nESI and cAPCI applications of a controlled ion activation stage ("ion tunnel")

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Introduction

Ion activation stage

- activation of reagent ions/clusters (i.e. protonated water clusters) via rf heating
- elevated ion temperatures lead to high kinetic energies and therefore high energy collisions
- cleavage of weakly bound adducts

Different ionization mechanisms

The activation stage works well with gas phase ionization techniques, e.g., APCI and APPI. The use of well defined chemical reagent gas systems, as the protonated water cluster equilibrium, allowed a deeper insight into the rf induced processes occurring within the activation stage.

Regarding electrospray ionization, the situation changes dramatically. ESI generates a complex, multiphase system, thus effects observed with intermediate pressure ion activation cannot be explained by gas phase ion-molecule interactions. The differences between the two techniques in combination with the ion activation stage are presented.

Methods

Experimental Setup

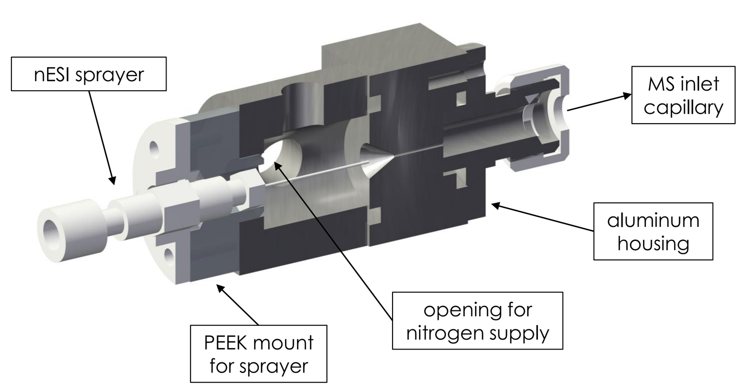
MS: Bruker micrOTOF, Bruker Daltonik GmbH

Ion Source: custom capillary Atmospheric Pressure Ion (cAPCI) Source; custom nano Electrospray Ion (nESI) Source

RF-Activation: custom RF stage ("ion tunnel")

GC: 7890A, Agilent Technologies Inc.

Transferline: Custom temperature-controlled GC-transferline



Figue 1: Model of the custom nESI source, the sprayer consists of a nano spray tip (15 µm PicoTip™, New Objective) connected to a non-coated fused silica capillary (75 µm i.d.) via a stainless steel union; the union is held at high voltage, the source chamber at ground potential; liquid flow is supplied via a syringe pump; the source chamber is flushed with nitrogen

cAPCI Experiments

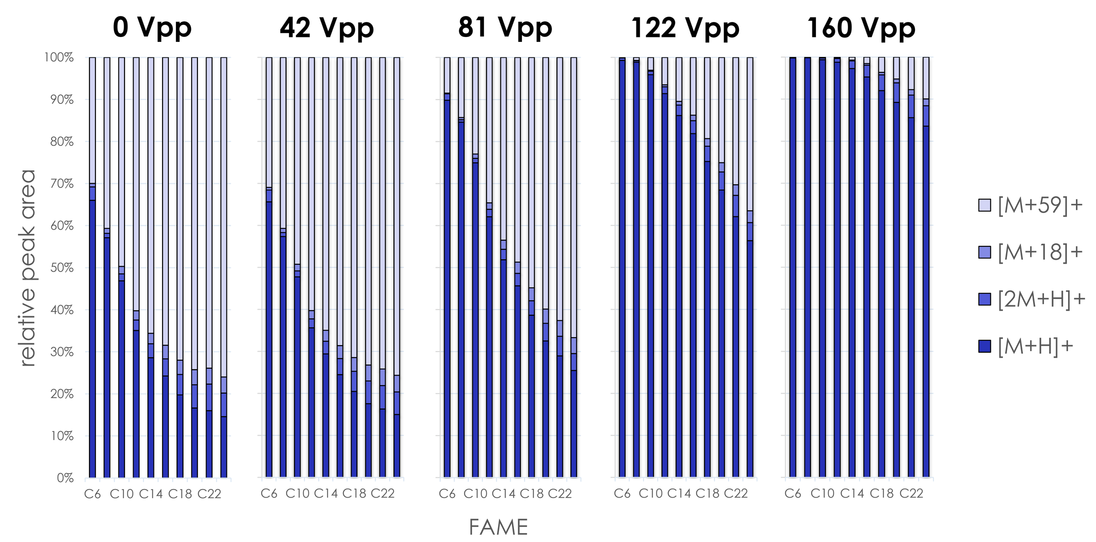


Figure 2a: *Relative peak areas of the detected ion species of 1 ng on column fatty acid methyl ester (FAME) mix (C4-C24 even carbon saturated FAMEs in hexane, Supelco Analytical)*

- adducts are significantly cleaved at high rf amplitudes, which leads to clear mass spectra (*Figure 4b* bottom left)

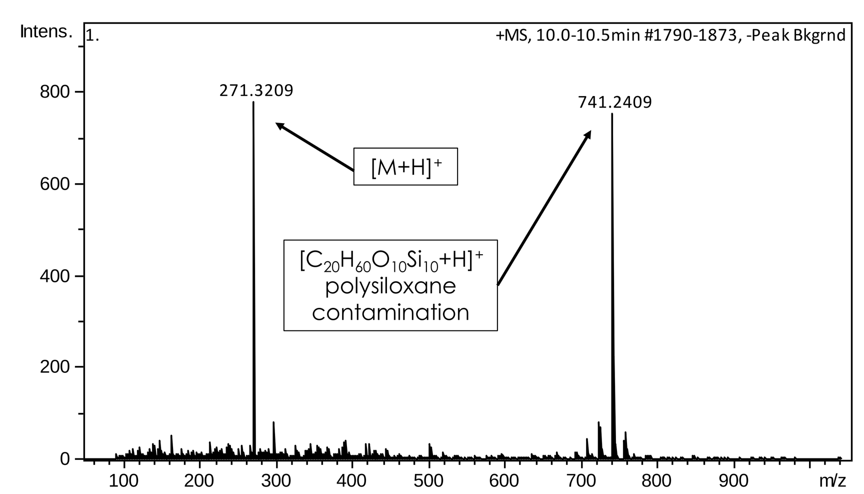


Figure 2b: *Mass spectrum of methyl palmitate, 1 pg on column*

- adduct cleavage and high transmission lead to limits of detection in the low pg range
- setup optimization and exclusion of contaminants may further reduce LOD

nESI Experiments

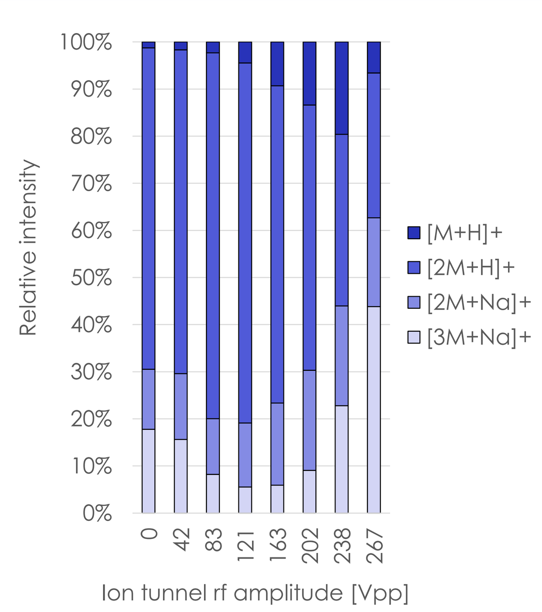


Figure 3a: *Relative intensities of detected ion species of methyl palmitate obtained with nESI*

- slight decrease of Na^+-adducts and simultaneous increase of protonated ion species when the rf amplitude is increased up to 160 Vpp
- at higher amplitudes the overall intensity decreases while the Na^+-adduct fraction increases

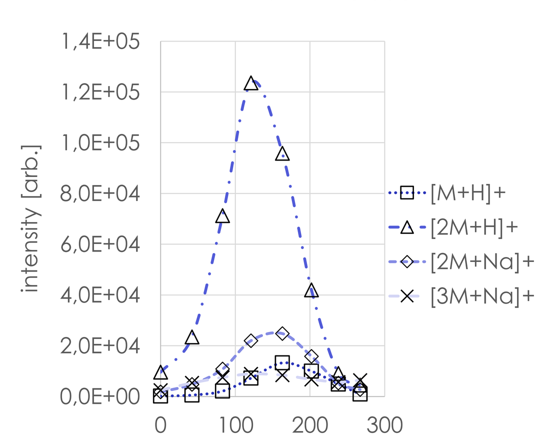


Figure 3b: *average intensities of extracted ion chromatograms of the detected ions*

- the intensities of all detected ion signals increase up to 160 Vpp
- above 160 Vpp a significant decrease of the overall intensity is observed

cAPCI vs. nESI

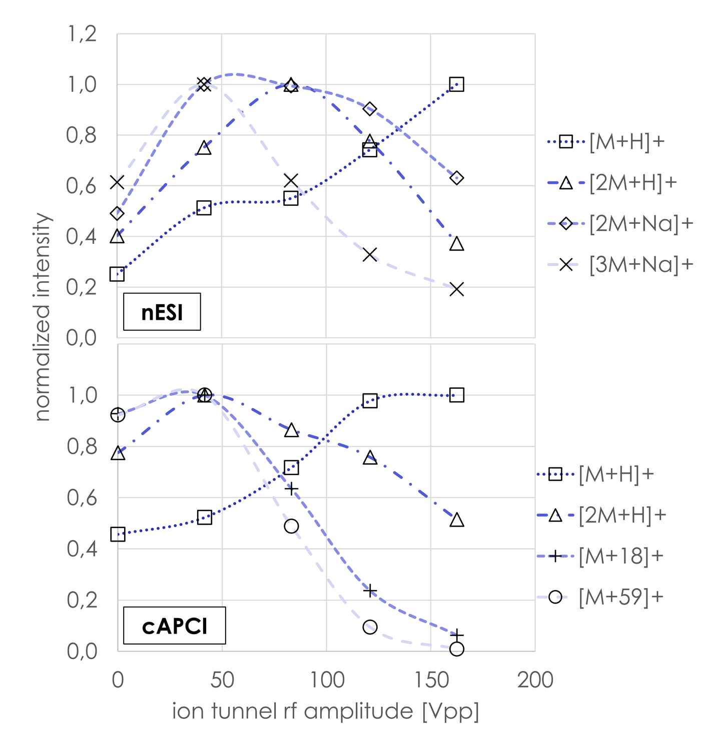


Figure 4a: *Methyl palmitate intensities normalized with TuningMix intensities to visualize non-transmission effects (top: nESI, bottom: cAPCI)*

- *trends with ESI and APCI are comparable, the increase of the $[M+H]^+$ signal is not only due to improved transmission*
- *above 50 Vpp formation of adducts is declining*

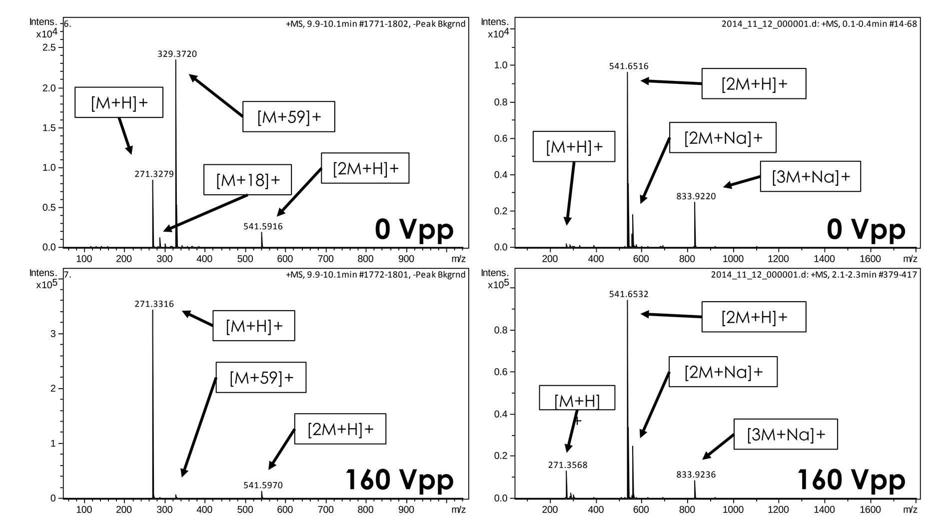


Figure 4b: *Mass spectra of methyl palmitate with cAPCI (left) and nESI (right) with ion tunnel rf field turned off and on*

- adducts are effectively dissociated at high rf amplitudes at APCI conditions (→ gas phase ions)
- ESI yields completely different mass spectra and the rf induced adduct dissociation is far less pronounced, even though the $[M+H]^+$ formation is significantly promoted, adducts are still present with high abundances

Transmission Effects

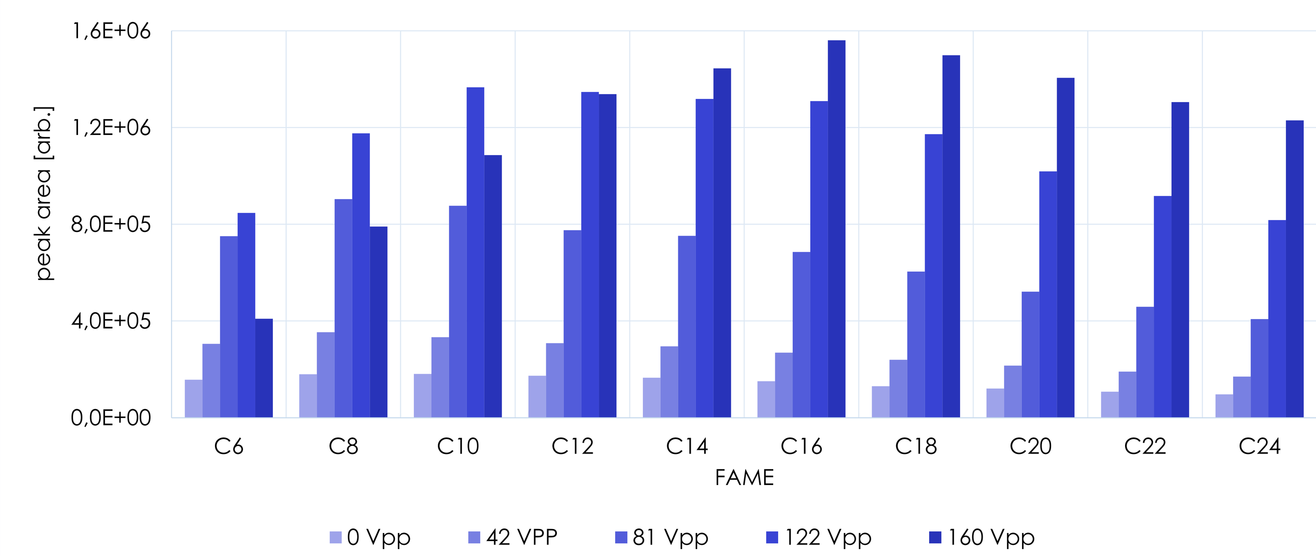


Figure 5a: *Sum of peak areas of all detected ion species of the FAMEs with cAPCI at different ion tunnel rf amplitudes*

- overall signal intensity increases at higher rf amplitudes (up to a factor of 12 in this example)
- the intensity gain appears to be mass dependent, which may be due to superimposed chemical effects (i.e., reactivity-increase of reagent ions)
- mass discrimination: the ion tunnel works as a high-pass mass filter, at 160 Vpp the FAMEs C6 – C12 show declining overall intensities compared to those at lower rf amplitudes

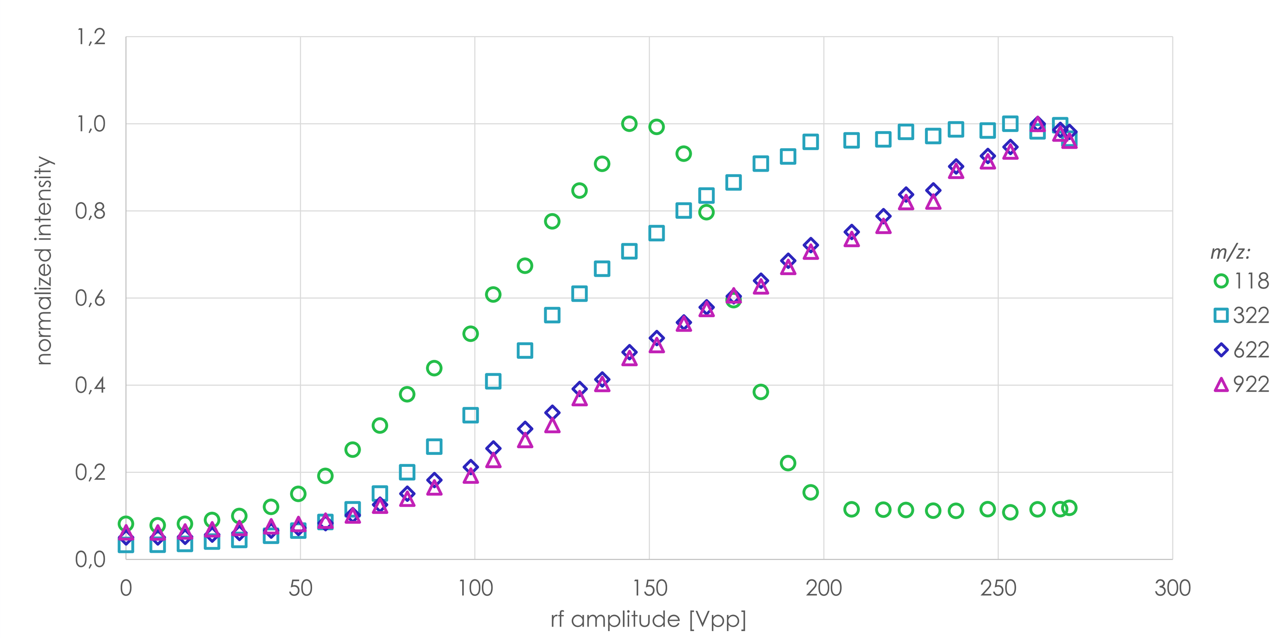


Figure 5b: *Normalized intensities of ESI TuningMix (Agilent Technologies Inc.) compounds in dependency of the applied ion tunnel rf amplitude.*

- ions with lower m/z are cut off eventually when the rf amplitude is increased, which was also observed in APCI experiments
- TuningMix compounds form solely singly protonated molecular ions and undergo no transformation. Therefore they are promising candidates for the use as „transmission markers" to investigate chemical effects
- m/z 118 (betaine) shows a sharp cut-off at 150 Vpp, in contrast to m/z 322 (hexamethoxyphosphazene) whose intensity reaches a plateau. This may be due to different chemical properties and therefore different transformation processes

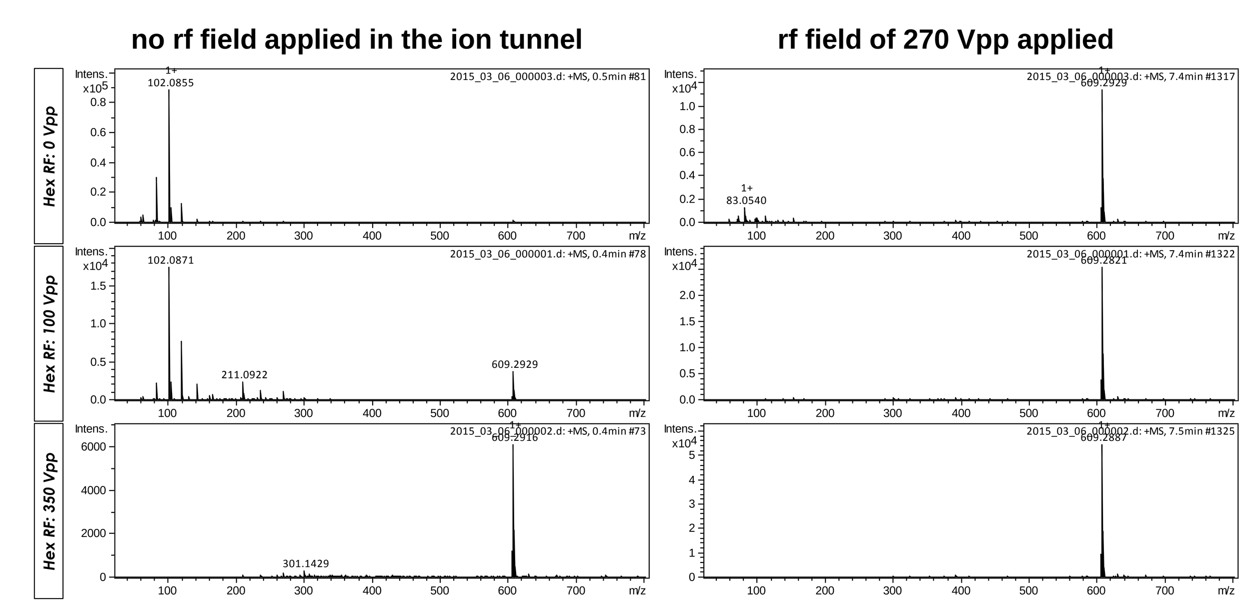


Figure 5c: *Mass spectra of Reserpine (608.28 Da, $[M+H]^+$ at m/z 609.29) obtained with nESI at different transfer hexapole settings (Hex RF), without (left) and with maximum (right) ion tunnel rf amplitude*

- no detection of protonated Reserpine without rf guiding (ion tunnel and hexapoles), only low-mass solvent clusters are detected
- maximum signal of m/z 609.29 with hexapole rf amplitude at 350 Vpp, low m/z region is cut off (mass discrimination)
- ion tunnel rf field increases signal intensity roughly by a factor of 10
- with the ion tunnel rf field at maximum amplitude the $[M+H]^+$ signal at m/z 609.29 is detected even with the hexapole rf turned off; solvent clusters with low m/z are still visible in the spectra

Conclusions

Adduct cleavage

It was shown that the ion activation stage clears up mass spectra effectively. By applying an rf field to an ion population generated by gas phase ionization methods in an intermediate pressure range, adducts are effectively dissociated due to rf heating. In ESI experiments only a slight shift in ion species distribution was observed. In conclusion, the impact of the rf activation is strongly dependent on the character of the ion population.

Transmission Effects

In all experiments with the ion tunnel, a change in signal intensity was observed. Additionally, the ion tunnel shows characteristics of a high-pass mass filter. The effect occurred in the same way with APCI and ESI, regarding intensity gain and mass discrimination. Furthermore it was shown, that the ion tunnel strongly focuses the ion population. Reserpine was readily detected (hence transmitted to the mass analyzer) *without* rf guiding of the transfer hexapoles, when the ion tunnel rf field was turned on. With no rf guiding at all, only low m/z solvent clusters were detected.

Outlook

- Characterization of transmission effects
- investigation of rf induced chemical effects and transformation processes with ESI
- new rf driver to access higher amplitudes

Literature

[1] Y. Brachthäuser, S. Klee, D. Klink, M. Thinius, K. J. Brockmann, T. Benter, *GC-MS Performance of a Novel Capillary Atmospheric Pressure Chemical Ionization (cAPCI) Source*, Proceedings of the 61th ASMS Conference on Mass Spectrometry and Allied Topics, Minneapolis, MN, USA, **2013**

[2] S. Klee, A. Brockhaus, M. Thinius, W. Wißdorf, T. Benter, *Fundamental ion-molecule reaction studies at elevated ion temperature and analytical application of an ion activation stage ("ion tunnel")*, Proceedings of the 62th ASMS Conference on Mass Spectrometry and Allied Topics, Baltimore, MD, USA, **2014**

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