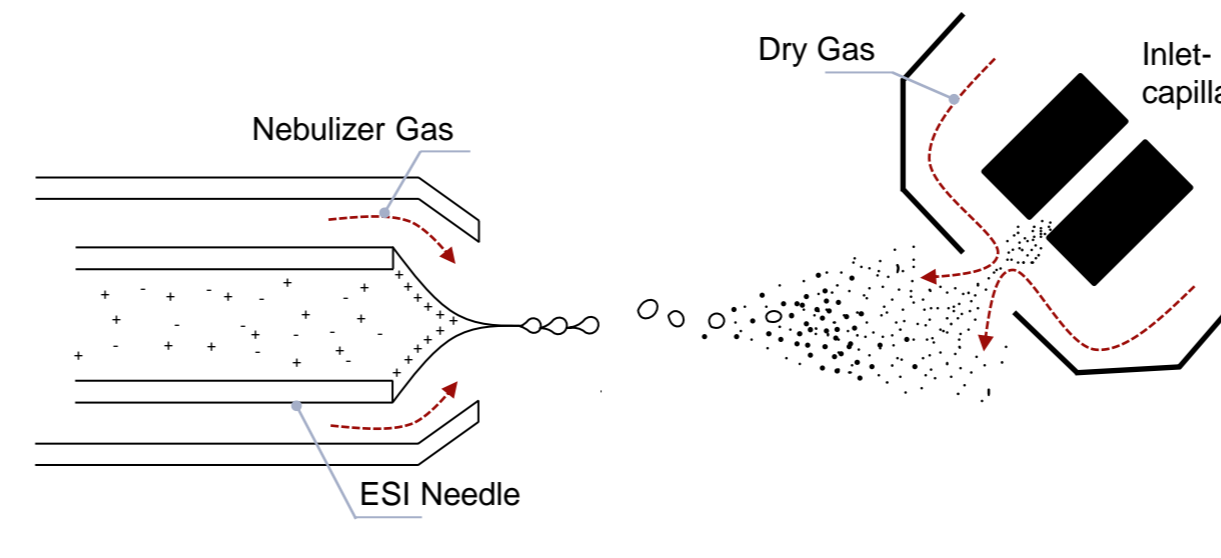


Fig. 1 Scheme of ESI process

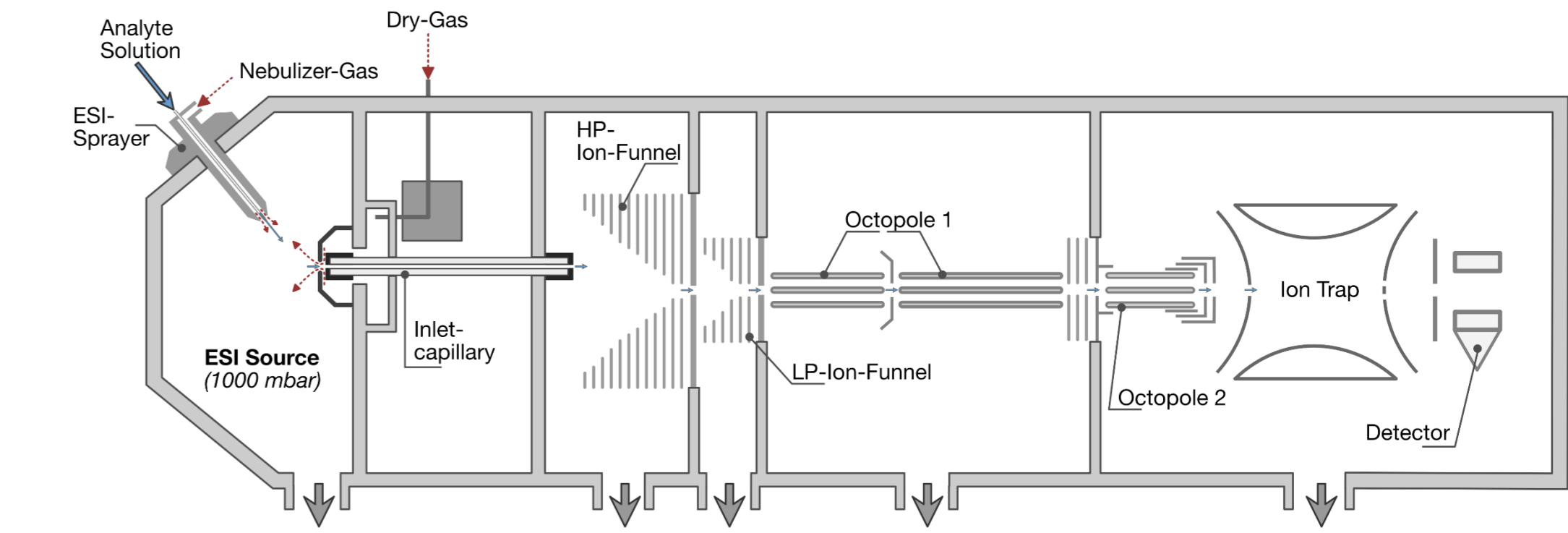


Fig. 2 Scheme of the Bruker amazon ETD

ESI source: A liquid analyte solution is sprayed into a strong electric field between the ESI needle and the mass spectrometer entrance formed by the spray-shield and the inlet capillary tip. Nebulizer-Gas is injected at the sprayer tip to assist the spray process. An additional heated gas flow, the Dry-Gas, is introduced from the MS entrance towards the ion source, to support the droplet evaporation.

HPLC → ESI → Accumulation → Isolate → Analyzer

Droplet Signatures - Fragmentation

Reserpine in Acetonitril

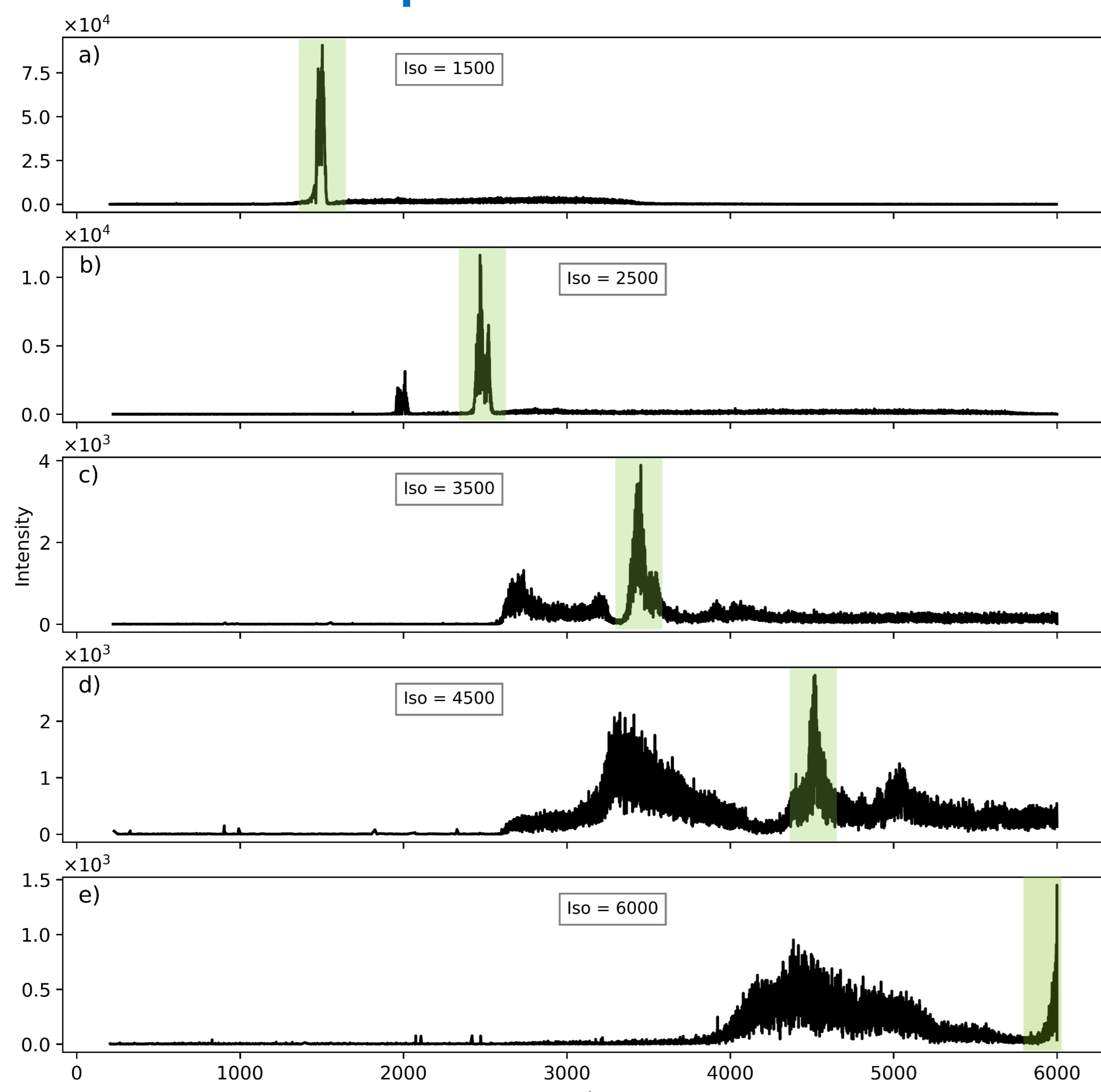


Fig. 3 Isolation range variation Reserpine in Acetonitrile

Reserpine ($M=608.7$ g/mol) was used as analyte in isolation / fragmentation experiments. Intensive signals of isolated ions above $m/z = 2000$ clearly indicate the presence of large, multiply charged aggregates in the ion trap. The signals outside the isolation range are generated after isolation and thus from the initially isolated particles. With ESI, large, multiply charged particles are visible in the ion trap, which are fragments of the initially aspirated, very large liquid droplets. Variation of the isolation range indicates that the particle distribution in the ion trap spans over a very wide m/z range with a high total amount of ions.

Reserpine in Isopropanol

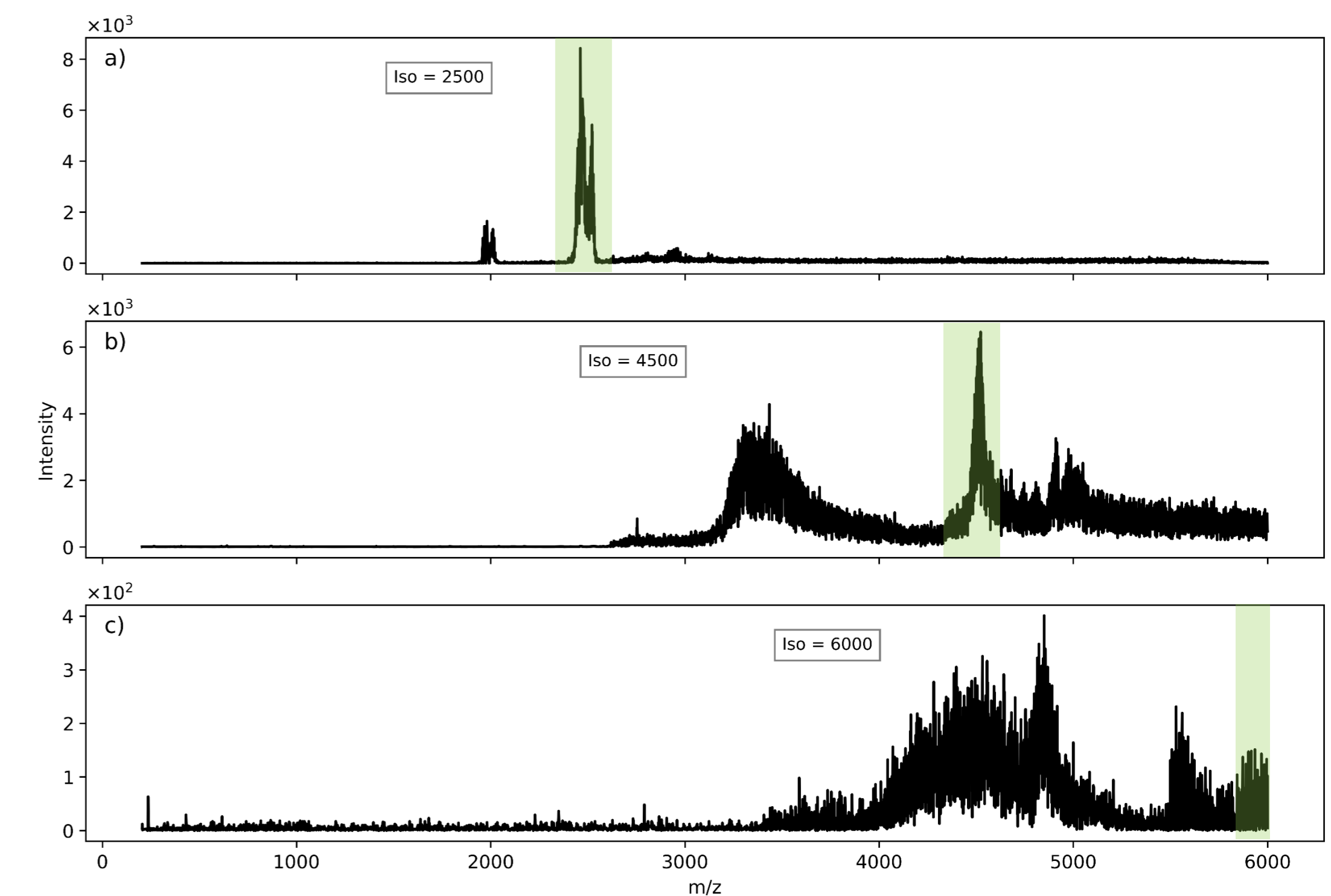


Fig. 4 Isolation range variation Reserpine in Isopropanol

The similar but different fragmentation patterns indicate effects of the solvent composition on the fragmentation reactions of the isolated aggregates. Figures 3 and 4 clearly shows the complex fragmentation dynamics of the isolated aggregates. Remarkably, signals with *higher* m/z than the isolation range are observable with both solvents. Since significant cluster growth in the ion trap is unlikely due to the lack of neutral reaction partners, the signals above the isolation range are the result of charge loss processes of the multiply charged isolated particles.

Ion source parameter

Dry Temperature

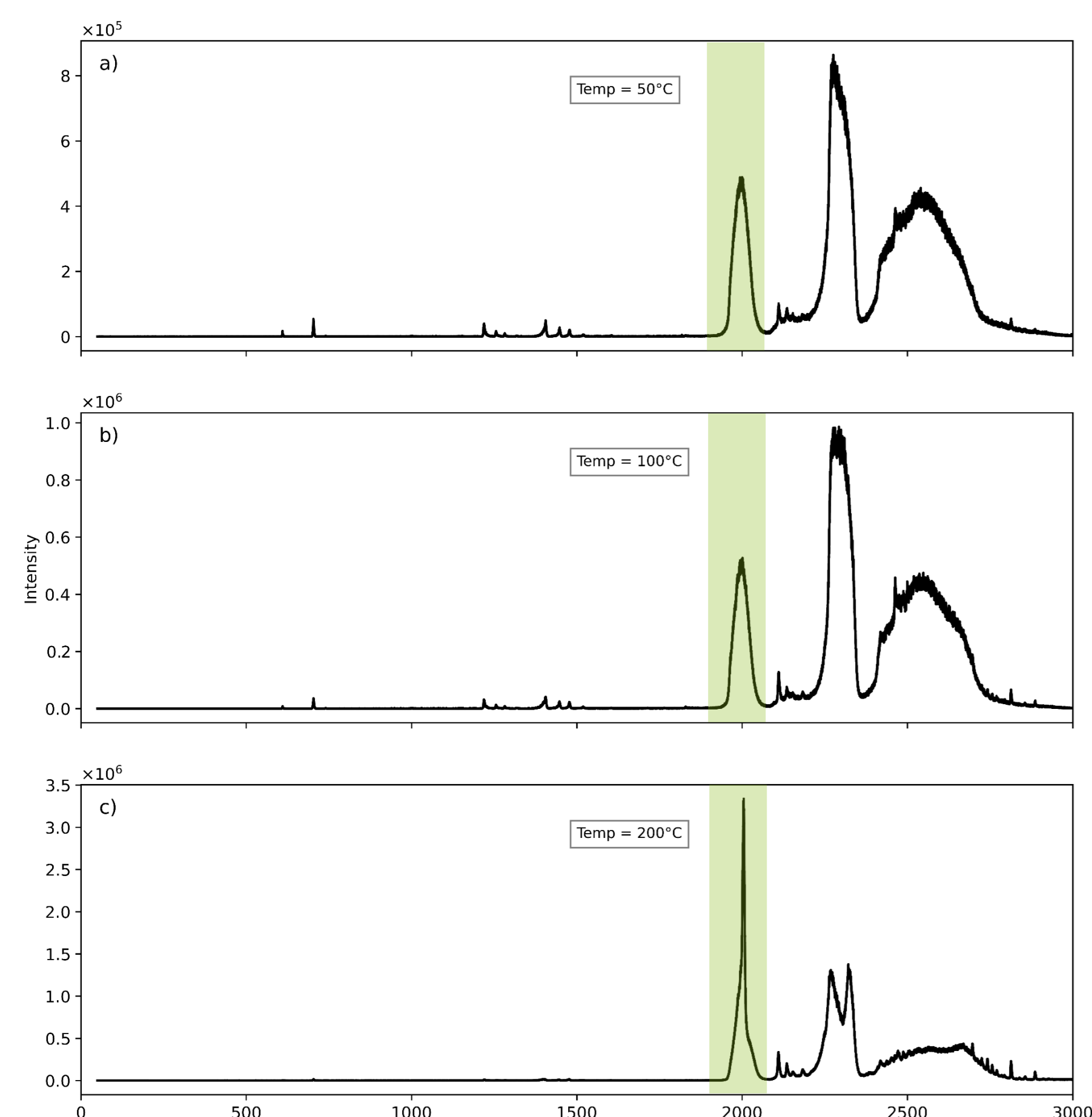


Fig. 5 Dry Temperature variation Reserpine in Ethanol

- Reserpine in $H_2O/EtOH/CH_2O_2$
- The intensity increases
- Intensity is not affected as much as expected, but the structure of the signals above the isolation ranges significantly.
- EtOH stabilized the cluster with Hydrogen-bridge-bonds (ACN is an acceptor)

Dry Temperature

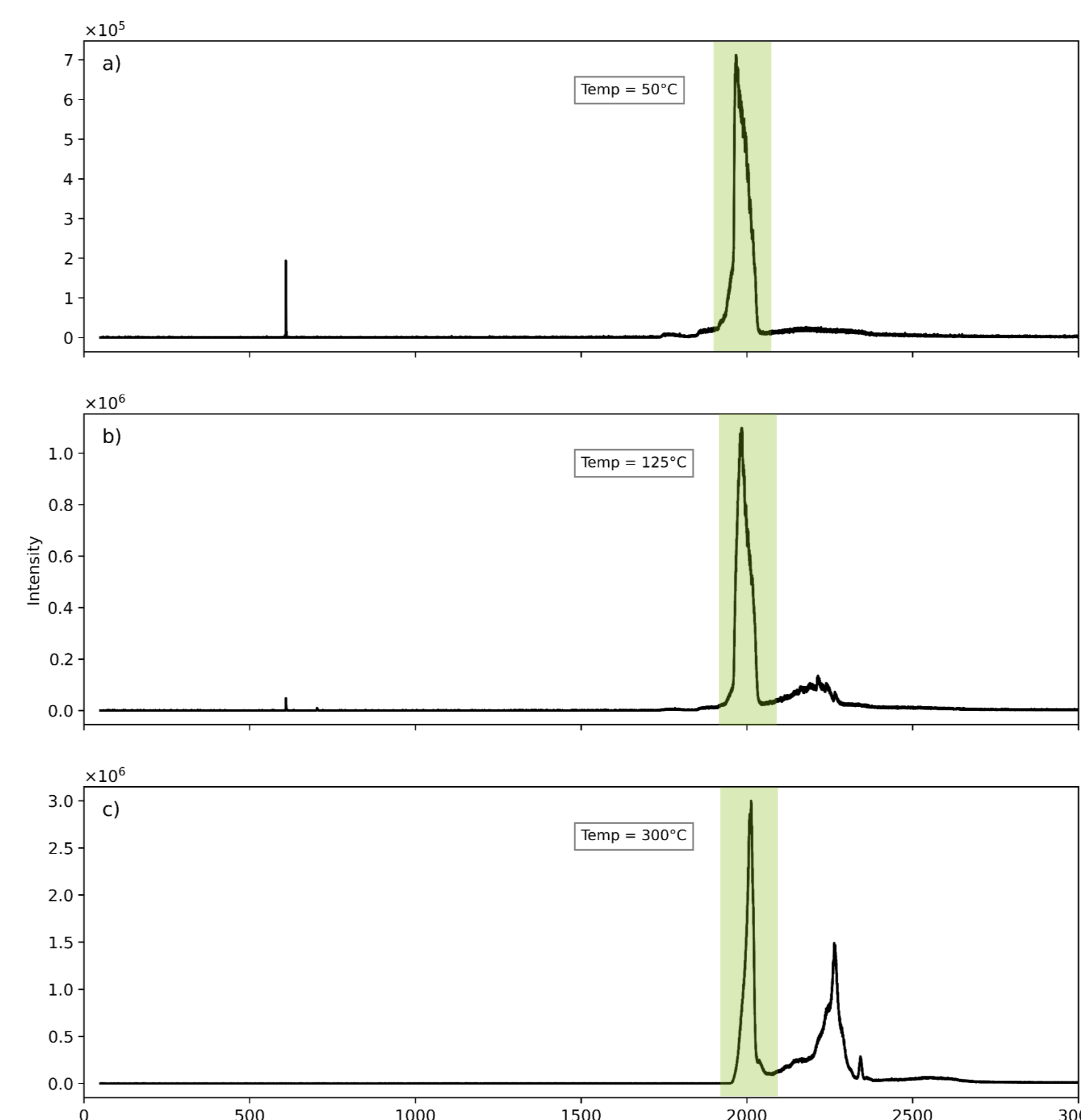


Fig. 6 Dry Temperature variation Reserpine in Acetonitrile

- Reserpine in $H_2O/ACN/CH_2O_2$
- An analyte signal appears when using the solvent acetonitrile
- The mass signals above the isolation range, resulting from charge loss, are increasing with higher Dry Temperature
- Higher temperature leads to increased charge loss reactions

Conclusions

- Strong signatures of aspirated droplets are observed in the Amazon Ion Trap with Reserpine in different solvents
- Variation of isolation range show a very wide range of charged aggregates in the ion trap originating from droplet fragments
- The shape of mass signals within, above, and below the isolation range and as well as the relative intensities of charge-loss signals depend on the ions source parameters and the isolation range
- The Dry Temperature has a pronounced effect on the observed stability of droplet fragment species

References

- [1] Kang, Y.; Schneider, B.; Covey, T. R.: On the Nature of Mass Spectrometer Analyzer Contamination. *J. Am. Soc. Mass Spectrom.* 28, 2384-2392 (2017). <https://doi.org/10.1007/s13361-017-1747-3>.
- [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. *Anal Bioanal Chem* 2021. <https://doi.org/10.1007/s00216-021-03452-y>