Real-time analysis of trace metals in air by microwave induced plasma time-of-flight mass spectrometry (mipTOF)

ETH Nanoparticles Conference

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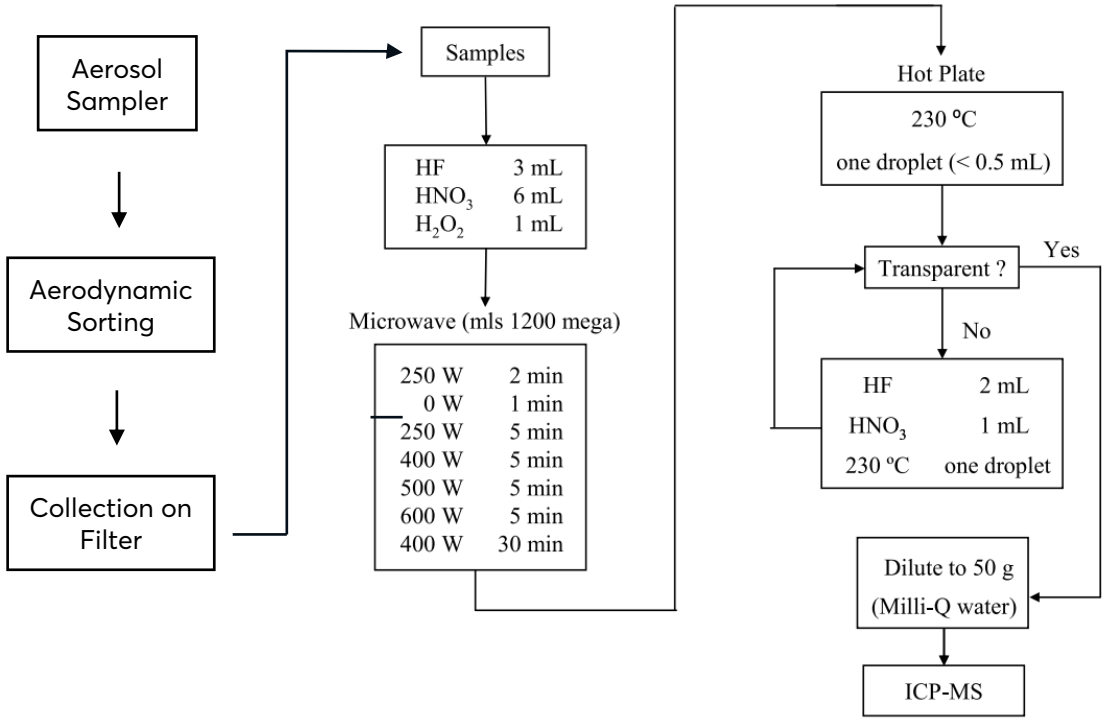
Alex Gundlach-Graham
Martin Tanner

Conventional Analysis of Metals in Air

Lab-Based:

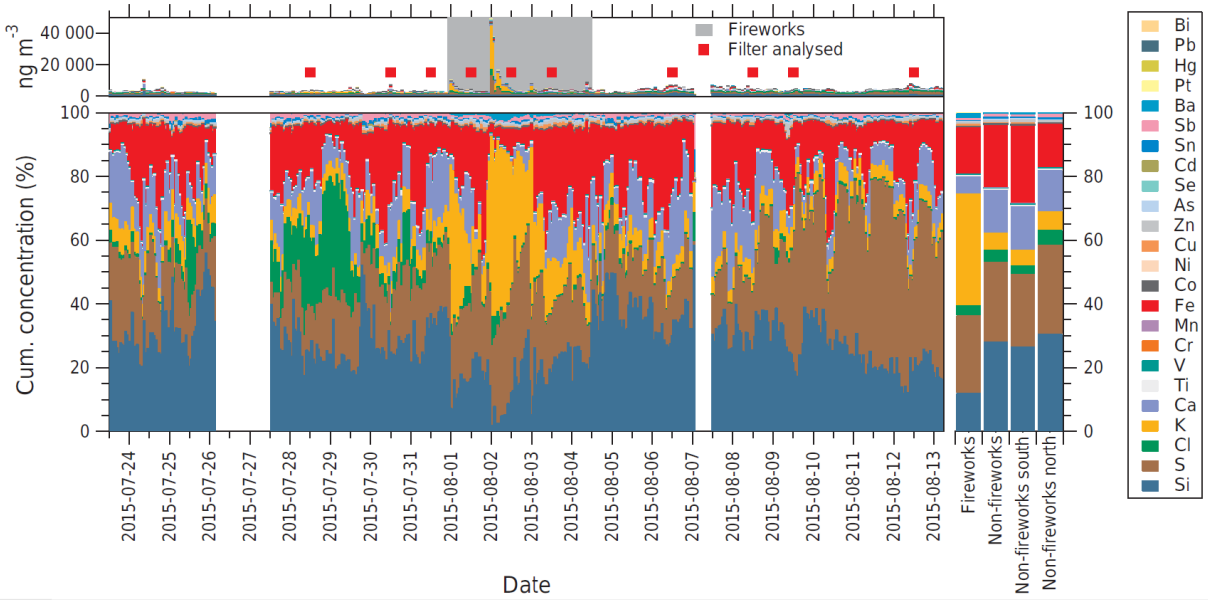
- Collect particles on filters
- Analyze samples in the lab by ICP-MS



Suzuki, Y.; Suzuki, T.; Furuta, N. *Analytical Sciences* ***2010, 26 (9), 929-935.***

In-Field Sampling and Analysis:

- Samples collected on a filter and then analyzed by EDXRF
- Time resolution: 30-120 min
  - Provides bulk metal concentration information, LODs from 0.3-500 ng/m³



Furger, M.; et al. Atmos. Meas. Tech. 2017, 10 (6), 2061-2076.

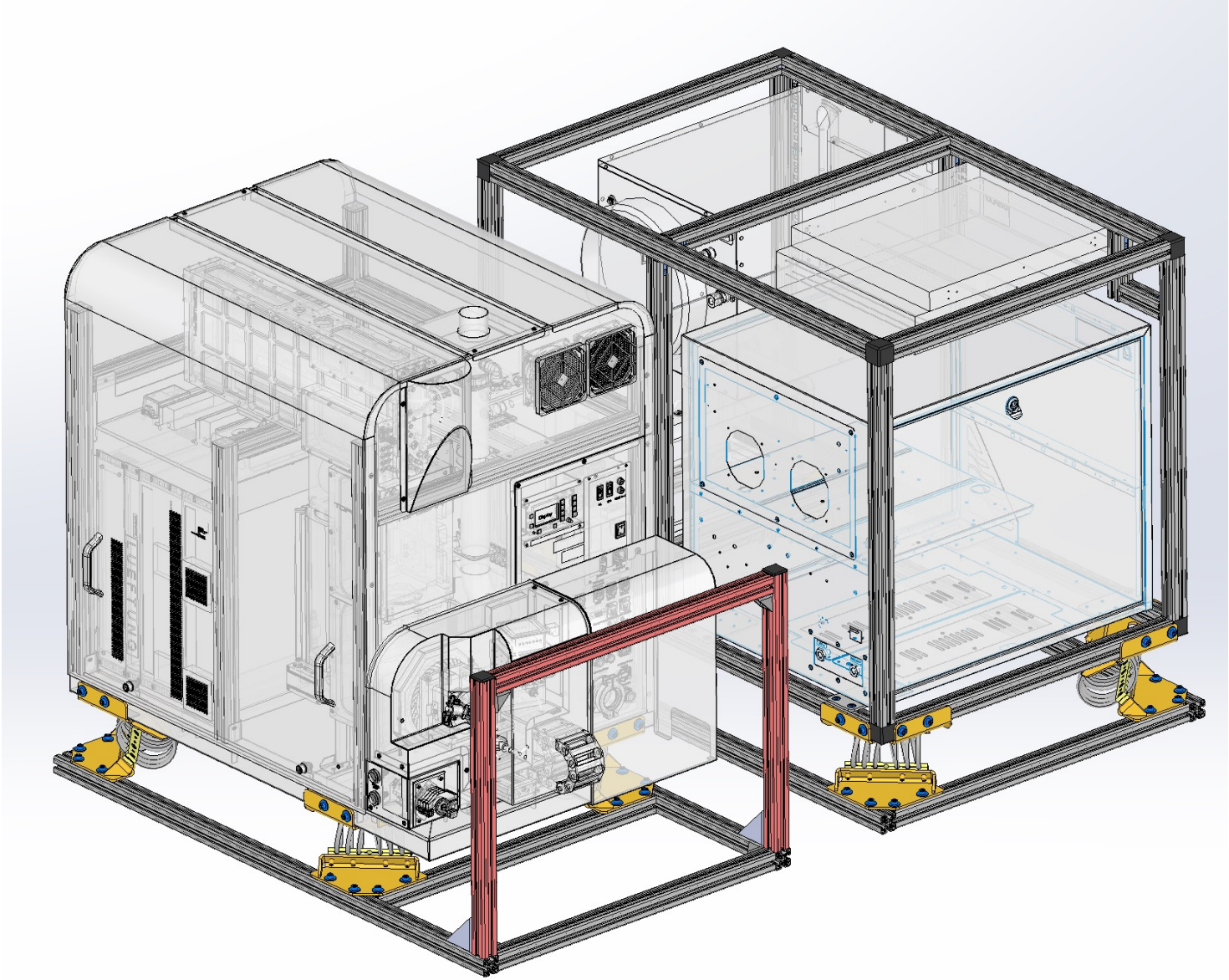
mipTOF Overview

Instrument for real-time trace-metal particle analysis

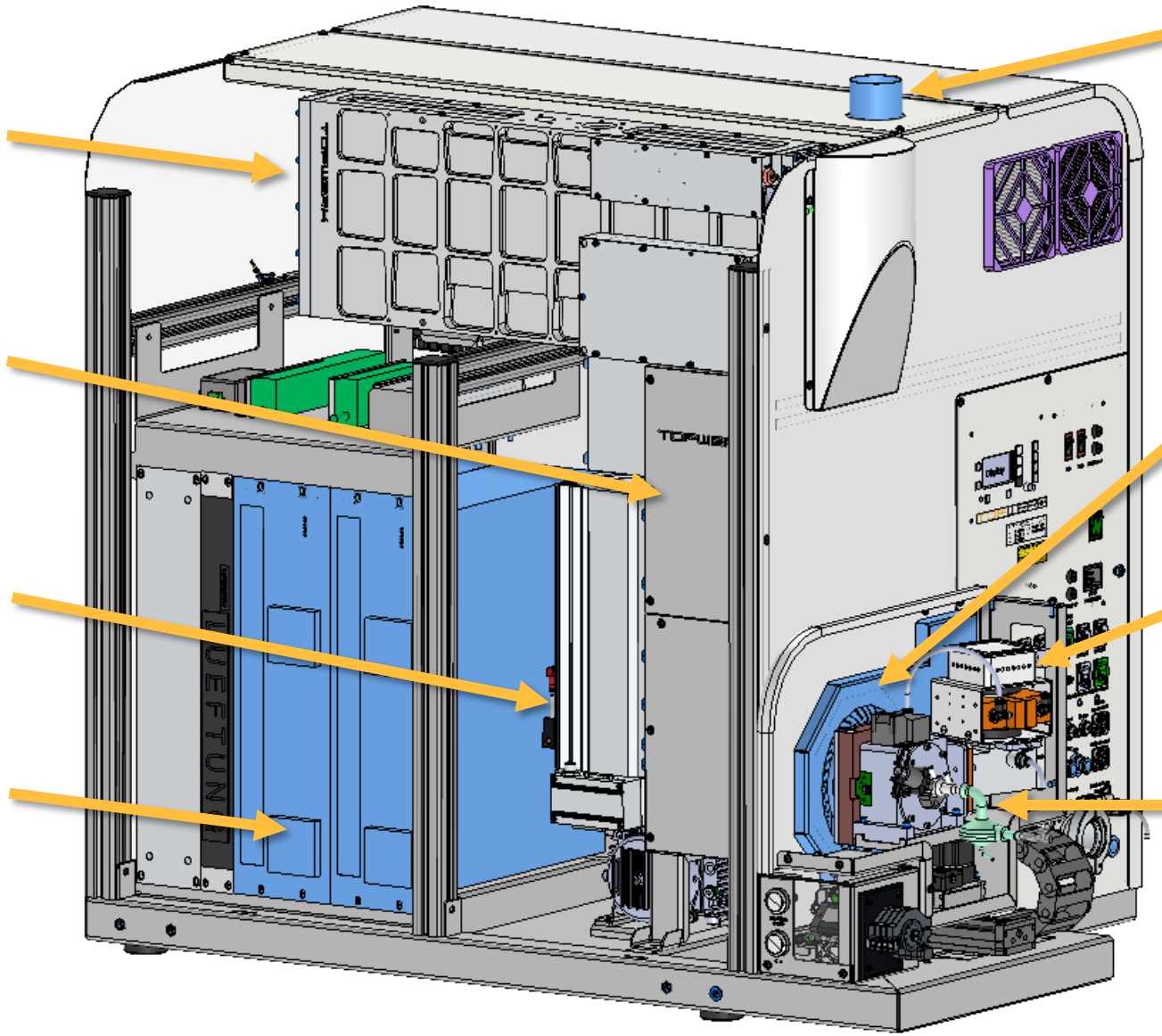
- Microwave Inductively Coupled Atmospheric-Pressure Plasma (MICAP, RADOM Corp.) coupled to TOFMS instrument
- Plasma source can be operated with nitrogen (N_2) gas or directly with air.
  - Eliminates need for compressed gases and allows for instrument **deployment in the field**.
- mipTOF be used to **directly sample air** for **real-time, continuous particulate analysis**
- Sensitive detection of metals in individual particles: attogram to femtogram detection limits

mipTOF Instrument Design

- Field-Deployable or Lab-Based options
- Power Consumption
  - Active: 5.5 kW
  - Standby: < 350 W
- Size:
  - Main Unit: 0.8 × 1.2 × 1 m: 196 kg
  - Supplies: 0.8 × × 0.9 m: 225 kg



mipTOF Instrument Design



Orthagonal acceleration TOF mass analyzer

Ion Optics: Turning optic, RF Collision cell, RF Notch Filter

Split-flow turbo pump

Electronics and computer

Exhaust with integrated fan

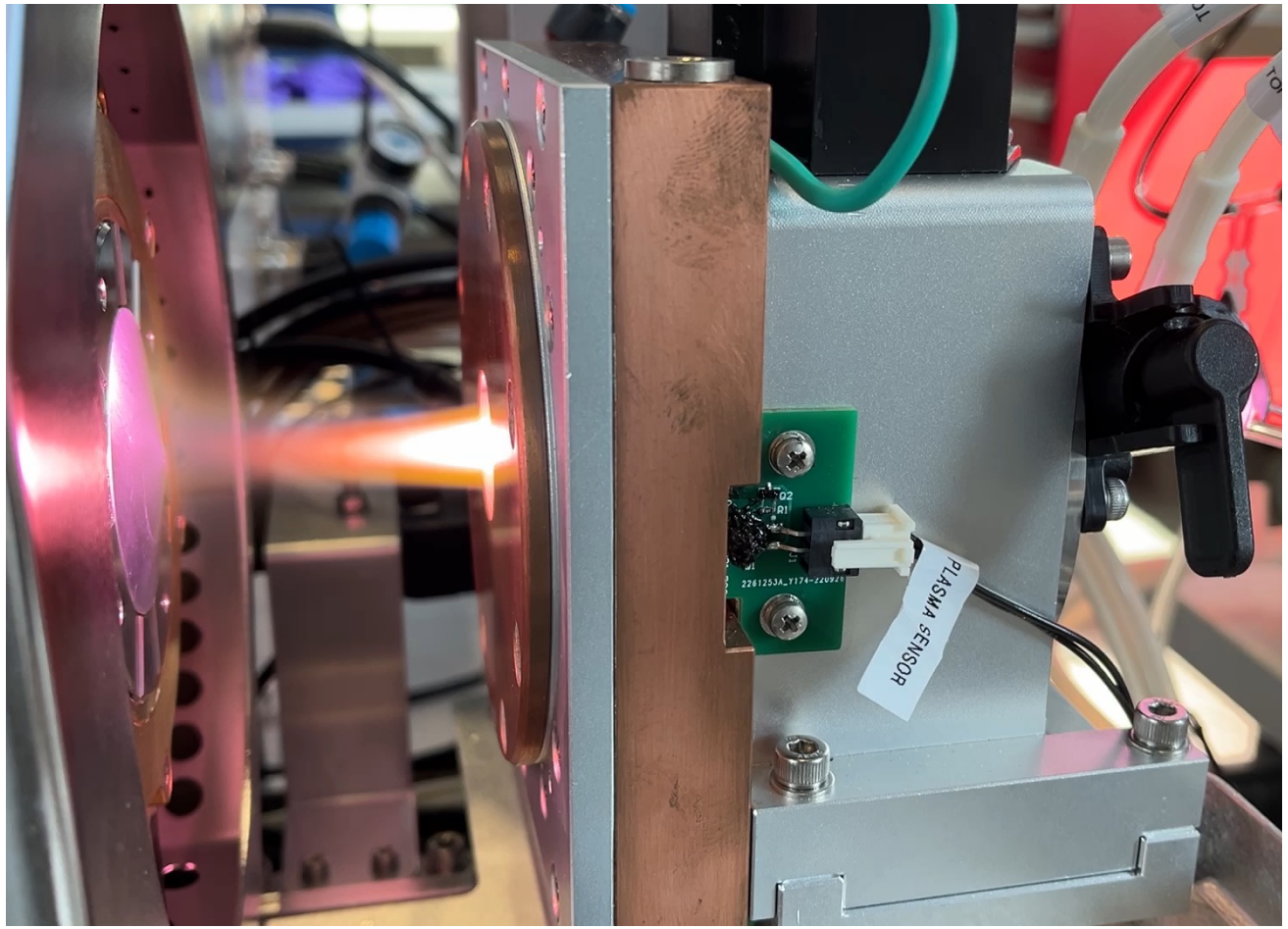
Water-Cooled Interface

MICAP Source on 3D translation stage

Sample Introduction

MICAP Source Characteristics

- Toroidal Plasma sustained with N_2 or air
- Argon is used during ignition for spark propagation
- Powered inductively at 2.45 GHz via ceramic resonator
- Water-cooled magnetron for stable sustained operation
- "Conventional" Fassel ICP torch
- 800-1500 W
- Gas temps: > 5000 K
- Source of vaporization, atomization, and ionization
- >90% ionization of many elements

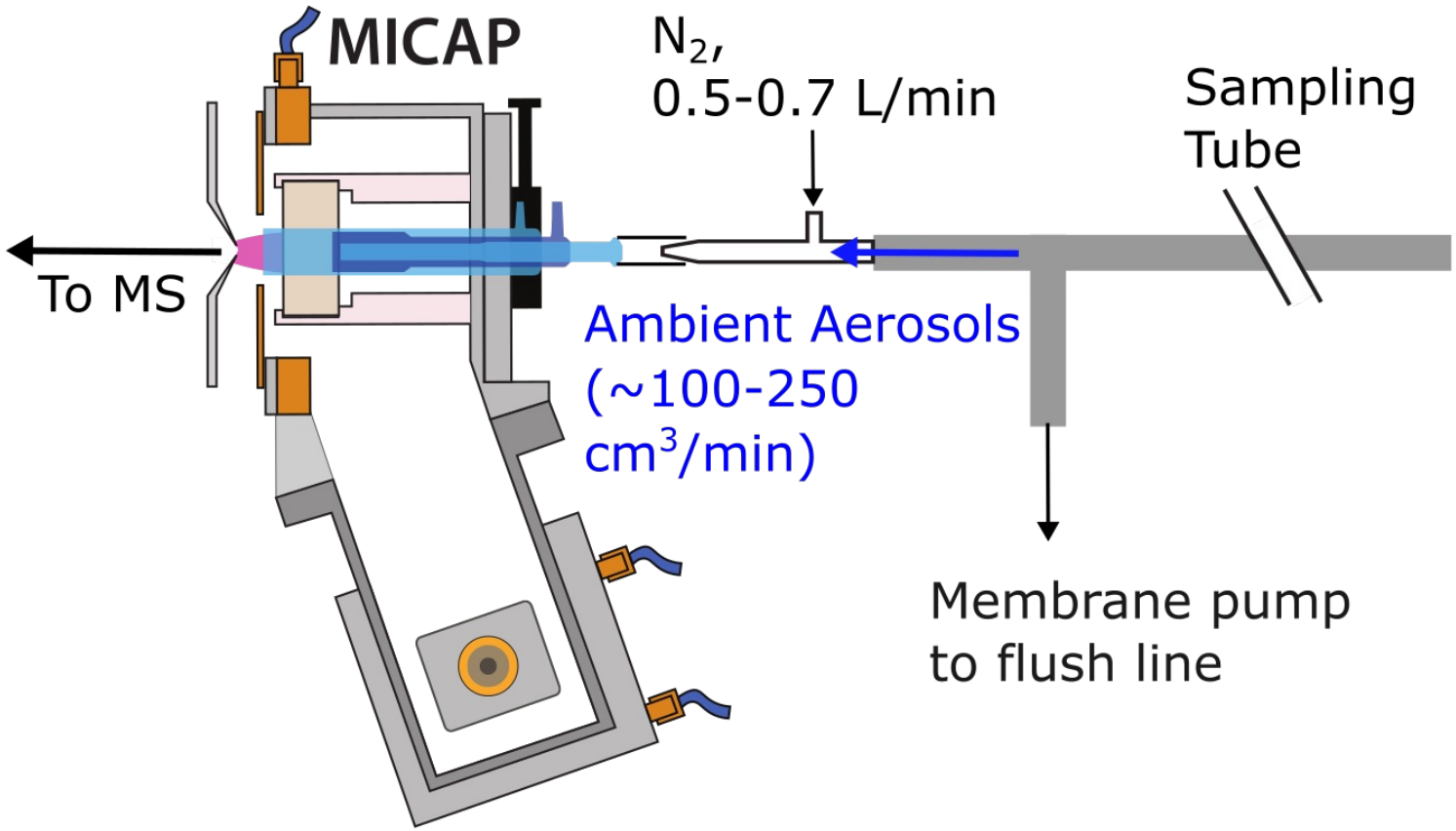


Jevtic, J.; Menon, A.; Pikelja, V. Plasma generator using dielectric resonator. PCT/US14/24306, 2015.

Schild, M. et al. *Analytical Chemistry* **2018**, 90 (22), 13443-13450.

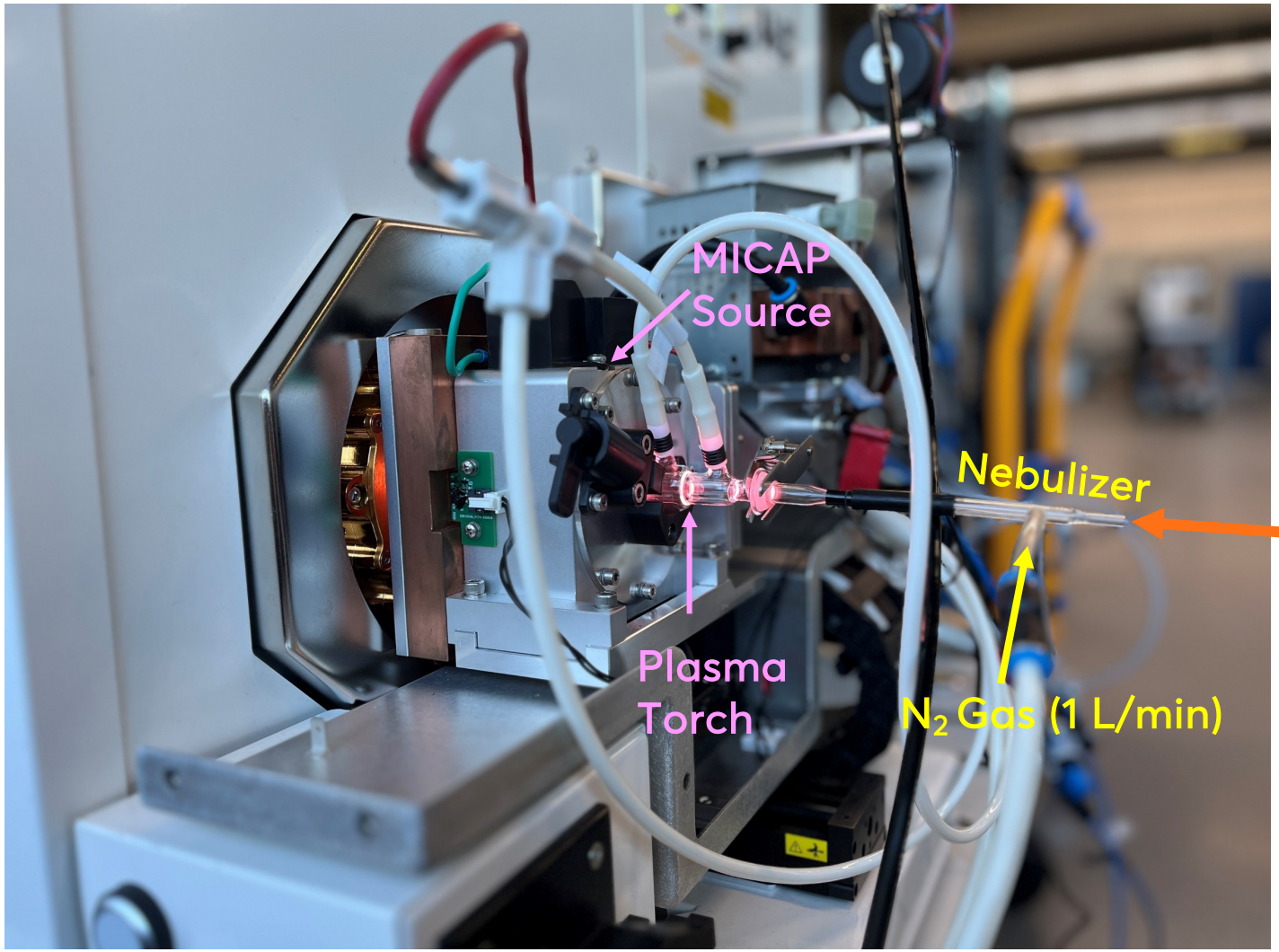
Direct Air sampling

Passive Sampling by Venturi Effect



- Air sampling without pump in the sample flow path to the ion source
- Use of conventional concentric nebulizer as a Venturi pump

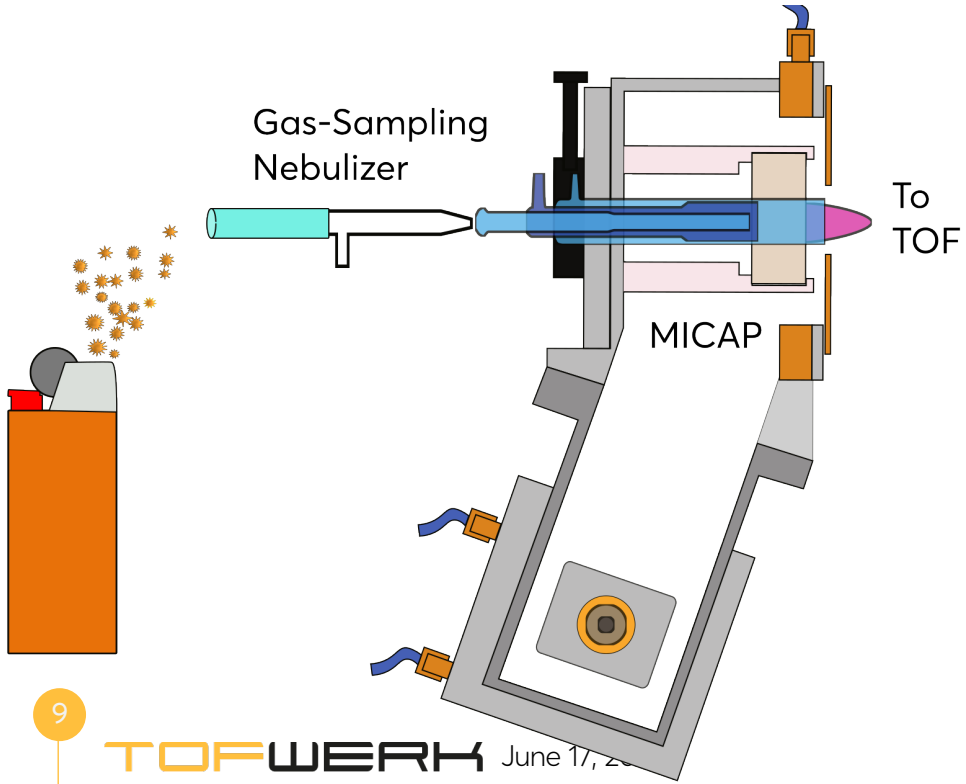
Direct Air sampling

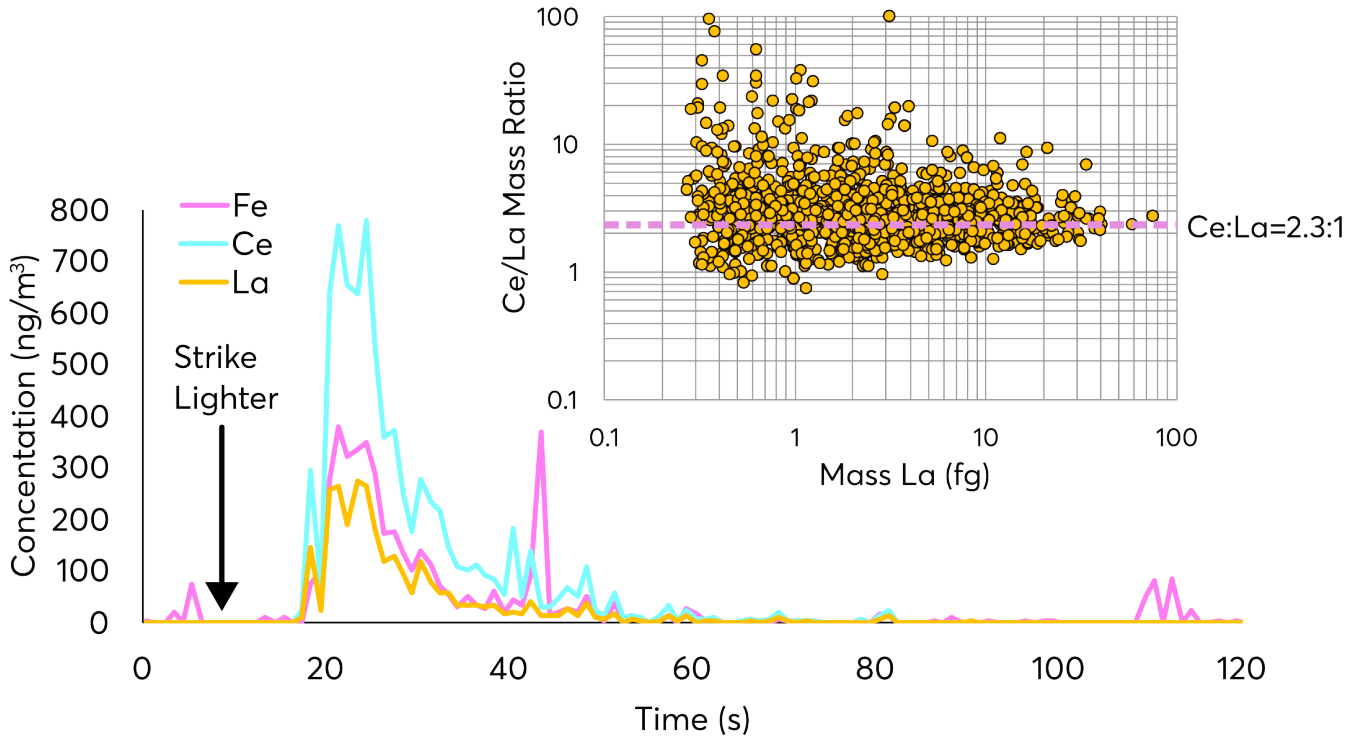


- Air sampling without pump in the sample flow path to the ion source
- Use of conventional concentric nebulizer as a Venturi pump

mipTOF Time Resolution: Bulk and Particle Resolved Measurements

- Complete average mass spectra collected at 5 ms time resolution
- Individual particles in plasma produce intense, fast transients (300-500 µs)
- Individual particles are registered as signal spikes
- If many particles are in the plasma within 5 ms, then individual particles cannot be resolved, but bulk quantification is achieved.
- Time resolution of mipTOF is tunable: milliseconds to min!

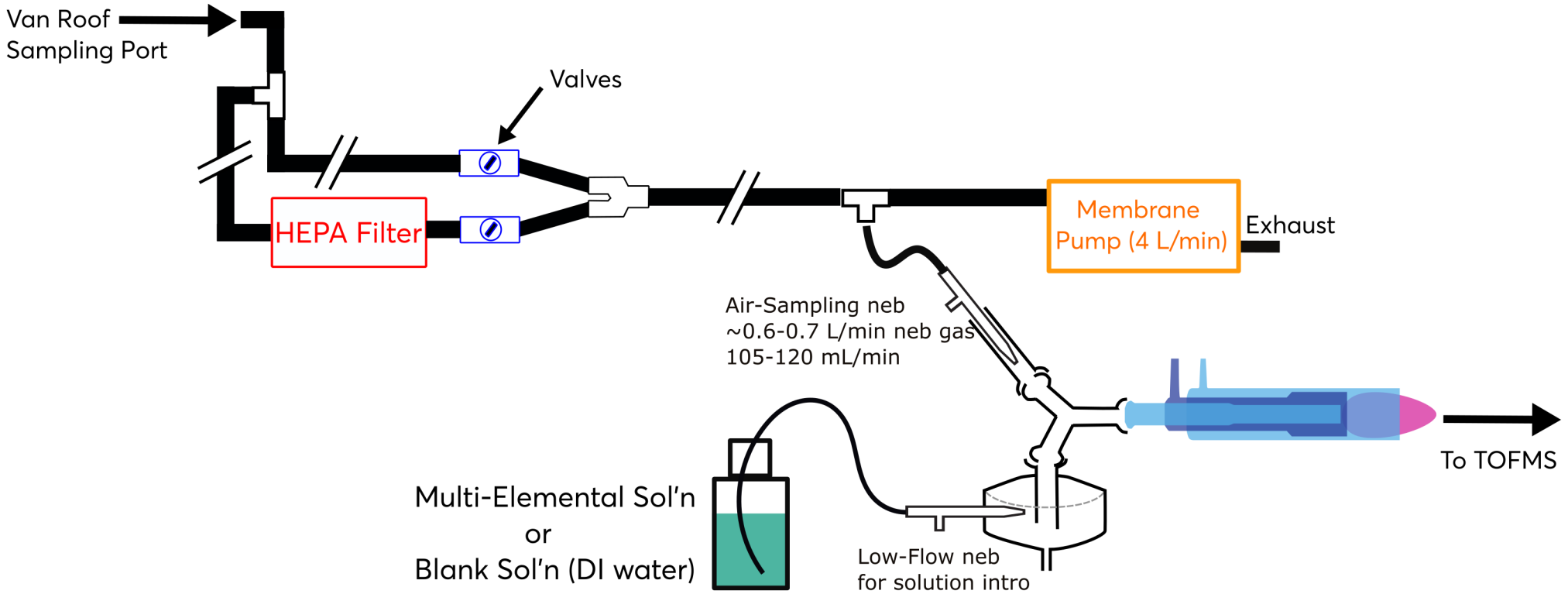




Calibration Setup

Calibration achieved with liquid standards!:

- Calibration: Std Sol'n aspiration + HEPA Filter (absolute sensitivities for elements)
- Gas Blank: Blank Sol'n aspiration + HEPA Filter (blank standard deviation)
- Measurement: Blank Sol'n aspiration + Particles from air

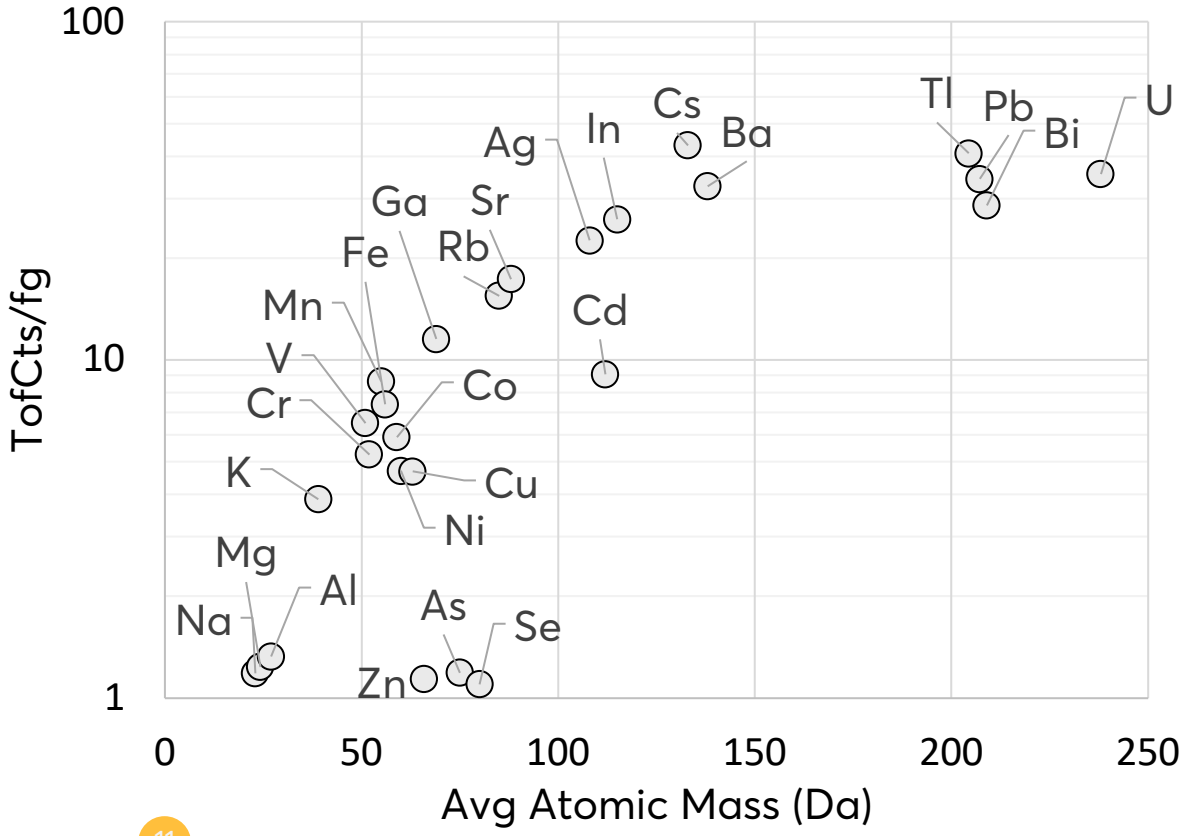


mipTOF Instrument for Real-Time Single-Particle Analysis

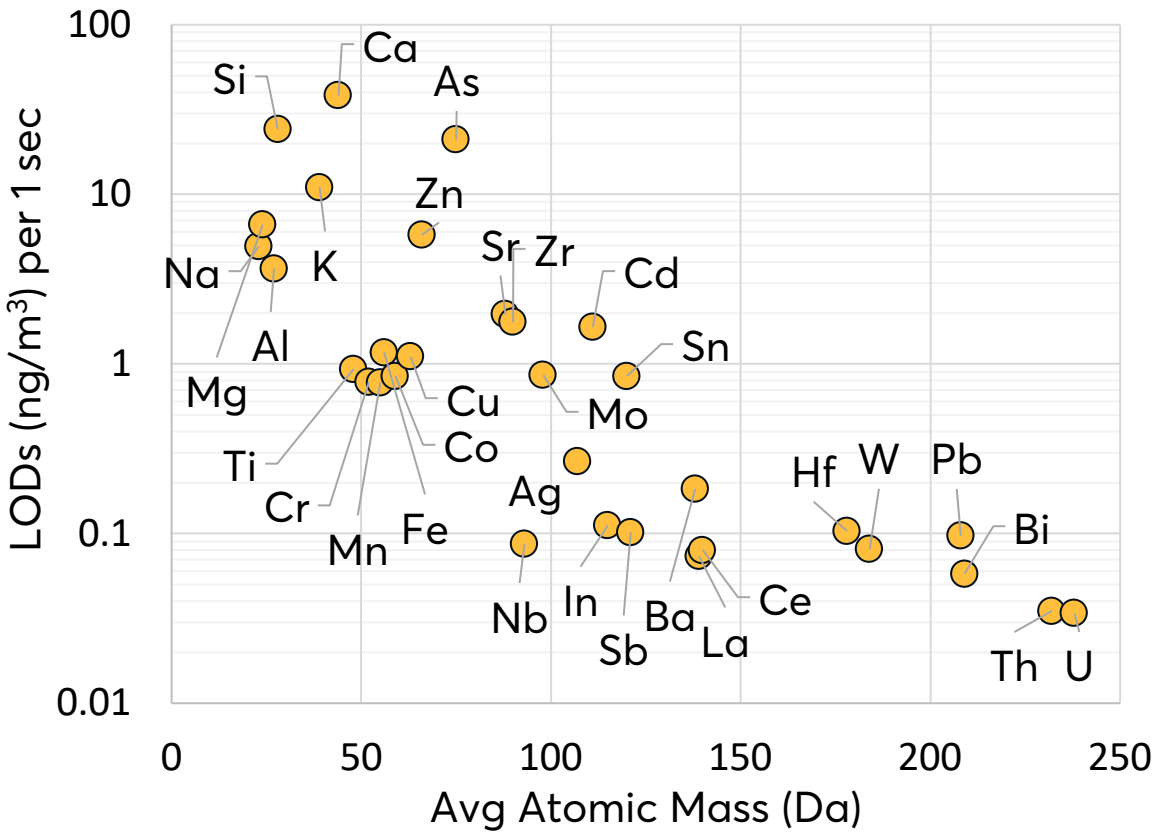
Most elements are measurable by MIP-TOFMS!

Elements not measurable: C, N, O, F, noble gases.

Absolute Sensitivities (Cts per femtogram):



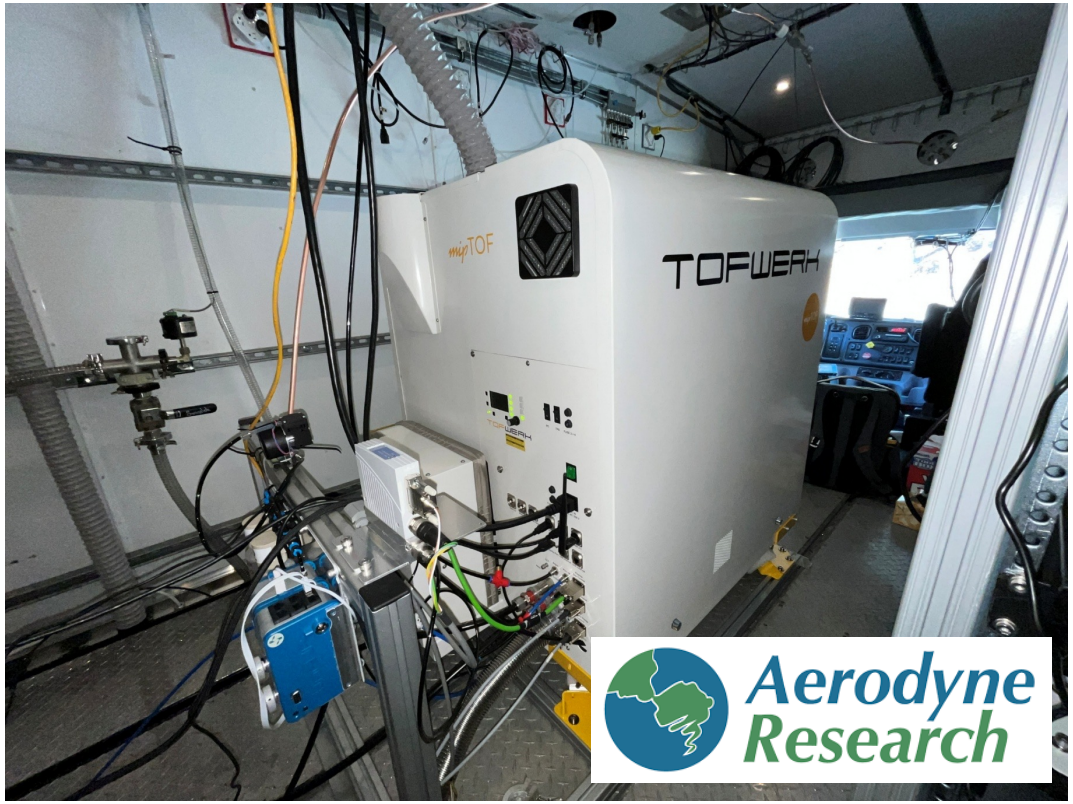
Limits of Detection (ng/m³) in one second:



mipTOF in the Field

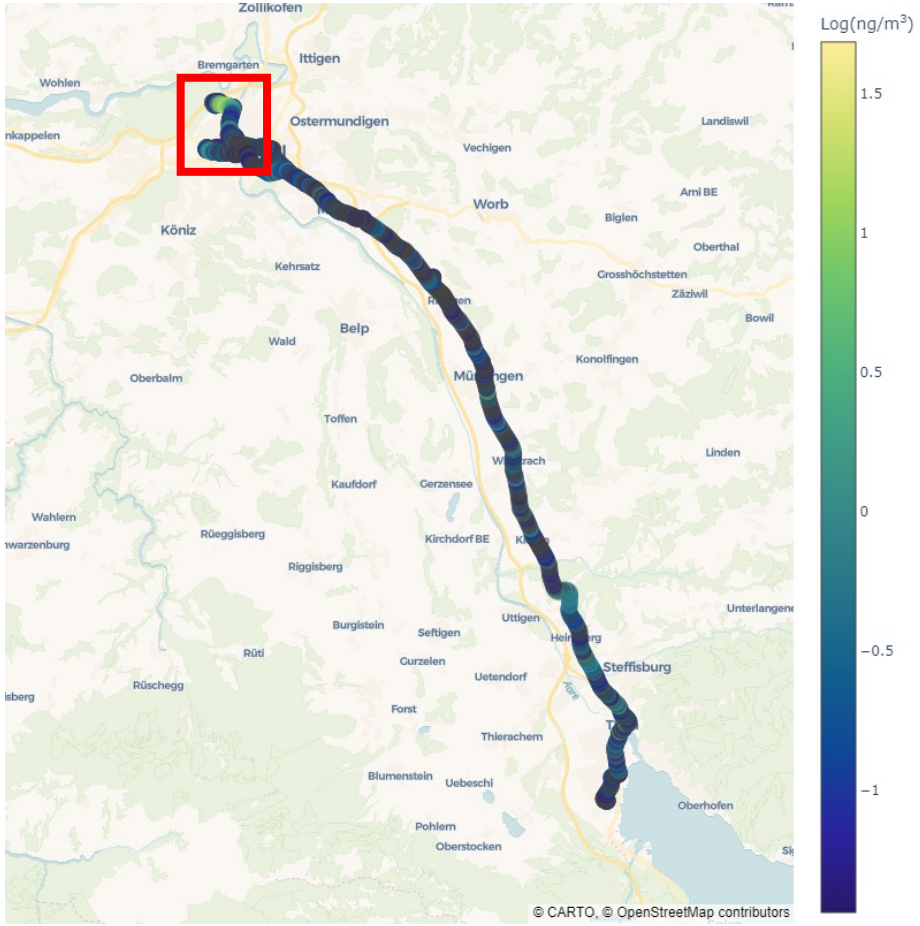
Field Campaign with the MOSQUITA
Jan 28 – Feb 4, 2025, Central Switzerland

Field Campaign with the Aerodyne Mobile Lab (AML)
March 17–28, 2025, Greater Boston Area

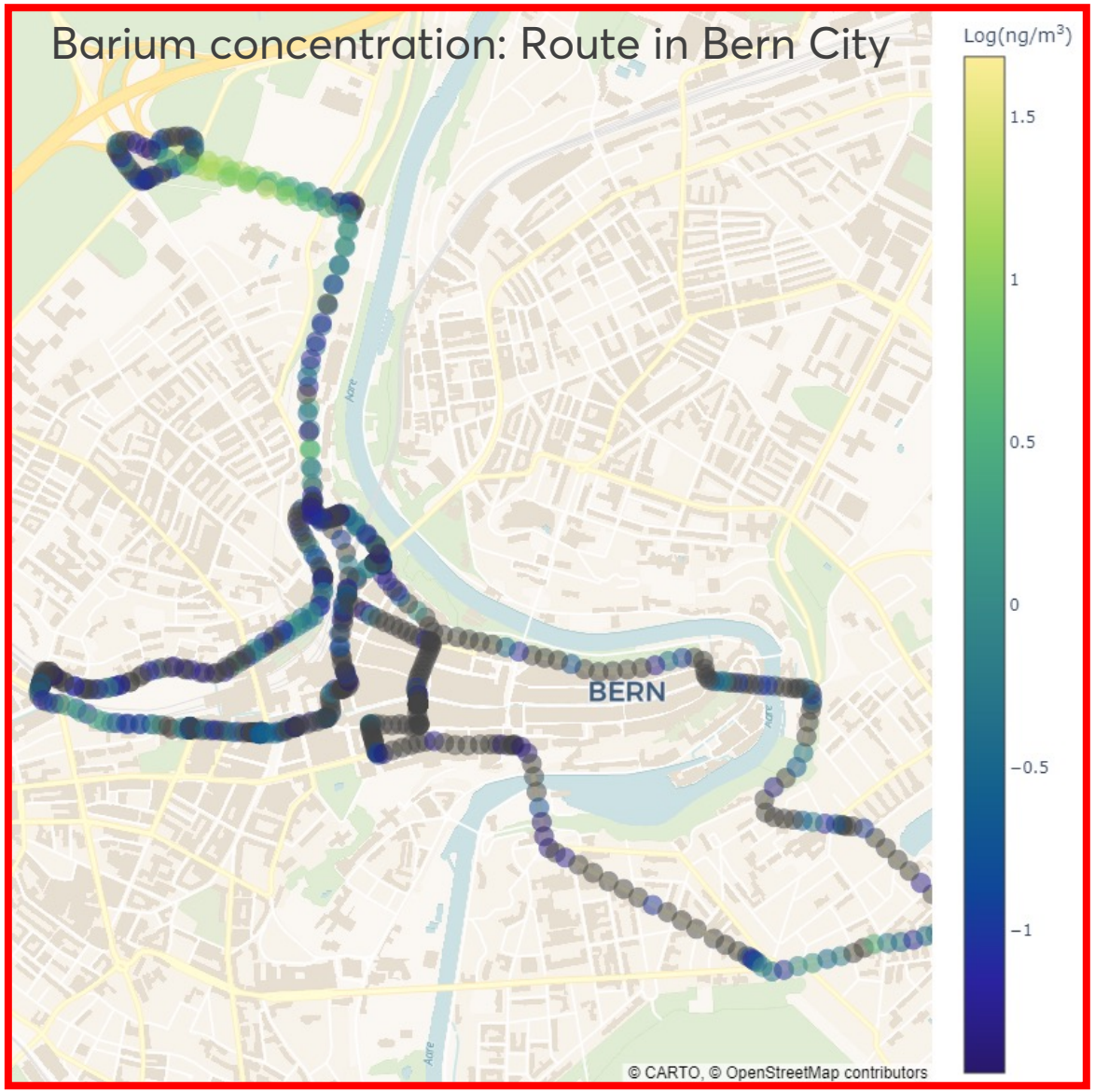


Mobile mipTOF measurements: Example Driving Data

Barium concentration: Route from Thun to Bern:

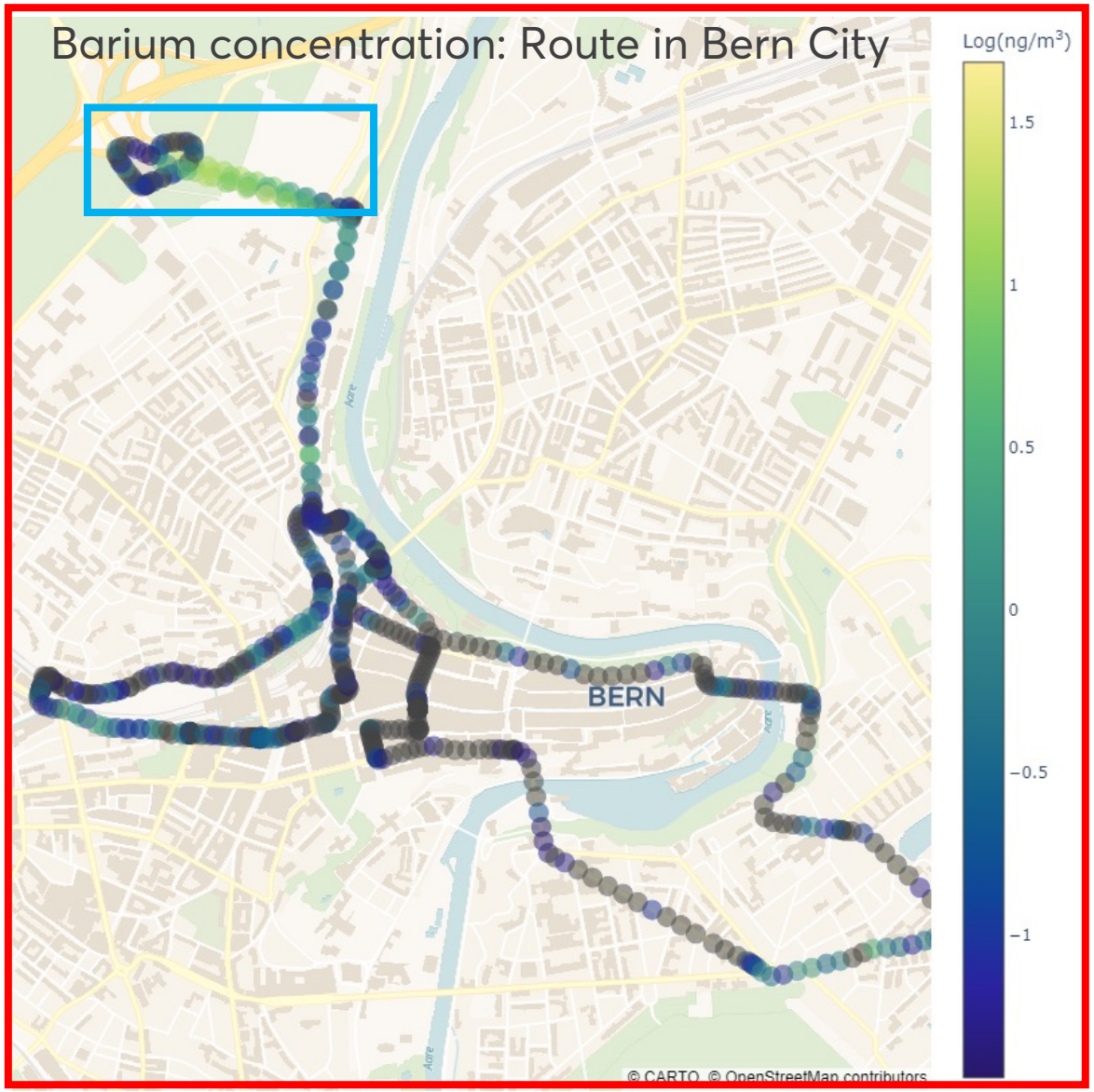


Barium concentration: Route in Bern City



Mobile mipTOF measurements: Example Driving Data

★ Driving up and down Neufeldtunnel in Bern

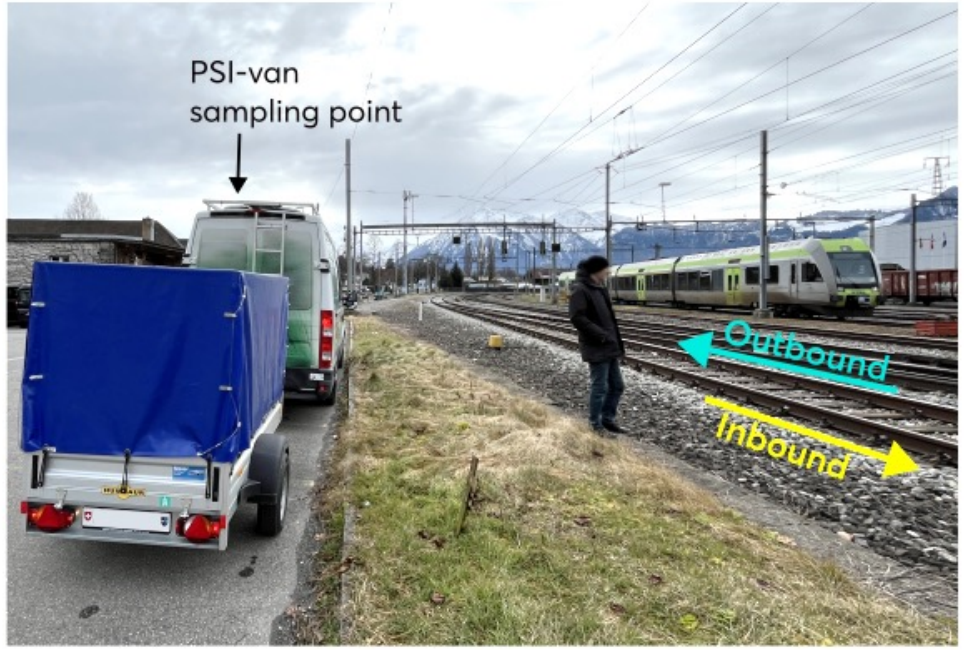


Example: mipTOF measurement of train-emitted metals

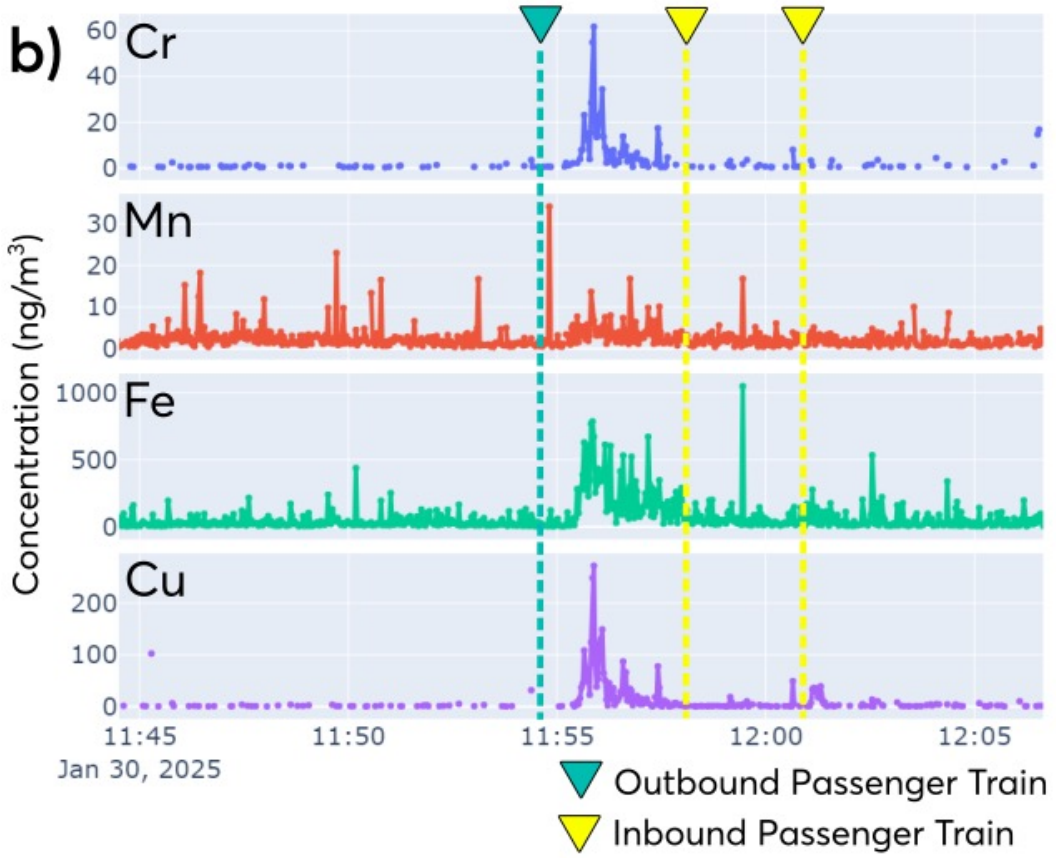
- Concentration of metal particles with Cr, Mn, Fe, and Cu are elevated immediately following train-passing event at Thun train station

Sampling position:

a)



Bulk quantification @ 2 second time resolution:



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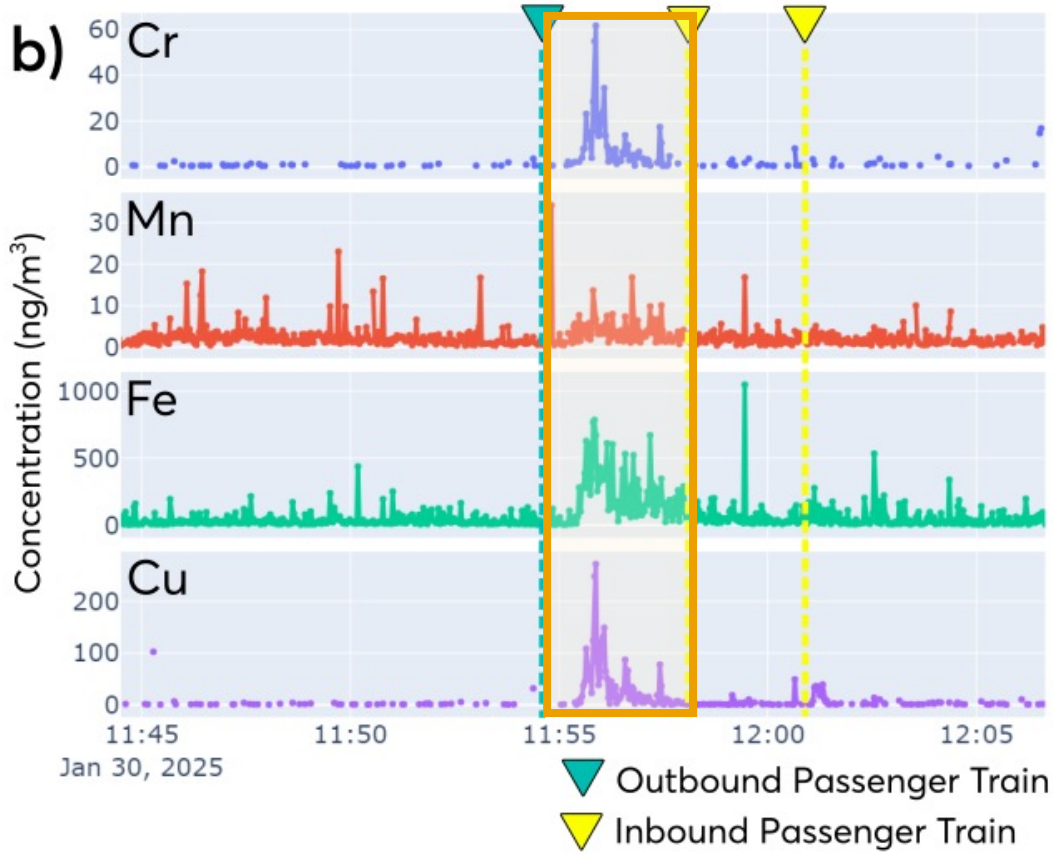
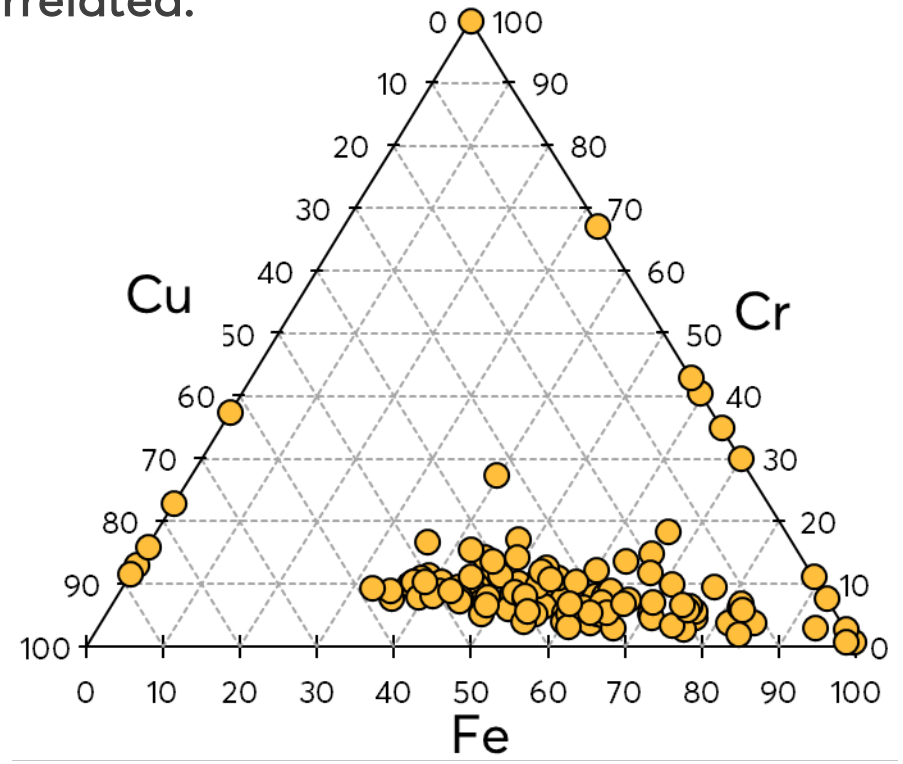


In 4-minute, window following train passing, 1800 particles recorded

At single-particle level, elements are correlated:



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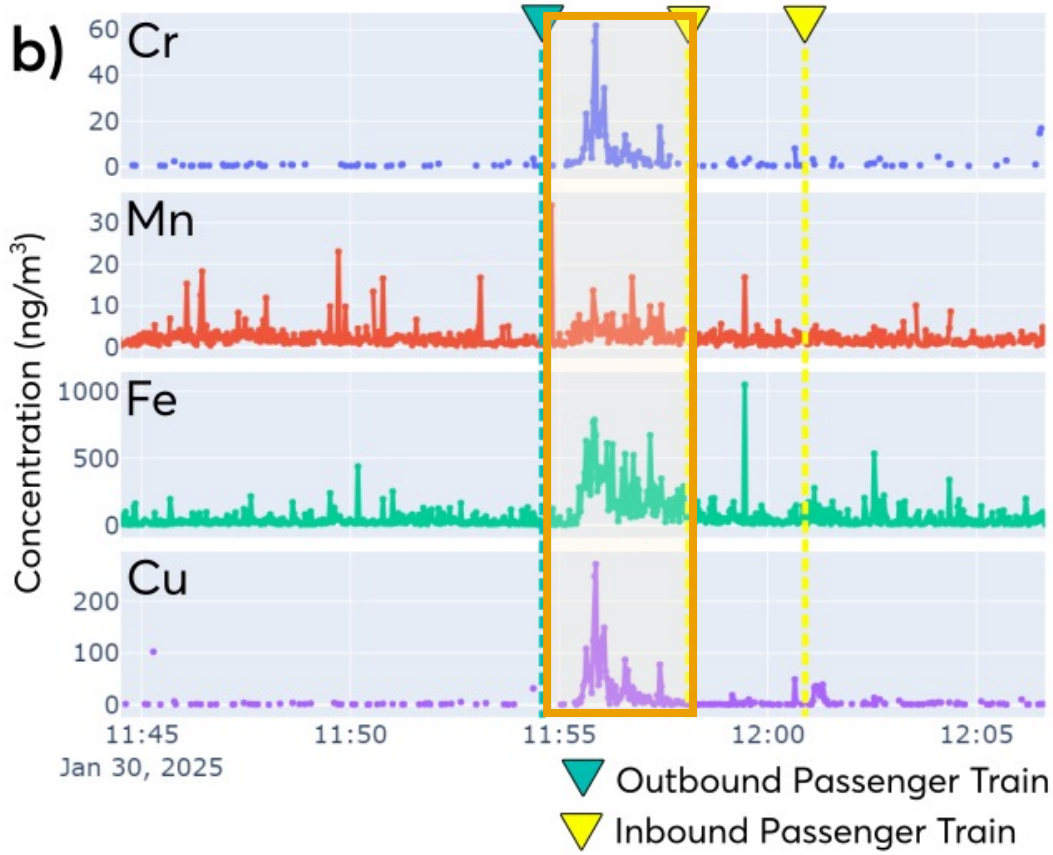
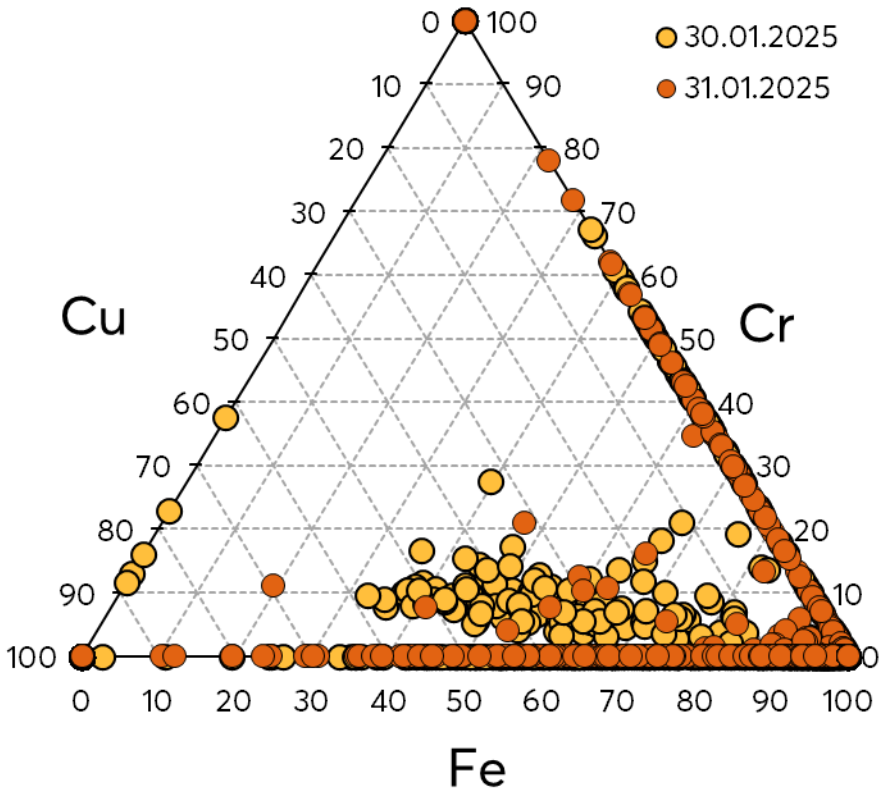
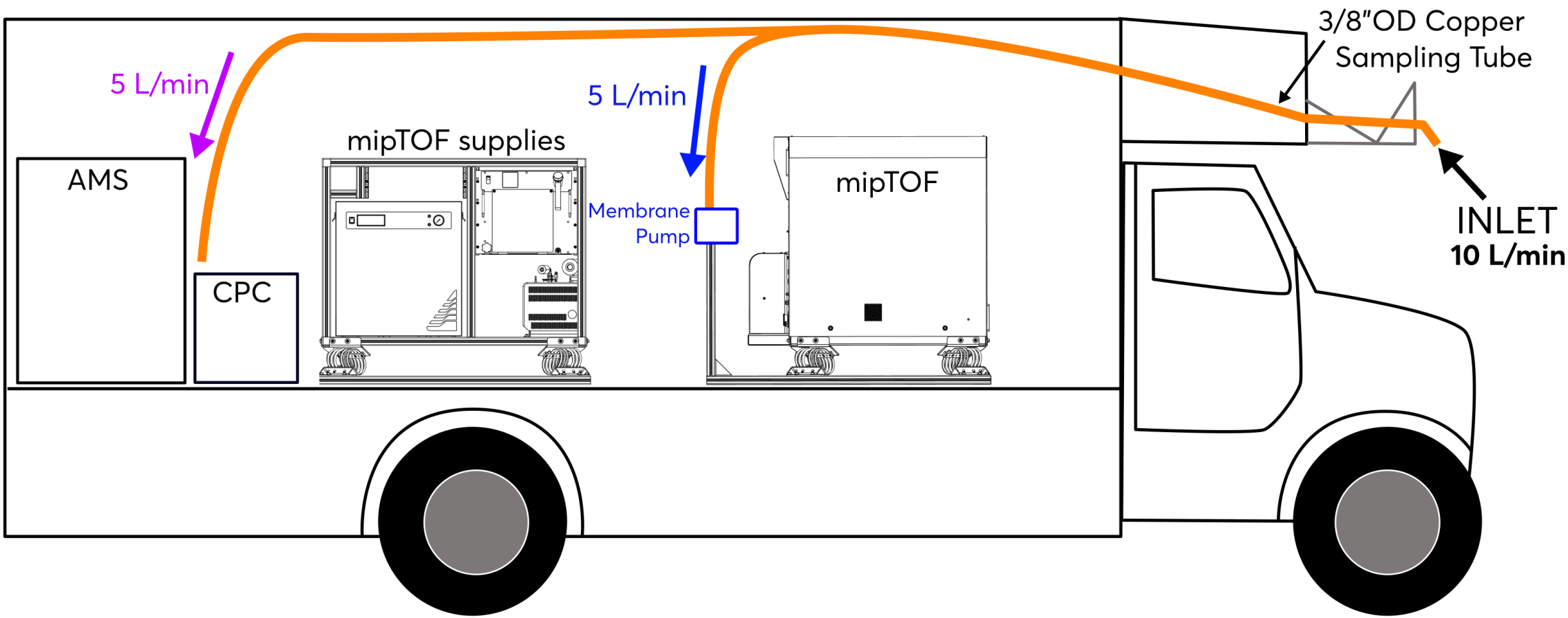


Cu-Fe-Cr particles from train-passing event may be unique to this particle source:

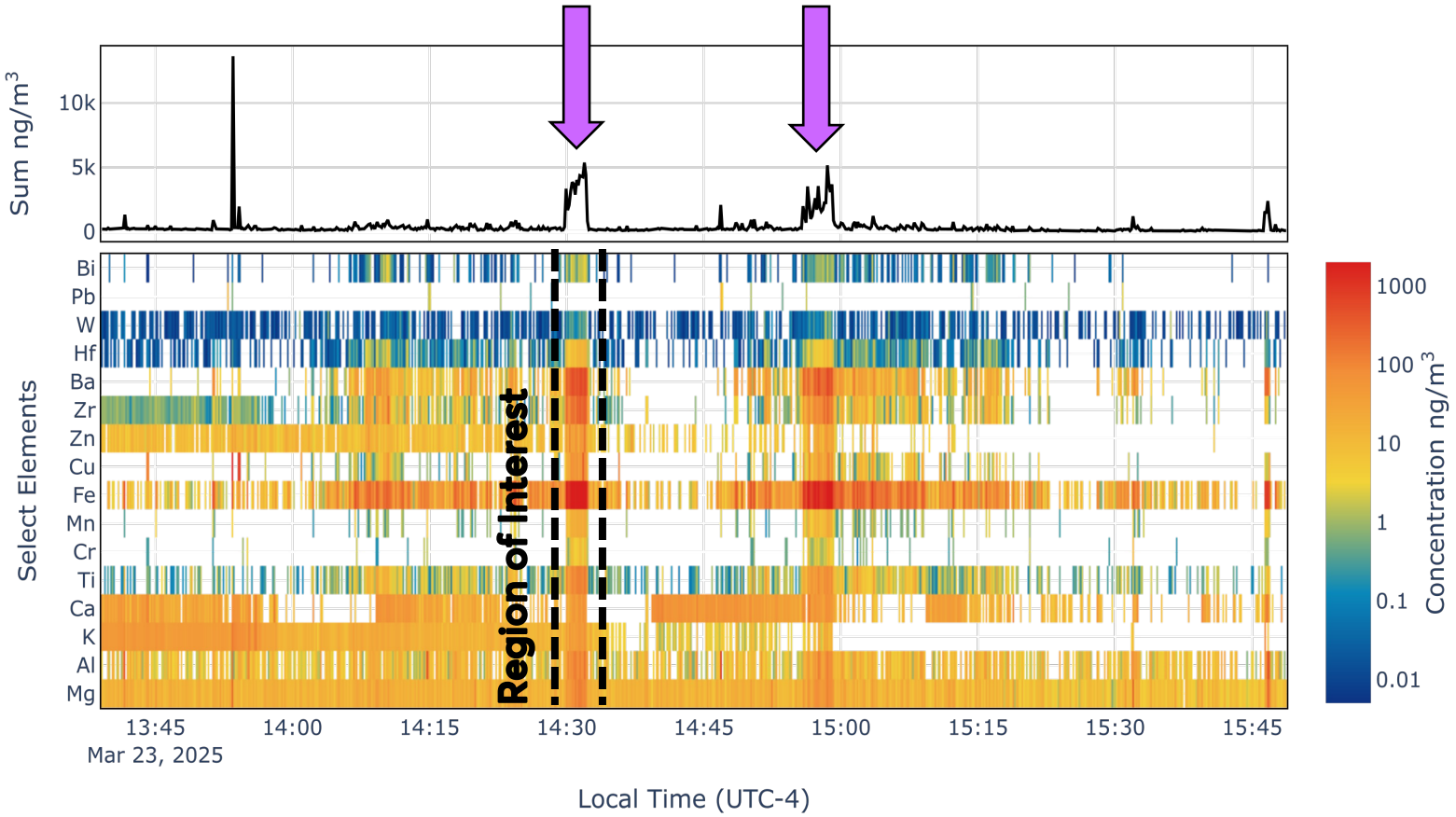


Sampling Inlet and Scheme for AML



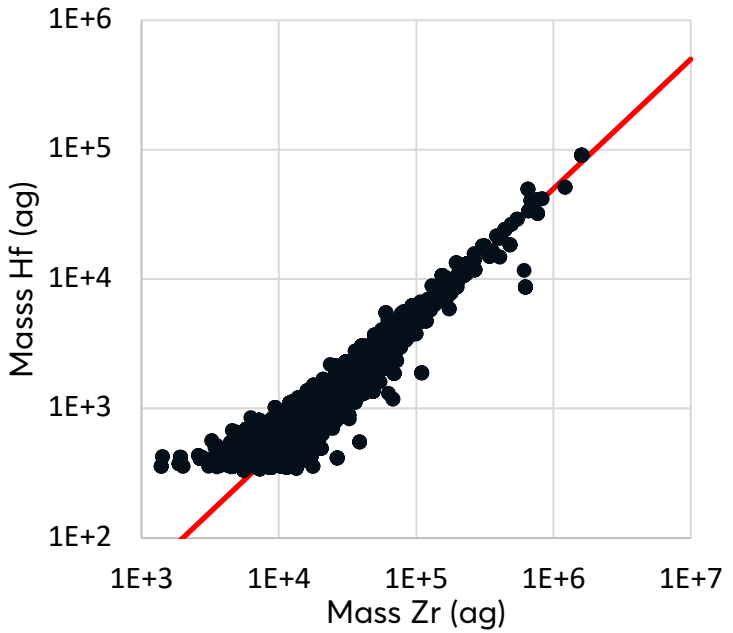
Example results: AML drive through Boston

- Signals obtained when driving thorough O'Neill tunnel
- Elevated concentrations of Cr, Mn, Fe, Cu, Zn, Zr, Ba, Hf, W, Bi are indicative of brake dust and road-dust



Particle-Resolved Analysis can be used to determine element concentrations at single-particle level

- ROI is 2.57 min,
- 4546 particles measured
- Strongest correlation: Zr vs. Hf



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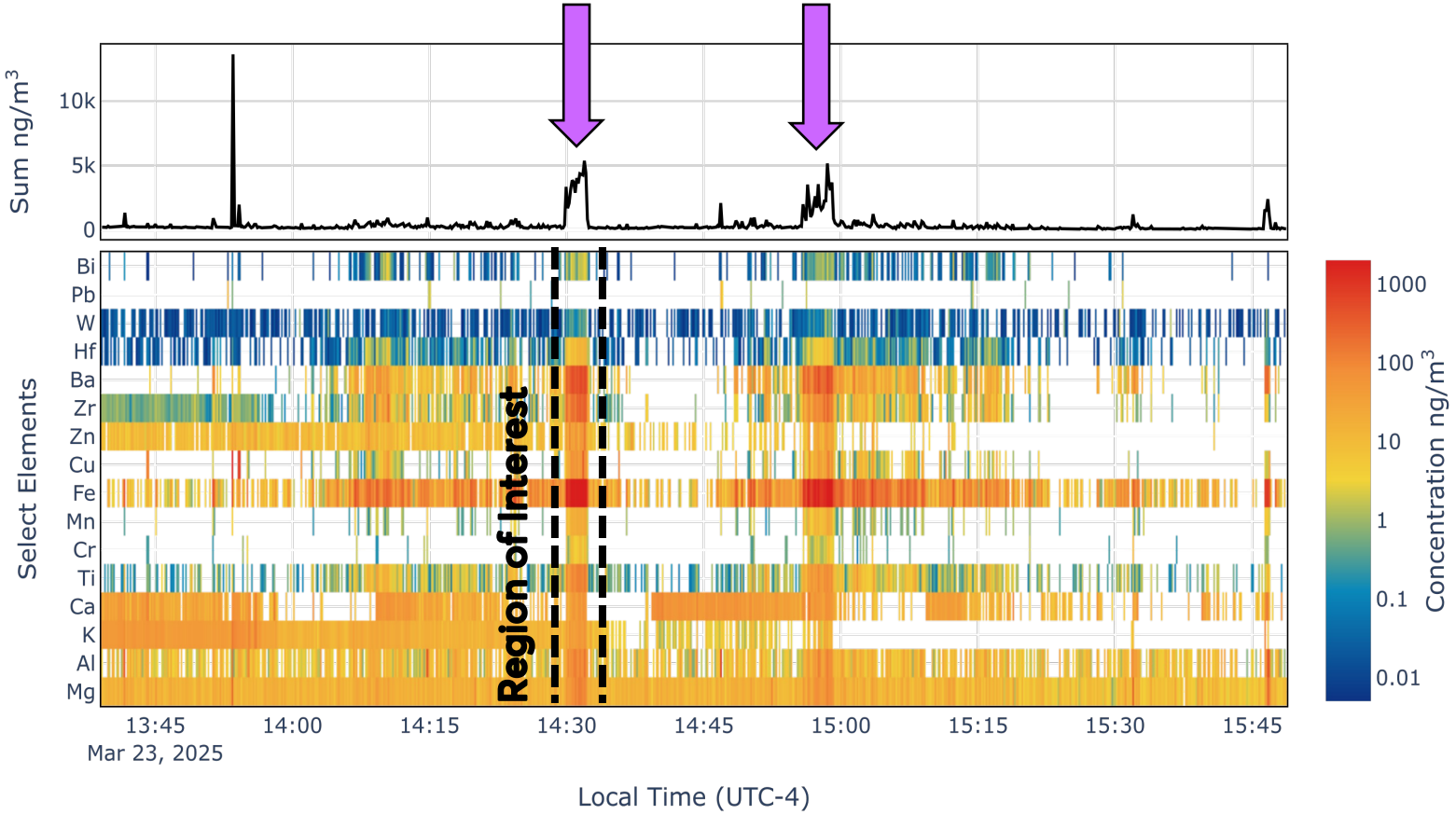
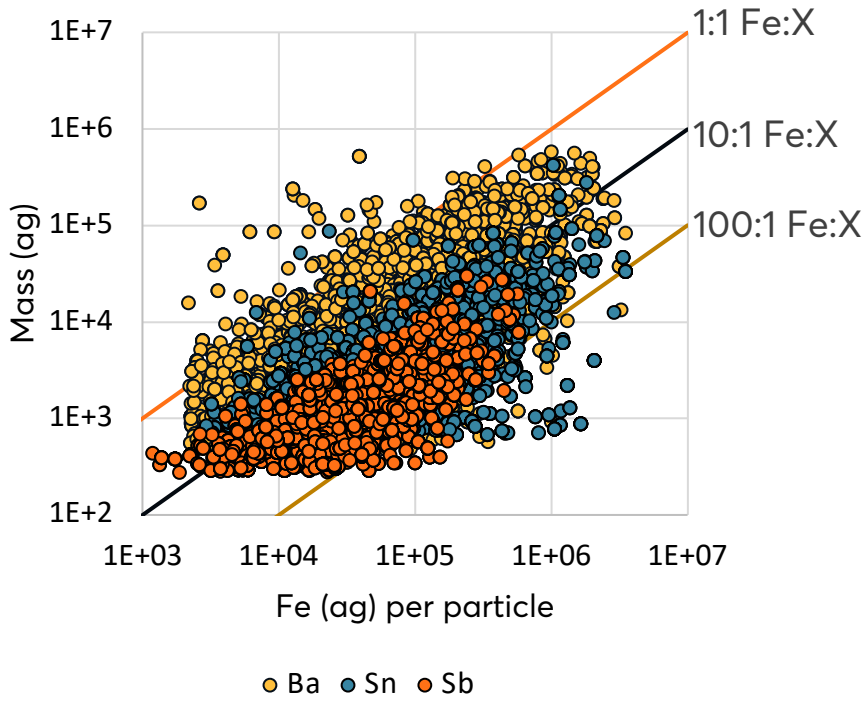


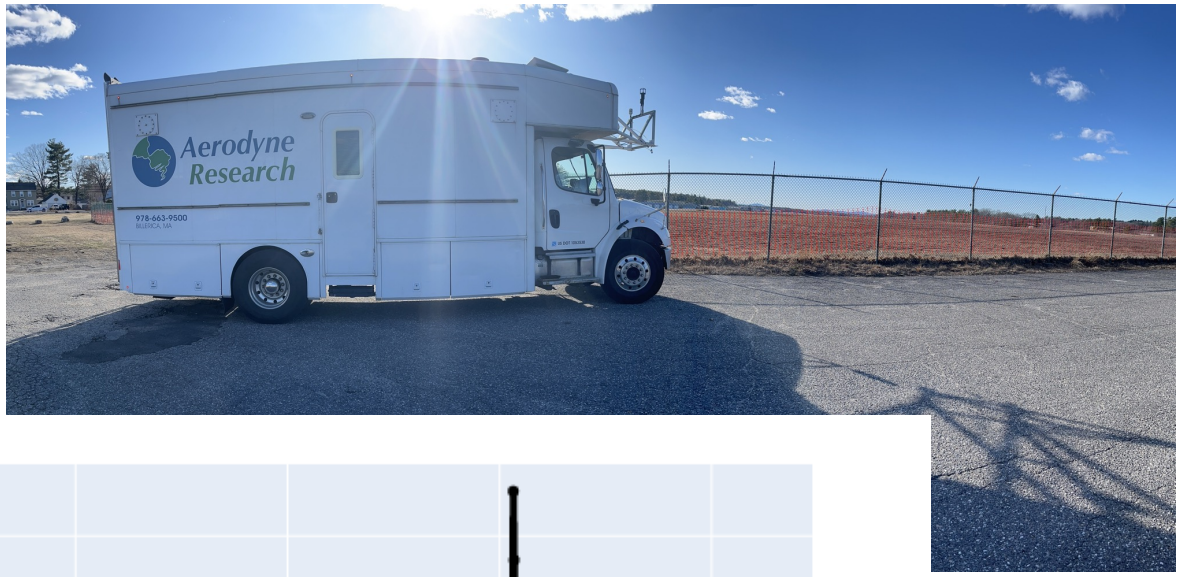
Particle-Resolved Analysis can be used to determine element concentrations at single-particle level

- ROI is 2.57 min,
- 4546 particles measured
- Moderate correlation: Fe with Ba, Sn, and Sb

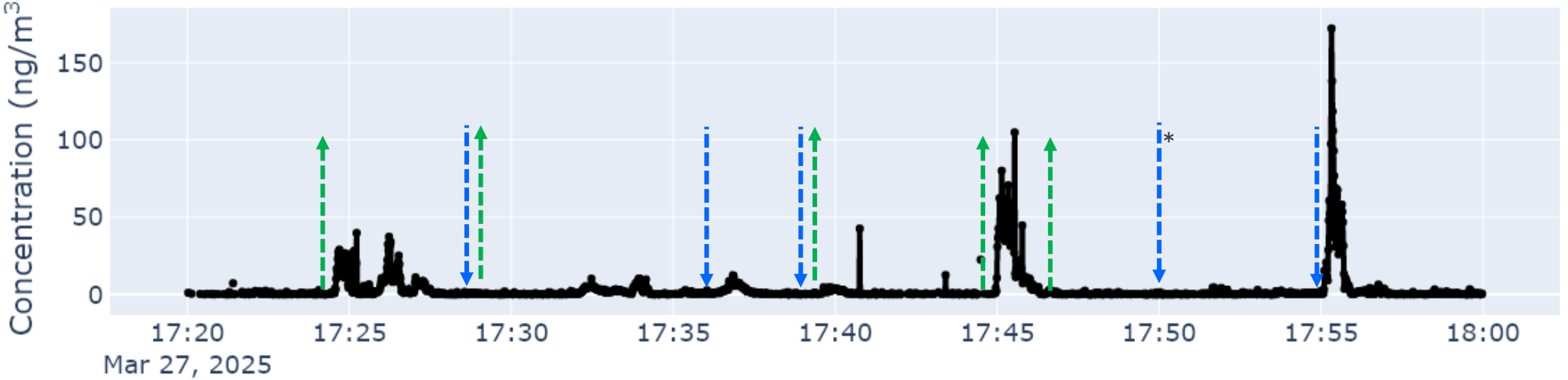


mipTOF measurement of metal emissions at regional airport

- With AML positioned downwind of runway at a regional airport, clear emission of lead particles from combustion of GenAv fuel coincides with take-off and landing of small propeller airplanes



Lead aerosol concentration:



Plane taking off

Plane landing

* Small jet landing: likely jet fuel instead of GenAv fuel

Conclusions

Information from mipTOF:

- Real-time measurement of trace-elements in air
  - Detection limits: 0.001-10 ng/m^3, depending on averaging period
  - Almost all elements on period table are measurable
  - Particle-Resolved Analysis

Applications Examples:

- Source Apportionment
- Air Quality Monitoring
  - Brake-wear emissions
  - Tire-wear particles
  - Urban dust
  - Mineral dust aerosols / weather and climate impact
  - Industrial emissions

Acknowledgments

- Jay Slowik
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- John Jayne

- Detlef Gunther
- Bodo Hattendorf

- Ashok Menan
- Velibor Pikelja
- Jovan Jevtic

THANK YOU

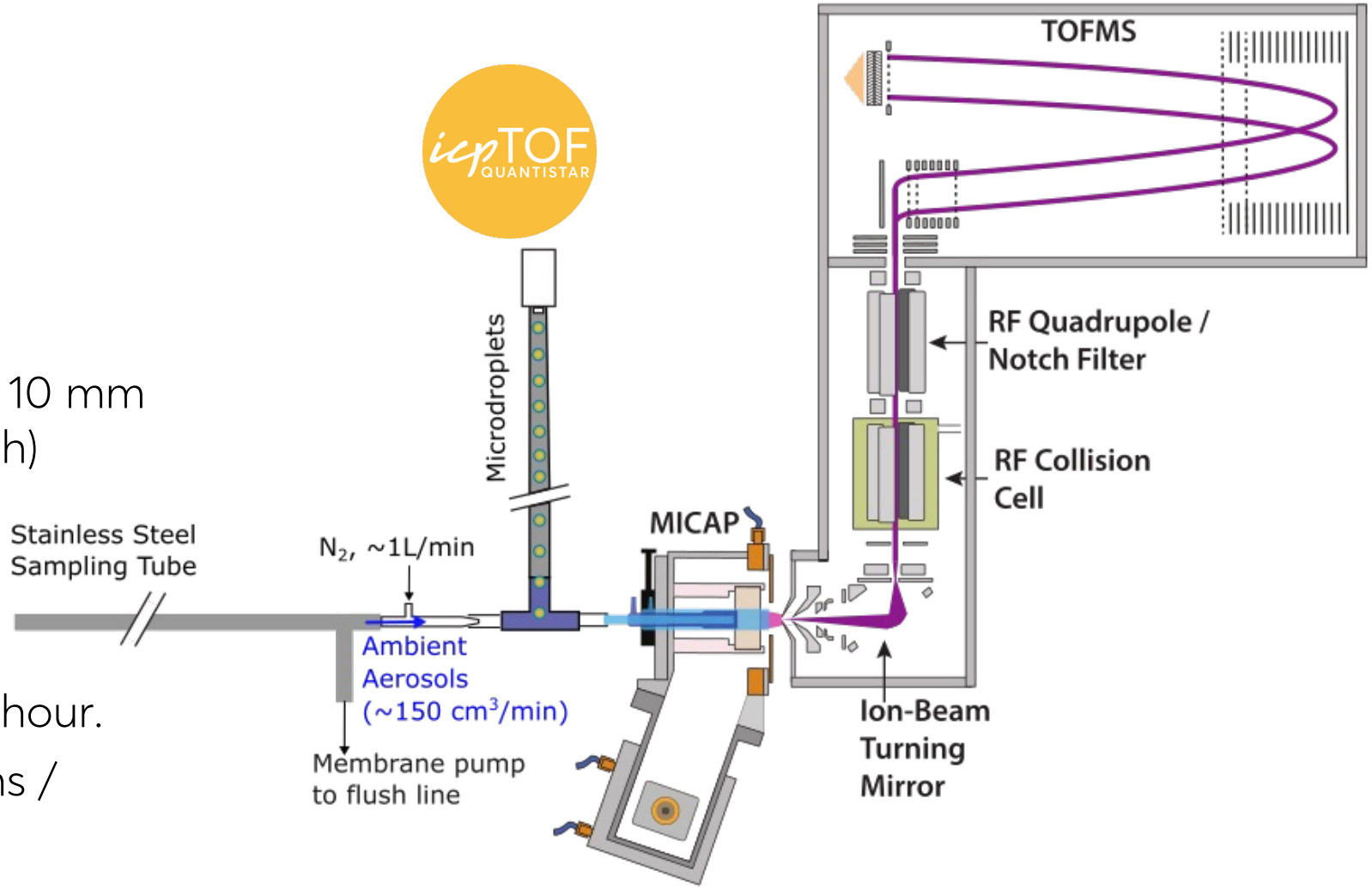
Alex Gundlach-Graham

a.gundlach-graham@tofwerk.com

Example: Four-Day Measurement via mipTOF

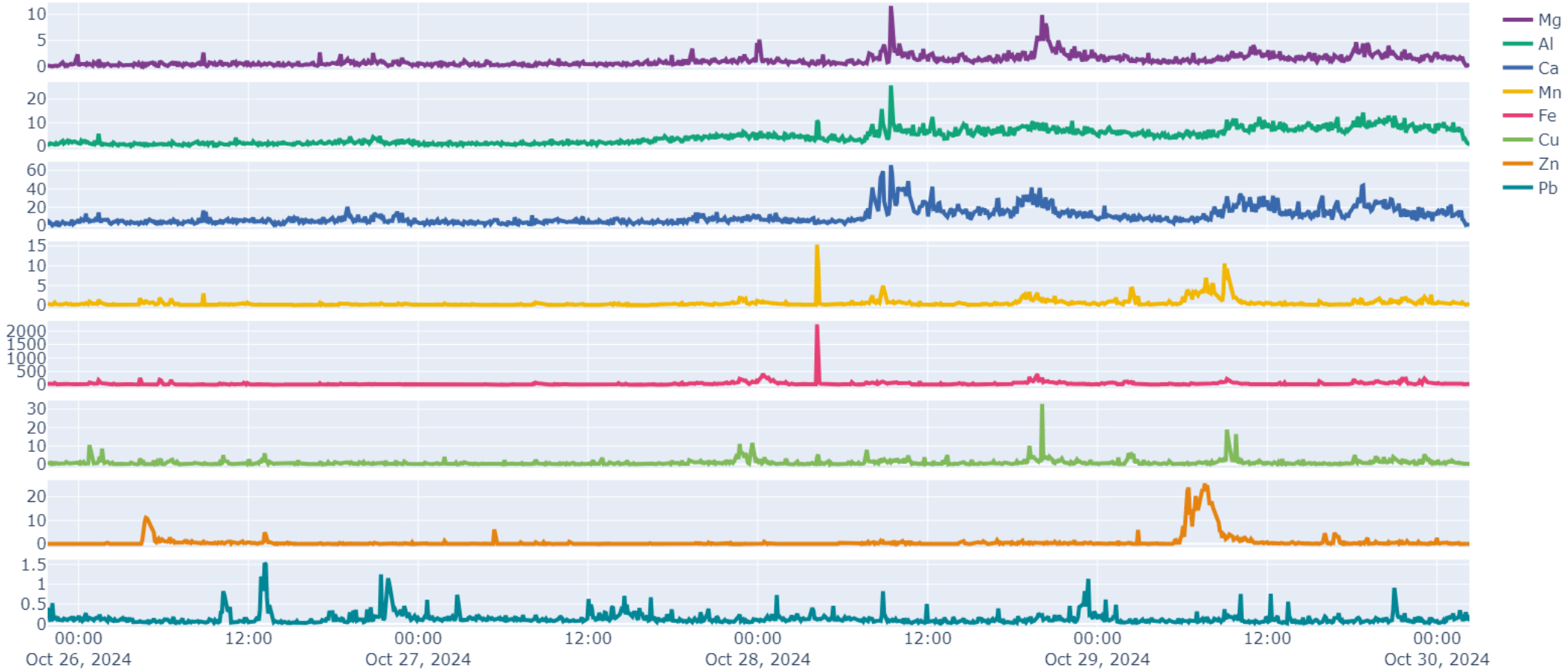
- Sampling position:
  - Thun, Schorenstrasse 39
  - Business Park Gwatt
  - ~10 m above ground (3rd floor)

- Outdoor Aerosol sampled through 10 mm id stainless steel tube (11 m in length)
- Online-Microdroplet Calibration used to determine absolute sensitivities (cts/g)
- Droplet calibration for 1 min every hour.
- Continuous TOF acquisition at 5 ms / mass spectrum



Example: Four-day measurement: Mass concentrations vs. Time

- Air sampling in Thun at Tofwerk facility
- Mass concentrations per 5 min averaging window:



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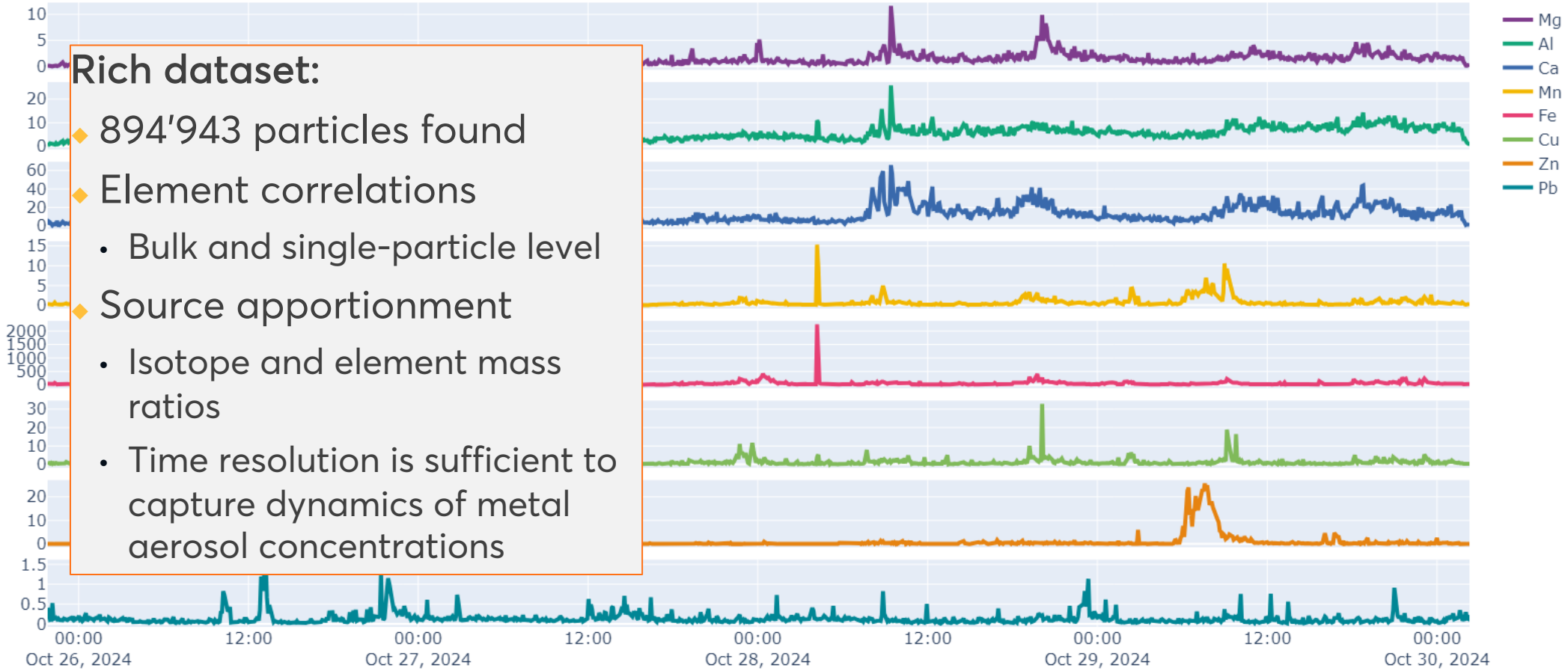

Rich dataset:

- 894'943 particles found
- Element correlations
  - Bulk and single-particle level
- Source apportionment
  - Isotope and element mass ratios
  - Time resolution is sufficient to capture dynamics of metal aerosol concentrations

Mass Distribution of Elements in Particles