Field deployable MS
-
the Tofwerk Experience

Marc Gonin & Benoit Plet

TOFWERK

contents

HEMS 1999

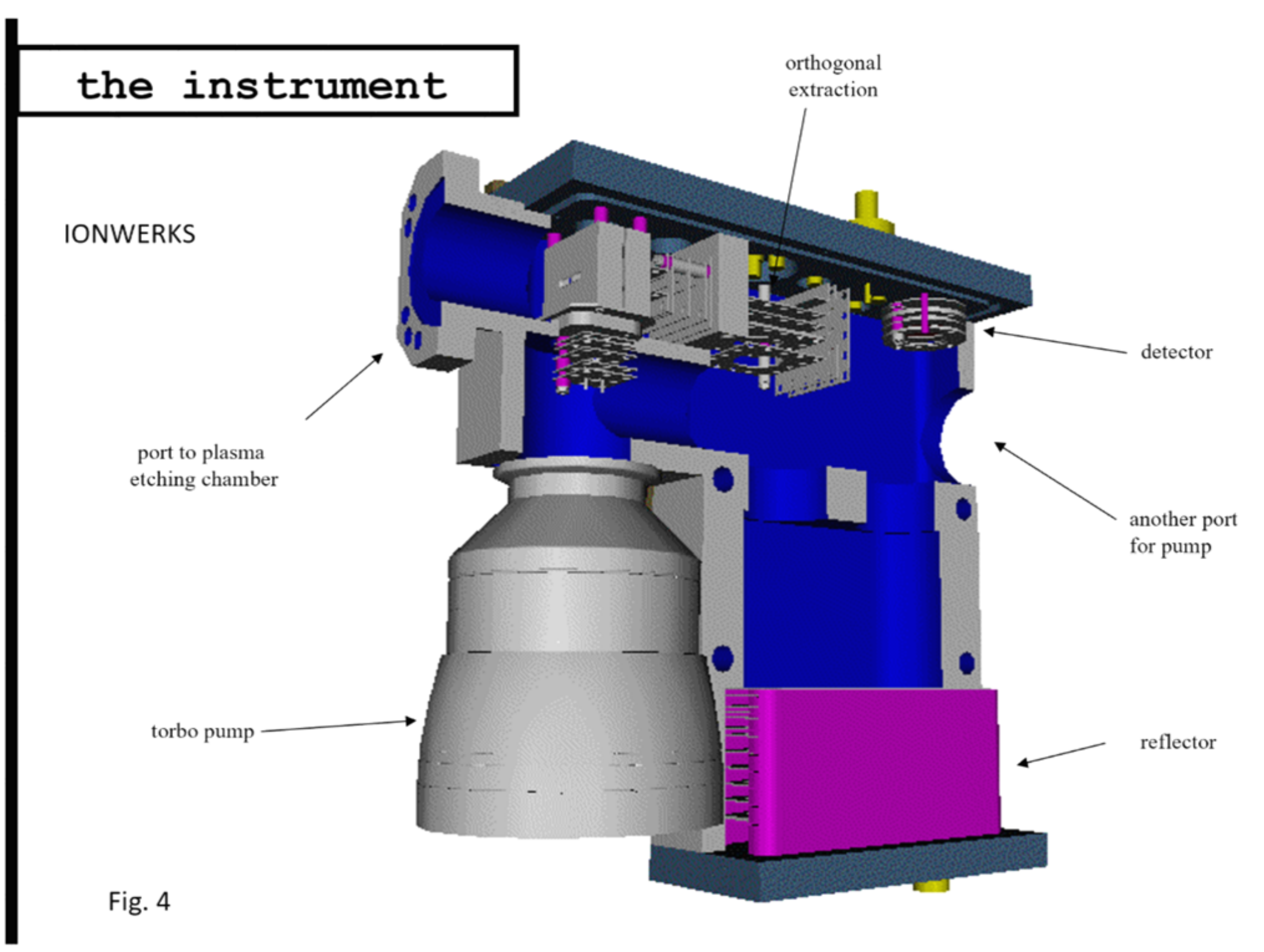
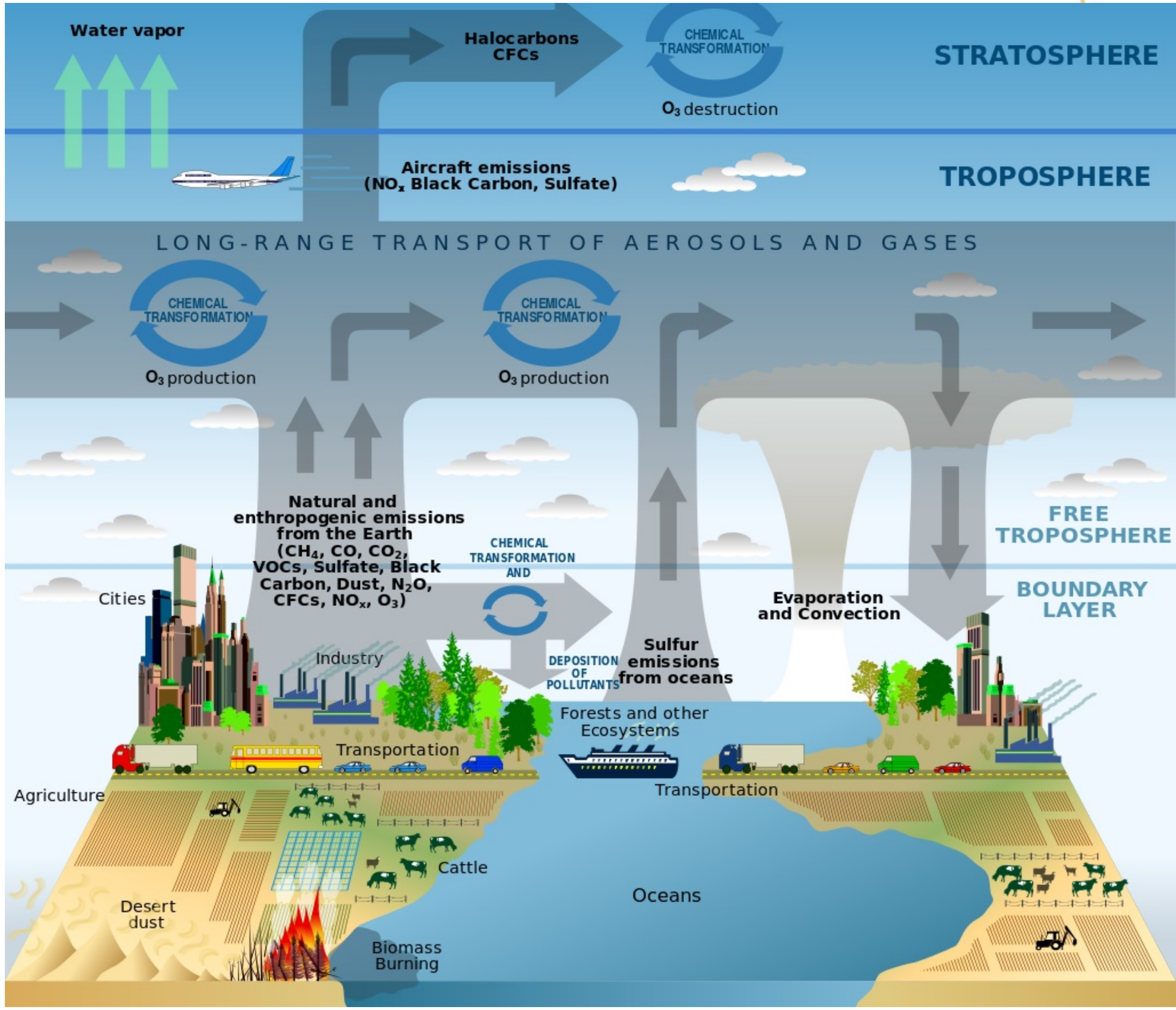


Fig. 4

financed by NASA

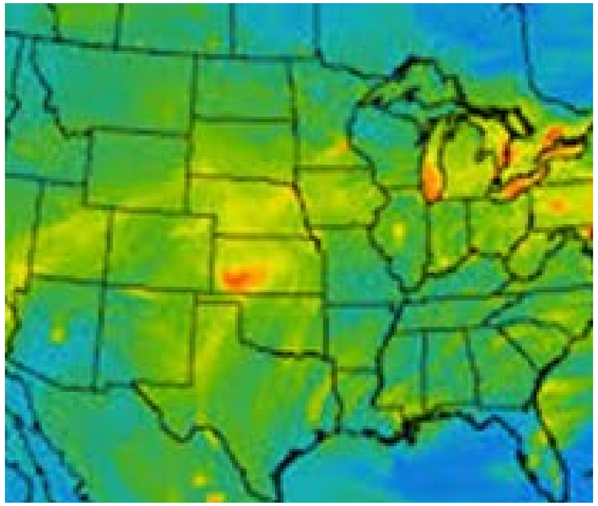
Atmospheric Chemistry

- Complex mixture
  - **Anthropogenic**
  - **Biogenic**
- Intricated processes
  - Local mixture
  - Transport
  - Multiphase processes
  - **Altitude**
  - Photochemistry conditions
- **Bring instrument anywhere**



- Credit: Phillipe Rekacewicz – Strategic Plan for the U.S. Climate Change Science Program, Public Domain

Atmospheric Chemistry



Models

Field

Laboratory

Operational Challenges

- Transported to remote places
  - Compact size
  - Survive to “exotic” shipment
  - Reasonable weight

TOF-CIMS on HI -SCALE campaign

Operational Challenges

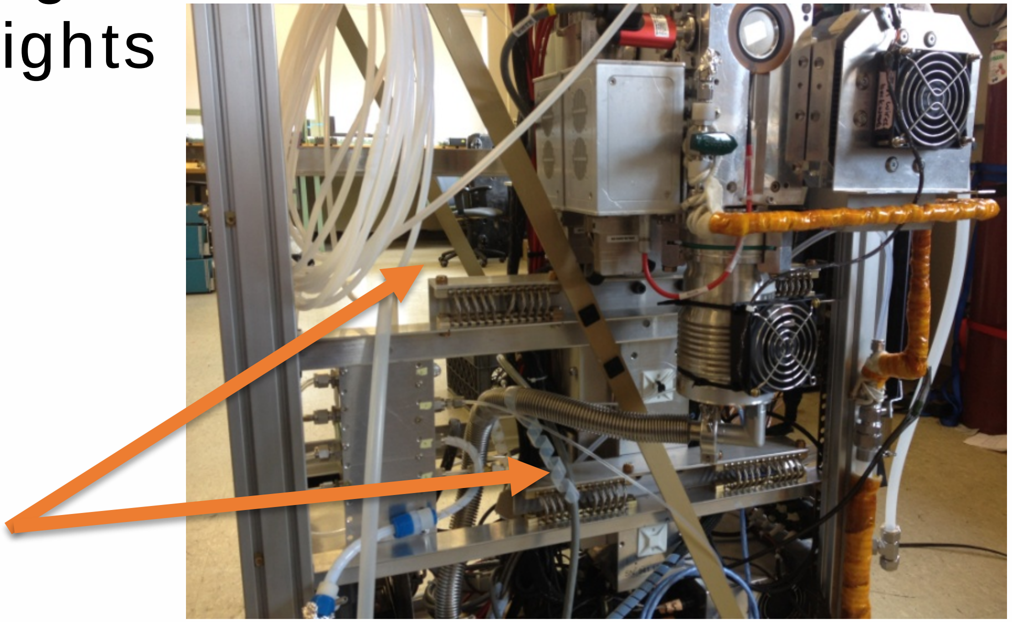
Operational challenges

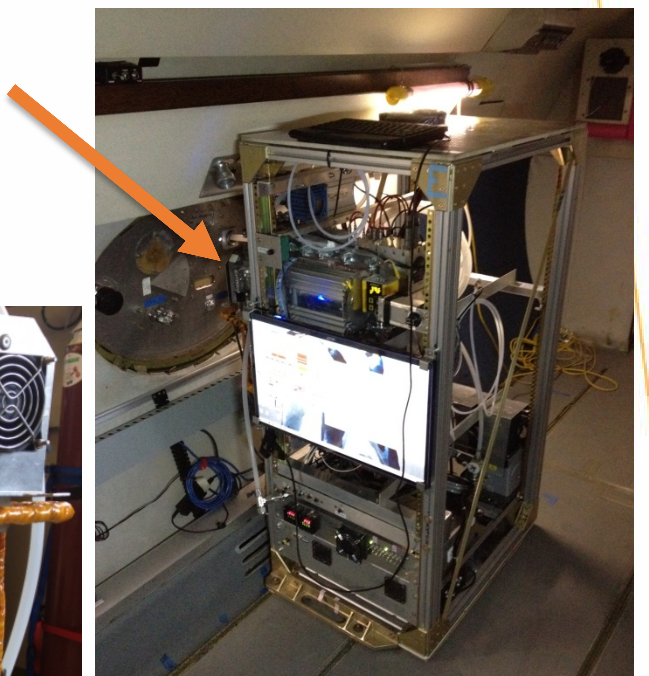
- Transported to remote places
- Work in “unspecified” environments
  - Pressure changes
  - Limited/unstable power
  - Survive power failures

Credits: Federico Bianchi, University of Helsinki

Operational challenges

- Transported to remote places
- Work in “unspecified” environments
- “Unbox your MS”
  - Fit customized ion-source / inlet
  - Comply with aircraft regulation
  - Survive to turbulent flights
    - Vibrations / Shocks
    - Heat





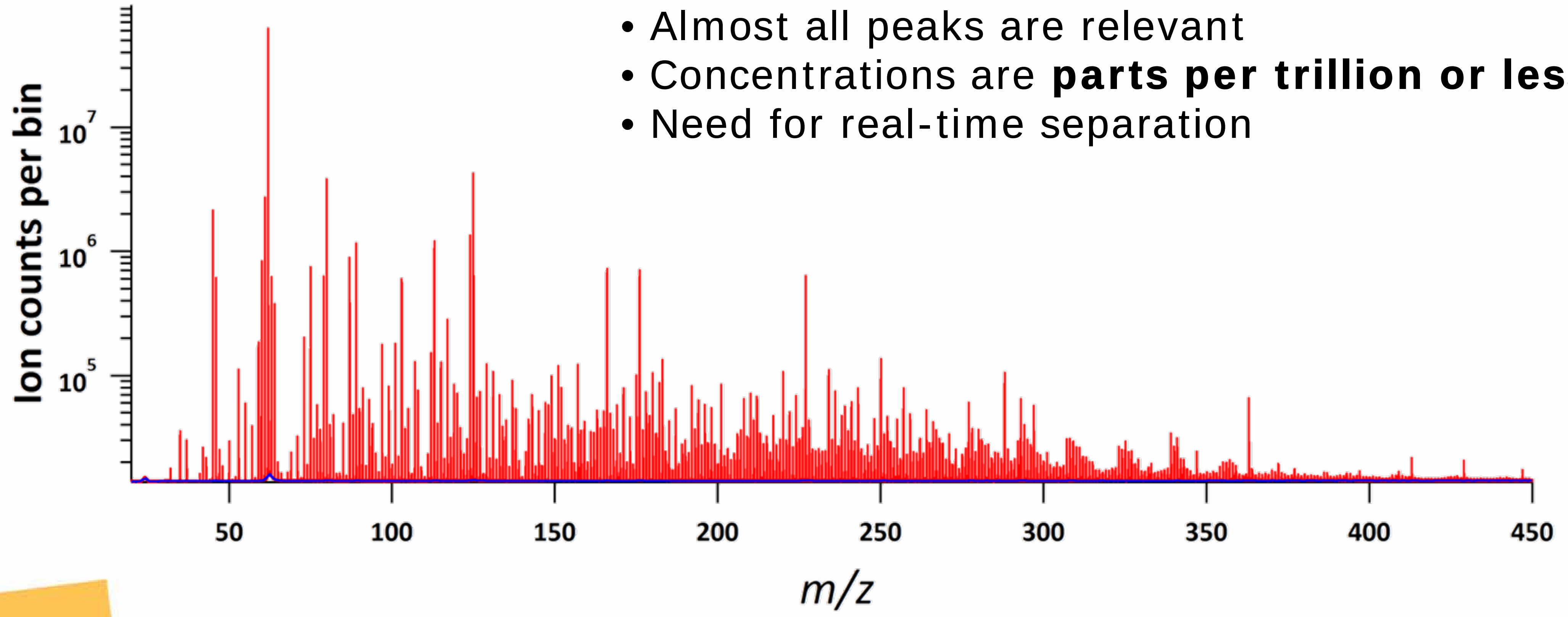
CIMS aboard G -1 aircraft

Credits: Siegfried Schobesberger , Uni. Washington

Analytical challenges

MS background *is* our measurement

- Almost all peaks are relevant
- Concentrations are **parts per trillion or less**
- Need for real-time separation

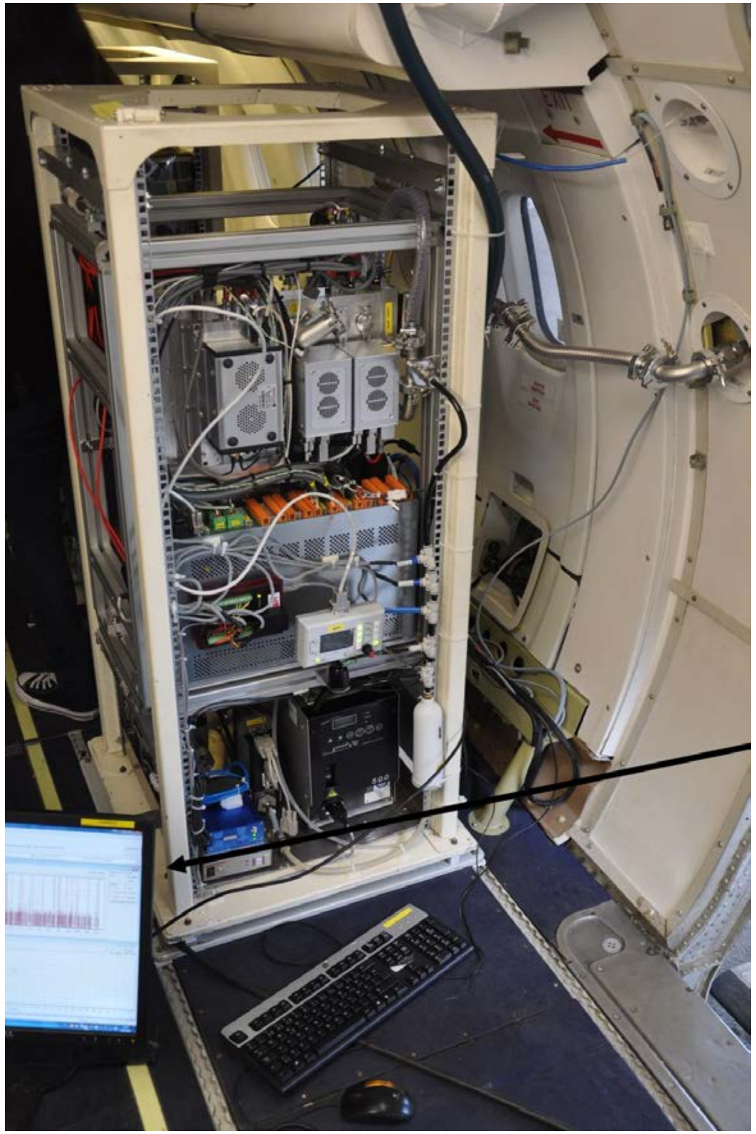


Comply with these challenges

APCI-TOF platform

- Top performance
- Compact
- Customizable
- Robust
- Scalable
- Upgradable (IMS)
- **Unconditional support**
- Open data format
- ...

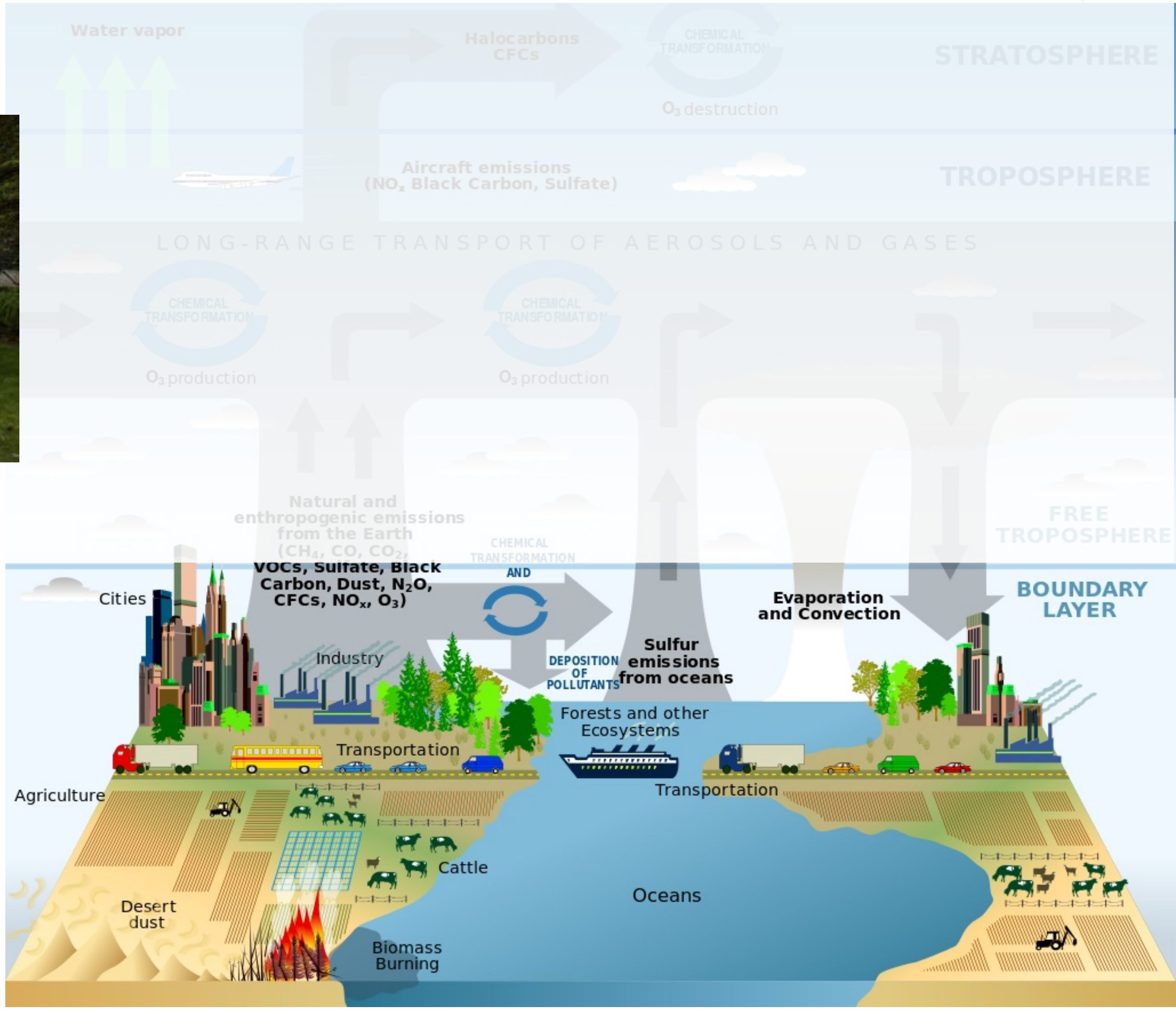
Instrument in airplane



by Jonathan Duplissy

Move your MS to the field!

Boundary Layer

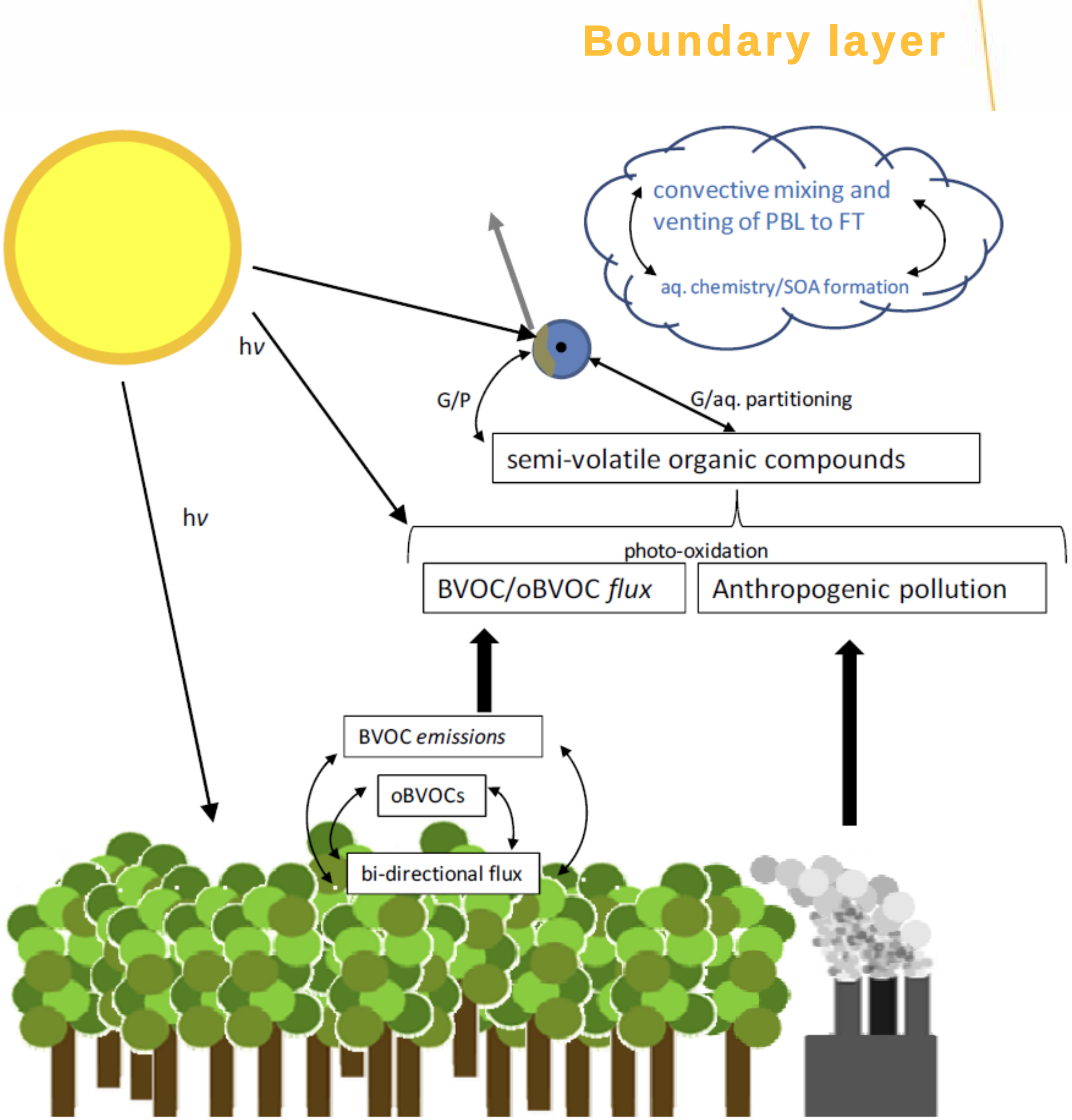


SOAS Campaign 2013

- Southern Oxidant and Aerosol Study

? Fate of biogenic compounds in anthropogenically-influenced environments?

- $HO_x/NO_x/O_3$/organics/aerosol distributions, fluxes, sources, sinks
- Focus on formation of Secondary Organic Aerosol (SOA)



Source: SOAS white paper

SOAS 2013: Instrumentation

Boundary layer

- **First deployment** of a **(NO_3^-)-IMS-TOF**
- Detection of **highly oxidized species** likely to form particles
- Detect **isomeric variants**
- Understanding reactions pathways
- Characterizing partitioning behavior

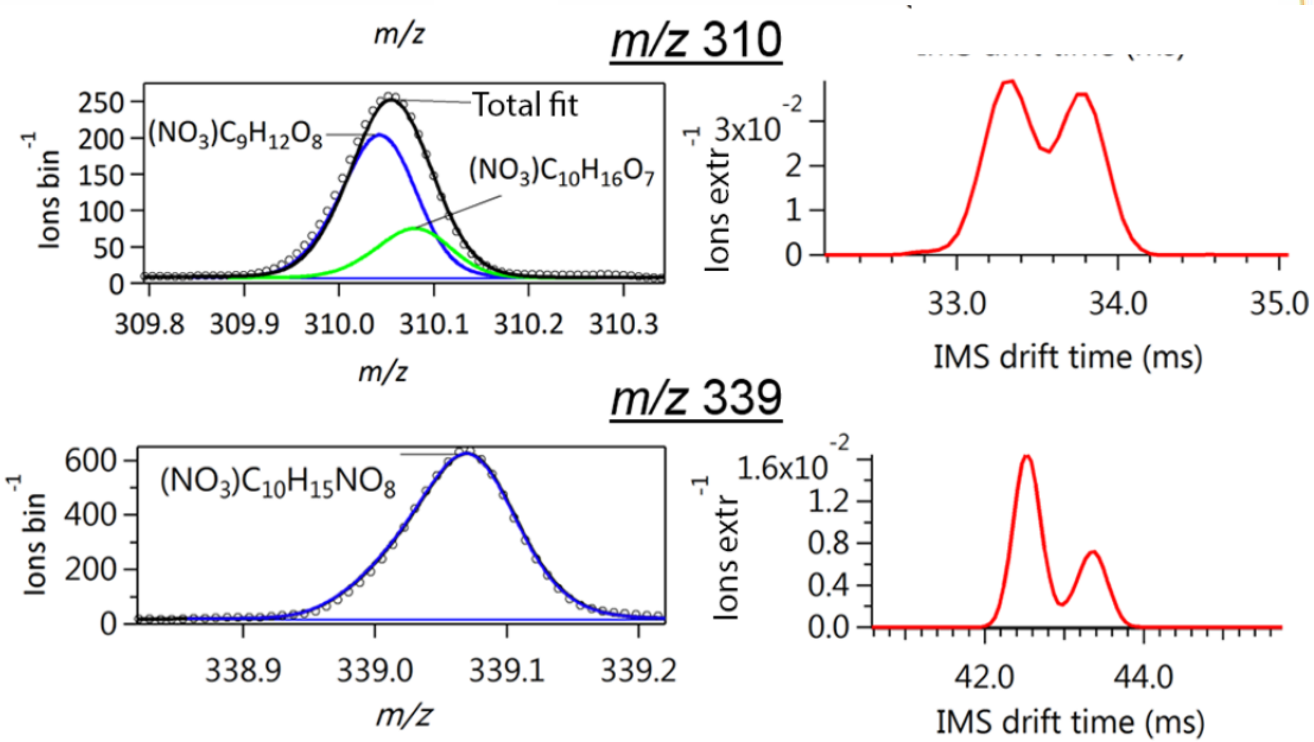
IMS-TOF in situ at SOAS 2013
Centreville Alabama field site, USA

Credits: Jordan Krechmer

SOAS 2013: Results

Benefits of IMS-TOF

- Increase separation
- Compensate for missing GC
- Compensate for limited mass resolution
- New information not available from MS alone



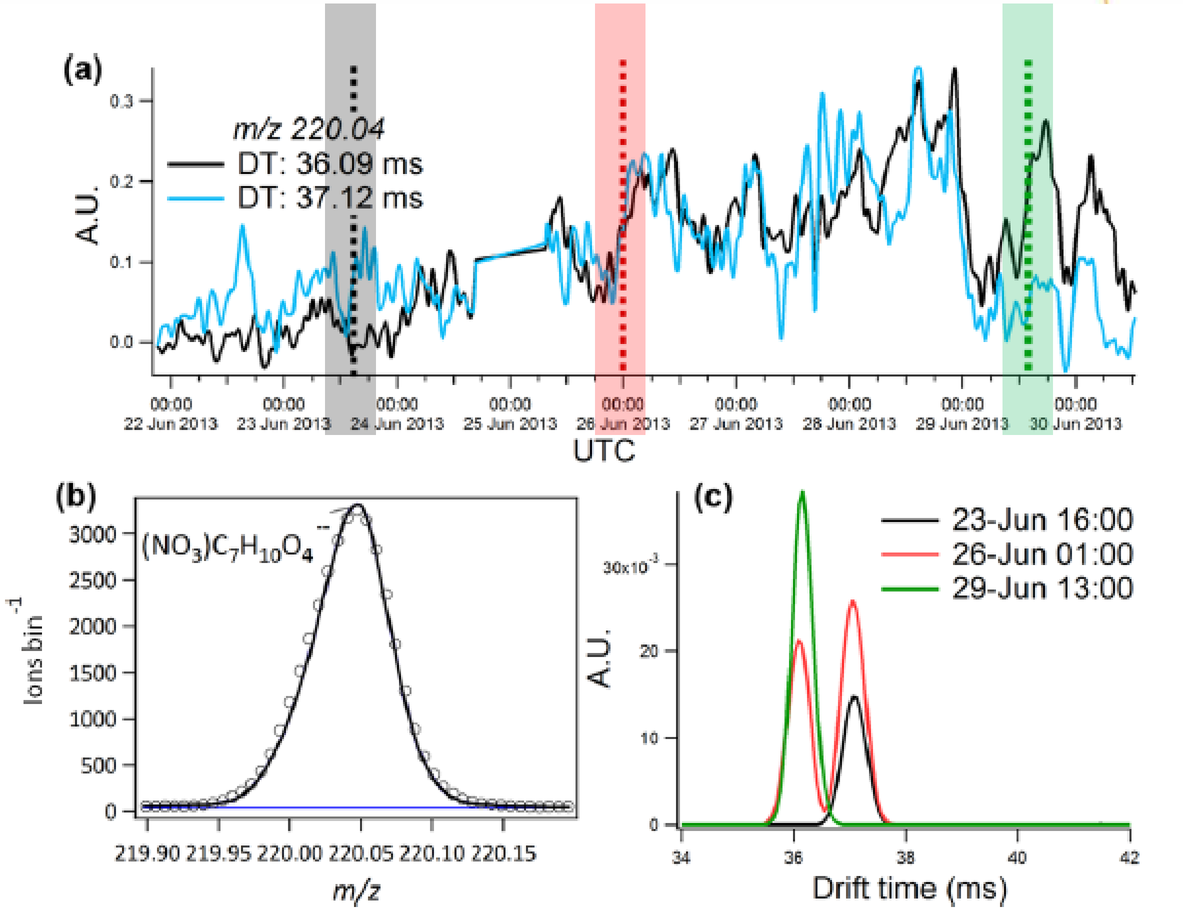
Krechmer , J. E. *et al* , Atmos. Meas. Tech., 9, 3245-3262, 2016

SOAS 2013: Results

Boundary layer

Benefits of IMS-TOF

- Compensate for limited resolution
- New information not available from MS alone
- Time-resolved measurements of gas-phase **isomers**



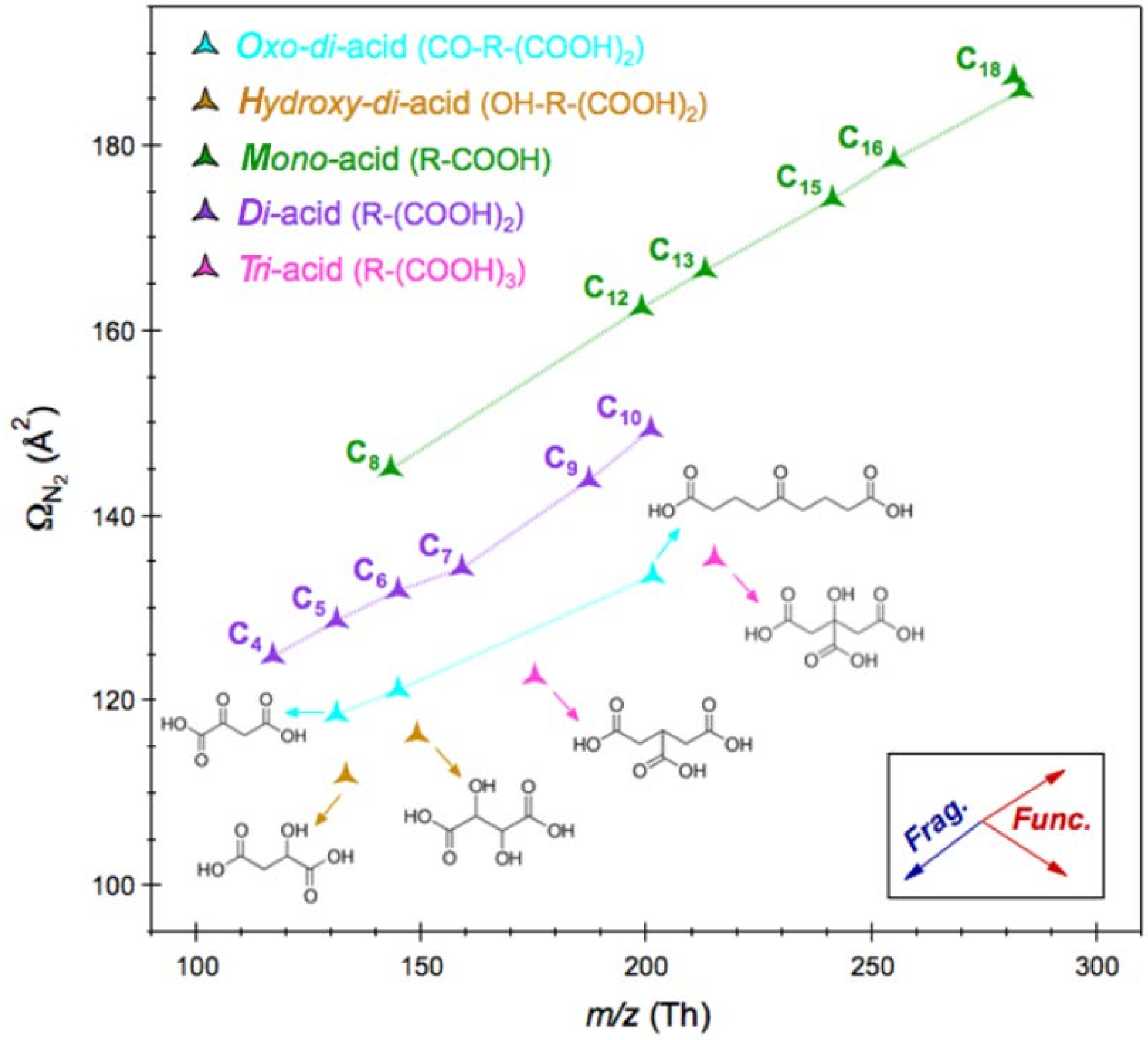
Krechmer , J. E. *et al*, Atmos. Meas. Tech., 9, 3245-3262, 2016

SOAS 2013: Results

Boundary layer

Benefits of IMS -TOF

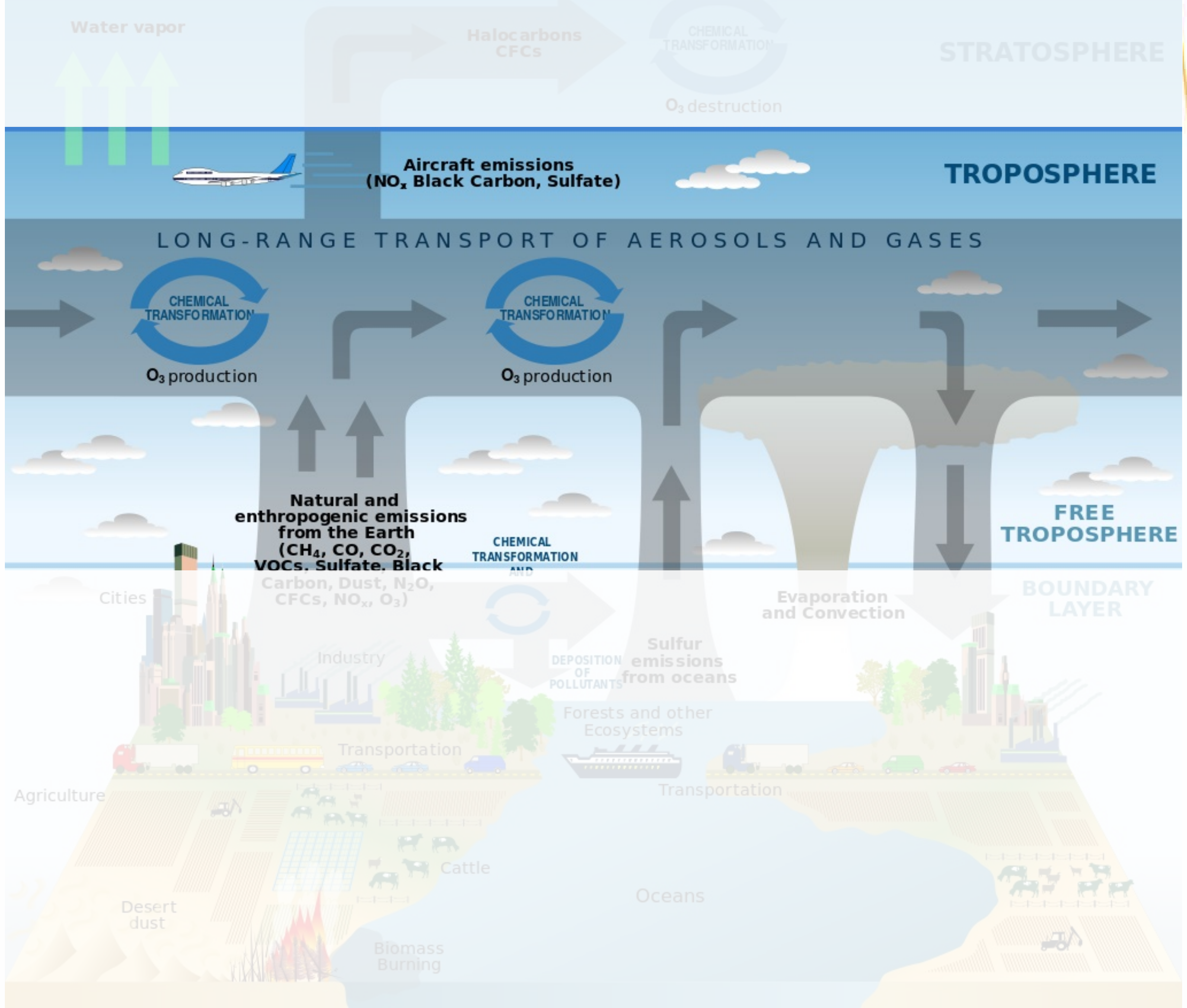
- Compensate for limited resolution
- New information not available from MS alone
- Time -resolved measurements of gas - phase isomers
- Chemical classes information / transformation of organics



Zhang, X. et al., Atmos. Chem. Phys., 16, 12945-12959, 2016

Move your MS to the sky!

Troposphere

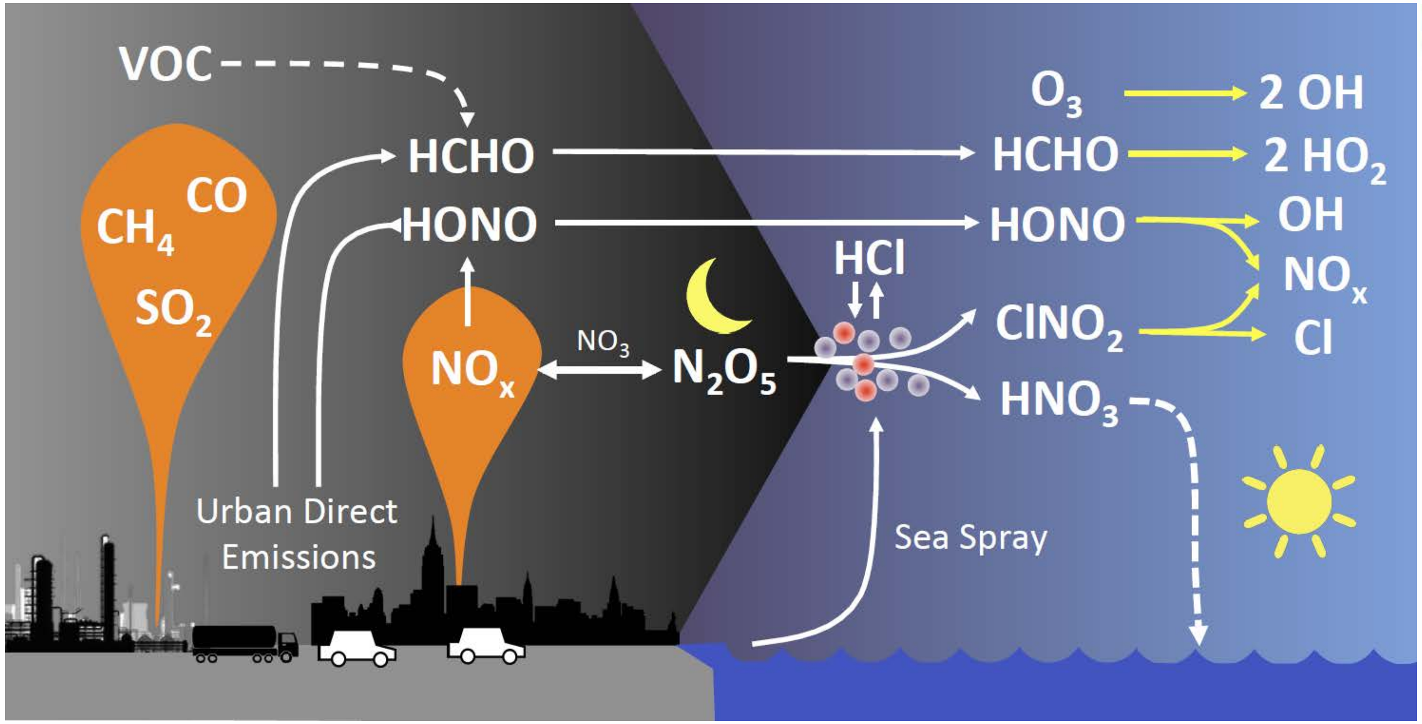


WINTER campaign 2015

- Studying the emissions and **fate of pollutants during winter** across the eastern U.S.

- Photochemistry slow
  - NO_3, N_2O_5

- Chemical transformations
  - At night
  - At sunrise
  - Over polluted area
  - Over sea



Source: Felipe Lopez -Hilfiker

WINTER 2015: Instrumentation

Onboard NSF/NCAR C-130 research aircraft

- APCI-TOFMS (iodide)
  $ClNO_2$, N_2O_5, HNO_3, ...

- APCI-TOFMS (acetate)
  HONO, HCl, HNO_3, ...

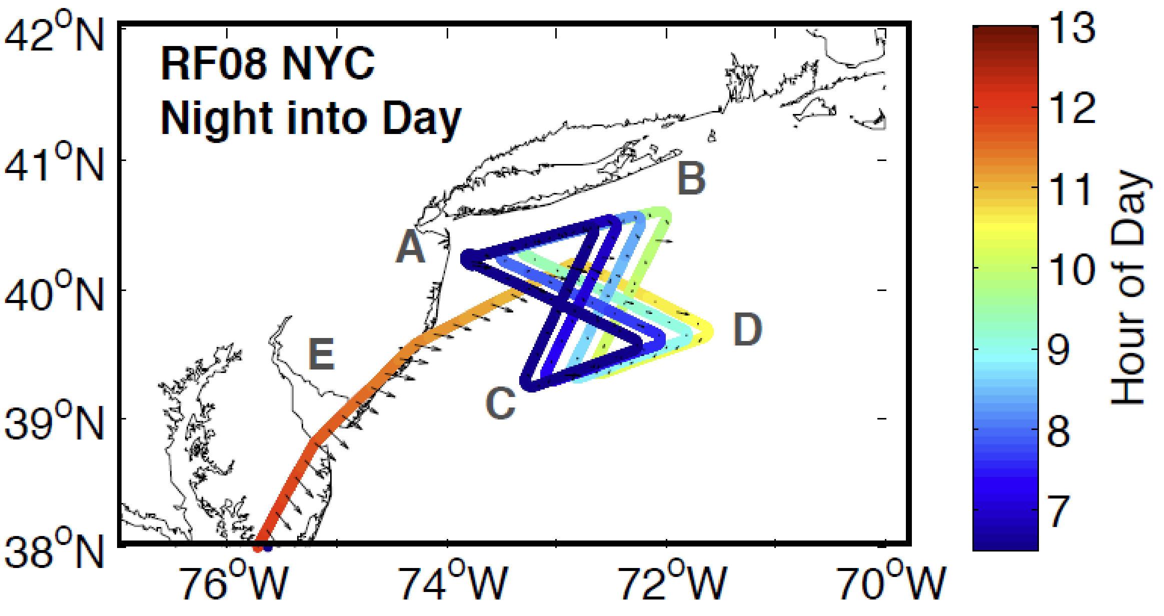
- One airplane = One rack

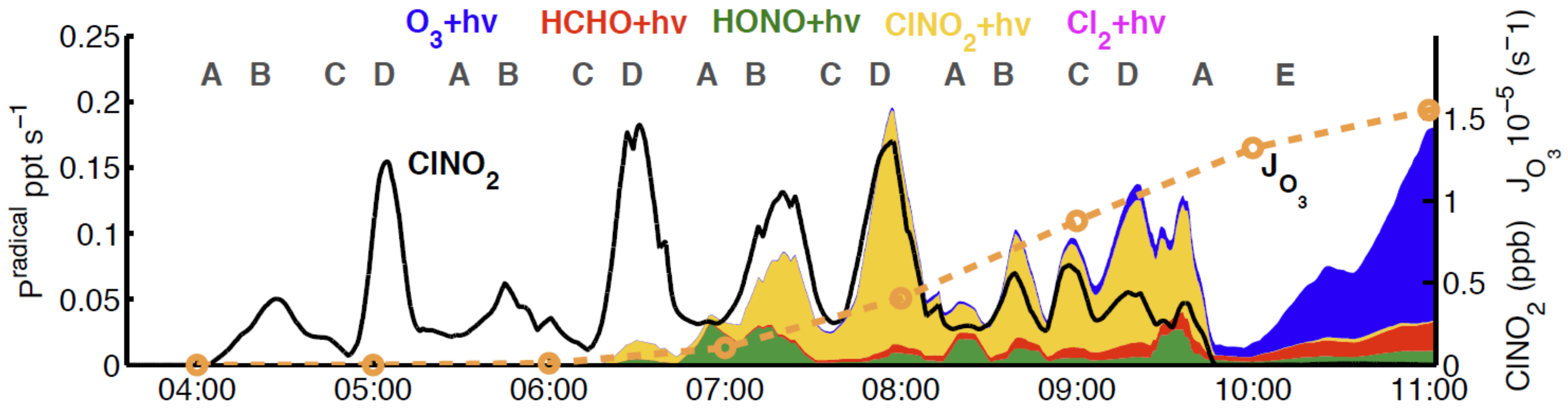
TOF-CIMS instrument in flight configuration

Source: Felipe Lopez -Hilfiker

WINTER 2015: Results

- **Radicals sources evolution** at sunrise
- Stagnant conditions
- Pollution plume from New Jersey that had aged overnight

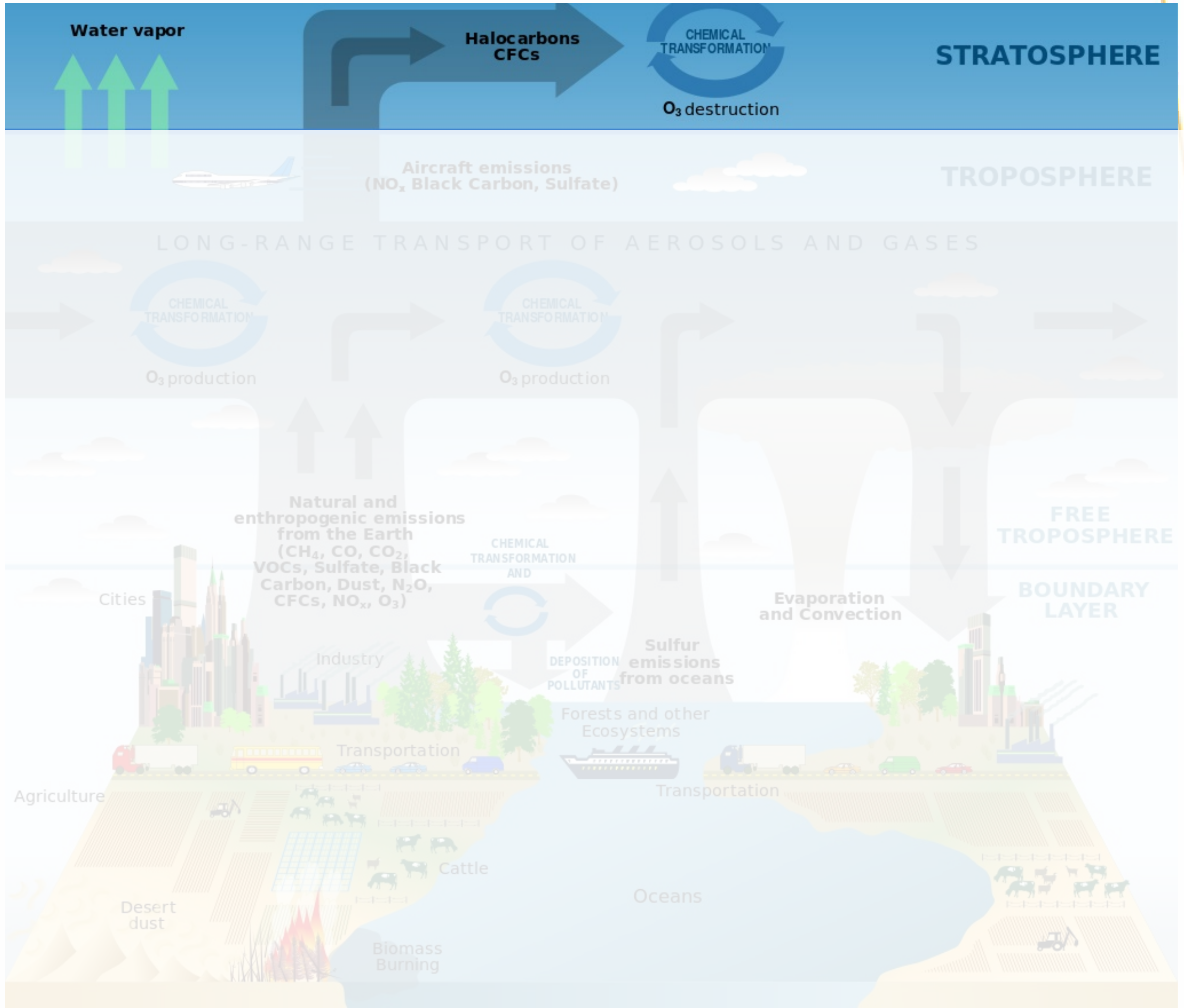




Felipe D. Lopez-Hilfiker et al, in preparation

Move your MS even higher

Stratosohere



StratoClim 2017

"Stratospheric and upper tropospheric processes for better climate predictions"

Measurements of:

- SO_2 (CO_3^- mode)
- bromine species (I^- mode)

- M55 Geophysica: High Altitude Aircraft

Source: Fred Stroh from IEK -7, fz -juelich.de

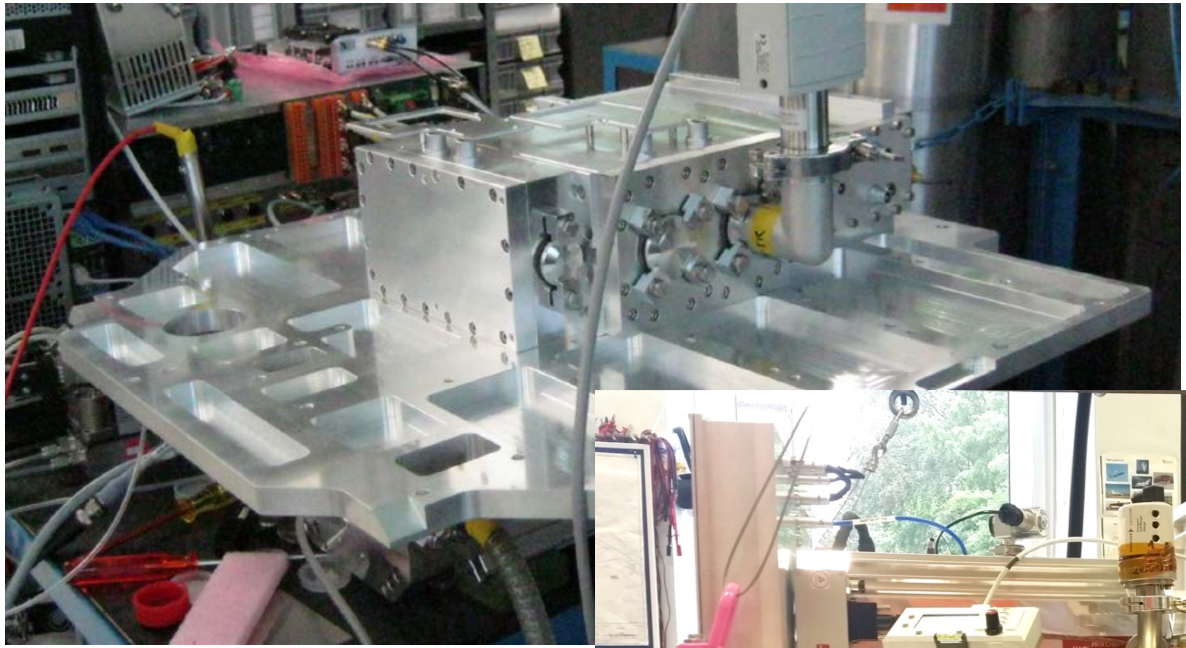
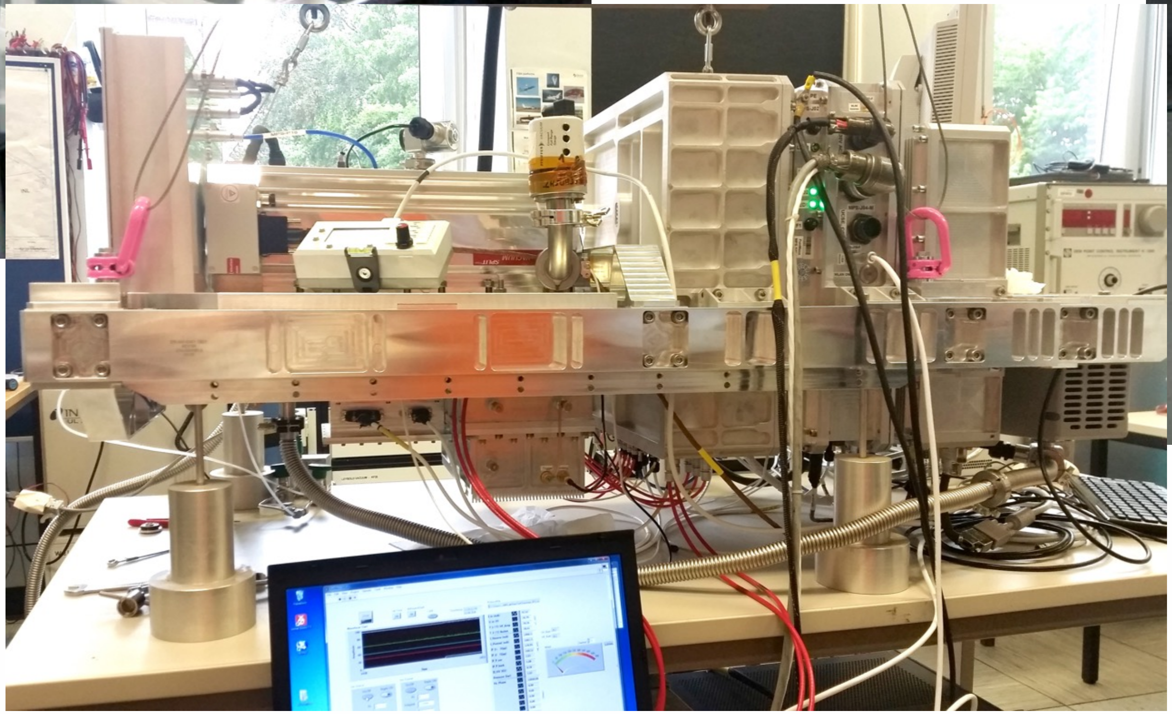
StratoClim 2017: FunMass

- Custom multi chemistry ion source
  - H2SO4, SO2 ➤ stratospheric aerosol
  - HCl, HNO3
- Flight unattended ➤ **autonomous**
- Extreme operating environment:
  - <-80°C
  - **No pressurized compartments** (50 hPa)
- Extreme mechanical and EMC specs
  - DO 160D standard, 9g loads
  - Weight, Size and **Power Constraints**
- Extreme "standby" conditions:
  - >+40°C
  - High humidity (India)

Source : Fred Stroh, IEK -7, fz-juelich.de

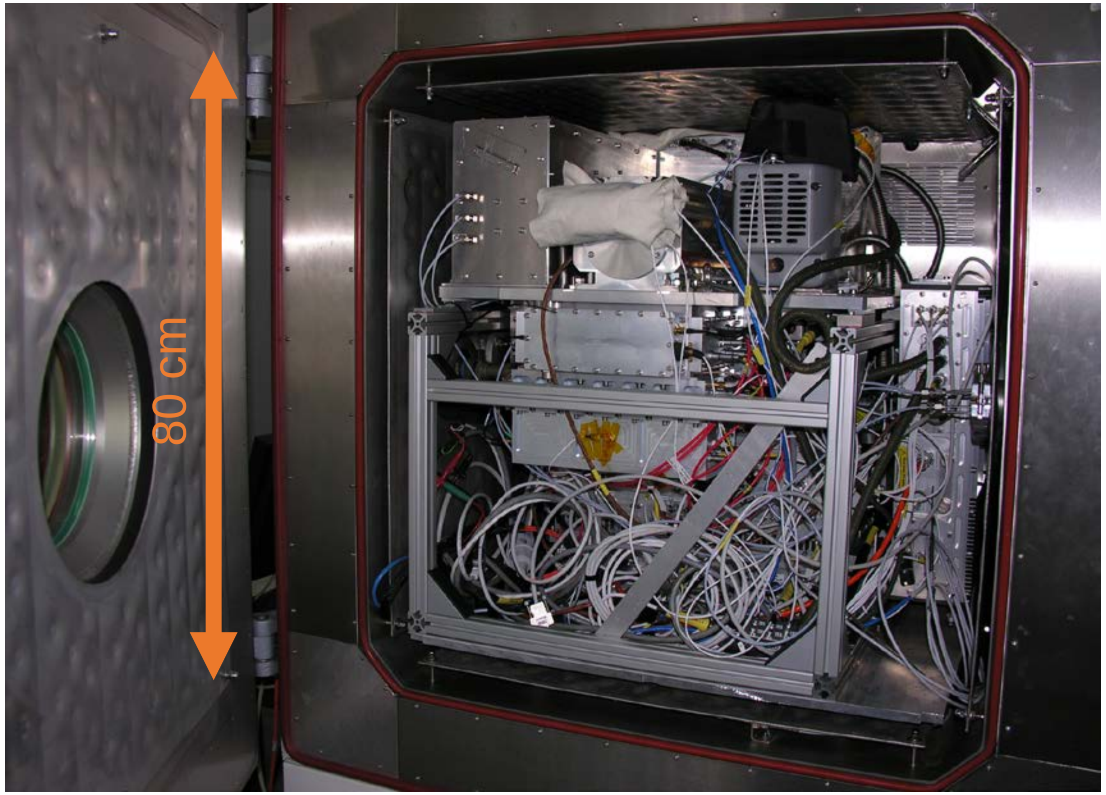
FunMass : Development

Stratosphere


FunMass: Stress Test

- Reconfigured instrument to fit climate chamber
- Full flight simulations (4-5h) with realistic T-p variations
- Stable under all flight conditions once insulation and heating/cooling measures taken.



- Weiss Climate Simulation Chamber

Source : Fred Stroh, IEK -7, Forschungszentrum Jülich GmbH

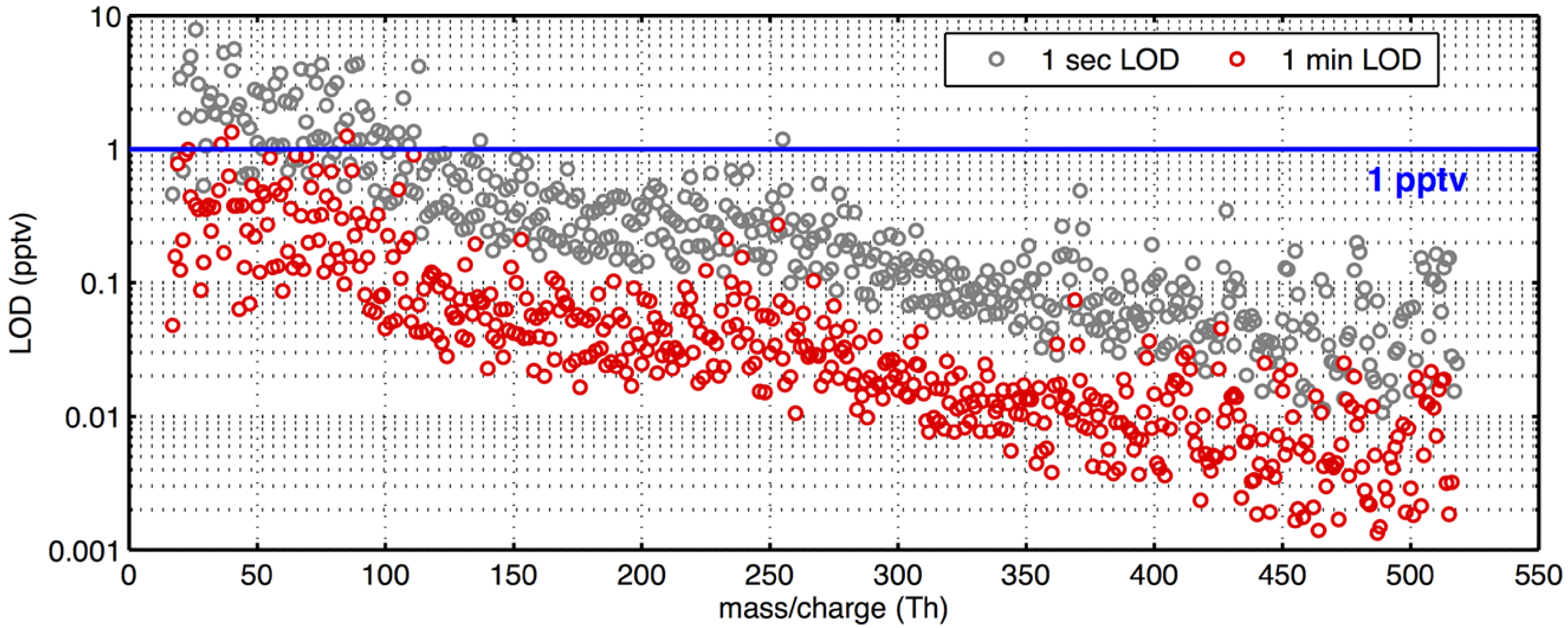
Vocus Model 2R

Medium Pressure Chemical Ionization: MPCI

- Height = 1480 mm
- Width = 480 mm
- Depth = 615 mm
- Volume = 0.45 m^3
- Mass = 160 kg
- Power < 1000 W
- Line Voltage = 100-260 VAC
- Line Frequency = 50/60 Hz
- Altitude = Tibet
- Temperature < 40 C

Vocus 2R

Level of Detection (LOD)



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

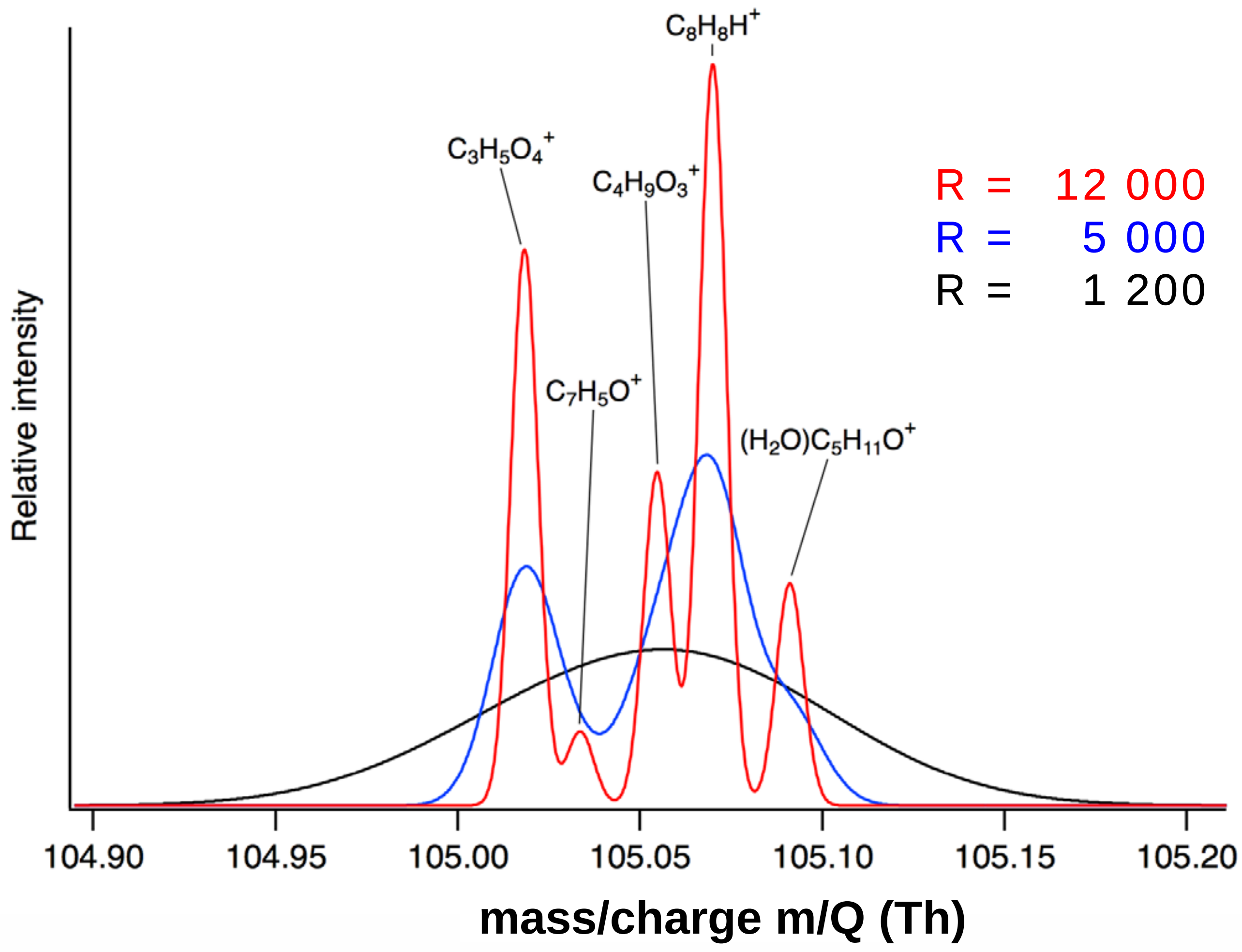
Mass Resolution

Vocus Specs

- **Vocus 2R** allows for
  - isobar separation
  - quantitative analysis
  - complex samples

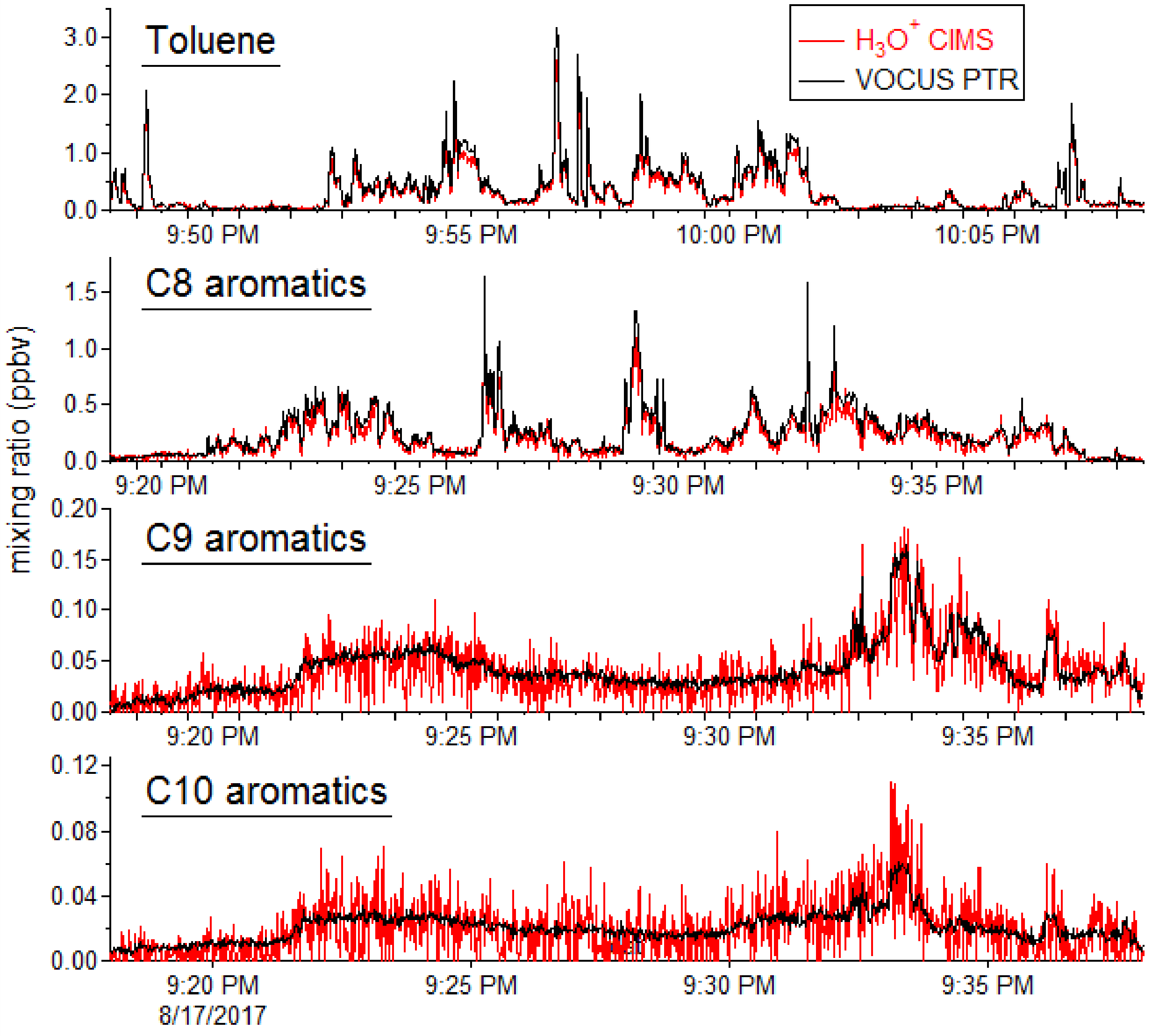
quantitative results require separation

high mass resolution



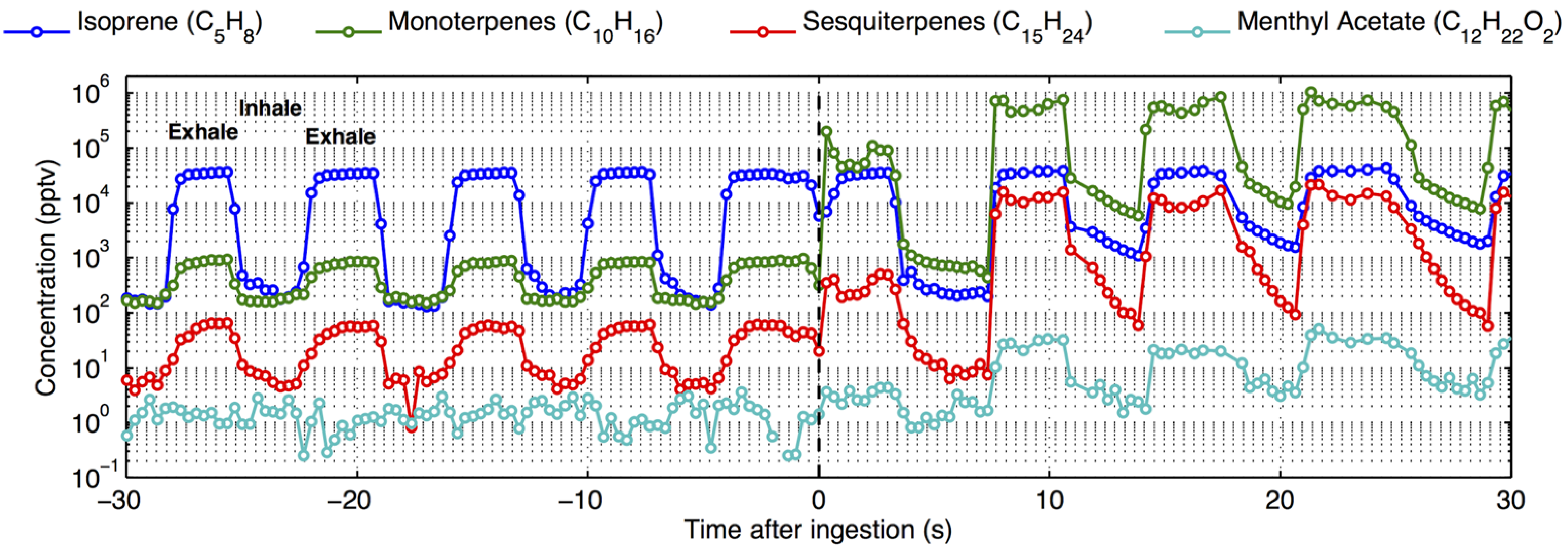
Sensitivity

- 1 Hz sampling of ambient air
- Side-by-side comparison with the
  1. NOAA PTR-TOF (**red**)
  2. Vocus 2R (**black**)
- The NOAA instrument is a state-of-the-art PTR-TOF
- **The sensitivity of Vocus yields better precision faster, especially at low concentrations.**



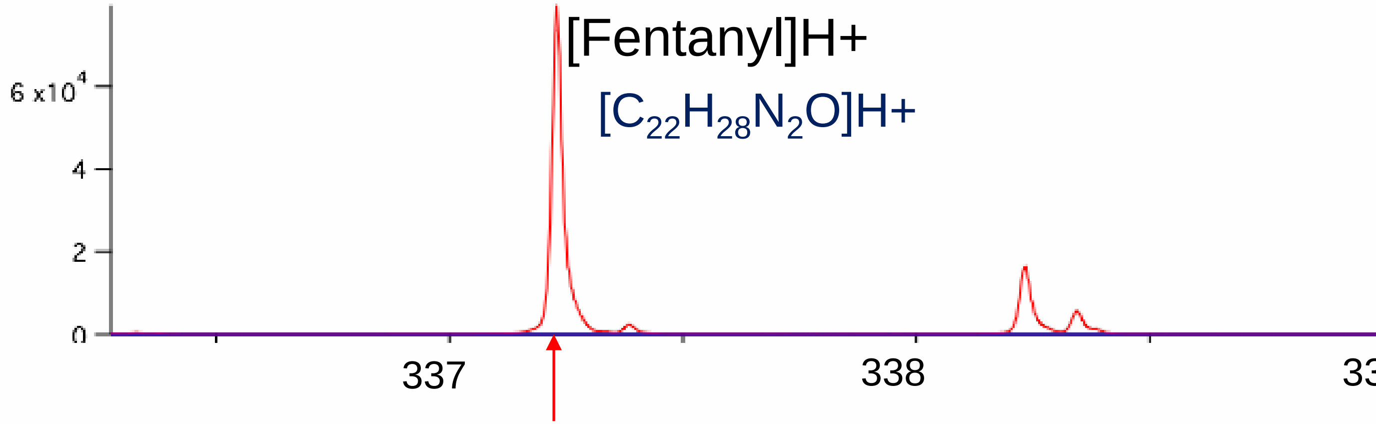
Data courtesy of Carsten Warneke, Joost DeGouw, Abby Koss

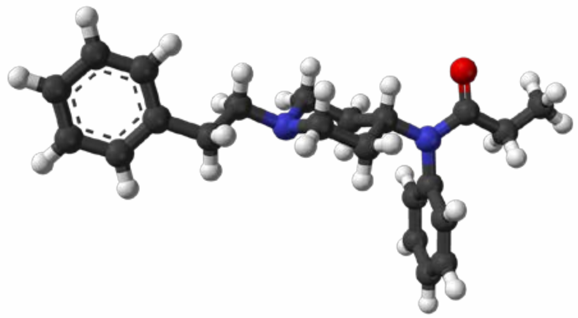
Dynamic Range



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

Confirmation with accurate mass

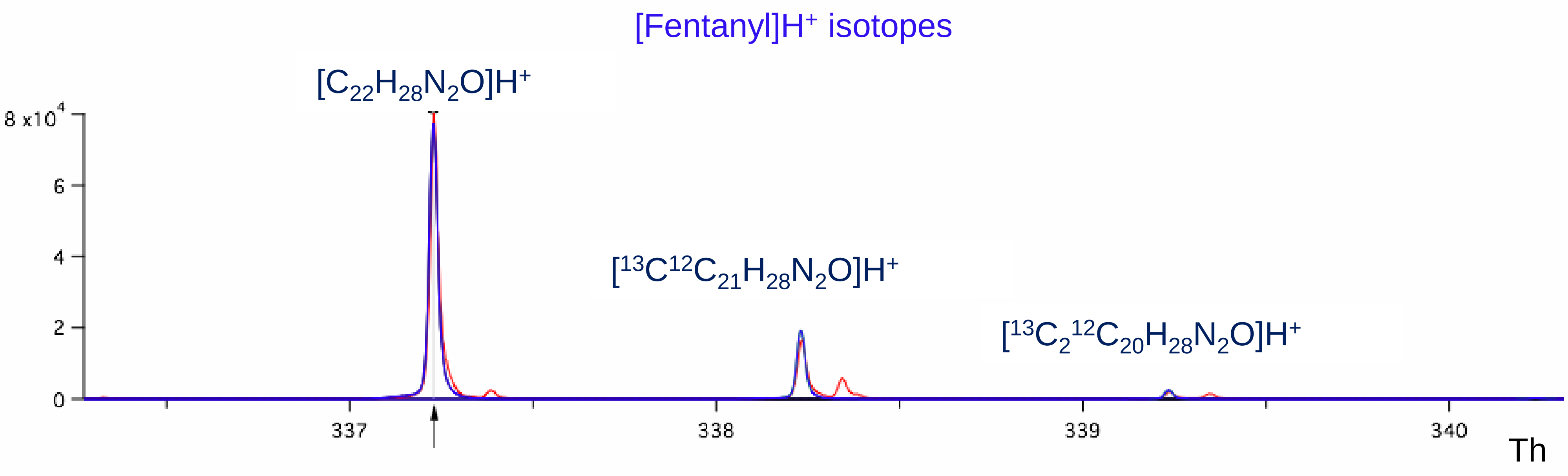




- Fentanyl exact mass: 337.22744 Da
- Fentanyl measured mass: 337.22650 Da
- mass accuracy: 0.94 mDa
- relative mass accuracy: 2.8 ppm

→ **mass accuracy** confirms the detection of protonated fentanyl

Confirmation with isotope pattern

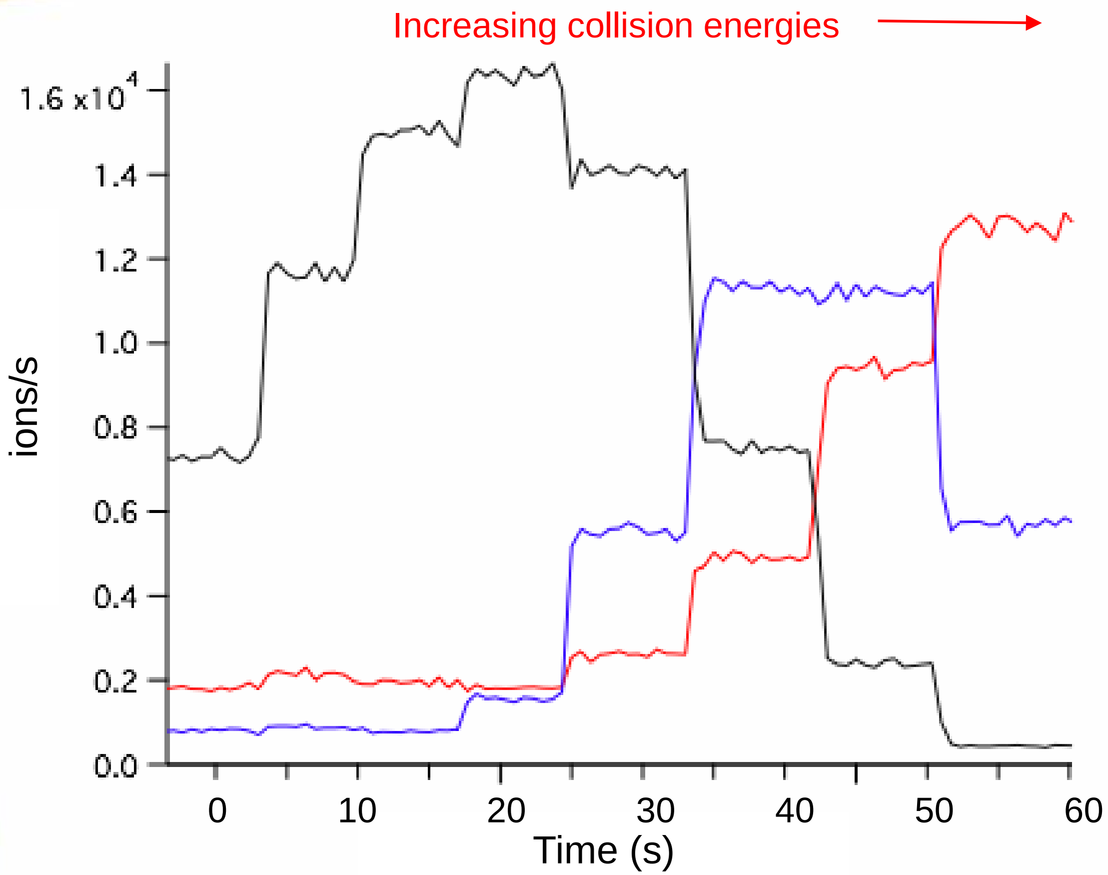


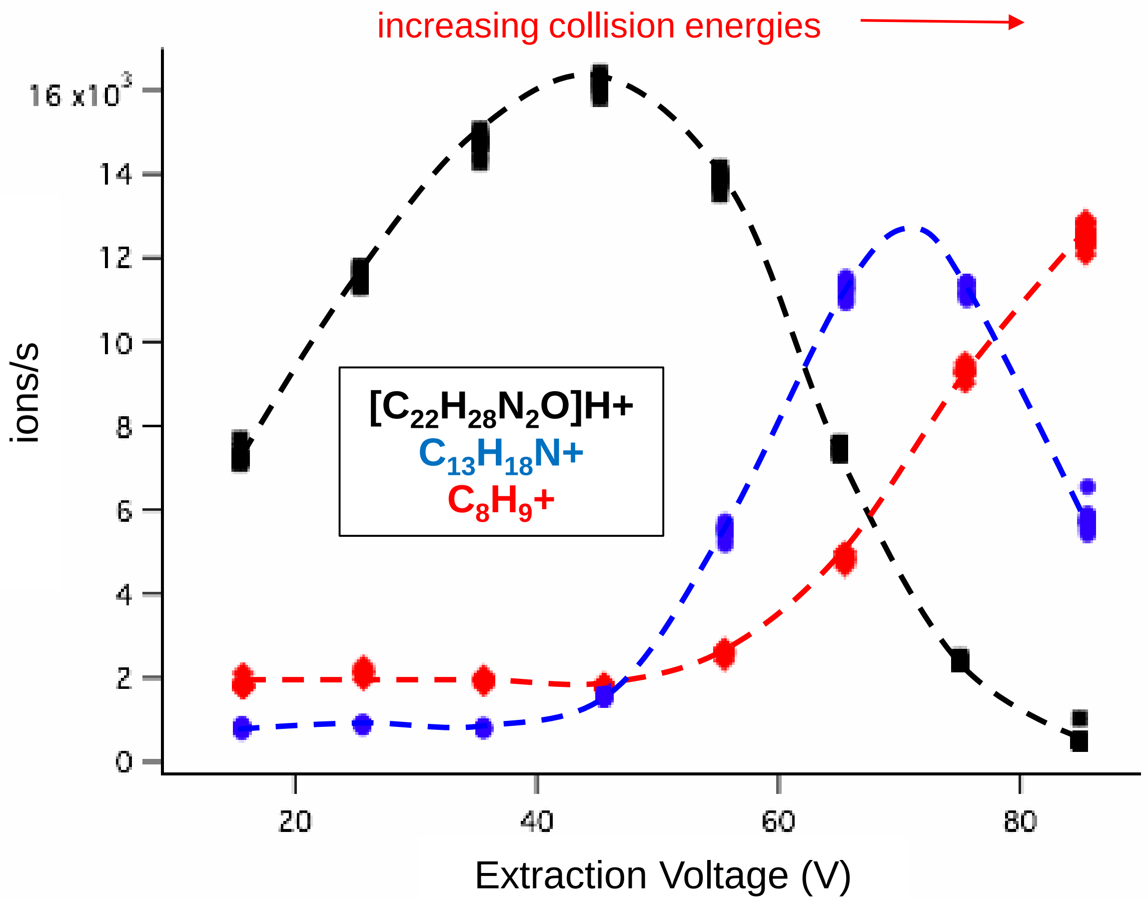
— synthetic spectrum of Fentanyl showing isotopes

— measurement of Fentanyl showing the same isotopes

→ **isotopic distribution** confirms Fentanyl

Fentanyl confirmation using CID



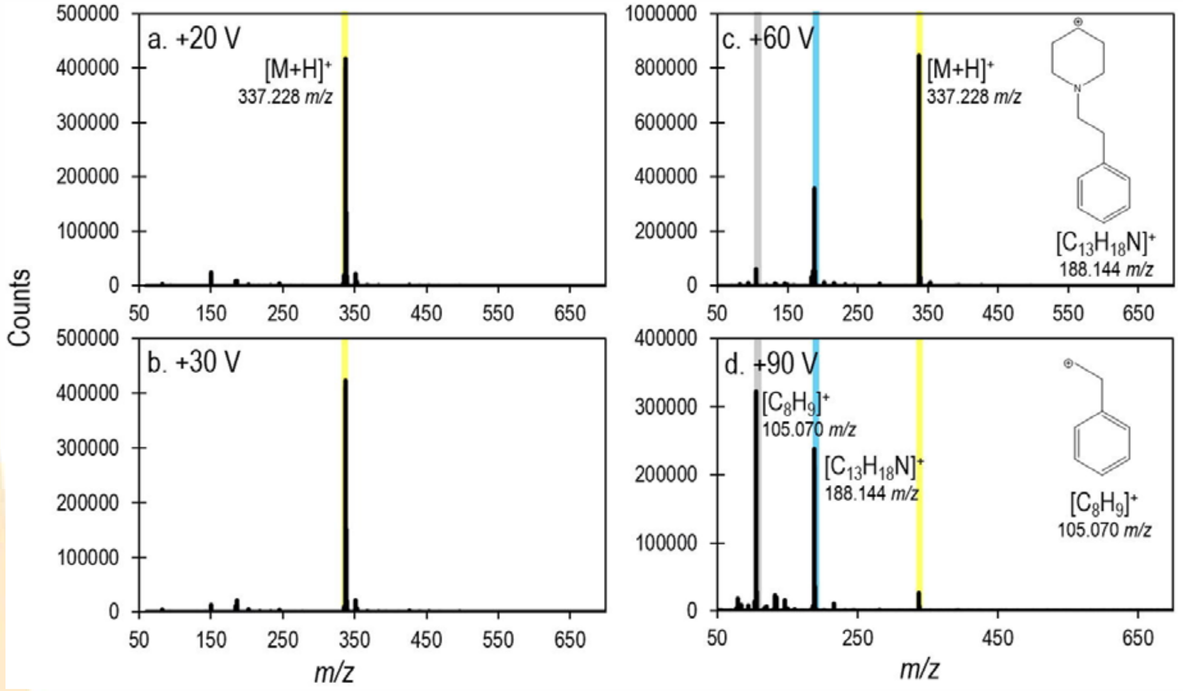


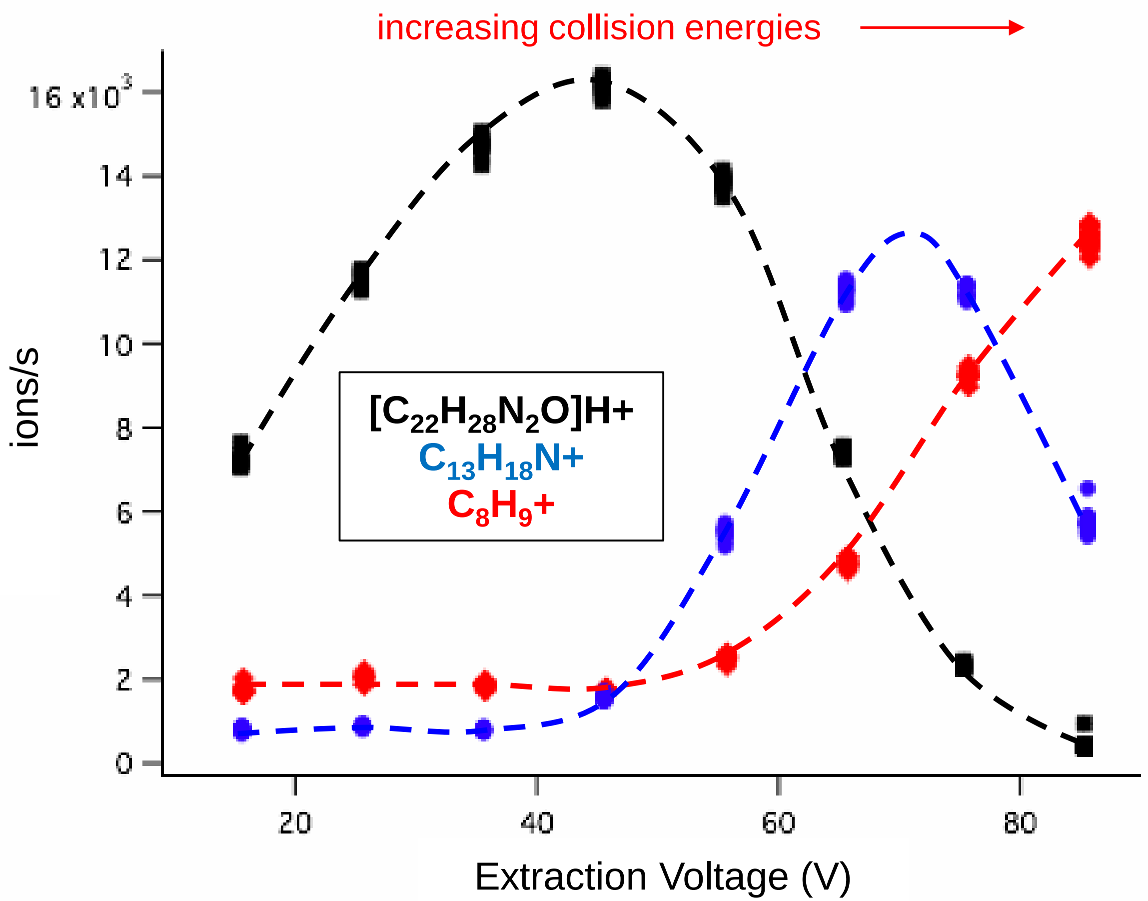
- By changing the collisional energy after the Vocus reactor, collisional induced dissociation can be used to confirm Fentanyl by formation of known fragments

Fentanyl confirmation using CID

CID fragments from library

https://doi.org/10.1016/j.forc.2017.04.001

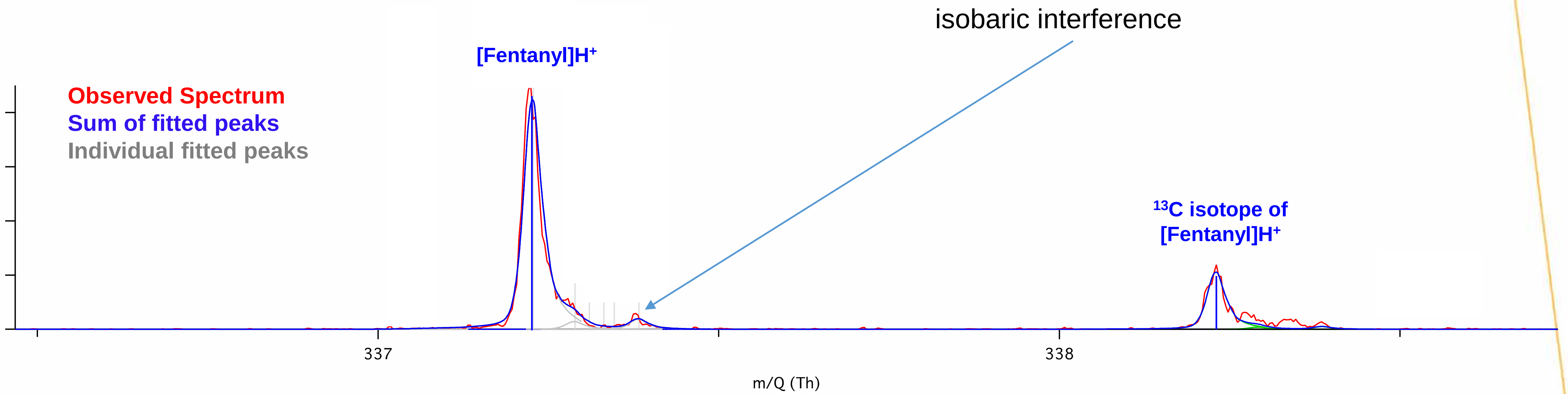




- The fragmentation patterns are the same as observed by previous studies using gas collision cells

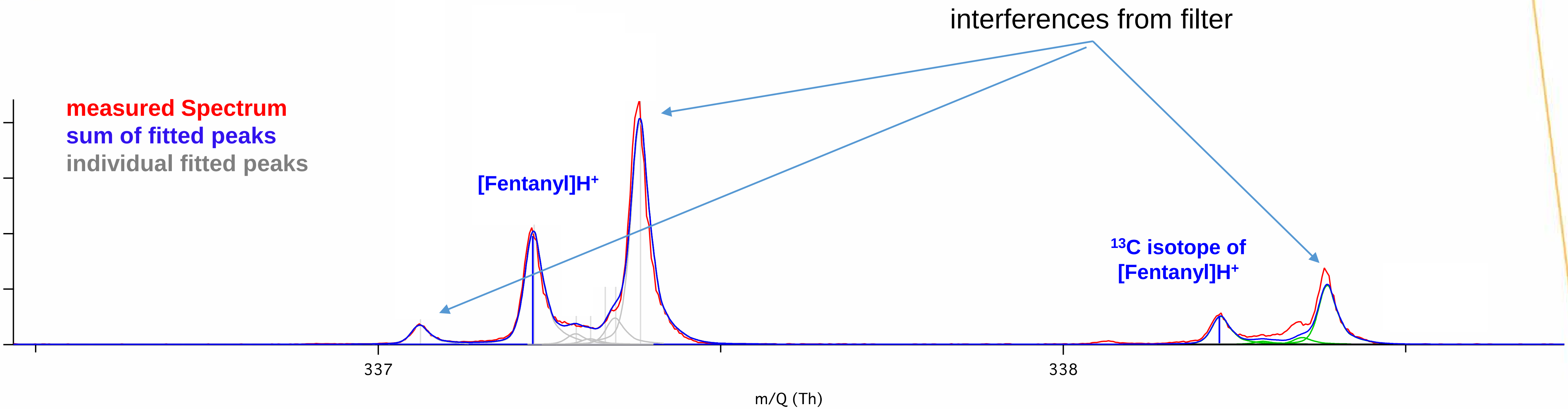
→ **fragmentation patterns** confirms fentanyl

Interference from clean glass



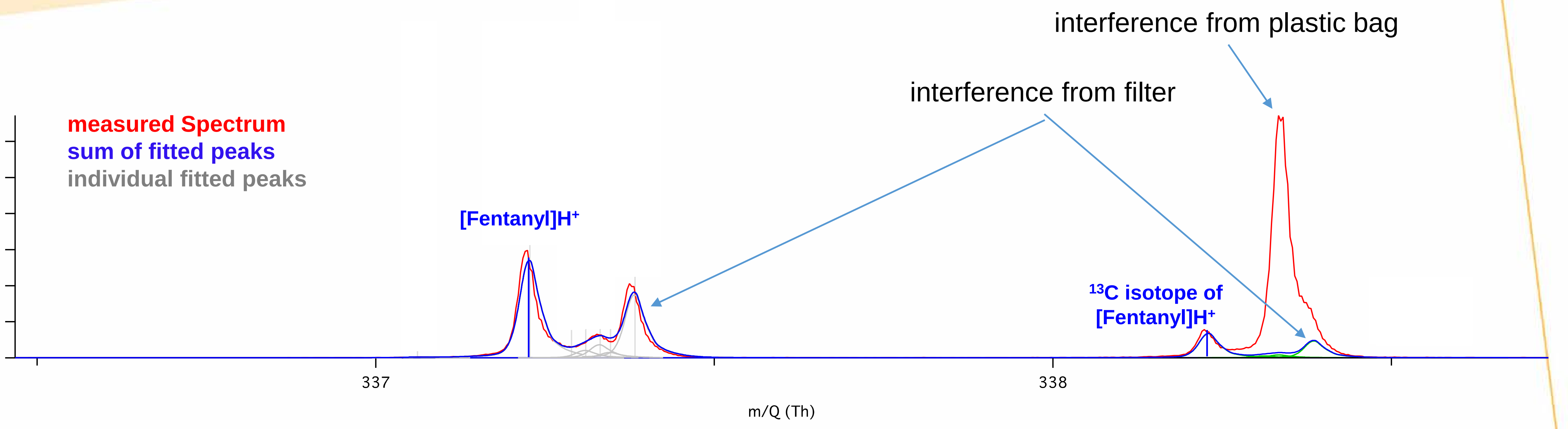
- Approximately 10 ng Fentanyl desorbed from a clean glass surface
- Very few isobaric interferences
- High resolution not required for pure detection

Interferences from filter paper



- 10 ng Fentanyl in water on a 3 cm^2 piece of filter paper straight out of a box (uncleaned)
- Isobaric interferences at both the protonated mass and the isotope which result in interferences
- High resolution required for robust separation of Fentanyl

Interference from plastic bag



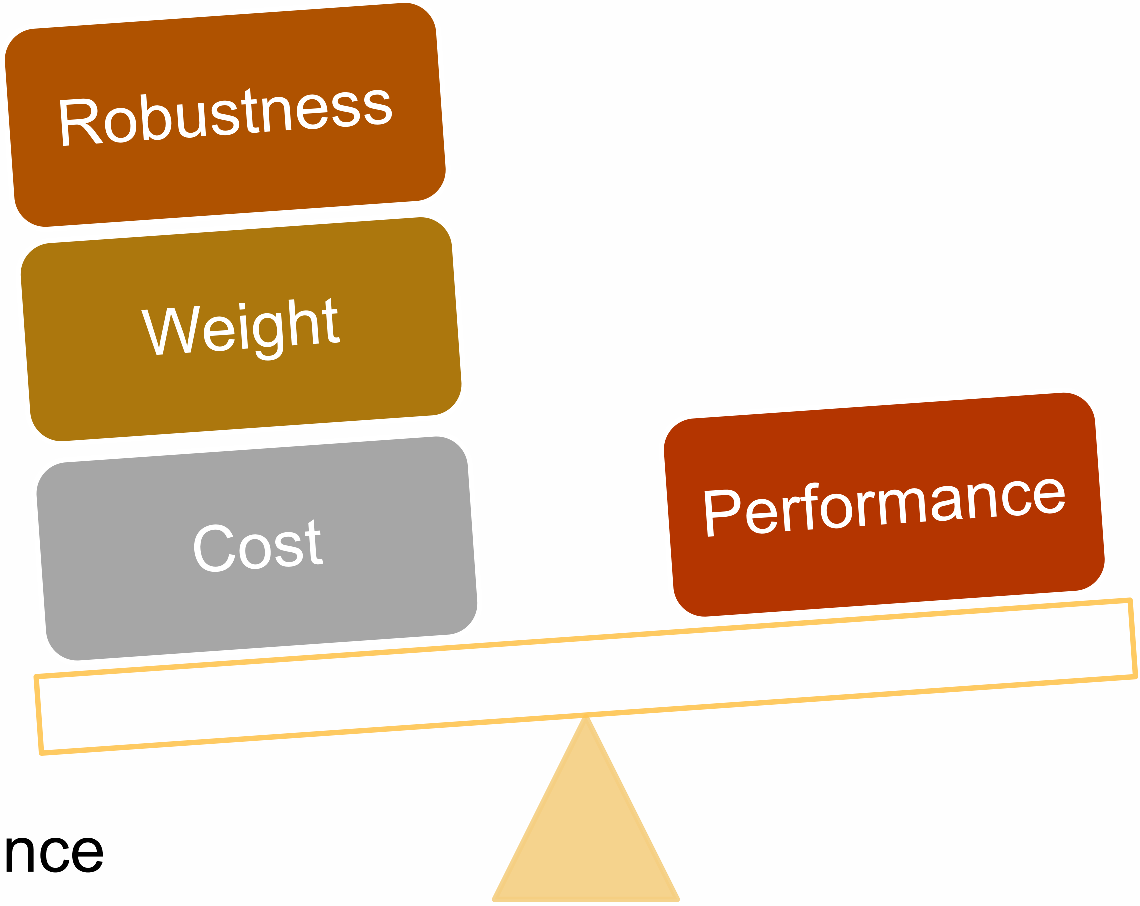
- 10 ng of fentanyl in water on a 3 cm^2 piece of filter paper which was rubbed on a plastic bag to add additional interferences (simulating material which is swabbed from a plastic bag).
- additional interferences are at different nominal masses (338 Th) in the region of interest.
- high resolution required

Summary

Field measurements are hard:

- Uncontrolled conditions
- Lot of background
- No sample prep
- Sometimes no expert users

→ You may require good performance



Find the right compromise

Acknowledgements

- Jordan Krechmer
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- Joel Thornton
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- TOFWERK, Switzerland