



EMPIR 16ENV17 AEROMET Project TXRF analysis of aerosol samples



Bruker Nano Analytics, Berlin, Germany
December 2018





TXRF analysis of aerosol samples EU EMPIR 16ENV07 AEROMET



Aerosol metrology for atmospheric science and air quality

www.aerometproject.com/

- Measurements of aerosol particles enforcing EU air quality regulations
 - to protect human health
 - research on climate change effects
- Metrics (mass concentration) as PM₁₀* and PM_{2.5} are in use
 - level of uncertainty is too high
 - traceability is insufficient
- The project aims at implementing improvements in
 - A) the uncertainty of particle mass, size, number of measurements
 - B) in the characterization of regulated components in PM



*) PM₁₀ / PM_{2.5} = particulate matter < 10 μm / 2.5 μm



TXRF analysis of aerosol samples

Objectives of work packages



Objectives

1. WP 1

- Development of reproducible reference methods for PM₁₀ and PM_{2.5}
- Design of aerosol chamber system for calibrating PM₁₀ and PM_{2.5} instruments
- Preparation of representative aerosols

2. WP 2 (Bruker involved)

- Traceable validated methods for the determination of major components of PM
- Elemental and organic carbon, total carbon, anions and cations
- Toxic metals (lead, arsenic, cadmium, mercury, nickel)

3. WP 3

- Development of calibration procedures for Mobility Particle Size Spectrometers
- Calibration facilities for measuring particle number concentration

4. WP 4 (Bruker involved)

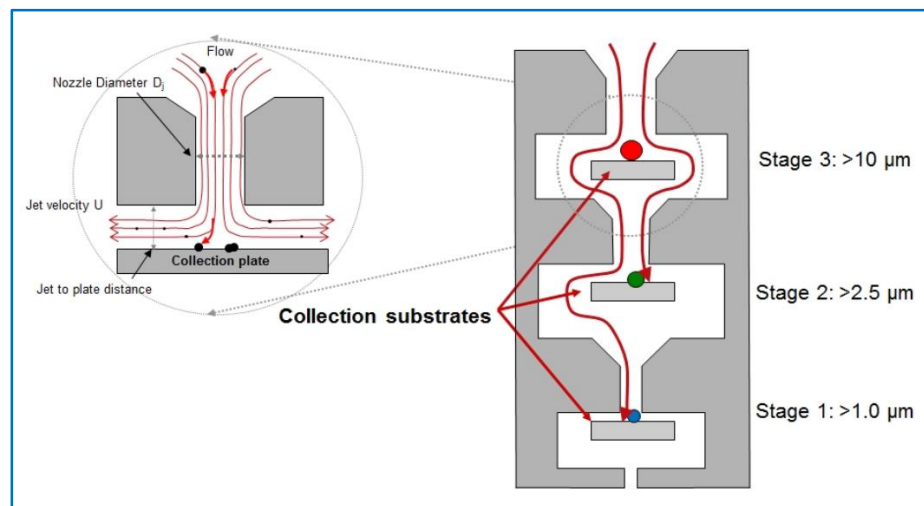
- Quantify PM with mobile x-ray spectroscopy combined with particle sampling
- Prove by lab-based methods

5. WP 5 (Bruker involved)

- Standardization, take up by accredited laboratories,

Aerosol sampling

- Aerosols are fractionated by size in an impactor
 - Typically aerosols are sampled on filter substrates
 - Long sampling time (~ 24 h) and digestion required for ICP analysis



Impactor working principle (www.dekati.com)

- Preliminary tests for TXRF
 - Direct analysis after sampling on acrylic discs is possible
 - Sampling times of down to 1 h deliver sufficient material for TXRF analysis



Special adapter ring for TXRF discs



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Activities WP 4



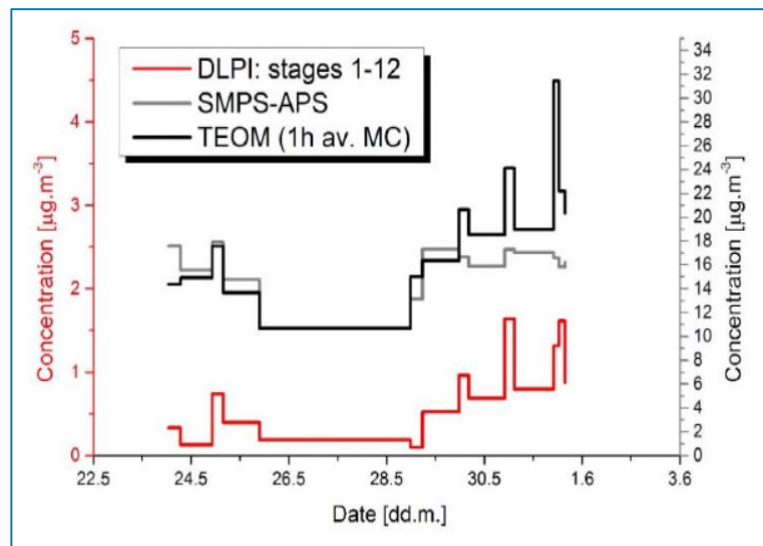
Two onsite campaigns

- Budapest, Hungary, May 2018,
Cassino, Italy, September 2018
- Sampling with 13-stage Dekati impactor,
sampling time 1 to 60 hours
- PM10 samplers for lab-based ICP-MS analysis,
 - sampling time ≥ 14 h !
 - no size fractions !
- Table shows all analytical tasks and instruments used (see last slide for more details)

Purpose	Details	Instruments
Sampling	Size range: 30 nm – 10 μ m	Cascade samplers (Dekati, May-type), PM10 samplers, ELPI
Quantitative element analysis	Mg to U down to 1 ppb	S2 PICOFOX TXRF spectrometer
Total particle mass concentration	PM _{2.5} , PM ₁₀ (black carbon)	TEOM, Aethalometer, DustTrak
Aerosol spectroscopy	Size range: UFP, FP, number conc.	OPSS, APS+MPSS, ELPI, CPC stand-alone, low-cost optical sensors

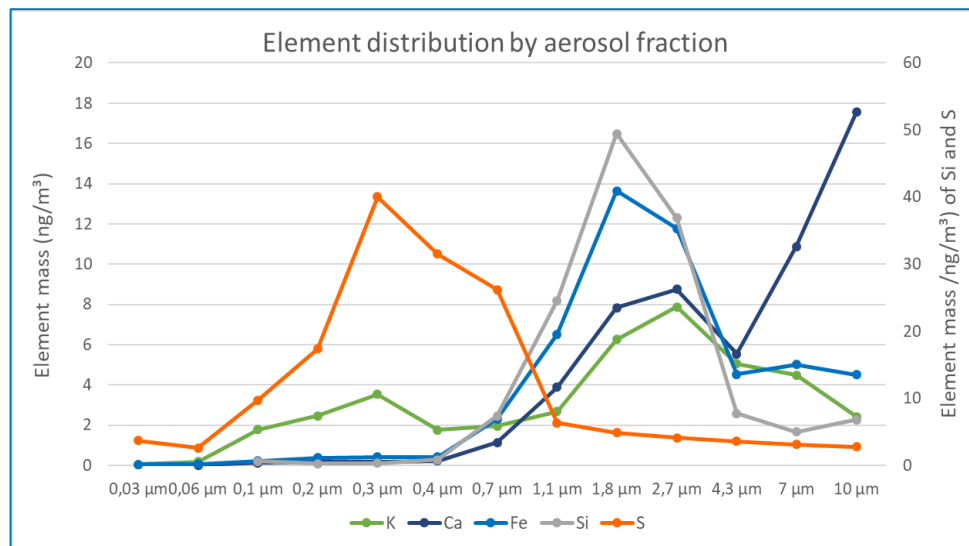
Trend of total mass

- Total particle mass was continuously measured with TEOM during 10 days (black curve below)
- Total inorganic mass detected with TXRF (red curve) shows exactly the same trend



Distribution of main elements

- Fractions from 1 to 4 µm typically contain geogene elements like Ca, Fe, Si
- Sulphur appears in particulate matter between 0,2 and 0,7 µm

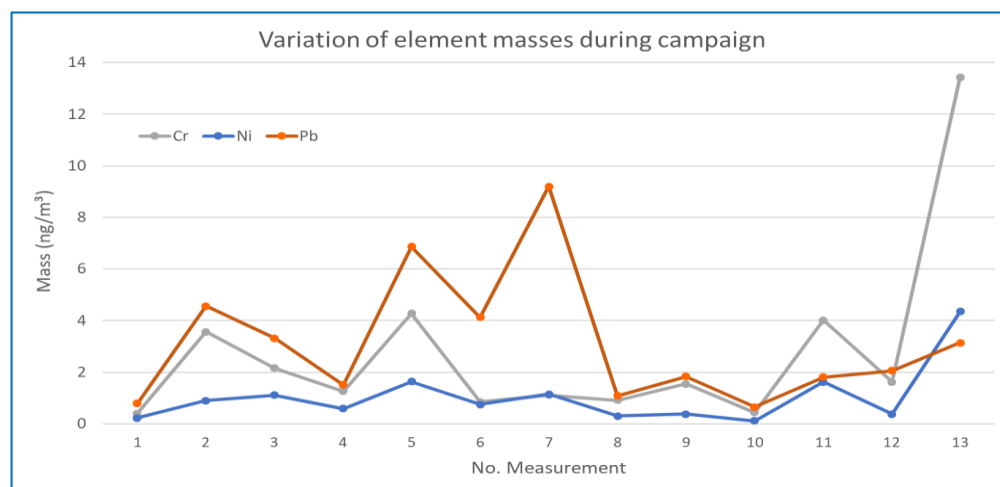
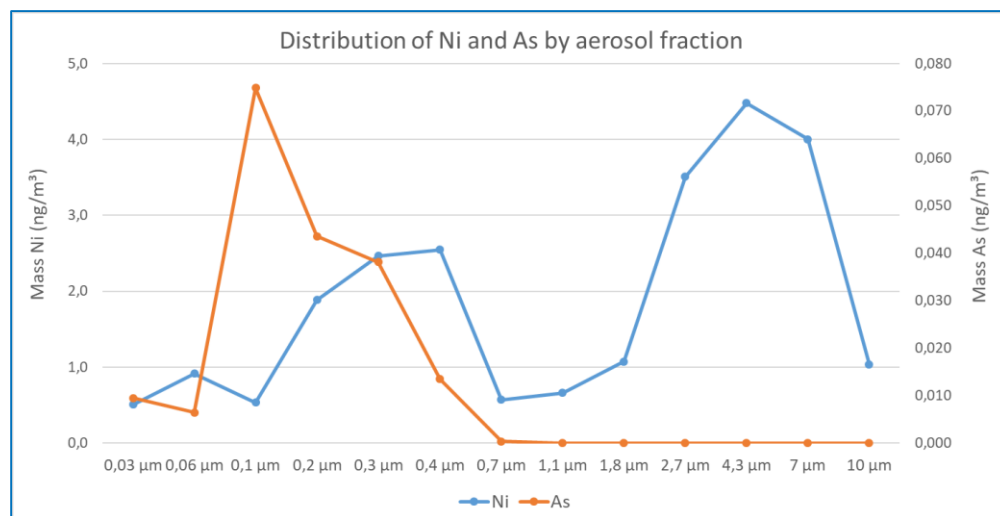


Toxic elements by particle fraction

- Ni (also Cr, Pb) detectable after short sampling times (mass up to 5 ng/m³ per fraction)
- As detectable after 14 h sampling time (< 70 pg/m³) present only in particles from 100 to 400 nm!

Trend analysis of toxic elements

- Cr, Ni and Pb mass variations could be monitored even at shortest sampling times (sum of all fractions shown)





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Outlook



Present work and outlook

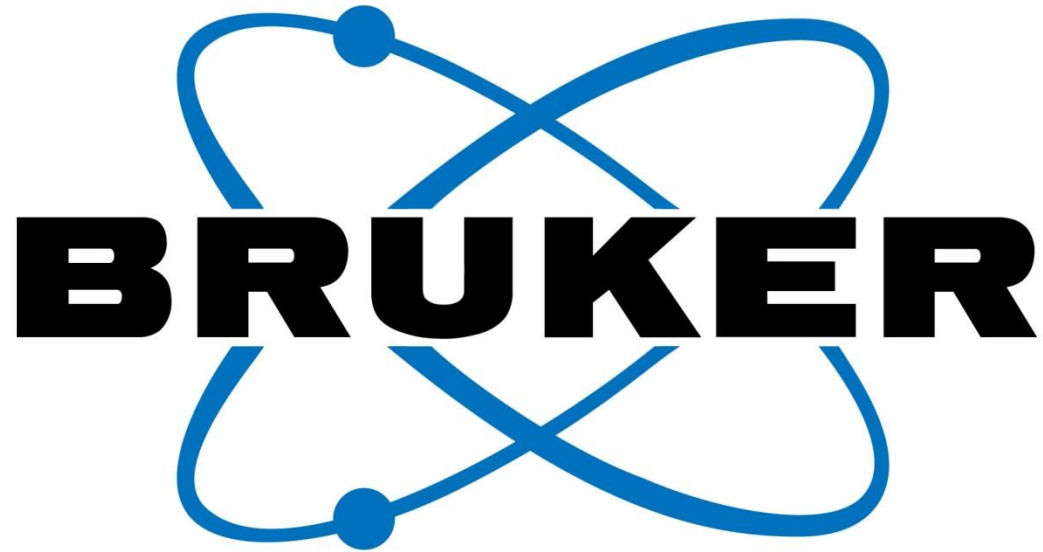
- In-field results will be compared with lab-based results (synchrotron-TXRF and ICP-MS)
lab system prove presence of more elements (e.g. Cd)
- Lab results and new aerosol standards will be applied to optimize results of direct TXRF measurements
- A draft standard operation procedure (SOP) for in-field TXRF measurements is available
- For standardization an ISO TR (technical report) will be proposed in 2019

Project funding

EMPIR



The EMPIR initiative is co-funded by the European Union's Horizon 2020 research and innovation programme and the EMPIR Participating States



Innovation with Integrity



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Background information



Instrumentation for aerosol metrology

- **MPSS:** Scanning Mobility Particle Size Spectrometer applied for particles below 1000 nm
- **APS:** Aerodynamic Particle Sizer
- **TEOM:** Tapered Element Oscillating Microbalance for real-time measuring of aerosol mass
- **Aethalometer:** concentration of optically absorbing (black) particulates