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MR-TOF-MS for Nuclear Physics Facilitate a New Class of Experiments in Analytical Mass Spectrometry

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Overview

- Motivation
- MR-TOF-MS for Analytical Mass Spectrometry
- Highly Resolving Tandem MS
- Applications
- Summary

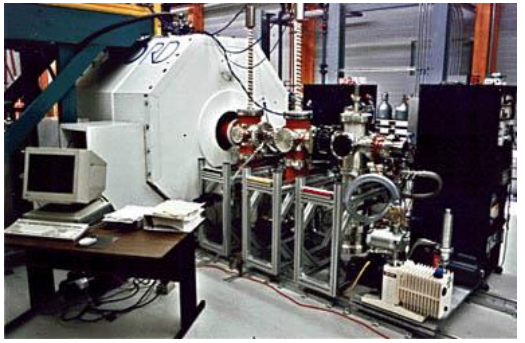
Mobile High-Performance Mass Spectrometry

High-Performance Mass Spectrometers

Very high resolving power ($m/\Delta m > 10^5$)

- Resolution of isobars at low/medium mass
- Isotopic resolution at high mass

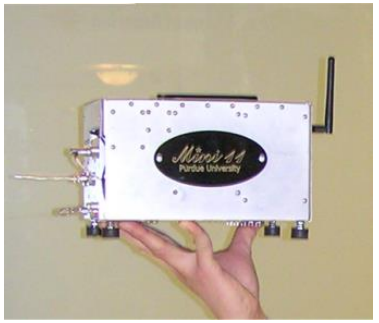
- Very high mass accuracy ($\delta m/m < 10^{-6}$)
- Determination of composition and structure



A. Marshall et al., 9.4 T FT-ICR-MS

Mobile Mass Spectrometers

- In-situ measurements
- Prompt results
- Investigation of time-dependent processes
- No sample storage required



R.G. Cooks et al., Mini 11 RIT-MS

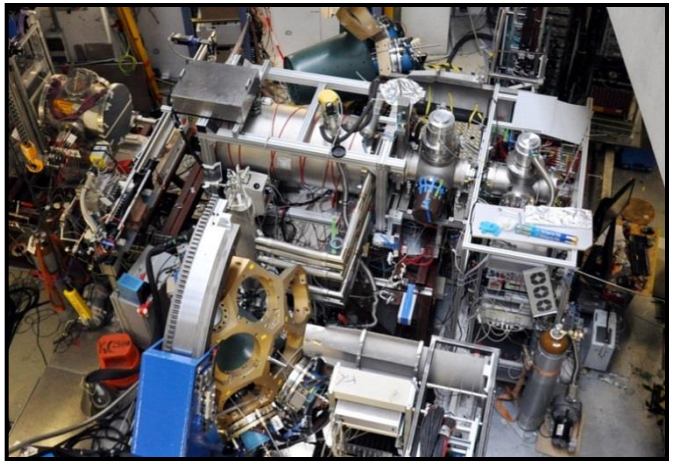
There is no mobile high performance MS yet

Goal: develop mobile high performance MS

MR-TOF-MS

Fast, sensitive, broadband, non-scanning, high resolving power

MR-TOF-MS for nuclear physics experiments



W.R. Plaß et al., NIM B 266 (2008) 4560
W.R. Plaß et al., Int. J. Mass Spectrom. 394 (2013) 134
T. Dickel et al., NIM A 777 (2015) 172

J. Ebert, Mo. 12:40
C. Hornung, Tu. 18:30
S. Ayet, Tu 18:30

Different fields of application

Synergy

No magnet, moderate vacuum requirements, size reduction is straight forward

MR-TOF-MS for in-situ analytical mass spectrometry

Identification of mycotoxins

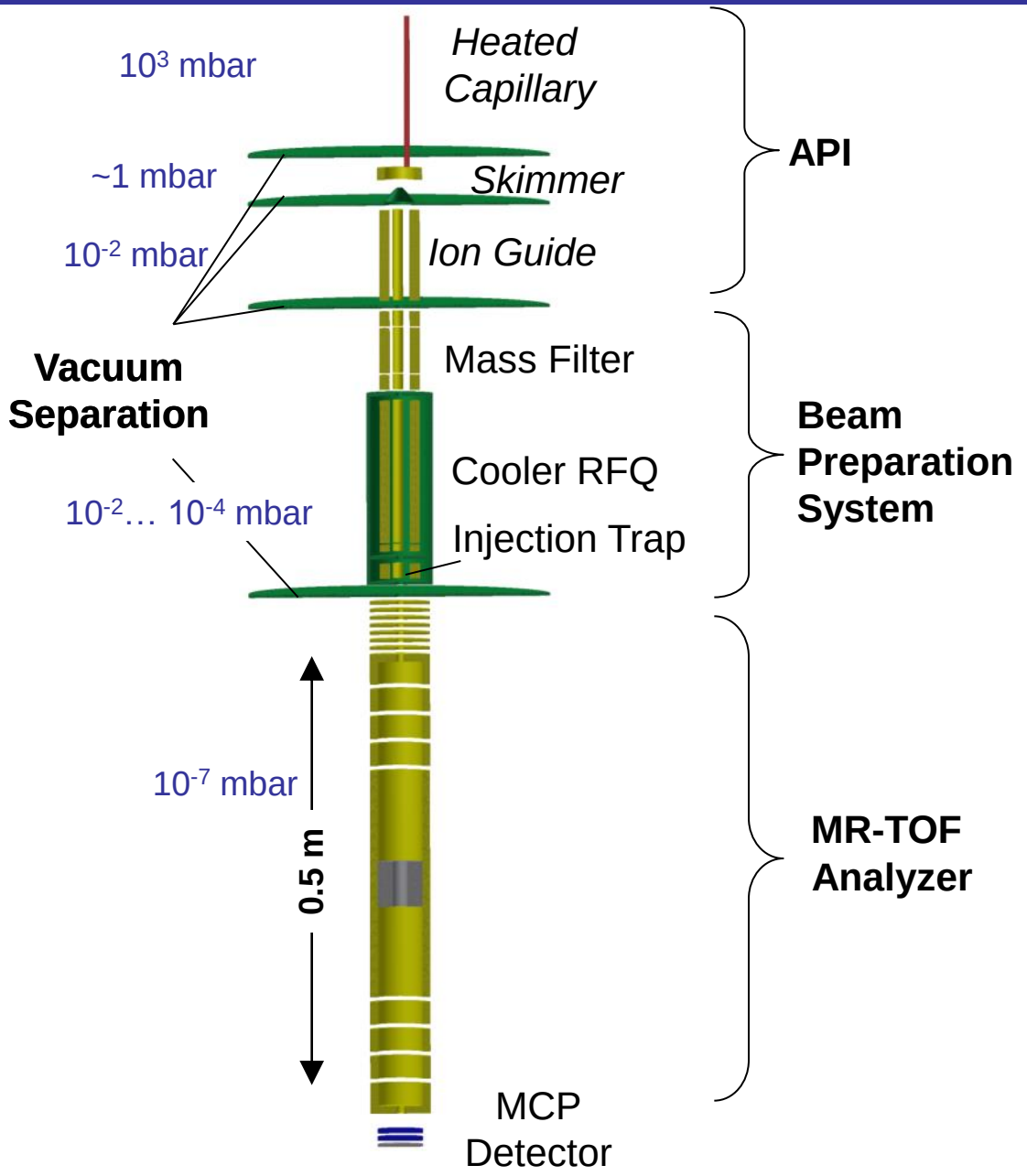
Water monitoring at ‘hot spots’

. . .

Mobile MR-TOF-MS for Analytical Mass Spectrometry

Design goals

- Mobile
- m/Δm > 100,000
- δm/m < 1 ppm
- Repetition rate ~ kHz
- Compatible with atmospheric ion sources



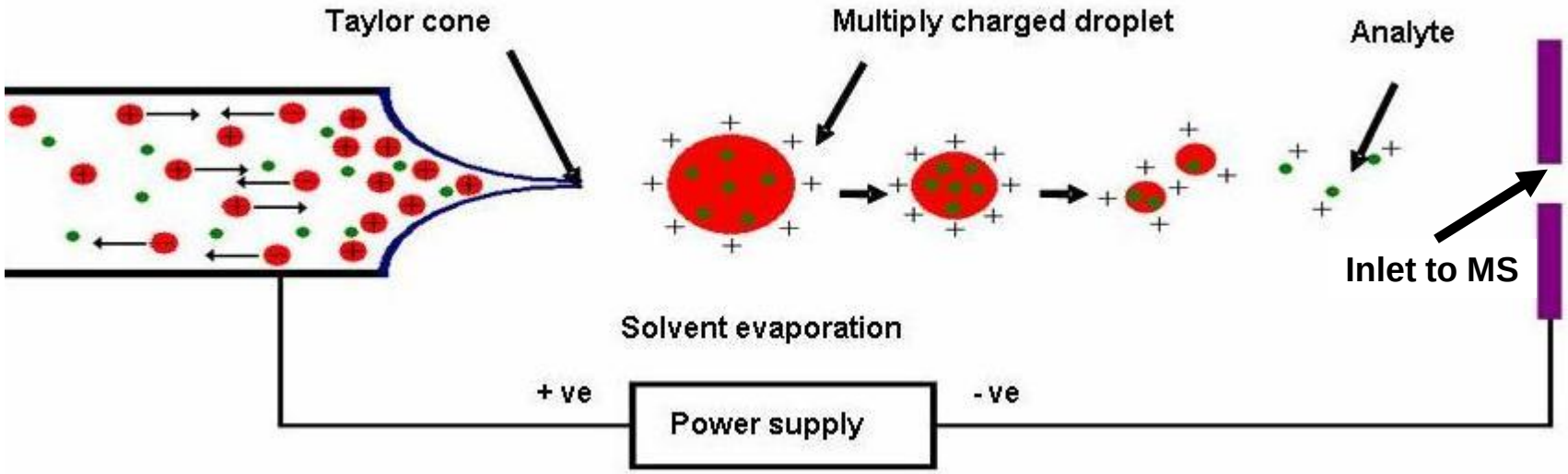
T. Dickel et al*, Nim B*, **317**, 779-784 (2013)
J. Lang, PhD thesis in preparation, JLU Gießen

Electrospray Ionisation

Soft ionisation technique for large molecules, e.g. proteins

Multistep process:

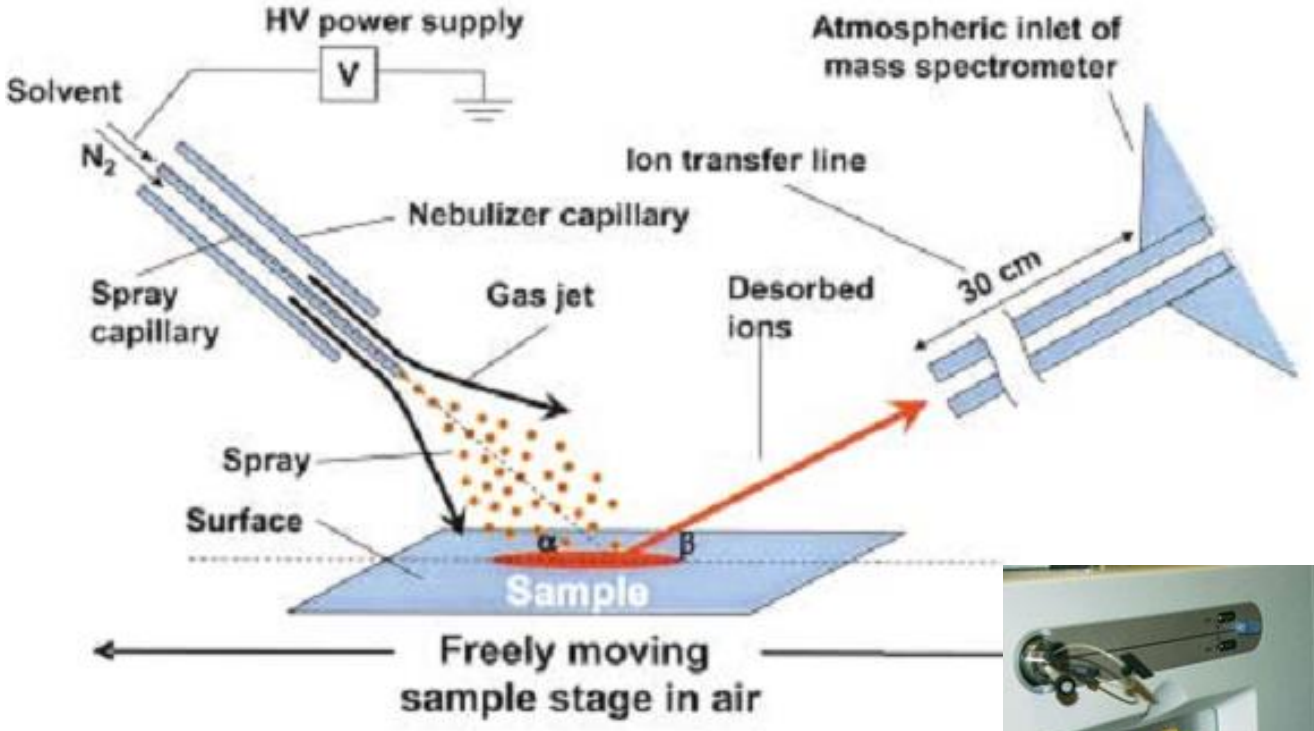
1. Analyte in solvent
2. Spray solvent towards the inlet of the mass spectrometer
3. Charged solvent droplets evaporate and intact charged macromolecule remain



Nobel Prize in Chemistry to John Bennett Fenn in 2002

Desorption Electrospray Ionisation

Z. Takats / R.G. Cooks, 2004



Advantage:
No sample preparation needed

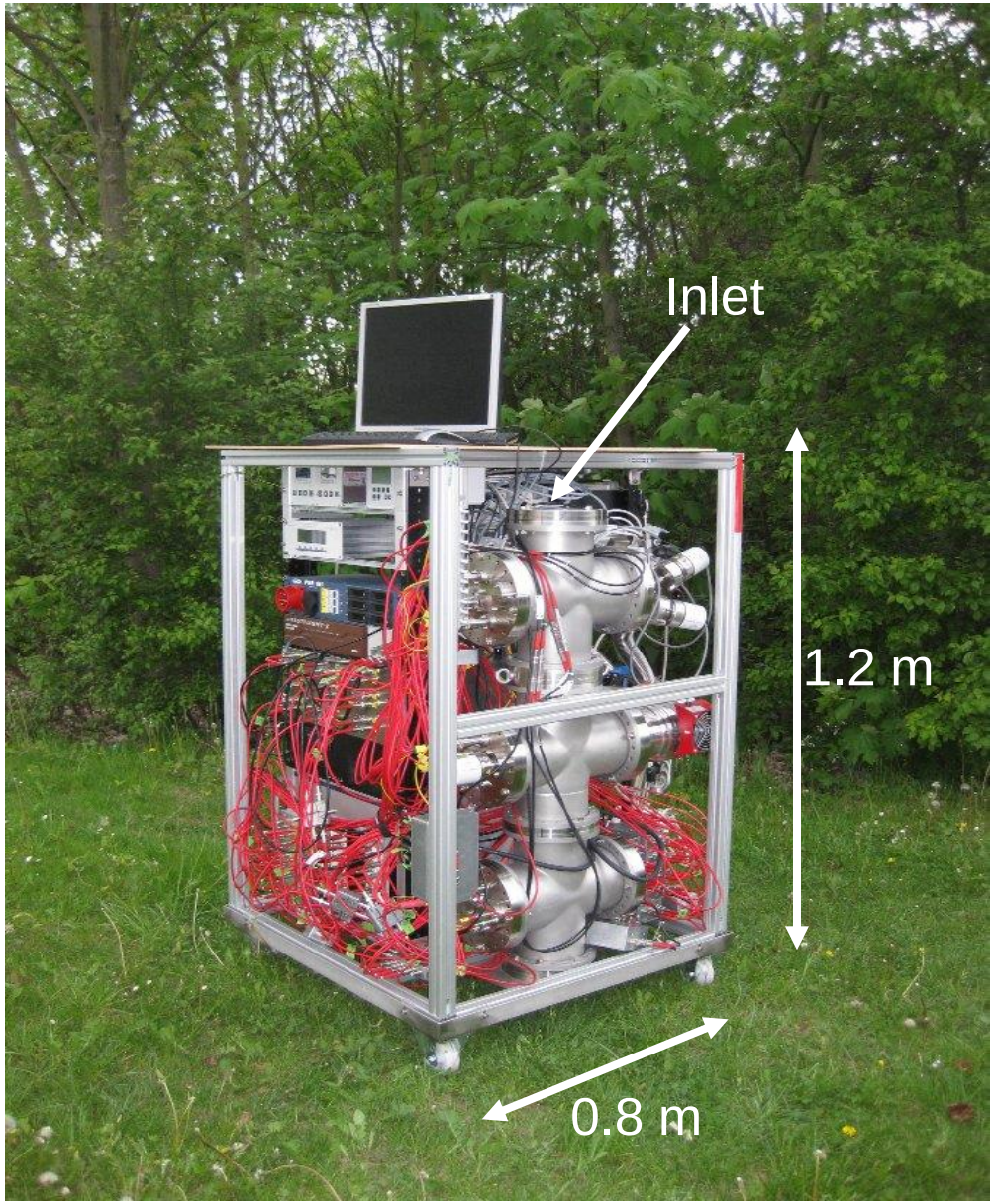
Mobile MR-TOF-MS for Analytical Mass Spectrometry

Design goals

- Mobile
- m/Δm > 100,000
- δm/m < 1 ppm
- Repetition rate ~ kHz
- Compatible with atmospheric ion sources

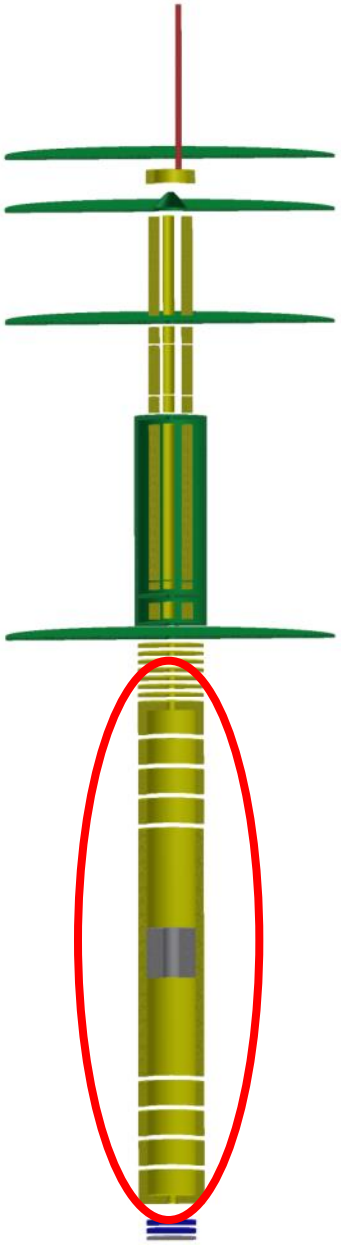
Rugged Setup

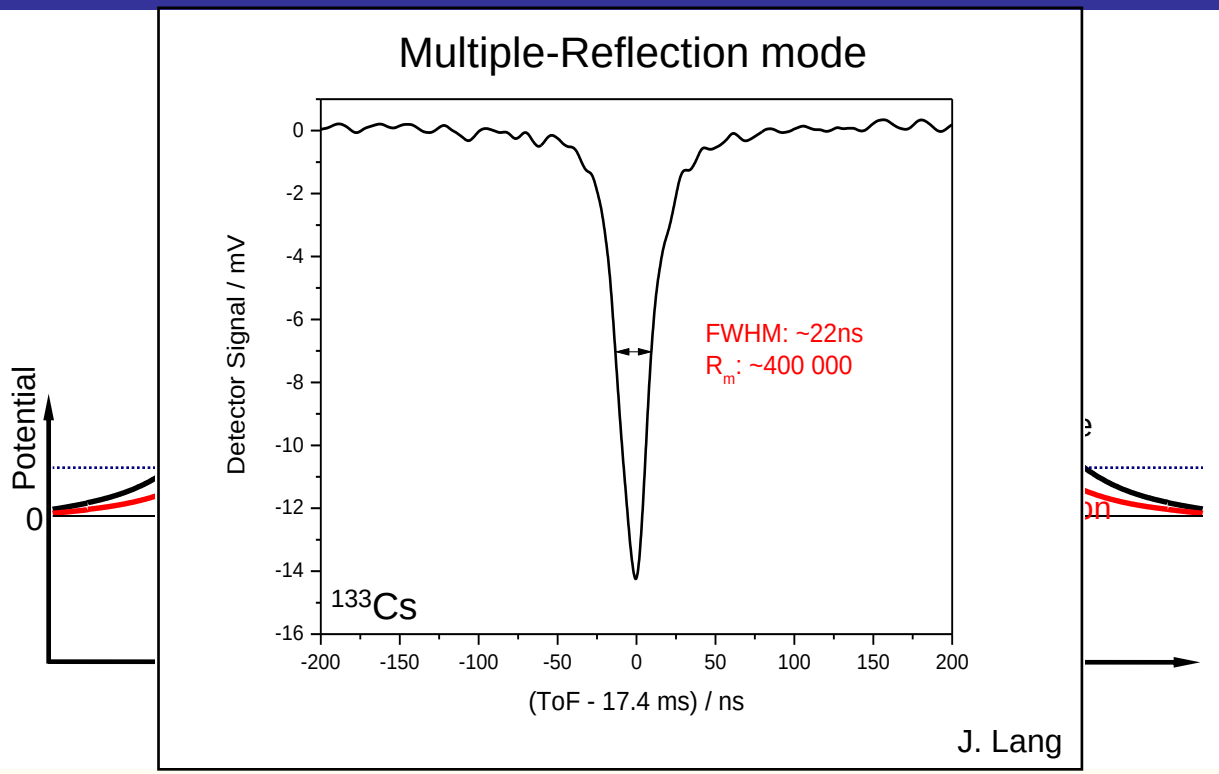
- 3 stacked DN150CF vacuum crosses as recipient
- 30 m^3/h rough pump integrated
- Volume ~ 0.8 m^3
- Weight ~200kg
- No further infrastructural needs except one power line

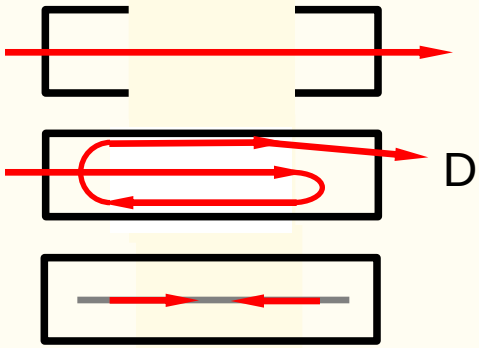


T. Dickel et al, *Nim B*, **317**, 779-784 (2013)
J. Lang, PhD thesis in preparation, JLU Gießen

Time-of-Flight Analyzer







Mode	Resolving Power	Mass Range m_{max}/m_{min} [1]
Linear	~100	" ∞ "
Dual-Reflection	>3000	~4.6
Multiple-Reflection	400.000	$\sim 1+\frac{1.6}{N}$

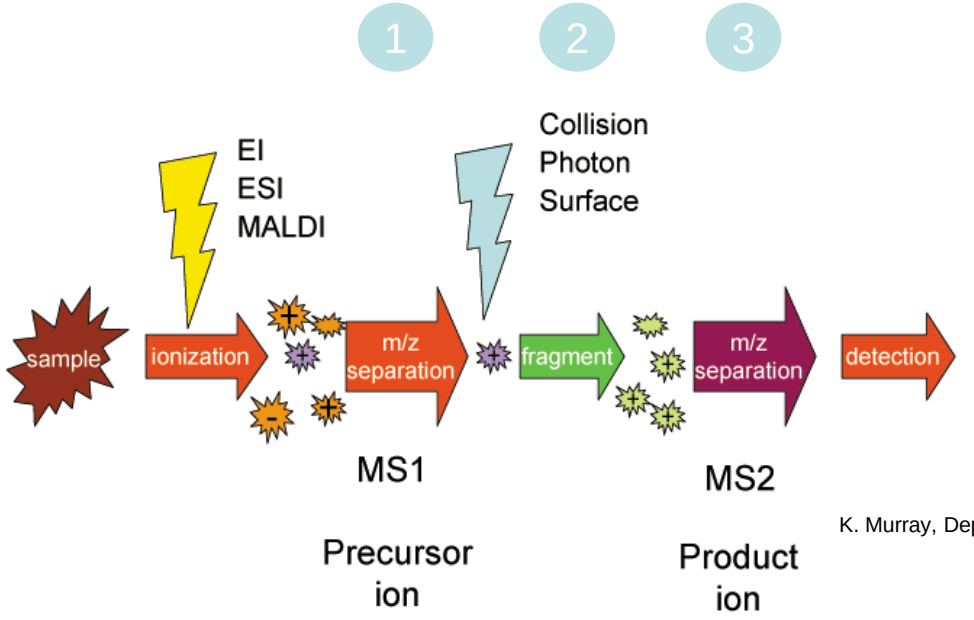
[1]M.I. Yavor, et al., Int. J. Mass Spectrom. (2015) in press, doi:10.1016/j.ijms.2015.01.002

Tandem Mass Spectrometry

Problem:

- Unambiguous identification of bio-molecules despite high mass multiplicity
- Structural information

Solution: Tandem-MS - two or more stages of mass analysis in space or time



K. Murray, Department of Chemistry, Louisiana State University
Baton Rouge, LA, USA

Advantages of MS^N with high resolving power in all steps:

→ no preseparation (GC, LC, IMS) neccessary

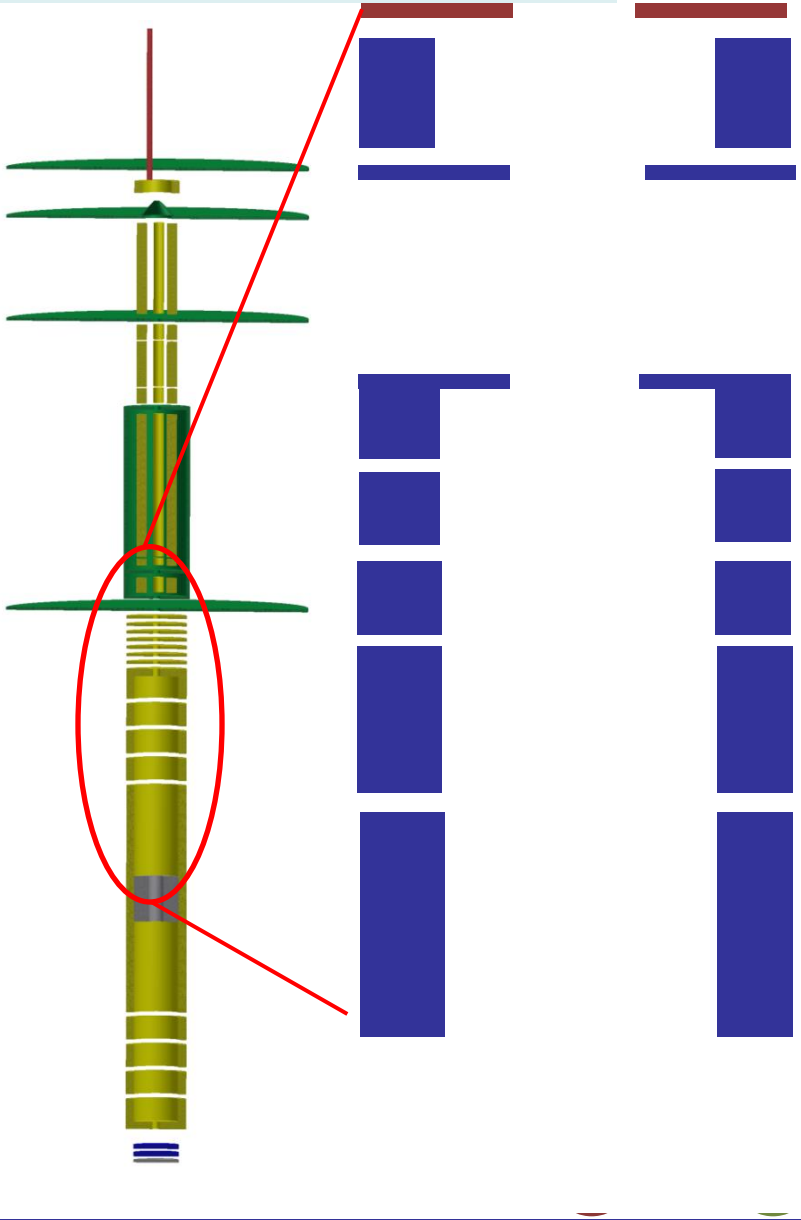
→ analysis of more complex mixtures

→ higher confidence in identification

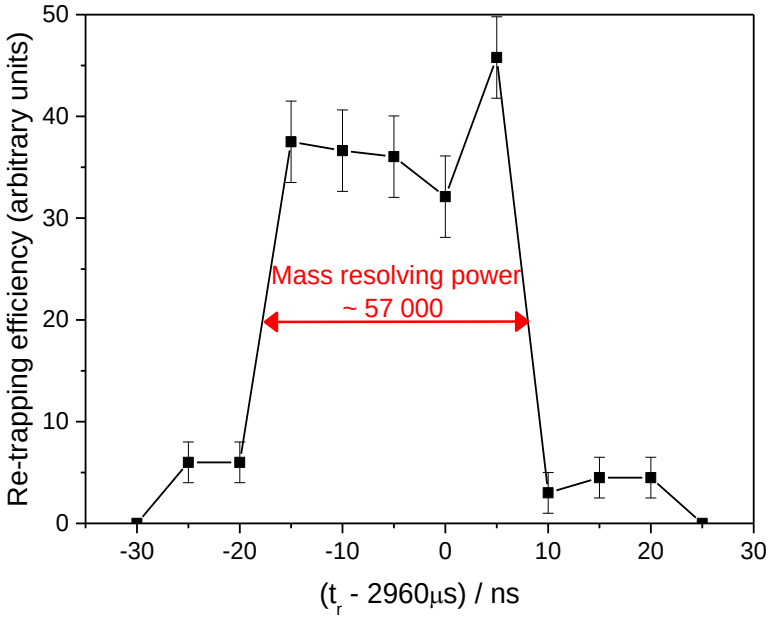
Ideal for In-situ analysis

Mass Selective Retrapping

1. Mass selective ion retrapping



1. Separate ions in time-of-flight
2. Inject ions back in RF-Trap
3. Close RF-Trap
   → only ions of interest are recaptured



J. Lang

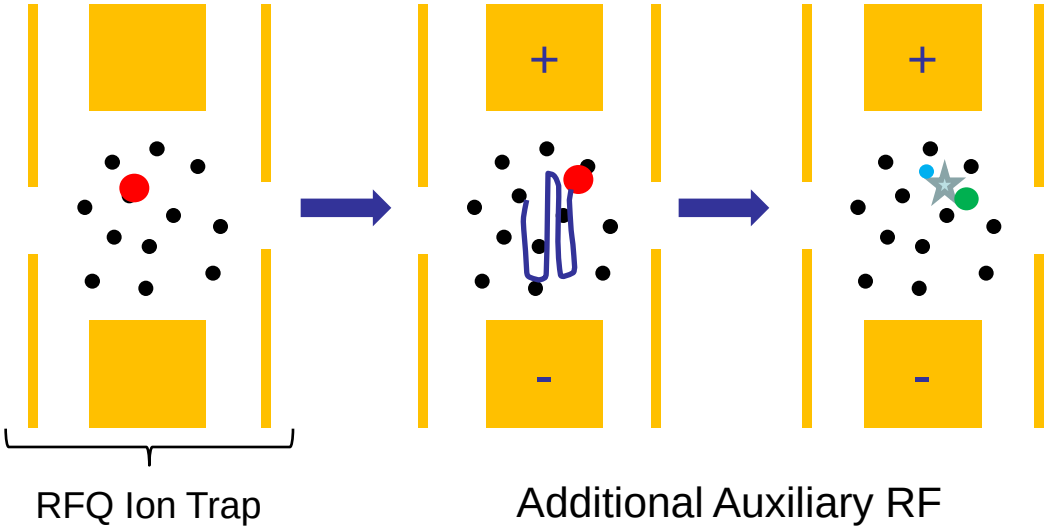
MR-TOF@TITAN
W.R. Plaß, Tu. 18:30

Collissional-Induced Dissociation

2. Collisional-induced dissociation in the ion trap

What is collisional-induced dissociation (CID)?

An ion/neutral species interaction wherein the projectile ion is dissociated as a result of interaction with a target neutral species.



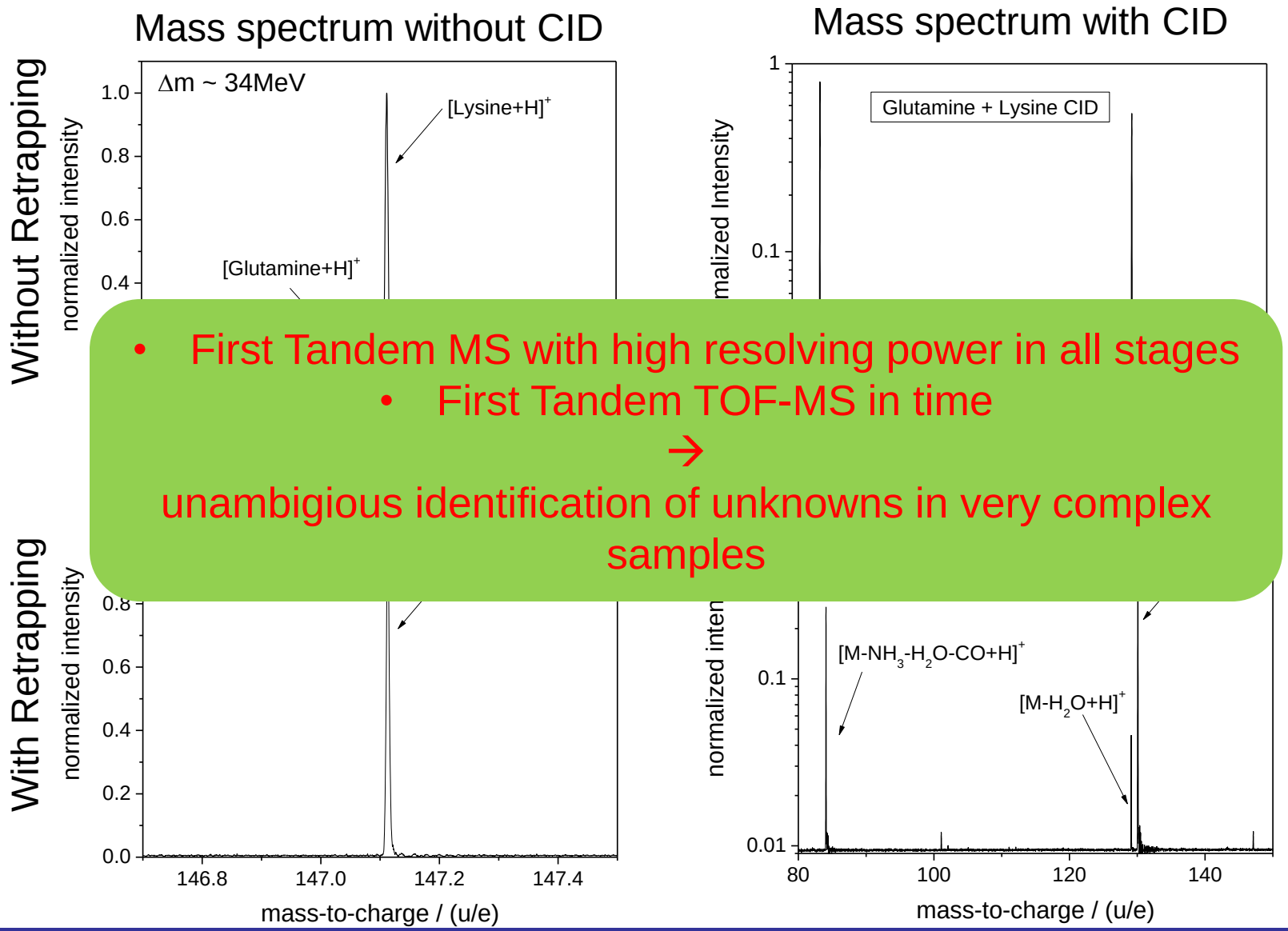
„Low-energy“ CID

Time scale	~ ms
Collision number:	10-100
Collision energy:	1-200eV

CID by resonant excitation in the ion trap

High Resolving Tandem Mass Spectrometry

1-3. Ion re-trapping → CID → mass analysis



- First Tandem MS with high resolving power in all stages
- First Tandem TOF-MS in time

→

unambigious identification of unknowns in very complex samples

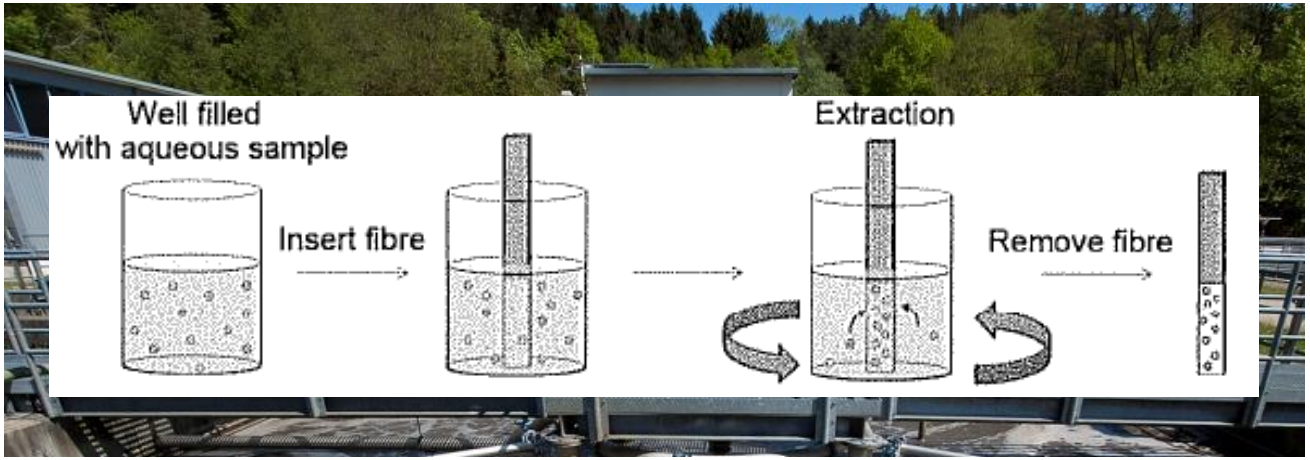
W. Lippert

Application I: Water-Monitoring at “Hot Spots”

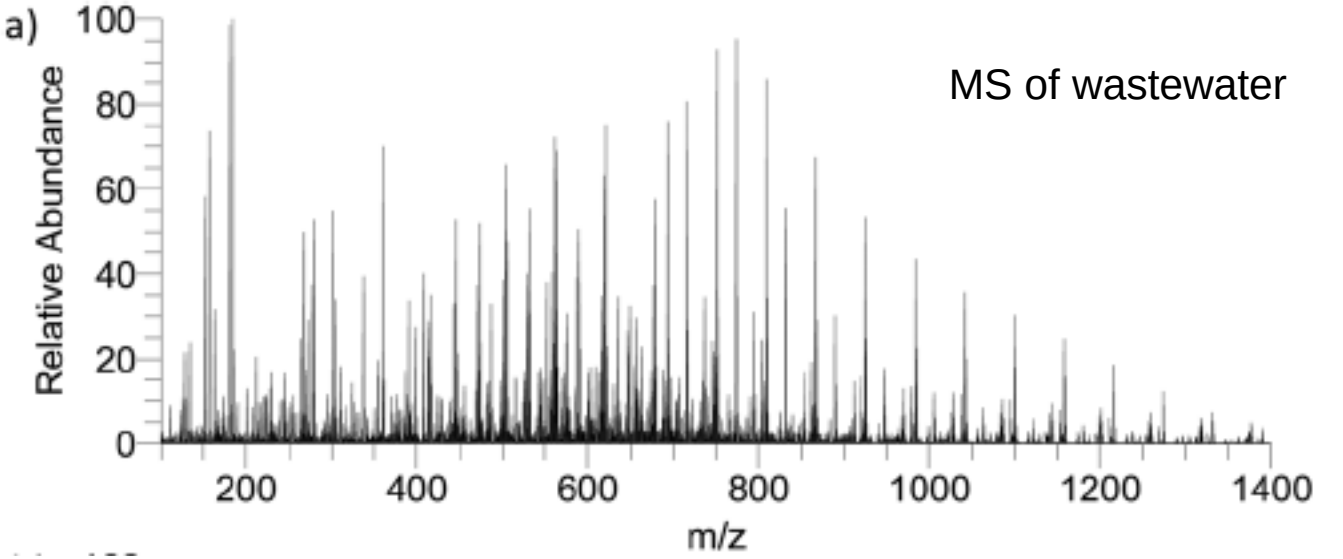
Check and monitor wastewater for pharmaceuticals (eg. Carbamazepine) and antibacterial agents (eg. Triclosan)

Two-step process:

1.
Enrichment of analyte by thin-film microextraction



2.
Sample analysis by high resolution DESI-MS



MS of wastewater

R. Düring, et al, Analyst, 2012, 137, 4037

Application II: Real-time Tissue Recognition

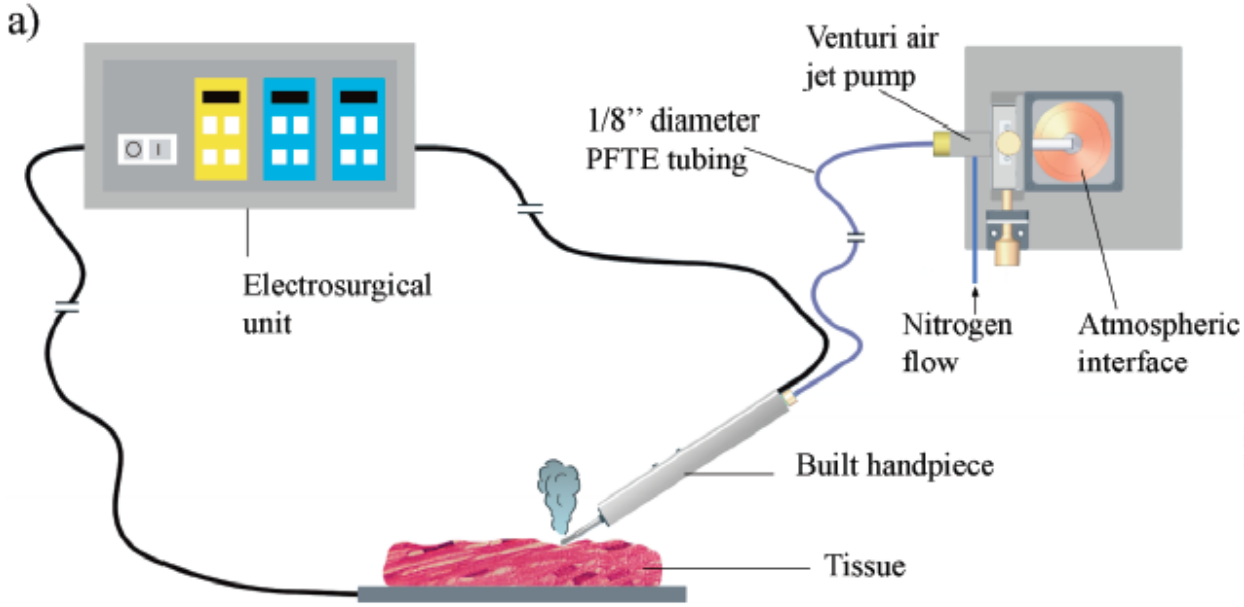
Problem:

- Histological examination of tissue is slow (hours)

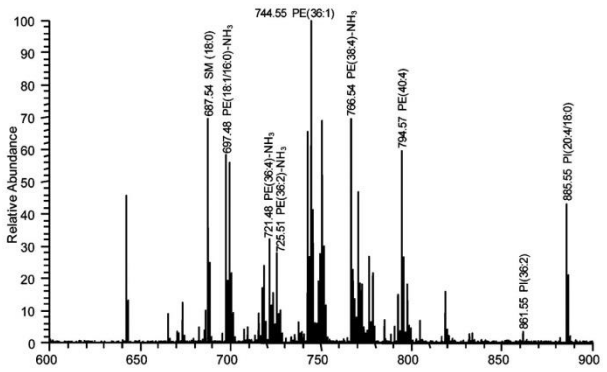
Solution:

Rapid Evaporative Ionization Mass Spectrometry (*REIMS*)

Identification of healthy and cancerous tissue in less than a second by the mass spectra



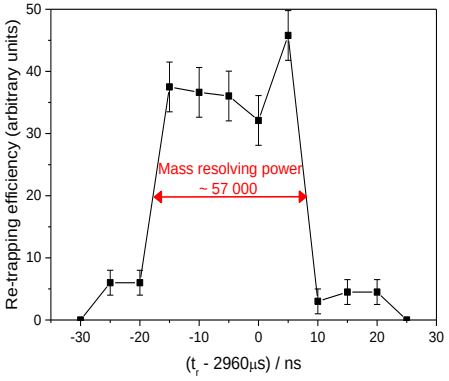
Vapor generated by a electrosurgery is pumped to API of mass spectrometer



Z. Takats, et al., Anal. Chem. 2010, 82, 7343-7350

Summary

- Motivation: High-resolution in-situ mass spectrometry
  Method: Mobile MR-TOF-MS
- Device has been developed and commissioned
  - $m/\Delta m = 4*10^5$
  - Atmospheric Pressure Inlet with various ionization techniques
- Highly resolving Tandem MS
  Mass selective Retrapping + CID
  → MS^N with high resolution $>10^4$ in all steps



- in-situ applications planned
  eg. Wastewater monitoring
- Next generation device: portable
  - Replace standard components by customized components
    → further saving in size, weight, power consumption, ...
- Future applications:
  - Space missions

Acknowledgments

IONAS Group at JLU Gießen

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