

# Evaluation of kinetic energy distributions in API-MS ion transfer stages



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## Introduction

The central task of transfer stages in atmospheric pressure ionization mass spectrometers (API-MS) is an efficient means of transport of ions from the source to the analyzer while removing as many neutrals as required [1]:

- API interface: Connection between the ion source and the vacuum system; capillary or orifice with diameters in the mm to sub-mm range
- Ion capture: Skimmer or RF-driven ion funnel, background gas is removed by the fore-pump
- Ion transport: RF ion guides (RF-only quadrupole or higher-order multipole guides) for radial ion confinement, and DC gradient for axial transport, pressure is further reduced
- Ion beam shaping to fit the requirements of the analyzer (e.g. ion trap injection)

Knowledge of the impact of the transfer voltages on the kinetic energy of the ions upon their journey to the analyzer is favorable because the efficiency of RF driven ion guides and traps is energy dependent [2] [3].

Upon collision free acceleration in an electric field the kinetic energy gain of ions corresponds directly to the applied acceleration voltage.

When collisions occur during or after the acceleration the resulting kinetic energy distribution may be completely different. In this contribution, a commercial API-MS transfer stage is characterized with regard to the impact of transfer voltages on the kinetic energy distribution of the ion beam and the effect on ion storage in a quadrupole ion trap.

## Methods

### Mass Spectrometry:

HCTplus and amaZon Speed ETD with Apollo ESI source (Bruker Daltonics, Bremen, Germany)

### Ion current measurement:

610C Solid State Electrometer (Keithley Instruments, Inc., Ohio, USA).

### Chemicals:

HPLC grade acetonitrile and Millipore water were used for preparation of the analyte solutions. All analytes (sodium formate, caffeine, pyridine) were diluted in water/acetonitrile (1/1) with 0.1% formic acid. All chemicals were used without further purification.

### Simulations:

SIMION® 8.1 (Scientific Instrument Services, Inc., Ringoes, NJ, www.simion.com) with hard sphere collision model (hs1)

### Data Processing:

DataAnalysis 4.1 (Bruker Daltonics, Bremen, Germany), Python 3

## Kinetic Energy Distribution (KED)

### Ion current measurement

- deceleration voltage ( $U_d$ ) scan
- absolute ion current (faraday cup)
- ion chromatogram (QIT)

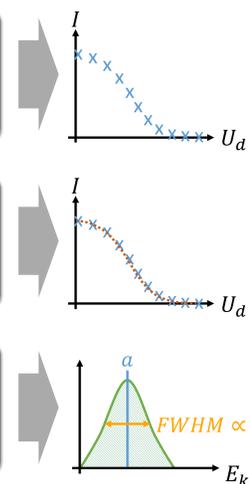
### Parameter fitting

$$f(x) = \frac{1}{1 + \exp\left(\frac{x-a}{b}\right)}$$

### Derivative $\equiv$ energy distribution

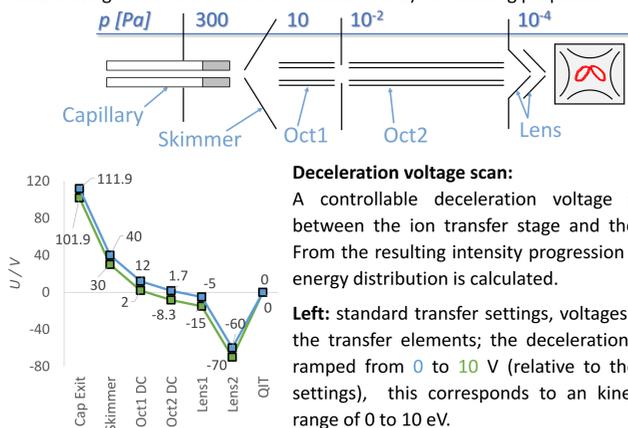
$$f(x) = -\frac{\exp\left(\frac{x+a}{b}\right)}{b\left(\exp\left(\frac{x}{b}\right) + \exp\left(\frac{x}{b}\right)\right)^2}$$

• area normalization



## Ion Transfer Stage

A schematic of the ion transfer stage of the HCTplus instrument is shown below. All ion optical elements are biased with DC voltages a) to create a potential ramp accelerating the ions towards the detector and b) for focusing purposes.



### Deceleration voltage scan:

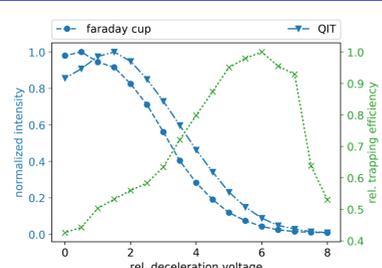
A controllable deceleration voltage is applied between the ion transfer stage and the detector. From the resulting intensity progression the kinetic energy distribution is calculated.

Left: standard transfer settings, voltages applied to the transfer elements; the deceleration voltage is ramped from 0 to 10 V (relative to the standard settings), this corresponds to a kinetic energy range of 0 to 10 eV.

## Faraday Cup vs. QIT Detection

Right: Experiments with the Faraday cup and the ion trap show different KEDs under otherwise identical conditions. In the ion trap experiments a significant intensity decrease is observed at low deceleration voltages.

→ The curves derived from QIT ion chromatograms do not solely show the KED  
→ Superimposed is the ion storage efficiency of the trap device

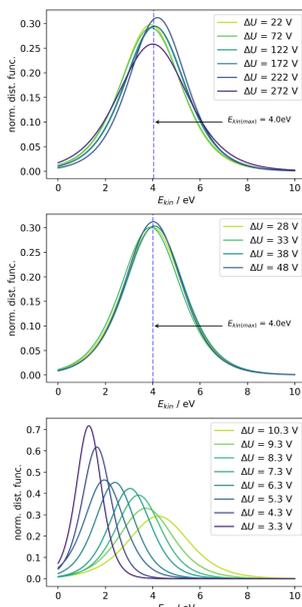


## KED

Using the ion trap for the kinetic energy scan has some advantages over the Faraday cup (e.g. mass resolved energies, easily automated, simpler data processing).

Left: KEDs obtained for different transfer settings (HCTplus)

- Between the capillary exit and skimmer ( $\Delta U_{std} = 72$  V) (top) and between the skimmer and Oct1 ( $\Delta U_{std} = 28$  V) (center), respectively, the collision rate is sufficiently high to prevent the ions from gaining kinetic energy.
  - Between Oct1 and Oct2 (bottom) the kinetic energy distribution curve is shifted towards higher kinetic energies when the acceleration voltage is increased
    - The width of the curve increases, which is attributed to the low number of collisions occurring while traveling from Oct1 exit to the detector.
- The shape and position of the KED is determined in the near-collision-free region

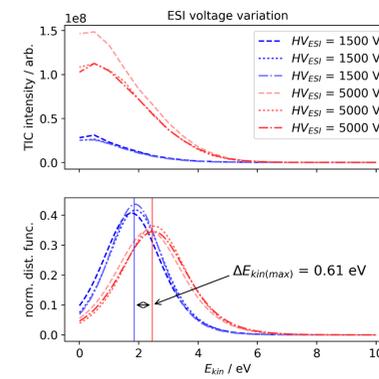


## KED as a Diagnostic Tool

Even though the KEDs derived from ion trap data are superimposed by the ion acceptance of the trap, changes of the KED still indicate a change of the kinetic energy of the analyzed ions. Therefore, the KED is a probe for processes, which modify the kinetic energy of ions in the transfer stage.

Right: TIC and KED for different electrospray voltages, recorded with the HCT instrument

- When changing the electrospray voltage a shift in the KED is observed
  - This may be attributed to a change of droplet size and, thus, droplet evolution and subsequent ion release
- The KED may be a valuable tool for further understanding of the ion release in ESI
- This is not observed with the amaZon Speed ETD
  - The amaZon instrument utilizes a double skimmer stage, in contrast to the skimmer inlet used in the HCTplus ion trap
- The funnel stage is designed for efficient declustering  
→ Changes of the initially formed droplets may very likely be masked by this stage



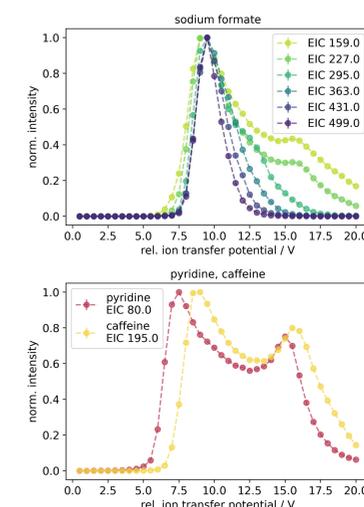
## QIT Ion Acceptance

### Extended Voltage Scans

The effect of the acceleration voltage applied between the ion transfer stage and the ion trap is systematically investigated over an extended voltage range, with ions of different m/z ratios.

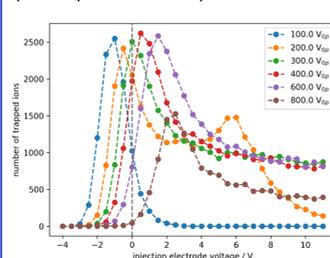
Right: Extracted ion chromatogram intensities of different analyte ions, recorded with the amaZon Speed ETD

- Sodium formate (top) forms clusters of the shape  $[nM+Na]^+$  ( $n = 2 \dots 6$  in the considered mass range)
    - The obtained intensity distribution changes significantly with the ion mass
    - The faster intensity loss at high ion transfer potentials (and therefore stronger acceleration into the trap) for heavier clusters may also be explained by fragmentation
  - Pyridine and caffeine protonated molecules (bottom) show similar intensity distributions
- For some ions a second intensity maximum is observed  
→ The position of the second maximum depends on the pseudopotential (cf. sodium formate plot)



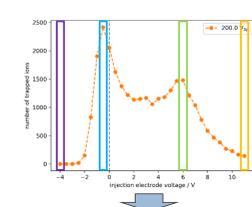
### Voltage Scan Simulations

For further investigating the occurrence of the second intensity maximum SIMION simulations of the voltage scan are performed. An ion trap model adapted from the SIMION pseudopotential example is used for modeling of the ion acceptance of an ion trap.



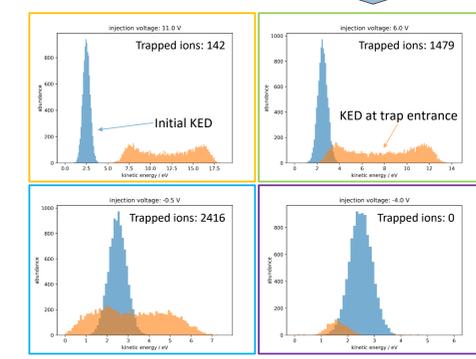
Left: Number of stable ions (m/z 100) after a simulation time of 1 ms in dependence of the injection electrode voltage, for different RF voltages

- When increasing the RF voltage the maximum of the intensity distribution moves to higher injection voltages
- The second maximum separates from the first as the RF voltage is increased



Right: Kinetic energy distributions of ions obtained from SIMION simulations for an RF voltage of 200 V

- The kinetic energy of ions entering the trap is modified by the fringe field at the trap entrance hole (depending on the RF phase)
  - Significant broadening of the energy distribution
- For high numbers of trapped ions a broad KED is favorable, e.g. as observed for injection voltages of 6.0 and -0.5 V
- If the injection voltage and thus the kinetic energies of the ions are too high the trapping efficiency is low, as for an injection voltage of 11.0 V
- If the injection voltage is too low (e.g. -4.0 V) a portion of the ions is deflected from the ion trap, as expected



## Summary / Conclusion

The ion current measured in the analyzer recipient of a commercially available ESI MS is in the range of a few picoamperes. The kinetic energy distribution obtained for standard transfer settings has a maximum around 3 eV with a FWHM of 3 eV.

The KED depends on the applied transfer voltages:

- Acceleration at intermediate pressure (Capillary-Oct1) does not change the KED because gained energy is rapidly re-distributed via collisions
- At lower pressure (Oct1-detector) the collision rate is lower and the gained kinetic energy is only partly lost
- This leads also to significant broadening of the KED compared to thermal conditions (several eV vs. tens of meV for nitrogen at  $10^5$  Pa and 298 K [4])

→ The KED of the ion beam is defined in the low collision environment of the transfer stage

KEDs obtained from ion trap data are superimposed by the ion acceptance of the trap

- The ion acceptance decreases with higher ion energy
- Nevertheless, changes of the kinetic energy of the ion beam are still observable
- The fringe field at the ion trap entrance significantly modulates the KED of the ion beam when entering the trap
  - Experimental and simulation data show a second maximum in the energy dependent intensity progression, which scales with the ion mass and RF voltage (→ pseudopotential)

## Literature

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