

TOFWERK

Vocus PTR-TOF

Real-time VOC Analysis with Market Leading Performance

Chemical analysis by mass spectrometry

- **Mass spectrometry measures the mass-to-charge ratio (m/Q) of gas-phase ions**
- **Analysis of ions by mass spectrometry enables identification and quantification**
- **Neutral molecules must be converted to ions, which requires a controlled ionization step to charge them in a quantitative manner**
- **Proton Transfer Reaction (PTR) is one such chemical ionization method that ionizes many classes of compounds**

PTR-MS is an established technique for sensitive, on-line VOC detection

PTR-MS

VOCUS PTR-TOF Combines Three Powerful TOFWERK Technologies

- Proprietary "VOCUS" ion source design
- High performance API-TOF platform
- Acquisition and analysis software suites

The Result

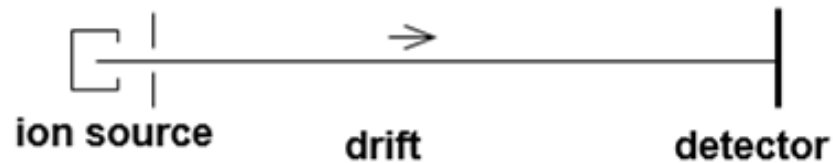
- Market leading sensitivity and speed
- Separate isobars in complex mixture with highest available mass resolving power
- Robust instrument for demanding lab or field
- Powerful, easy-to-use workflows



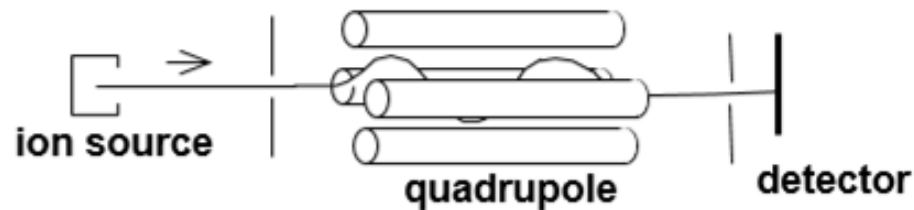
Selecting the right mass analyzer

- Mass analyzers apply electric and/or magnetic fields to ions in vacuum
- Resultant motion of ions depends on the ions mass/charge
- PTR-MS most commonly uses either **quadrupole** or **time-of-flight (TOF)** mass analyzers

Time-of-Flight (TOF)

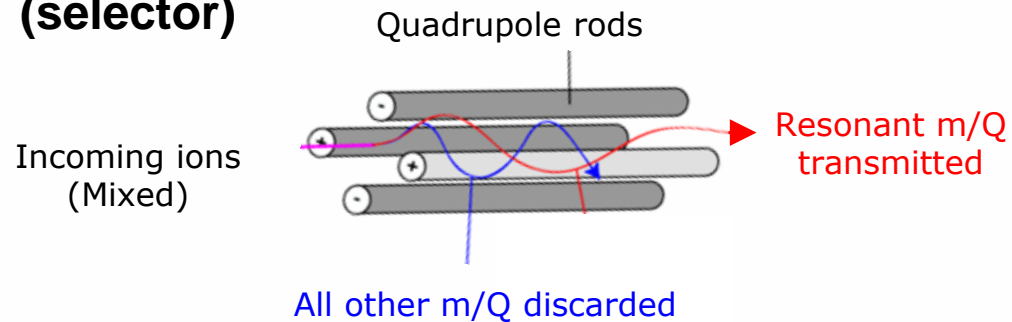


Quadrupole (Quad)



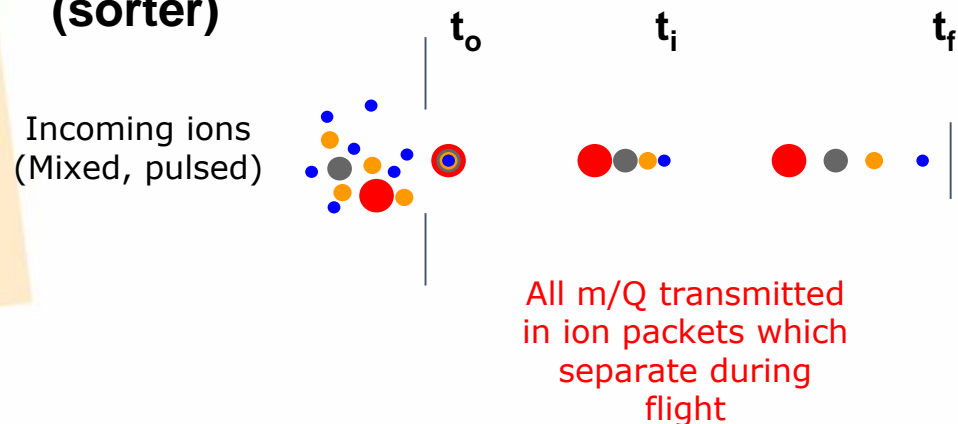
Selecting the right mass analyzer

Quadrupole (selector)



- Measures only one m/Q at a time
- Slow to measure complete spectrum (scan)
- Typically unit mass resolution
- Poor duty cycle when many ions are monitored

TOF (sorter)

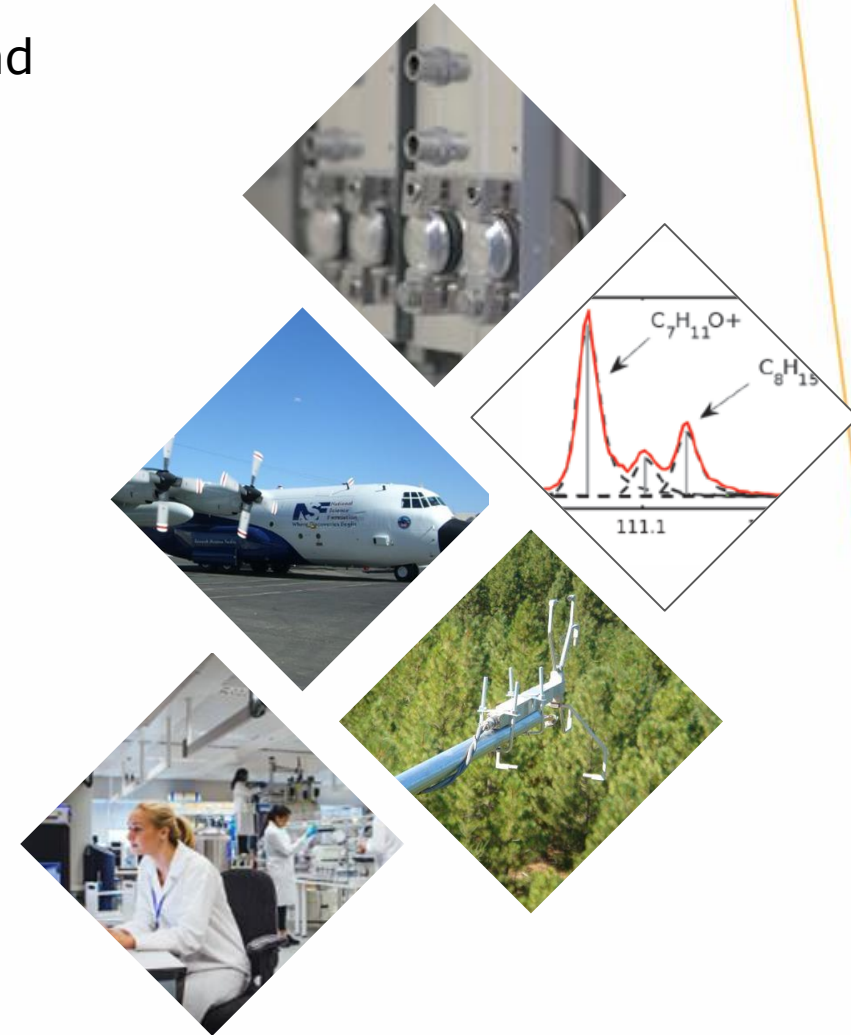


- Measure entire mass spectrum simultaneously
- TOF is fast: >40,000 unique spectra per second
- TOF can have high resolving power (M/dM) and good mass accuracy allowing
 - Separation of isobars
 - Elemental analysis allows identification of unknowns

Tofwerk is a global provider of TOF

TOF Technology

- Over **400** mass spectrometers delivered and supported around the world
- Family of end-user products and custom designs for OEM and research
- Broad range of designs, collaborations, and applications
- Expertise in field-deployable instrumentation
 - 15 year collaboration with Aerodyne Research in atmospheric science field
 - We uniquely bring laboratory performance to mobile platforms and difficult environments
 - Demands robust and reliable instruments



History of PTR-TOF at TOFWERK

PTR-TOF

- **2002 World's first PTR-TOF.** TOFWERK partners with University of Innsbruck to demonstrate the advantages of TOF for PTR-MS.
- **2005-2016 TOFWERK is OEM provider of TOF technology to Ionicon.** TOFWERK delivers TOFs for research and academic labs, and leads development of new interfaces to improve sensitivity and resolution (e.g. Qi-TOF interface).
- **2017 End of OEM Partnership.** Ionicon shifts strategy and releases new product line without TOFWERK TOFs.
- **2017 VOCUS Released.** TOFWERK patents Vocus drift tube design and ion source. Vocus PTR-TOF is launched with market leading sensitivity and resolving power.



VOCUS PTR-TOF built on field proven platform

PTR-TOF



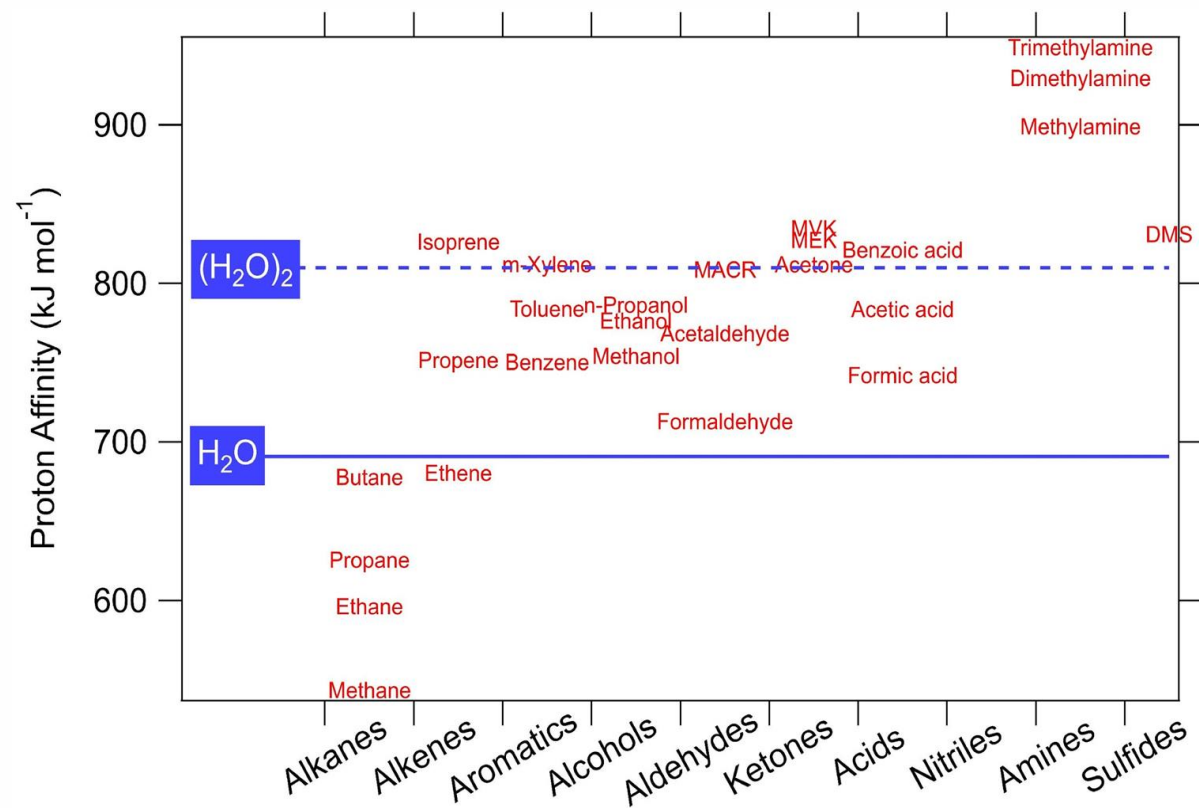
API-TOF

- API-TOF is a core TOFWERK product, compatible with many ion sources including VOCUS
- Deployed for field measurements on mobile labs and to research stations on every continent
- Compact, robust design, optimized for low power consumption and weight without sacrificing performance
- Key role in 100+ scientific publications, including numerous ***Nature*** and ***Science*** articles

PTR ionization efficiency depends on proton affinity



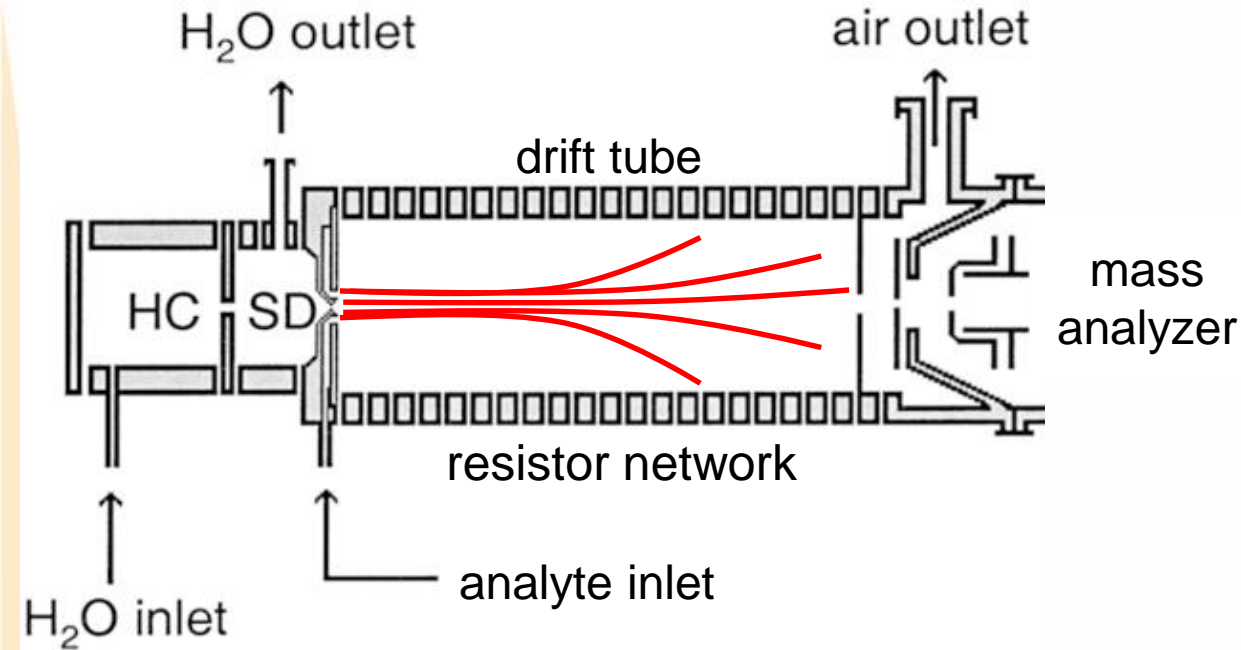
- **Transfer proton to R, Detect (R)H⁺**
- **Reaction occurs** if R has higher proton affinity than reagent ion [H₃O⁺ or (H₂O)H₃O⁺]
- **Exothermic and fast for**
 - Most alkenes
 - Aromatics
 - Most functional groups



Proton transfer occurs

No Reaction

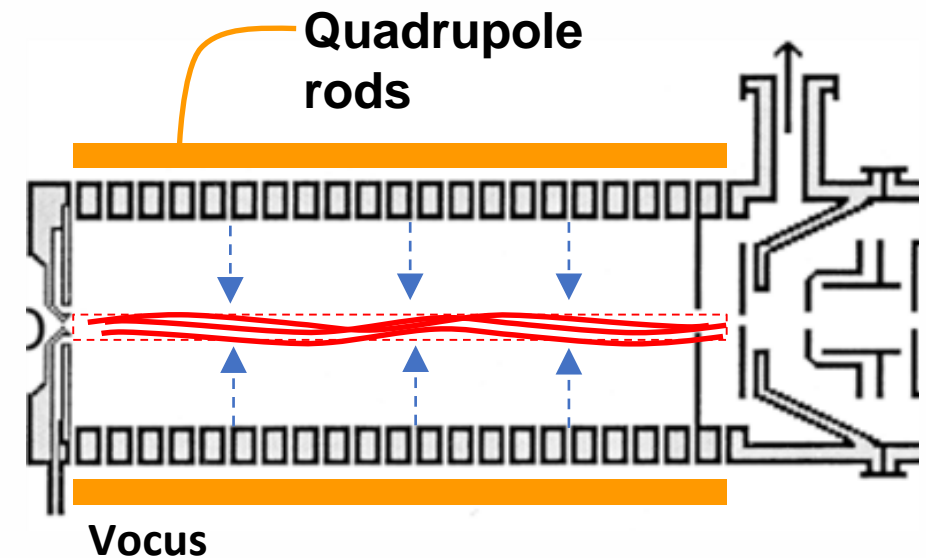
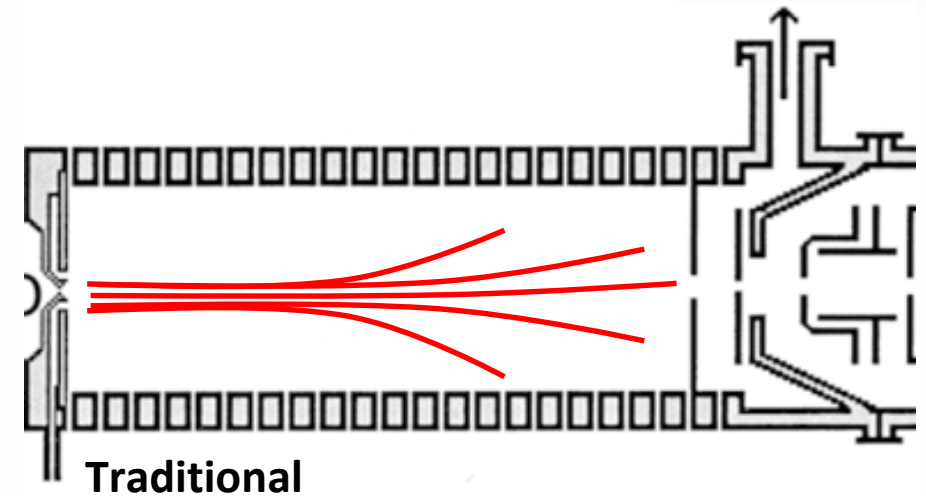
Traditional PTR Drift Tube



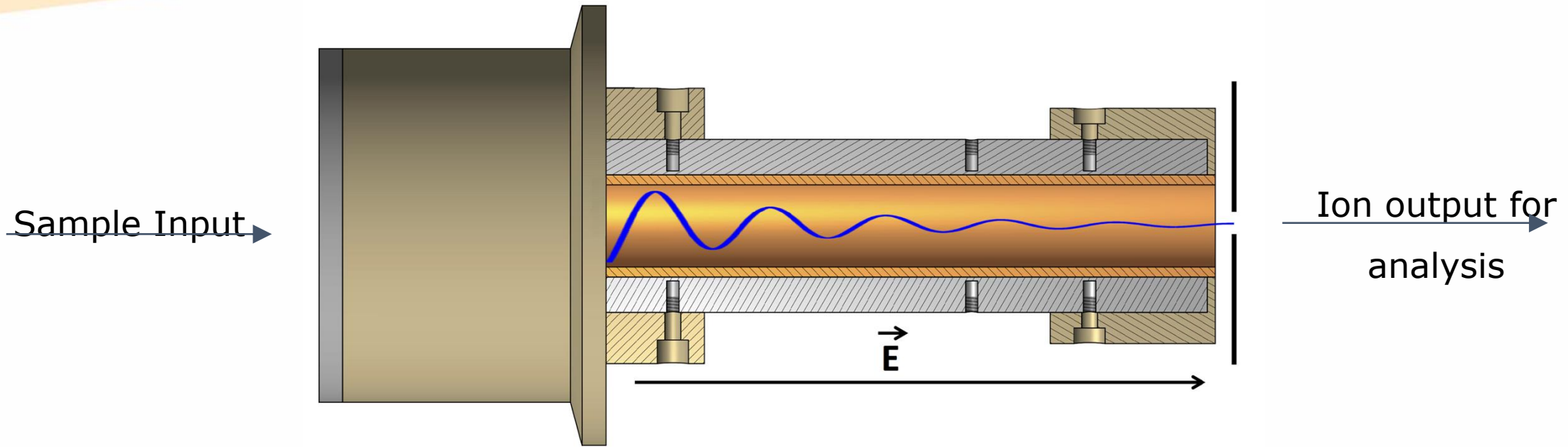
- **Low pressure** (1-3 mbar)
- **Linear electrostatic field** set by resistive network
 - Controlled cluster distribution
 - Fixed electrostatic reaction time
- Hollow cathode is **bright primary ion source**
- **Sample introduction** via a long, low pressure capillary with **unwanted wall interactions**
- **Scattering and diffusion of ions limits overall reactor efficiency**

The VOCUS concept

- **Maintain key features of traditional PTR drift cell**
 - Reaction conditions, parameterized calibration
 - Compact reactor with reduced pumping requirements
- **Superimpose RF fields on top of traditional linear field to increase sensitivity**
 - Focus ions into a beam for efficient sampling at exit orifice
 - Reduce reagent and product ion wall losses
 - **Not possible with traditional reactor design**



VOCUS PTR reaction cell (patented)



- **Use of resistive glass drift tube** (orange), rather than traditional lens stack, yields more uniform drift field.
- **Resistance of glass chosen to pass focusing RF field, but also allow the axial DC field**
- **The result: Sensitivity boost** by optimum product ion focusing and elimination of ion losses

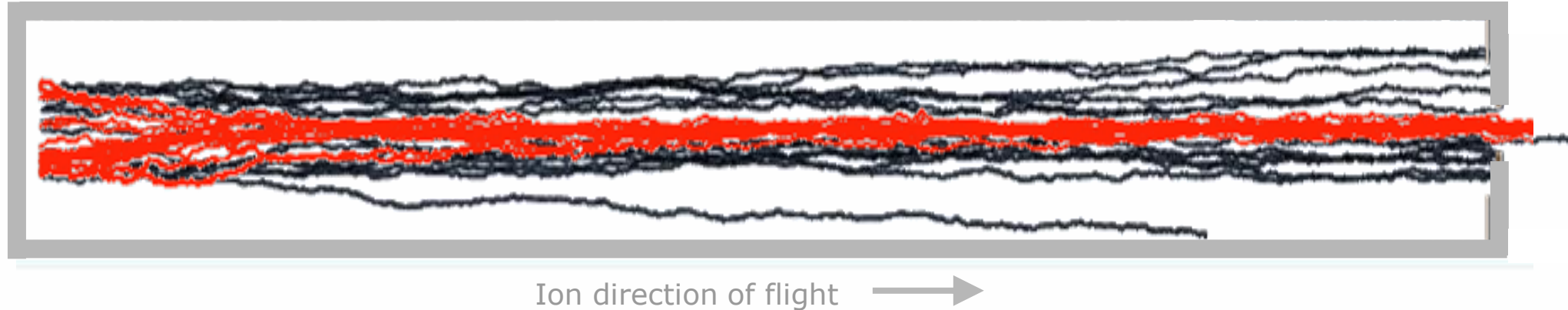
Modeling the effect of RF ion trajectories

VOCUS

DC only (Drift tube)

RF + DC (VOCUS)

Ion Injection
→



- SIMION modeling shows simulated ion trajectories during transit through a PTR reactor **with** and **without** RF added to the axial (DC) field.
- **Scattering and diffusion can be overcome with addition of RF field**, resulting in significant improvement of ion transmission exiting the reactor
- **This improved “transmission efficiency” directly results in higher sensitivity**

VOCUS PTR-TOF coupling

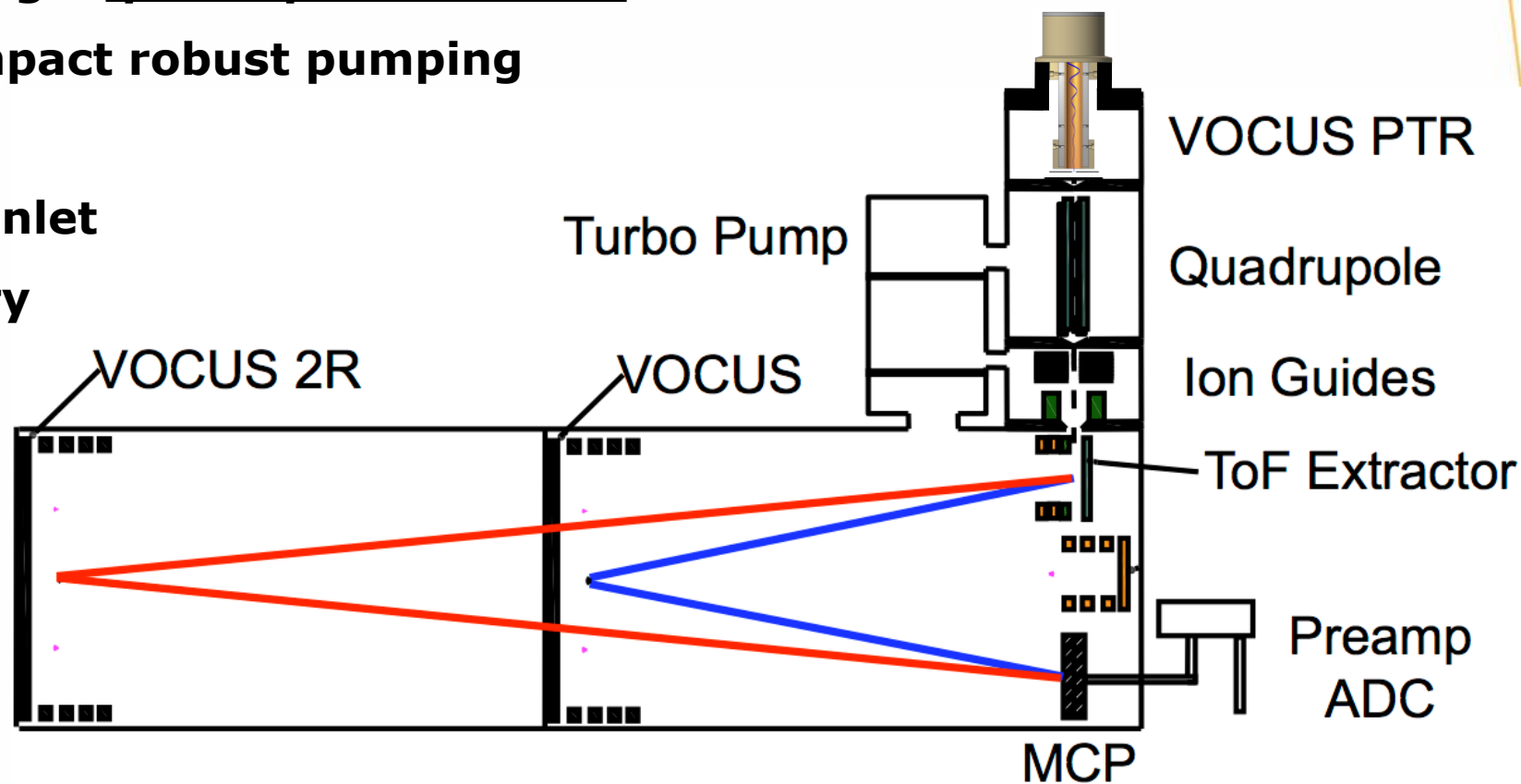
VOCUS

- **VOCUS reactor can be coupled to any TOFWERK TOF platform (C, Standard, 2R)**
- **Efficient ion analysis using a quadrupole interface**
- Custom turbopump for **compact robust pumping**
- Efficient VOC sampling

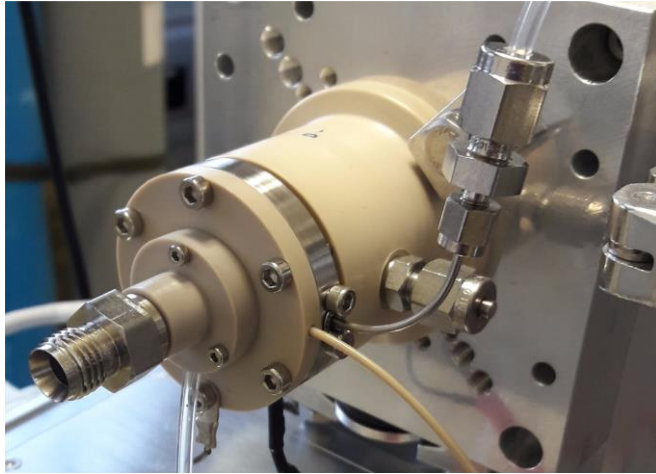
laminar core sampling inlet

heated transfer capillary

autosamplers



Vocus PTR-TOF configuration



- All components mounted inside rugged enclosure
- **Automatic internal zero and calibration** measurement
- Common axial inlet plate provides **adaptable inlet interface** for various sample flow rates and couplings

Vocus 2R

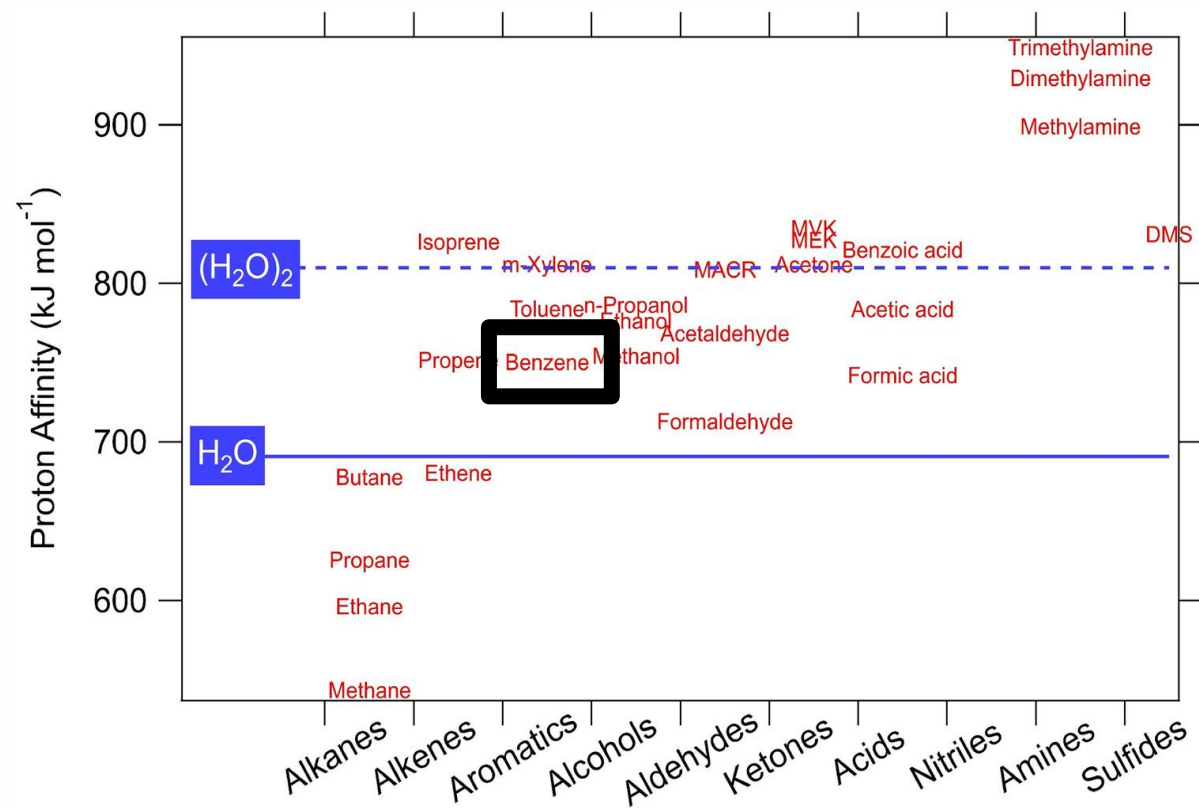


Volume: 0.45 m³
Mass: 160 kg

PTR ionization efficiency depends on proton affinity



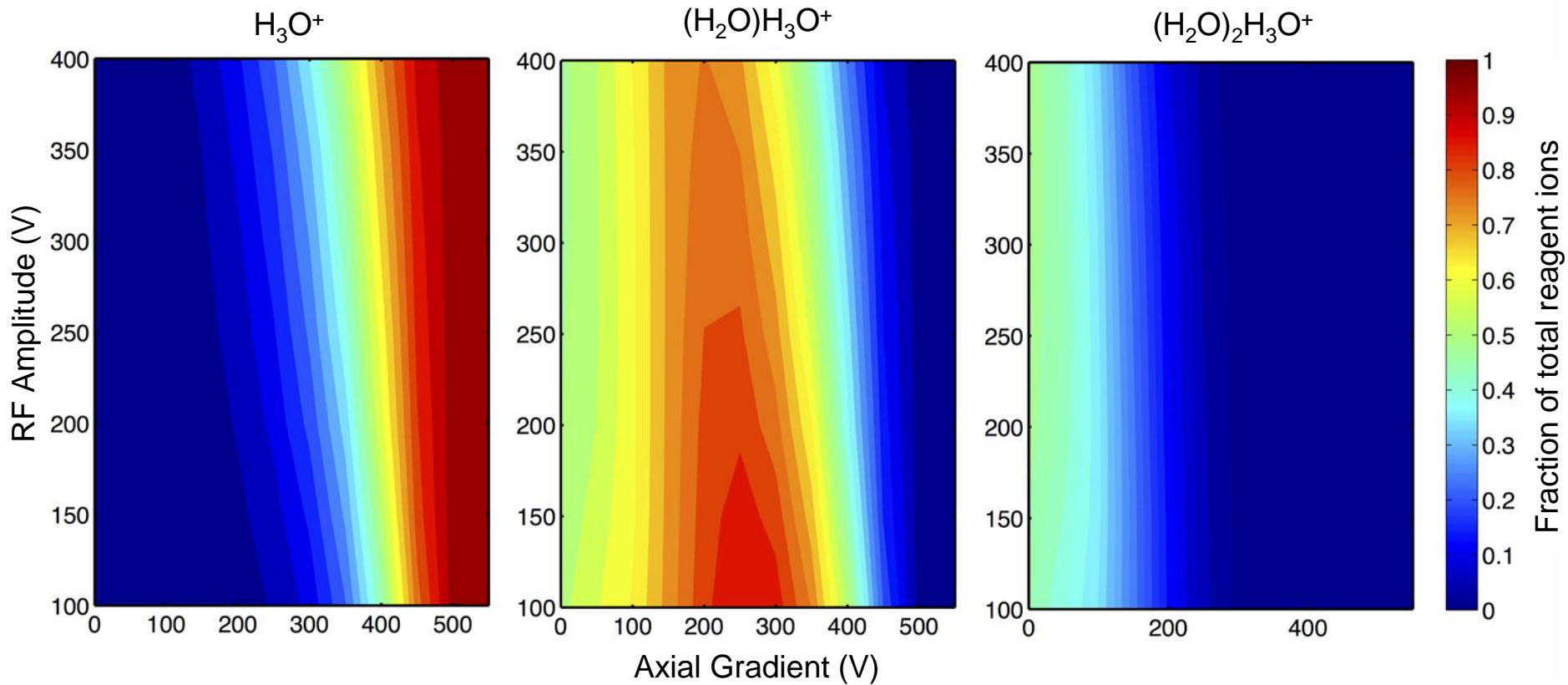
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No Reaction

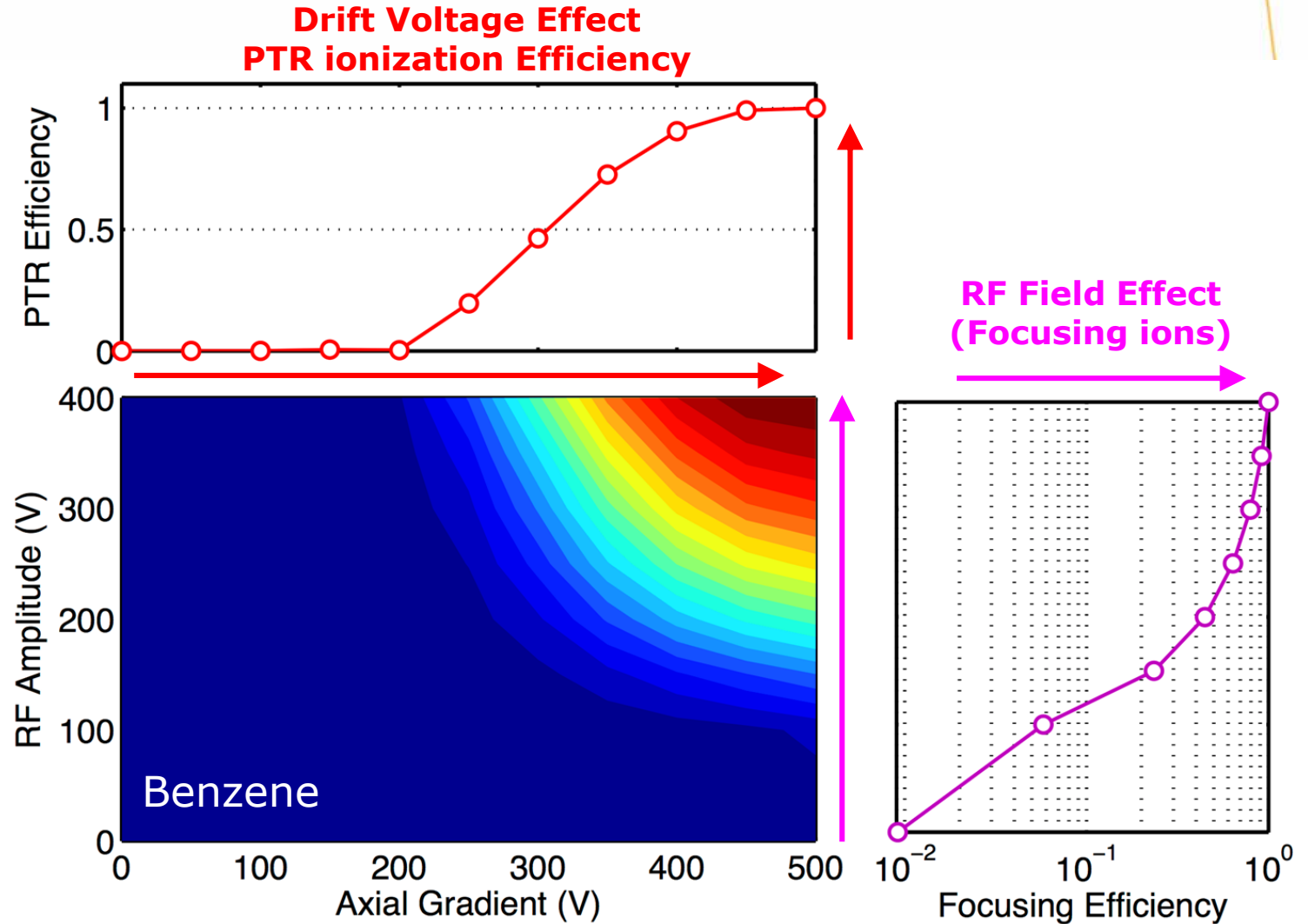
VOCUS reagent ions controlled with DC field



- **Sensitivity and selectivity depends on cluster distribution in the reaction cell** (ionization efficiency)
- **VOCUS DC field drives declustering** (RF has secondary effect) i.e. colors change primarily along horizontal axis (vertical organization)

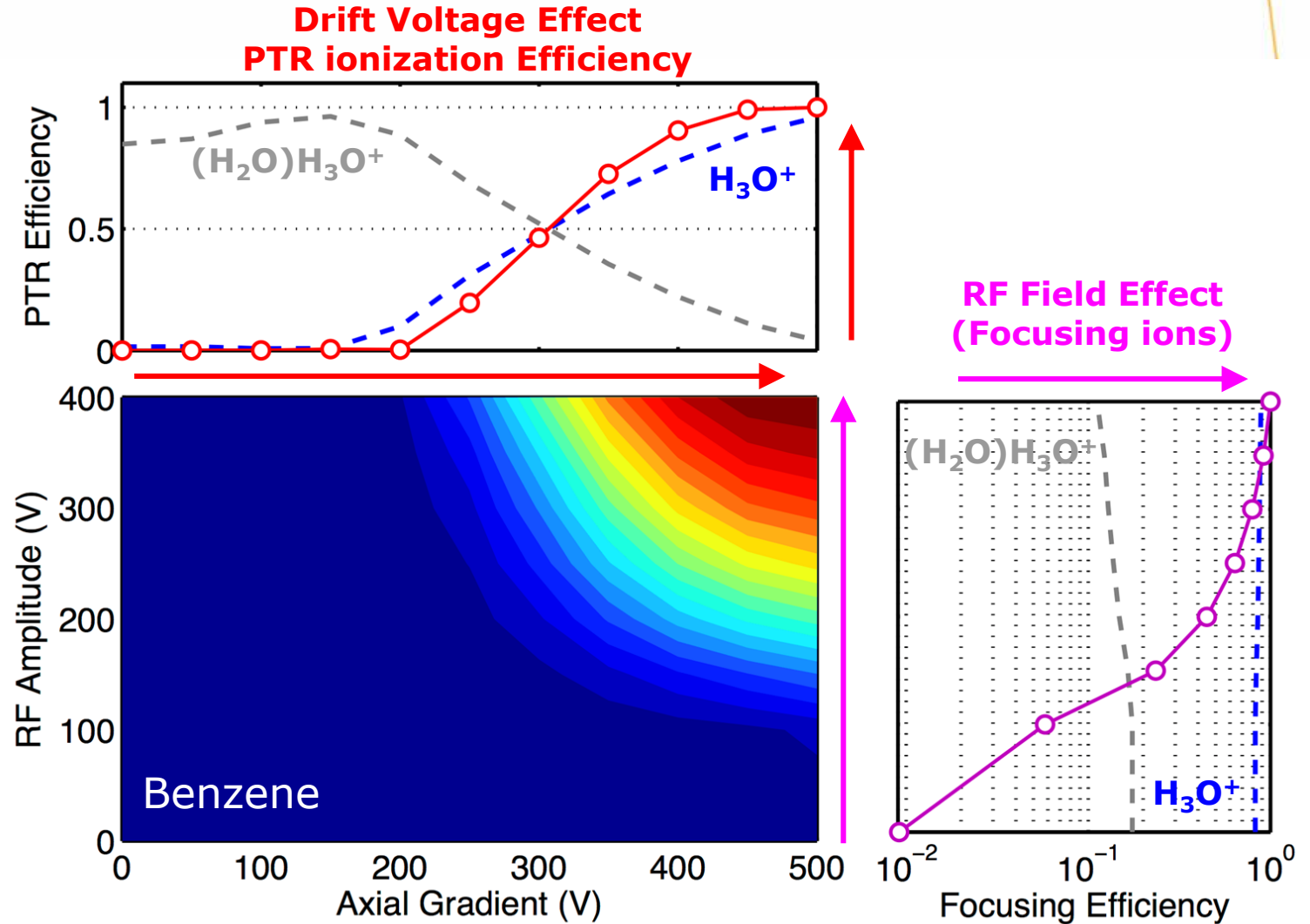
Vocus RF field drastically improves sensitivity

- Measured benzene sensitivity as function of DC and RF voltages (colormap)
- **The Vocus RF field results in nearly 100x increase in sensitivity compared to RF off**
- Conventional drift cell has RF=0 and has reduced sensitivity due to combined effects of wall loss and reduced sampling efficiency at the end of the drift cell



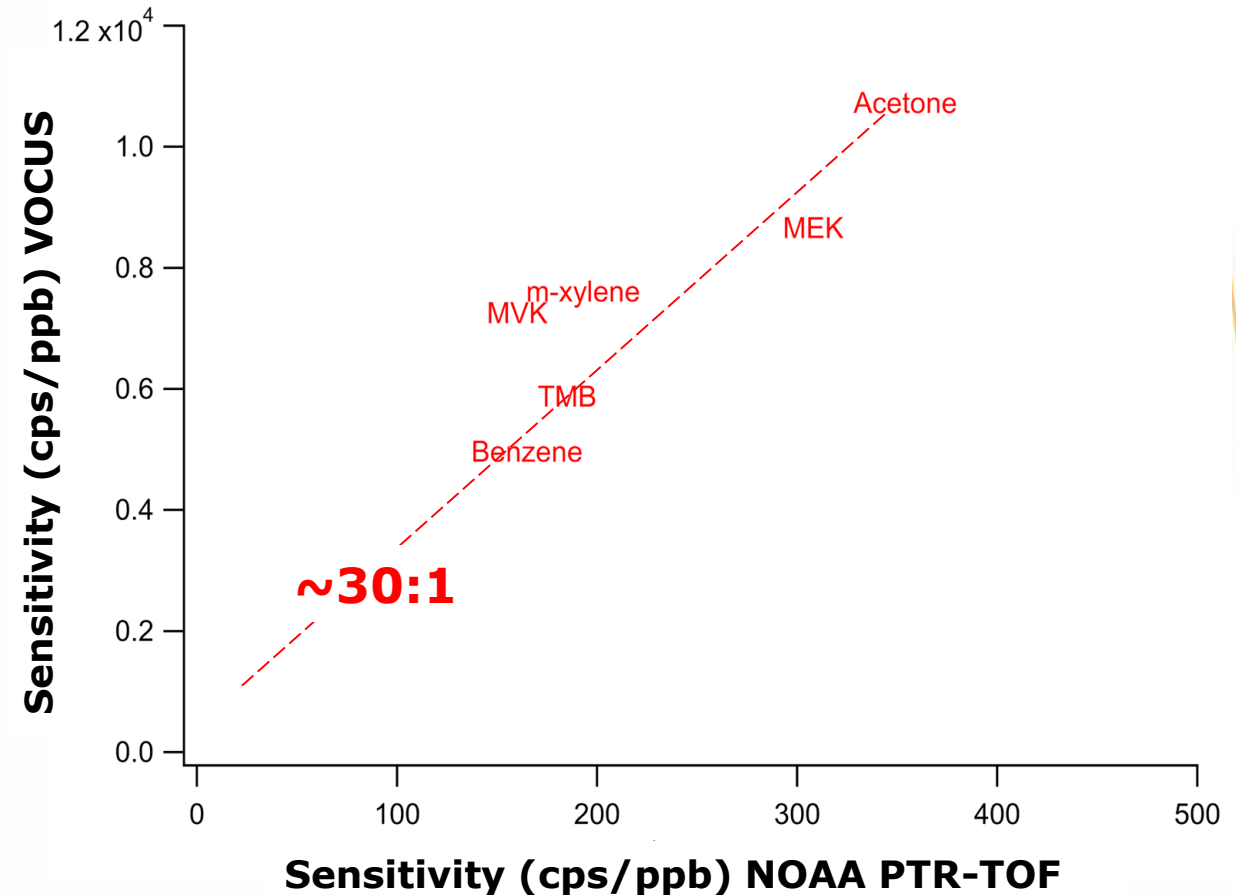
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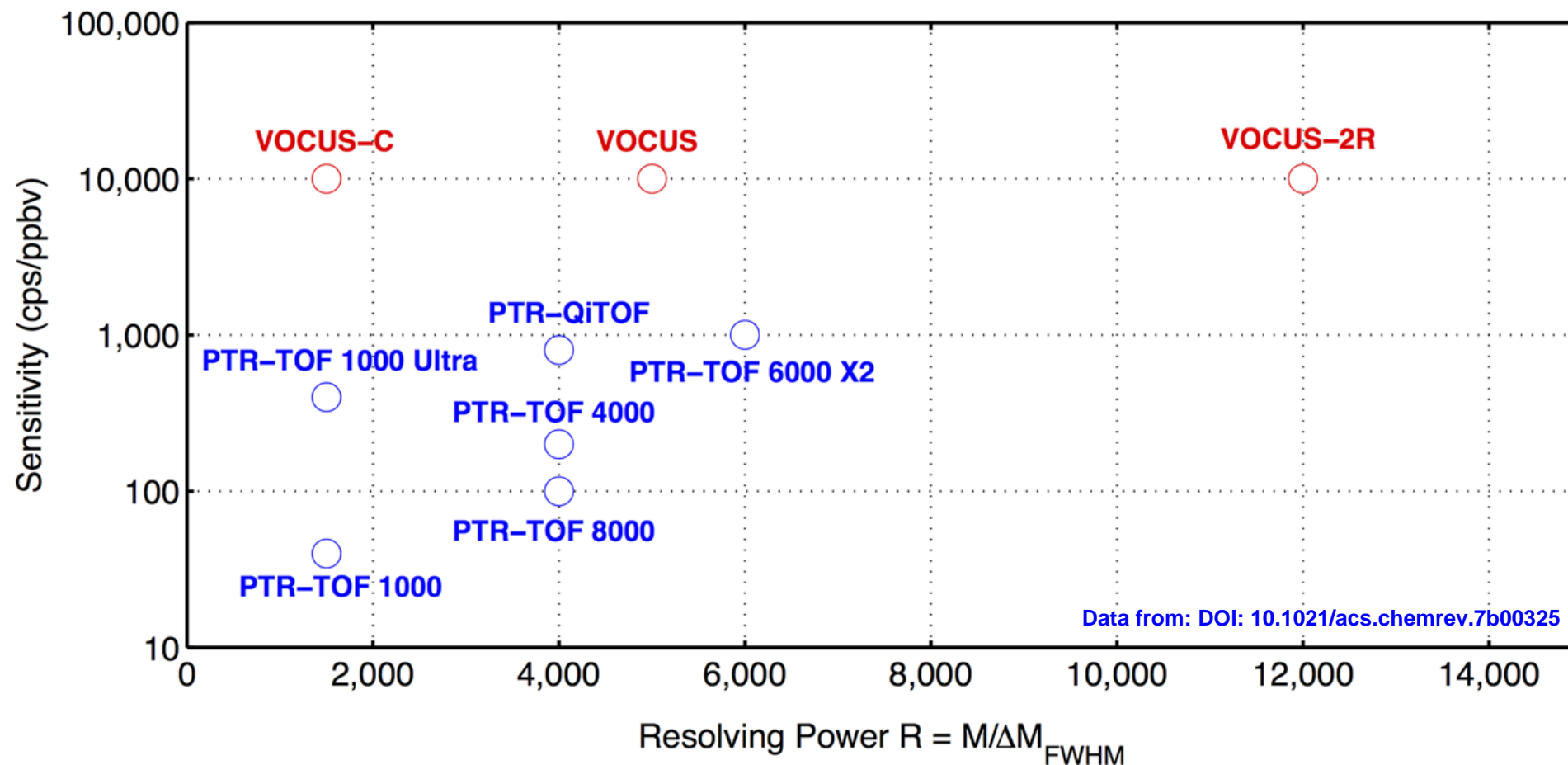
Standard PTR response, with order of magnitude higher sensitivity

- **~30x** improvement in sensitivity compared to state-of-the-art PTR-TOF instrument
- VOCUS still operates under traditional PTR conditions allowing sensitivity calculation to be utilized
- NOAA sensitivities from *Atmos. Meas. Tech.*, 9, 2735–2752, 2016



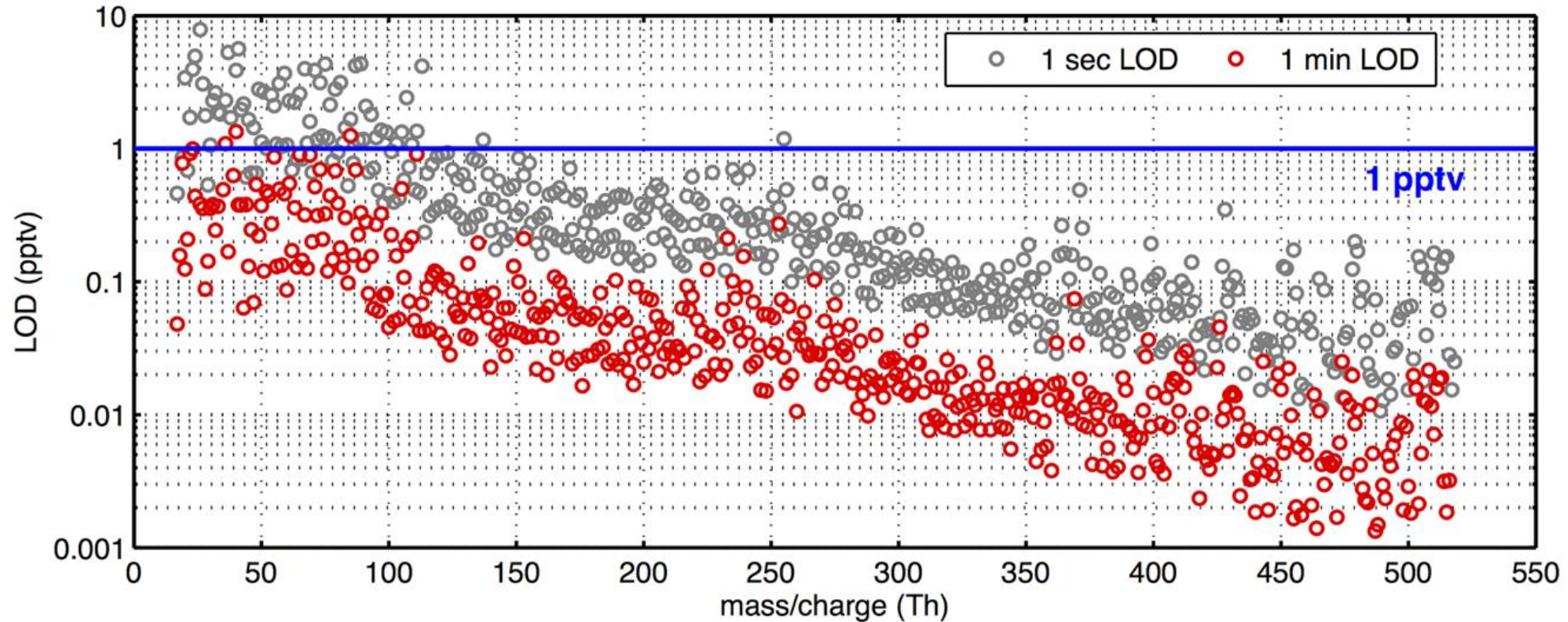
PTR-TOF performance map

VOCUS



- **VOCUS product line provides sensitivity and resolution which are unmatched by other commercially available PTR instruments.**

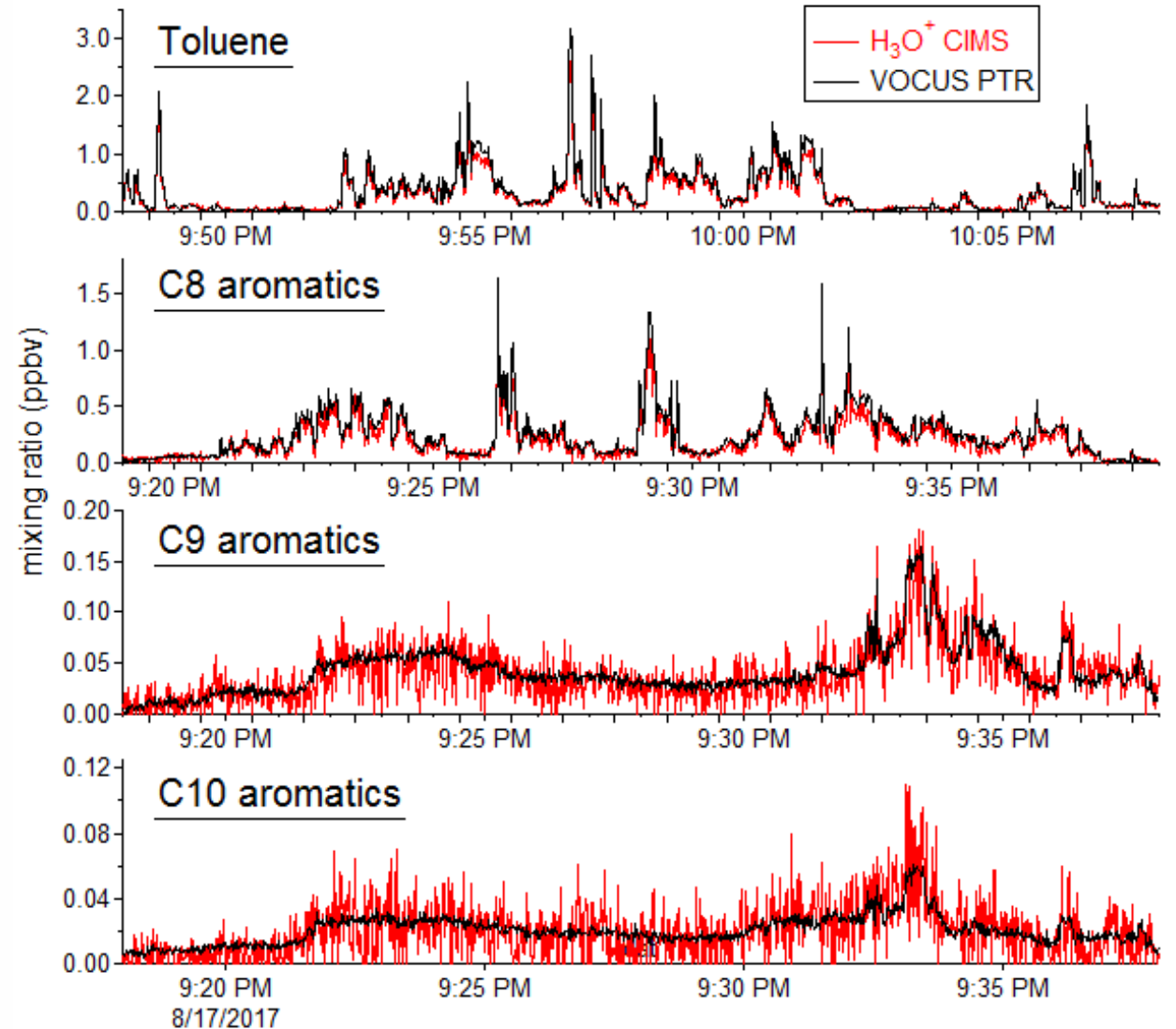
Achieve sub ppt level of detection in seconds.



- 3 times the standard deviation of a background measurement assuming the benzene sensitivity for the whole mass spectrum
- Background limited at low m/Q – counting statistics dominates at higher mass

VOCUS sensitivity results in better signal to noise, faster.

- 1 Hz, sampling of ambient air in Boulder, Colorado, USA showing quantitative response
- Side-by-side sampling with the NOAA PTR-TOF (**red**), VOCUS (**black**)
 - Data courtesy of Carsten Warneke, Joost DeGouw, Abby Koss
- **The sensitivity of VOCUS yields better precision faster, especially at low concentrations.**

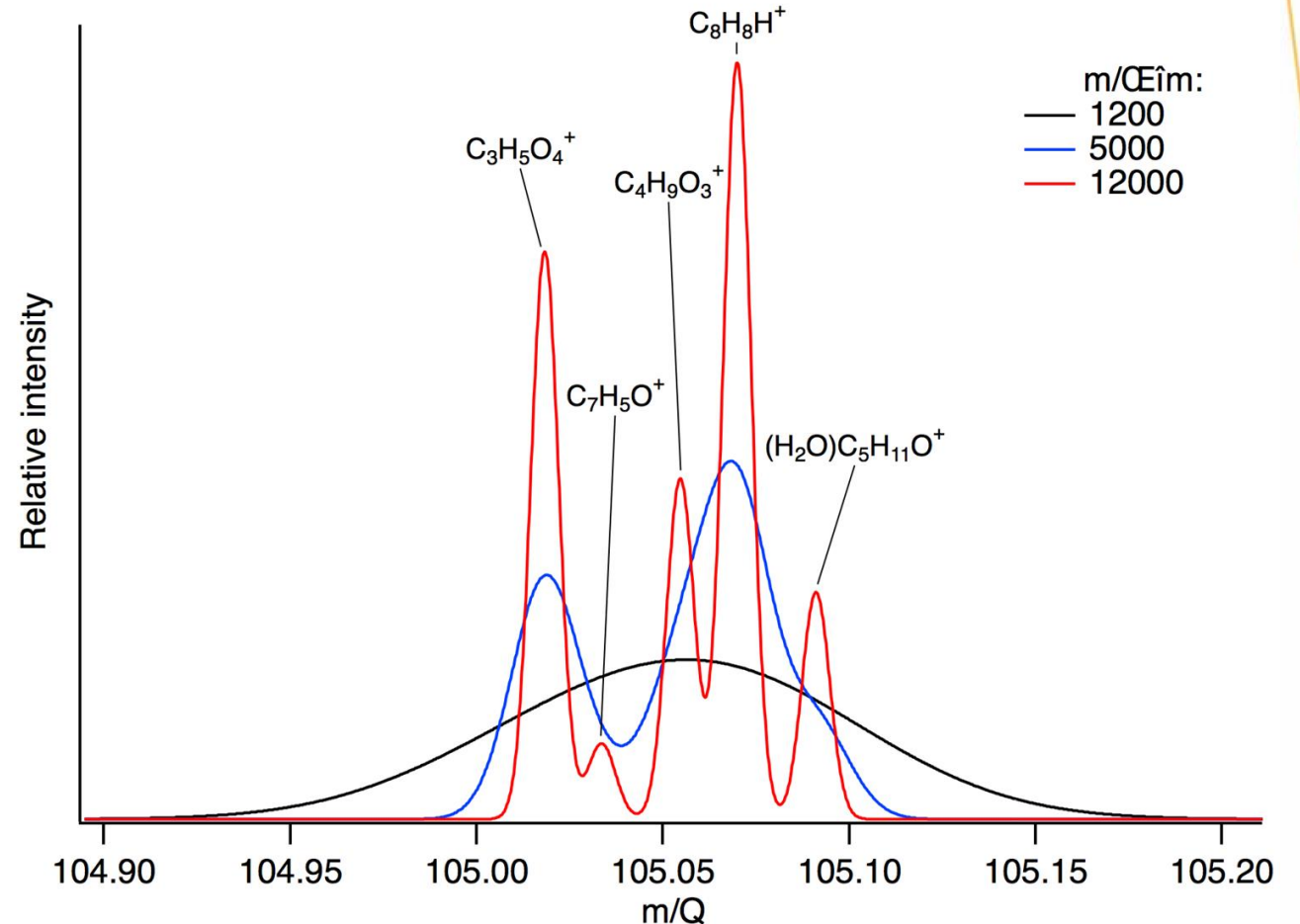


VOCUS PTR-TOF 2R is also a leap forwards in mass resolving power

VOCUS

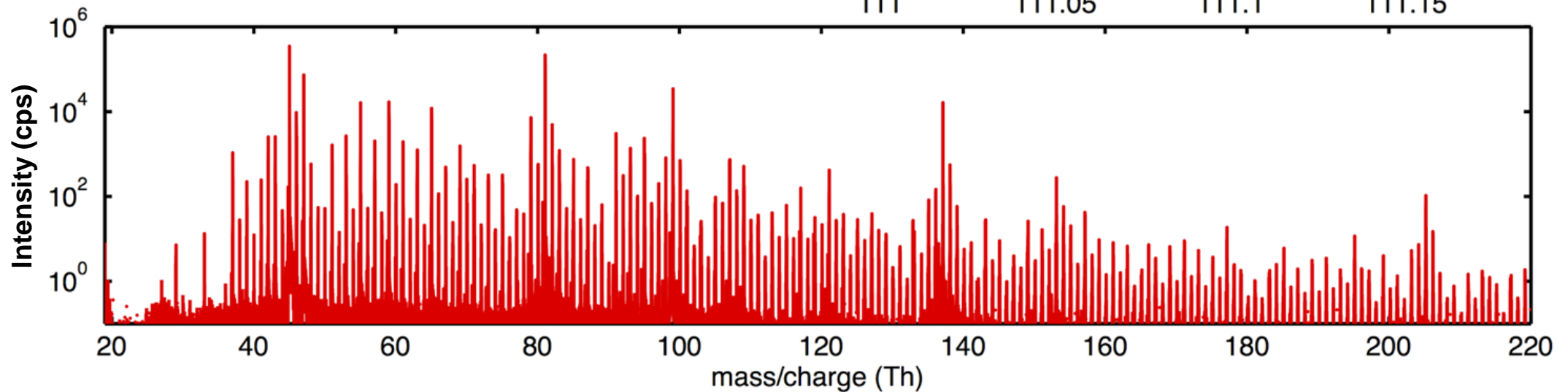
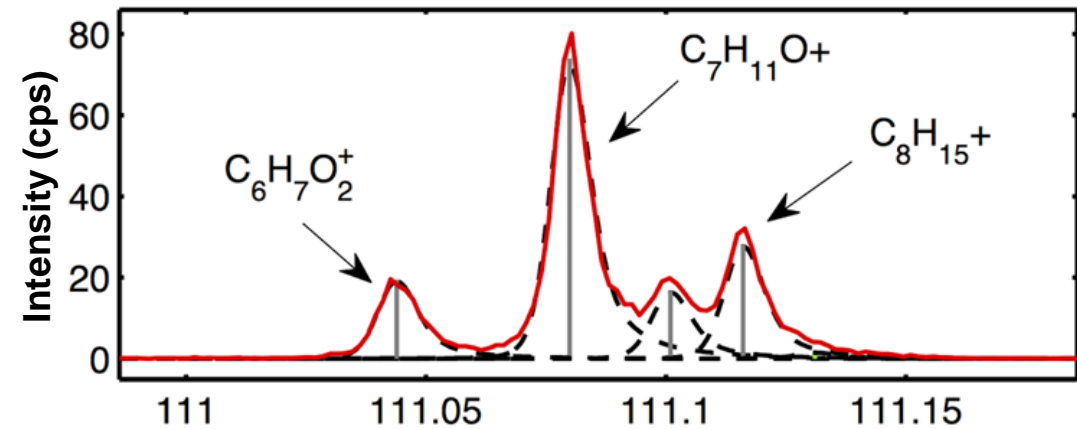
- Example mass spectrum from air measured in the Netherlands during ACTRIS by a VOCUS 2R (**red**)
- The spectrum is re-sampled to simulate the same spectrum, at different TOF resolutions (**blue** and **black**)
- **The VOCUS 2R allows quantitative analysis and robust isobar separation even in complex samples.**

12,000 m/dm
5,000 m/dm
1,200 m/dm

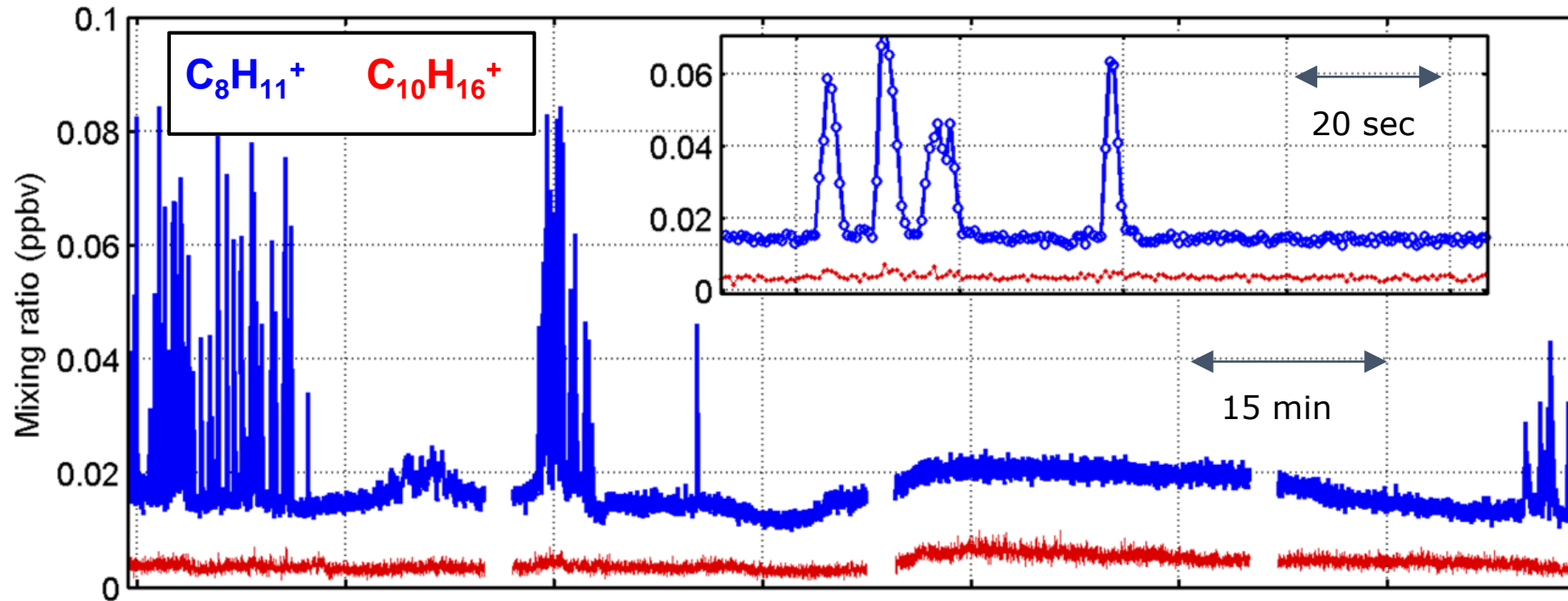


Separate complex mixtures with the highest available PTR resolution

- A single pine needle cut near the VOCUS inlet.
- High resolution separates isobars
- Molecular ions are identified

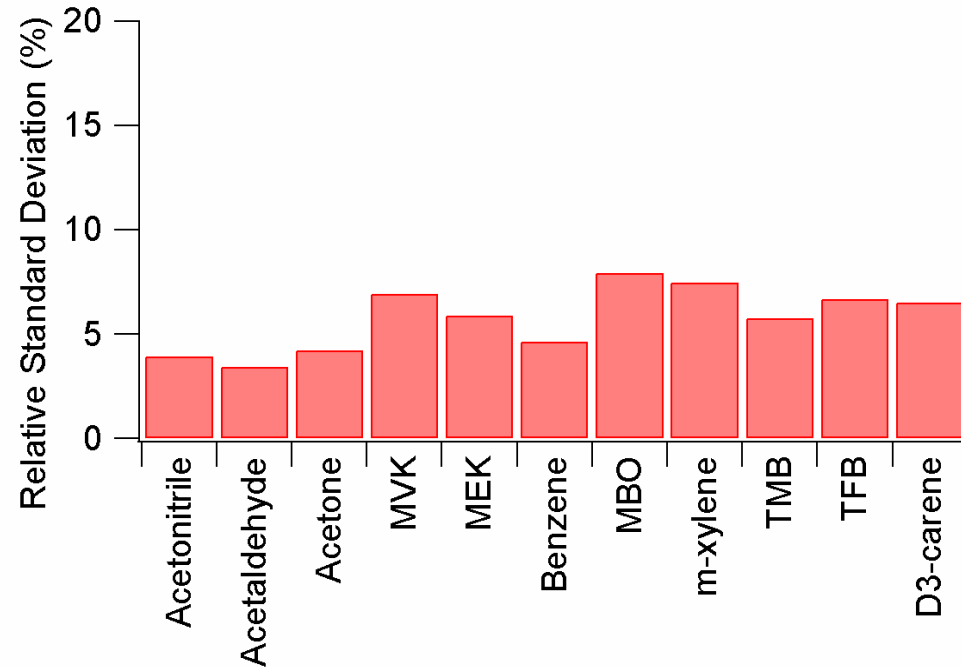


High frequency atmospheric measurements



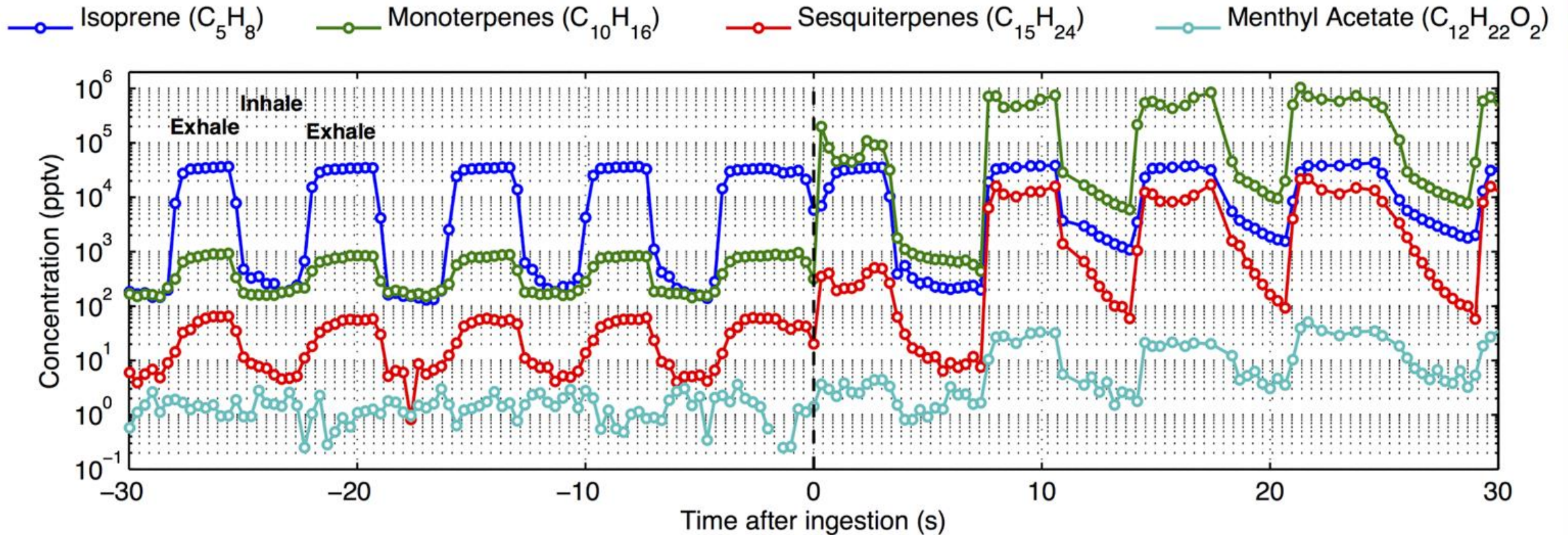
- **ACTRIS PTR inter-comparison in Netherlands** with 12 other PTR-MS, 9 with TOFWERK TOFs!
- **VOCUS measurements at 2 Hz show excellent signal to noise. VOCUS is ideal for high frequency measurements** like EC fluxes, even at low absolute concentrations.

Calibrations are automatic, stable and reproducible



- Automatic calibrations from certified cylinders ensure instrument performance accurately tracked
- **Integrated background measurement and calibration included as standard for all instruments**
- 3 days of standard additions to a VOCUS 2R during ambient measurements show excellent reproducibility

Monitor fast processes with large dynamic range



- Example of analysis of human breath **measured at 3 Hz** before and after ingestion of a Ricola herbal drop, where **concentrations span more than 6 orders of magnitude**

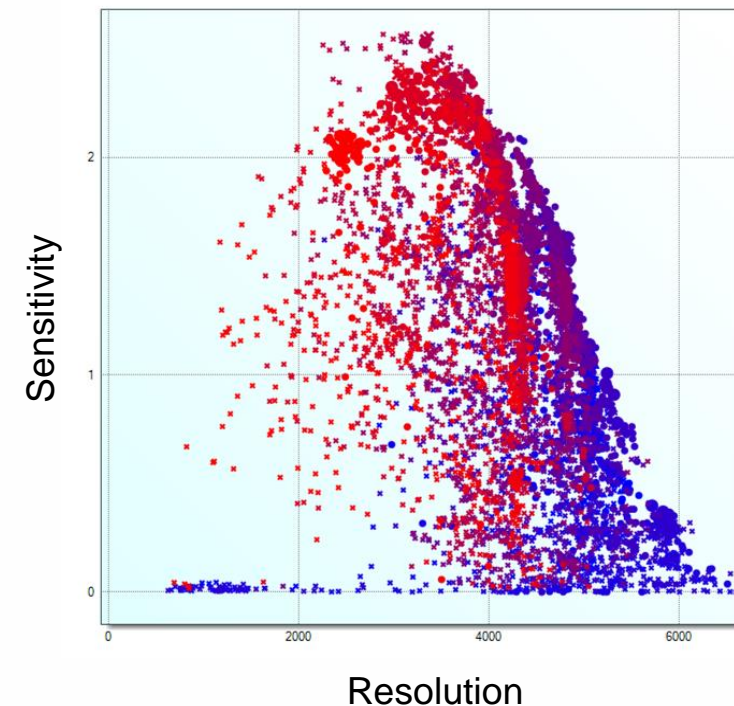
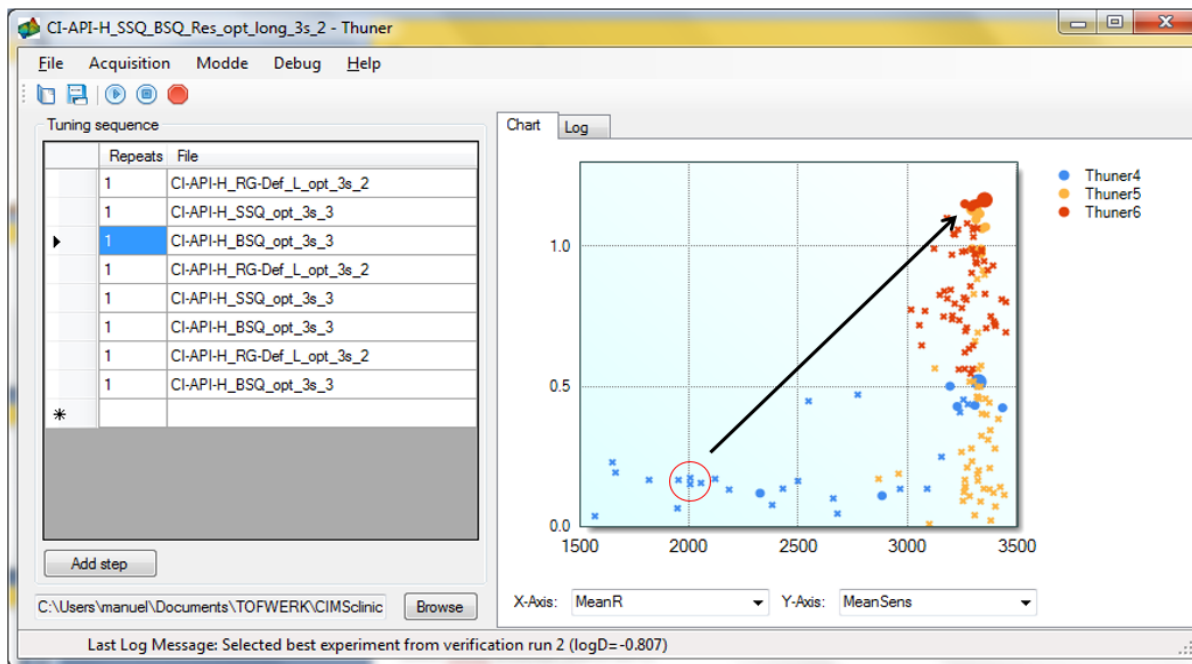
VOCUS software and workflow

Software

1. Instrument optimization and experiment setup (**Thuner**)
1. Data acquisition and quality control (**Acquility**)
 - Full instrument and process control
 - Automation and sequencing
 - Real time data viewing
1. Powerful and flexible post processing, high resolution analysis (**Tofware**)
 - Averaging
 - Mass calibration
 - Instrument parameters (resolution, peakshape)
 - Peak assignment
 - Time-series

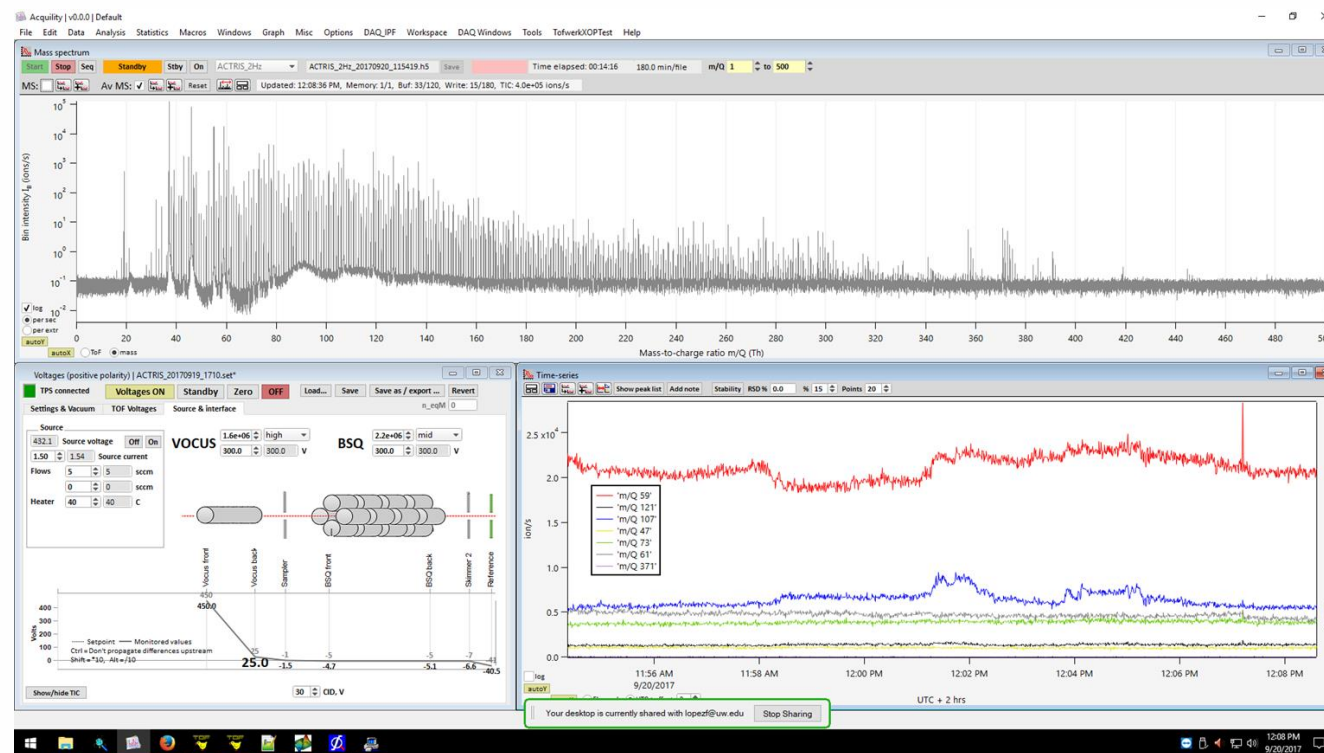
Thuner: automatic instrument optimization

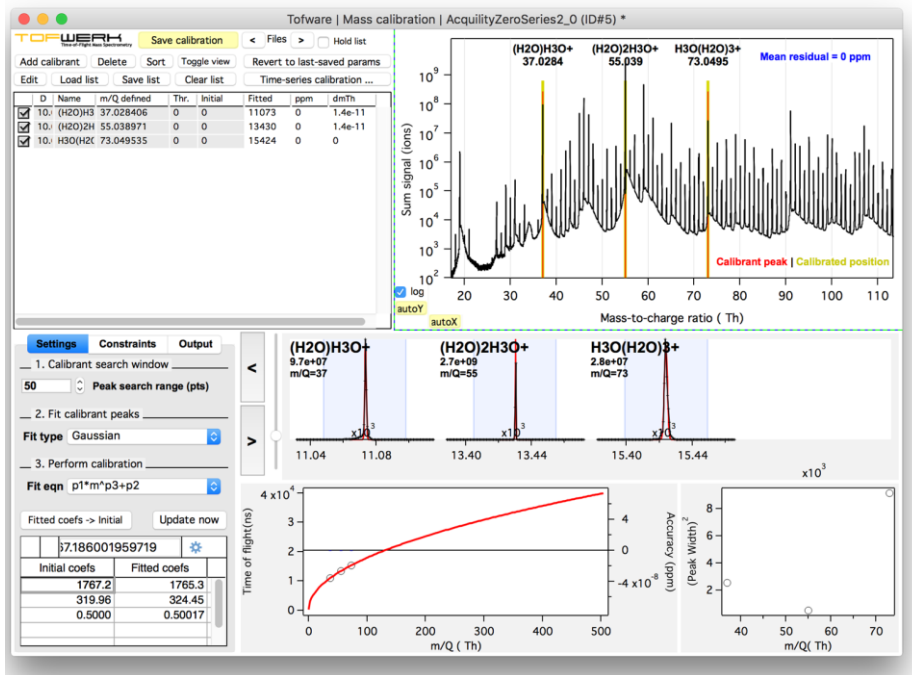
- One-button TOF re-tuning in a few minutes: Assures that instrument runs at top performance, even for users with no knowledge of instrument optimization
- Often used for instrument optimization for target compounds and parameter space mapping



Acquility: Data acquisition, automation and instrument control

- Customized interface for PTR
- **Sequencing and automation** of measurement workflow
 - e.g. zero and calibration valves
- **Complete instrument control**
 - voltages, pumps, heaters
- **User friendly** interface with customizable individual user profiles
- **Fully integrated with Tofware** post processing software

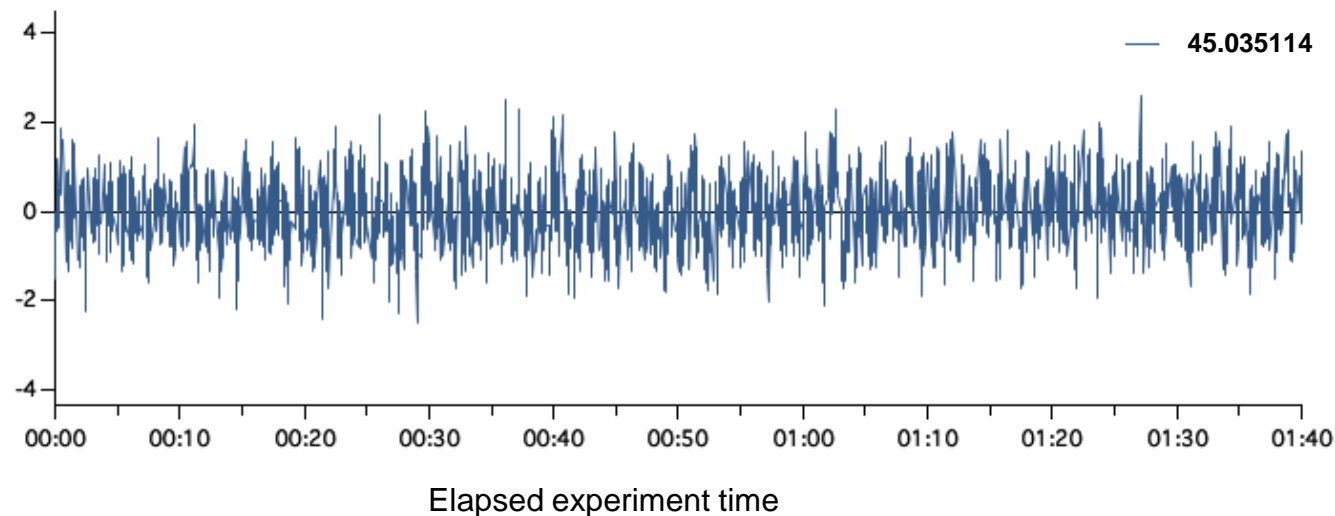




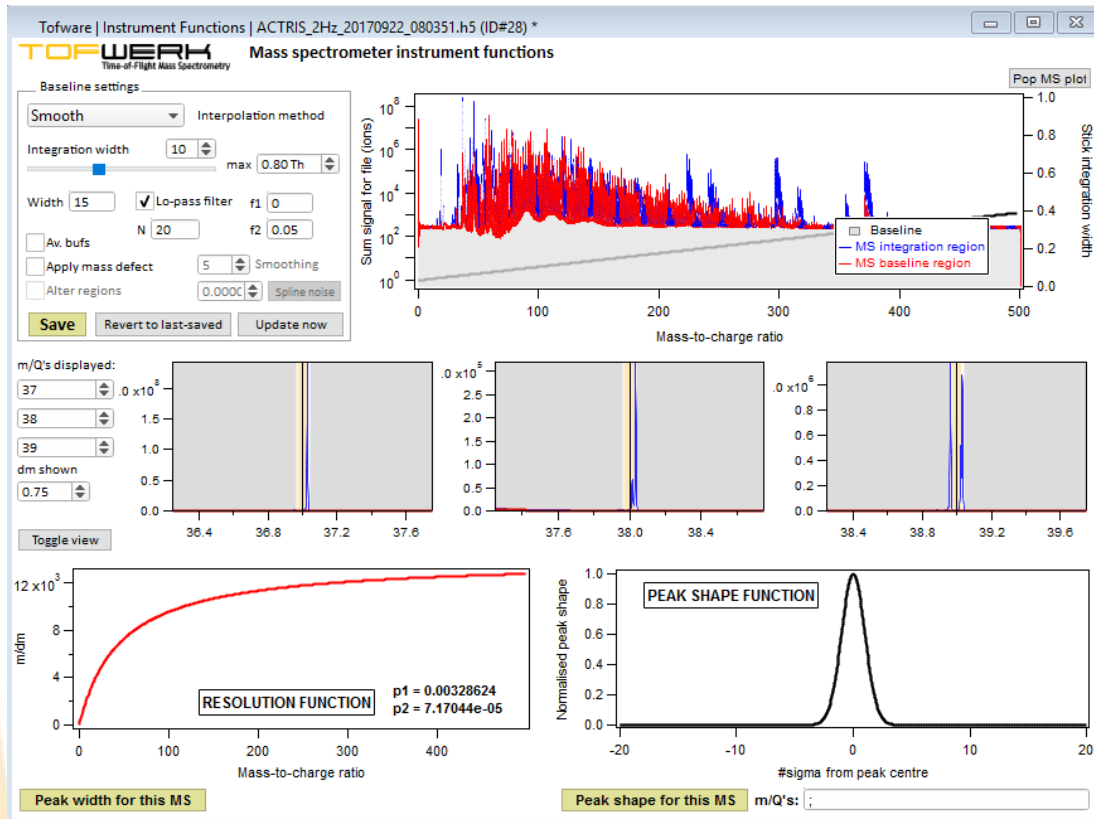
Mass calibration example of VOCUS-PTR

- Fully-featured GUI to optimize mass calibration
 - Simple and fast execution
 - Automated application to file series (batch run)
- 1 Hz data show std. dev. = 0.8 ppm = 0.000036 Th

Error in mass measurement (ppm)

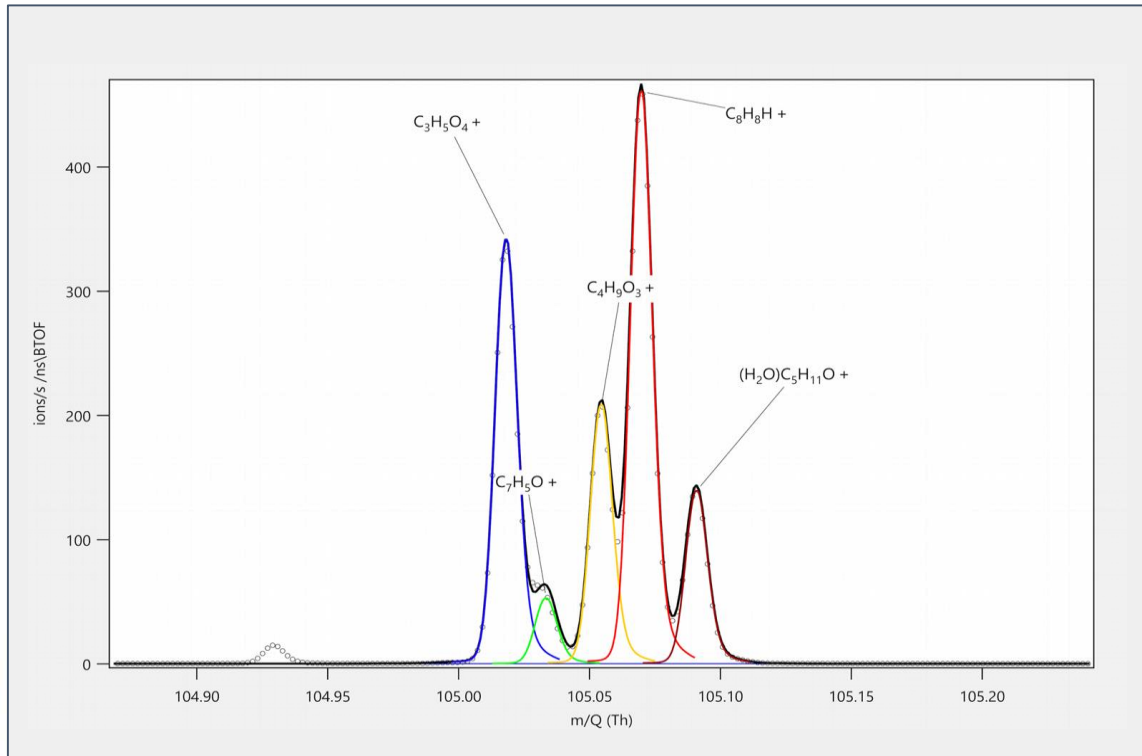


Tofware: Post processing and data analysis



- **Determination of instrument functions and parameters with the click of a button**
 - Resolution function definition
 - Peak shape determination for high resolution analysis
 - Intuitive and easy to use

Tofware: Peak Fitting



- Example of high resolution analysis using a VOCUS PTR-TOF 2R in Tofware from air sampled in the Netherlands
- A resolving power of 12,000 and nearly gaussian peak shape allows robust separation of isobars
- Streamlined workflows and functions utilized in Tofware allow easy assignment of molecular ion formulas even in complex mixtures

VOCUS PTR-TOF summary

VOCUS is a novel ion source and reactor, coupled with an established TOF-MS
VOCUS is ready for demanding lab or field measurements

VOCUS provides:

- **Market leading sensitivity**
 - Lower LOD
 - Better precision
 - Monitor dynamic changes at higher speed
- **Highest available mass resolving power**
 - Ability to separate isobars in complex mixtures
- **Powerful, easy-to-use workflows, automated operation and calibration**