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Poster-Abstract Form

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Title: Determination of trace elements in ambient aerosols by
synchrotron XRF

Abstract: (min. 300 - max 500 words)

Aerosols from combustion and abrasion processes often contain traces of metallic elements that are difficult to determine with conventional methods, which typically require long sampling times to accumulate enough mass for analysis. Synchrotron x-ray fluorescence (SR-XRF) spectrometry is a very sensitive method for elemental analysis that allows for very small amounts of material to be measured. This in turn can be profitably used for reducing the sampling time of individual samples to hours instead of days such that studies of diurnal variations become feasible.

We collected ambient aerosol samples with rotating drum impactors in different geographic settings (in an alpine valley, close to a freeway, in a city) with time resolutions of two hours in the winter of 2005/2006. The impactors segregated the particles into three size bins (PM₁, PM_{2.5}-PM₁, and PM₁₀-PM_{2.5}). Accidentally two of the three field campaigns coincided with heavy pollution episodes, where the legal thresholds of 50 µg/m³ (daily average) were exceeded by up to a factor of 3. The samples were then analyzed with SR-XRF at the Swiss Synchrotron Light Source (SLS) at PSI.

The elemental compositions did not differ much between the sites in northern Switzerland. Heavier elements were found mainly in the largest size fraction, which is usually considered to originate from (mineral) dust resuspended into the air or from mechanical abrasion. The smaller particle size fraction showed high amounts of carbonaceous material not detectable with our XRF setup and is more typical for combustion processes. K, Si, Fe, Ca, Al, Na, Mg, Ba, Zn were identified as the important metallic contributors, while Ti, Cu and Cr were found only in traces. K is an indicator for wood combustion, but is also a component of mineral dust and de-icing salts applied to roads during wintertime.

The elemental fingerprints determined with SR-XRF will be used for source apportionment studies to help determining specific emission reduction strategies.

Short CV:

I studied physics at ETH and acquired a PhD degree in geography (climatology) at the University of Berne in 1990. Since then I have been working at PSI in the fields of air quality and air pollution meteorology in complex terrain, atmospheric fluxes and – more recently – aerosol chemistry. I spent a post-doc year at Pacific Northwest Laboratory in the U.S. in 1992/93. My research emphasis is on experimental work, especially field studies in mountainous terrain.

Determination of trace elements in ambient aerosols by synchrotron XRF

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Motivation and Background

Aerosols from combustion and abrasion processes often contain traces of metallic elements that are difficult to determine with conventional methods, which typically require long sampling times to accumulate enough mass for analysis. **Synchrotron x-ray fluorescence (SR-XRF) spectrometry** is a very sensitive method for elemental analysis that allows for very small amounts of material to be measured. This in turn can be profitably used for reducing the sampling time of individual samples to hours instead of days such that studies of diurnal variations become feasible.

We collected ambient aerosol samples with **rotating drum impactors** in different geographic settings (in an alpine valley, close to a freeway, in a city) with time resolutions of two hours in the winter of 2005/2006. The samples were then analyzed with SR-XRF at the **Swiss Light Source (SLS) at PSI**. The combination of sampling and analysis methods allow for

- High temporal resolution of measurements (hours)
- Size segregated detection of (metallic) trace elements (in concentrations as low as pg m^{-3})
- Fast analysis of a large number of individual samples

The elemental fingerprints determined with SR-XRF will be used for source apportionment studies to help determining specific emission reduction strategies.

Aerosols from wood burning

It has been realized in recent years in Switzerland, that the combustion of wood contributes significantly to the amount of particulate matter in the air, especially during winter (Szidat et al. 2007). Therefore, rural areas may suffer more from air quality problems than previously assumed. How emissions from wood stoves and open fires influence the composition of particulate matter is the subject of the **Aerowood project**, which is performed in collaboration between PSI, Empa, the University of Bern and ETHZ.

Acknowledgement

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References

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Szidat, S., A. S. H. Prevot, J. Sandradewi, M. R. Alfarra, H. A. Synal, L. Wacker, and U. Baltensperger, 2007: Dominant impact of residential wood burning on particulate matter in Alpine valleys during winter. *Geophys. Res. Lett.*, **34**, L05820, doi:05810.01029/02006GL028325.

Rotating drum impactor sampling

Particulate matter can be sampled with various instrument types. We use rotating drum impactors (RDI). RDIs provide

- high time resolution in aerosol sampling (on the order of hours)
- particles segregation into three different size fractions ($10 - 2.5 \mu\text{m}$, $2.5 - 1.0 \mu\text{m}$, $1.0 - 0.1 \mu\text{m}$)

The particles are collected on a Mylar tape coated with Apiezon-L grease. The size segregation depends on the flow geometry and the design of the orifices at the entrance of each stage. The air volume flow is $1 \text{ m}^3 \text{ h}^{-1}$. The drums were rotated in steps every 2 h, yielding a total sampling time of ~ 10 days per drum set.



Fig. 2: Mylar tape of stage B ($1 - 2.5 \mu\text{m}$) with collected particles. Each 'bar' corresponds to 2 h of sampling.

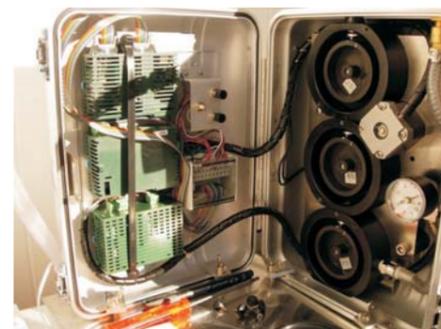


Fig. 1: Rotating drum impactor. Left side: Instrument control. Right side: Impactor drums (open) for 3-stage particle size segregation.

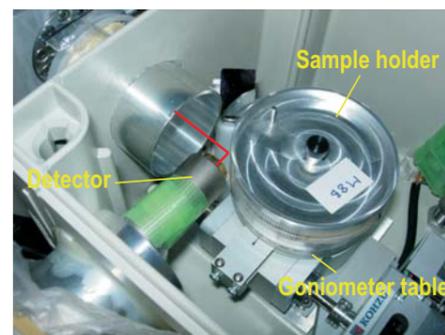


Fig. 3: Synchrotron-XRF setup showing the sample holder on the goniometer table in the Helium chamber. The x-ray light path is indicated with a red line.

Synchrotron-XRF analysis

X-ray fluorescence (XRF) analysis is a standard method to determine the elemental composition of a sample. The technique is based on the excitation of electrons on the inner shells of an atom with x-rays. When the atom returns to its basic state, light of characteristic wavelengths is emitted (a process called *fluorescence*) that allows to identify the emitting element. The signal intensity depends on the number of atoms in the sample and the excitation light intensity. The lower the light intensity, the higher the detection limit for a given element and the longer the required sampling time for the detectable elements.

Analysing hundreds of samples with tiny masses of aerosols in reasonable time requires the high flux of synchrotron light. Each bar's spectrum can then be measured with 30 s of irradiation. We used monochromatic light of 16 keV to determine the elements with $Z < 40$ at the Swiss Light Source (SLS) at PSI.

Elemental composition of a 2-hour sample

Three simultaneous spectra from Roveredo, Switzerland, are shown at right (Fig. 4). Ambient aerosol in Roveredo is composed of particles from traffic emissions and from fossil fuel and biomass combustion for domestic heating. The share of wood burning for heating purposes is quite high in this valley (50 - 100 %).

Stage A ($2.5 - 10 \mu\text{m}$)

A predominance of Cl, Ca, Fe, Cu and Zn is visible.

Stage B ($1 - 2.5 \mu\text{m}$)

A predominance of Ca, Fe, and Cu can be recognized.

Stage C ($0.1 - 1 \mu\text{m}$)

The largest peaks belong to S, K, and Fe. Elements of lesser importance are Ca, Cu and Zn.

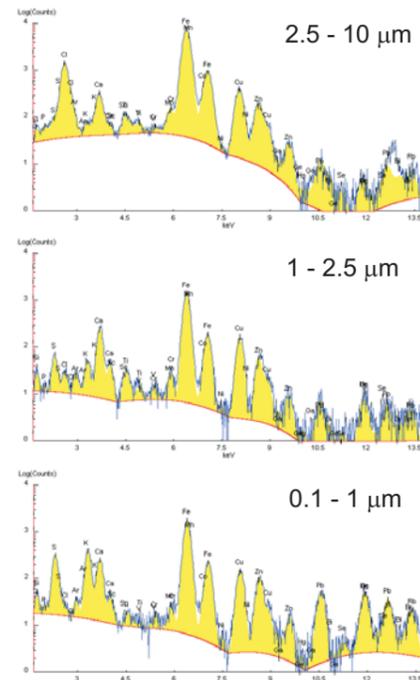


Fig. 4: Element spectra for Roveredo samples of 2005-12-09, 1700 CET. Each spectrum represents a particle size range (or impactor stage). Yellow: calculated peak area. Red line: continuum ('background').

Time series of elements in three size bins

An example of the time series of sulfur in three impactor stages measured in Zurich from 10-21 January 2006 are shown in Fig. 5. A warm front passing by on 17 Jan 2006 caused an airmass change that led to the end of the winter smog episode. This is clearly seen in the low PM concentrations after this date. In general, sulfur occurs in comparable amounts in stages B and C, while signifi-

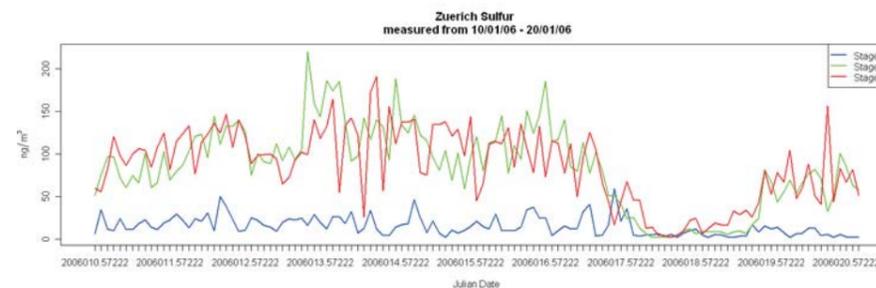


Fig. 5: Time series of S in ng m^{-3} for the three different size bins (blue: stage A, red: stage B, green: stage C).

Average elemental composition of winter smog aerosols in Zurich

Iron (Fe) can be found in significant amounts in all size fractions, although decreasing with decreasing size. This may be a strong indicator of traffic emissions, mainly of abrasion of mechanical parts in cars, engines, and on road surfaces. Coarse particle elements Cl and Ca are probably the result of road dust and of the application of de-icing salts on the roads. In contrast, K increases with decreasing size fraction. The large amount in the smallest size fraction hints towards biomass burning in domestic heating.

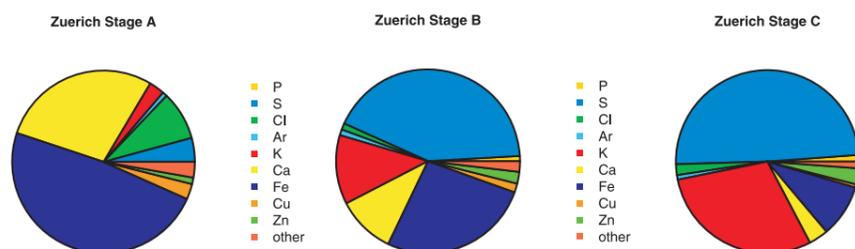


Fig. 6: Trace element composition of aerosols measured in Zürich during the smog episode of January 2006.

Sulfur is almost absent in the largest size fraction, but amounts to about half in the B and C stages. Fine mode S can thus be assigned to secondary sulfate aerosol.

Conclusions

The results presented here demonstrate

- the advantage of size-segregated aerosol sampling with rotating drum impactors
- the applicability of the SR-XRF method for analysing small amounts of aerosol mass
- a gain in information on emission characteristics from various sources in different size fractions