Structural elucidation of a medium-heavy **crude oil** sample and MS^N using **tandem mass spectrometry** with **isobaric precursor isolation** in a **multiple-reflection time-of-flight** mass spectrometer

Julian Bergmann[1], Timo Dickel[1,2], Jens Dreschmann[3], Tobias Murböck[1], Wolfgang R. Plaß[1,2], Christoph Scheidenberger[1,2,4], Wolfgang Schrader[3], Alessandro Vetere[3]
[1]II. Physikalisches Institut, Justus-Liebig-Universität Gießen, Germany; [2]GSI Helmholtzzentrum für Schwerionenforschung, Darmstadt, Germany;
[3]Max-Planck-Institut für Kohlenforschung, Mülheim an der Ruhr, Germany; [4]Helmholtz Forschungsakademie Hessen für FAIR (HFHF), Germany

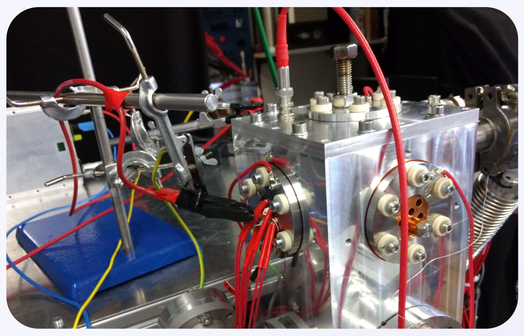
Introduction

Structural elucidation of complex mixtures using tandem mass spectrometry is typically limited by low mass separation power to isolate precursors. A multiple-reflection time-of-flight mass spectrometer (MR-TOF-MS) with sub-ppm accuracy, and ultra-high mass resolving power has been developed to overcome these limitations [1,2]. A new API, ion sources, software system, and analysis techniques have been implemented. The device offers multiple-stage tandem mass spectrometry with very high mass separation power in every stage [3,4].
Precursors were isolated in an MS^2 experiment with a separation power of 250 000, and MS^4 was demonstrated. MS^2 was performed on a crude oil sample with a precursor isolation window of 10 mu adjacent to a dominant peak, allowing the identification of 26 new structures.

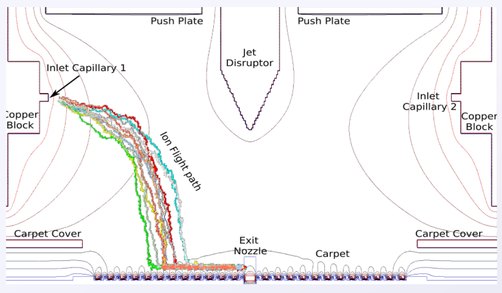
Atmospherical Pressure Interface

Features

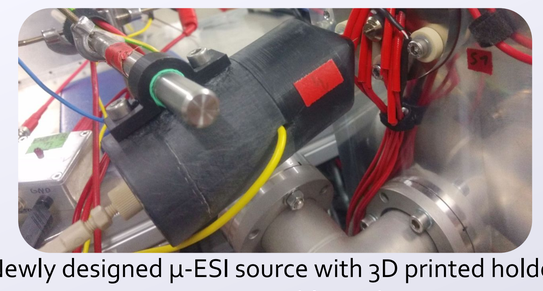
- Parallel use of up to four ion sources
  - Chemically inert mixing of ions
  - Simultaneous use of different ionisation techniques with individual settings
  - Features nano-ESI, µ-ESI, thermal ion source and heated inlet capillaries
- RF carpet funnels ions fast and efficiently
- Modular design, easy to clean and expand



Newly designed and built API



Simulations for ion trajectories of different masses and ion mobilities



Newly designed µ-ESI source with 3D printed holder
Syringe pump generates stable ion beam
Metal capillary allows electrochemical ionisation

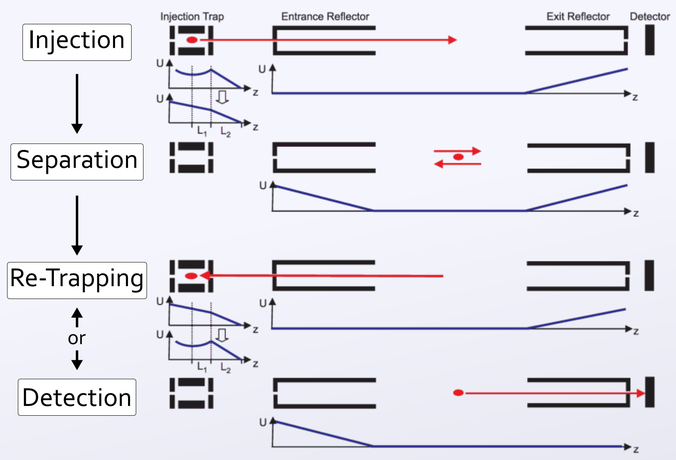
Mass-Selective Re-Trapping: Tandem-in-time

Features

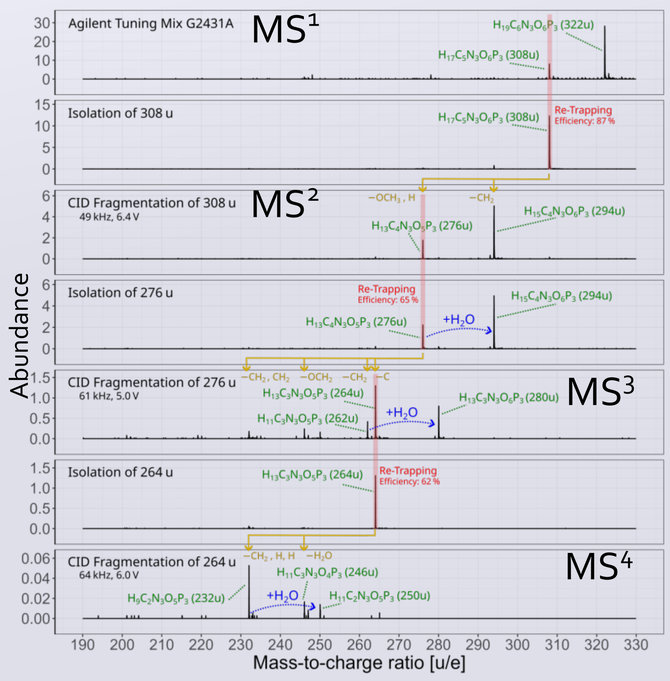
- Tandem-in-time with ultra-high precursor separation power
- Novel technique for closed-path MR-TOF-MS devices
- Re-trapping with the same RFQ trap
- Theoretically unlimited number of MS^N stages
- Fragmentation with low energy CID between each stage

For the first time

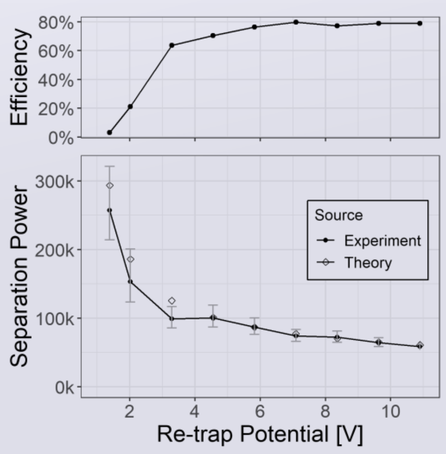
- **Precursor separation power up 250 000 demonstrated**
- **MS^4 in an MR-TOF-MS**



Schematic workflow for mass-selective re-trapping [4]

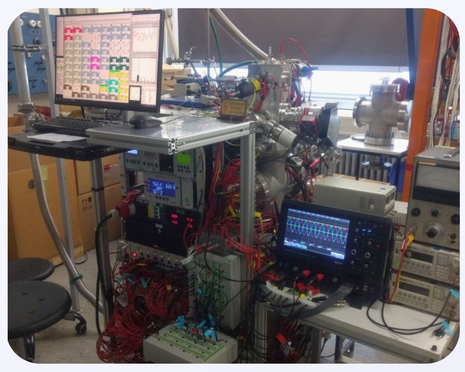


MS^4 Process of $H_{19}C_6N_3O_6P_3$ (322 u)



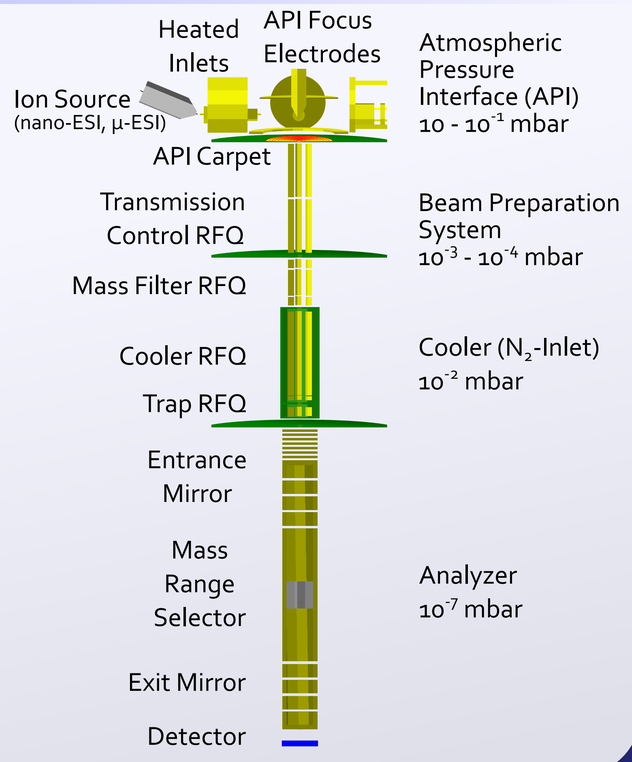
Precursor separation power and efficiency, measured at MS^2 of 118 u and in theroy

MR-TOF-MS Setup



Performance

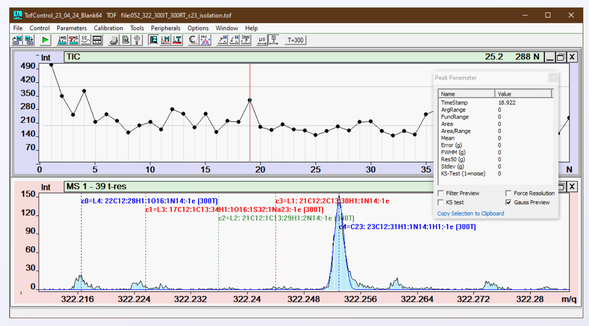
- Mass resolving power: 280 000
- Mass accuracy: < 1 ppm
- MS^N precursor separation power: 250 000
- Detection limit: < 10^{-9} mol/l
- Many additional features (mass filter RFQ, gain control, mass range selector, ...)



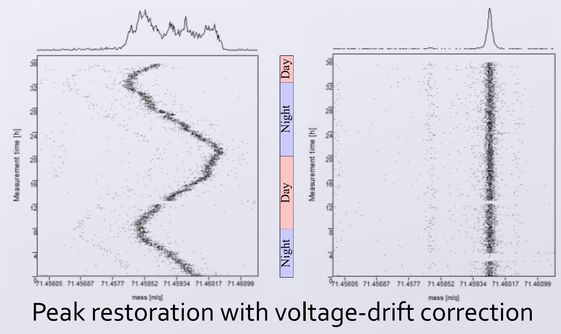
TOFControl Software System

Features

- Hardware control
  - Voltages, frequencies, timing sequences
  - Parameter scans and optimizers
- Data acquisition
  - Supports parallel use of TDC/ADCs
  - Life-visualisation and online-analysis
  - Self-optimizing systems
- Data analysis
  - MR-TOF-MS tailored calibration
  - Voltage drift and dead time corrections
  - Determines chemical composition
- Versatility
  - Used for analytical MS and for MS at accelerator facilities (GSI, TRIUMF)
  - Applied in more than 48 scientific publications

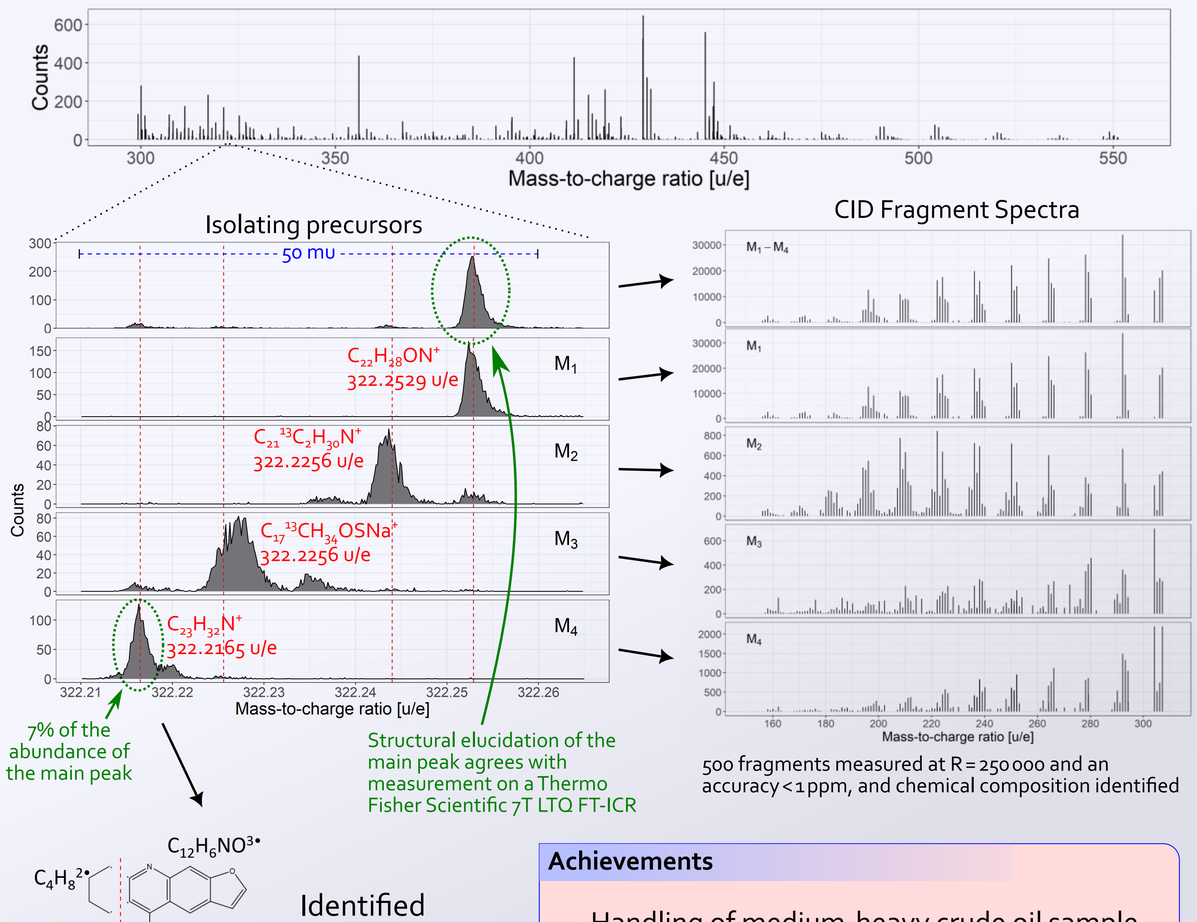


User interface of TOFControl

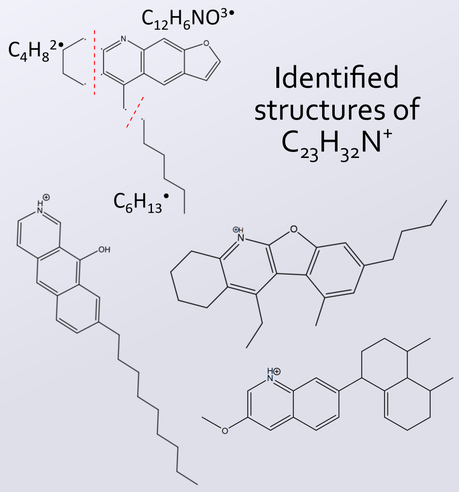


Peak restoration with voltage-drift correction

Ultra-high Res. MS^2 of Medium-heavy Crude Oil



500 fragments measured at R = 250 000 and an accuracy < 1 ppm, and chemical composition identified



Identified structures of $C_{23}H_{32}N^+$

Achievements

- Handling of medium-heavy crude oil sample
- New analysis technique: high-resolving, fast, and non-scanning measurement of a wide mass range in a closed-path MR-TOF-MS
- Precursor isolation window of 10 mu
- Isolation of a precursor at 322.2165 u with only 7 % abundance of the dominant signal at 322.2529 u
- 26 new structures derived

References and Contact

[1] T. Dickel et al., Nucl. Instrum. Methods B 317 (2013) 779
[2] J. Lang, PhD thesis, 2016, JLU Gießen
[3] W. Lippert, PhD thesis, 2016, JLU Gießen
[4] T. Dickel et al., J. Am. Soc. Mass Spectrom. 28(2017) 1079
[5] T. Dickel et al., Int. J. Mass Spectrom. 412 (2017) 1-7

Julian Bergmann
AG Scheidenberger
II. Physikalisches Institut
Justus Liebig Universität Gießen
julian.bergmann@physik.uni-giessen.de

Presented at DGMS 2024