Trace elements in ambient aerosols analyzed and quantified with synchrotron radiation induced XRF

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Aerosol samples were collected with rotating drum impactors (RDI) in two field campaigns in 2010. The first campaign took place in Paris, France, in January/February 2010 at a site near the city center and at a more rural site in a suburb. The goal of this campaign was to characterize urban particulate matter (PM) composition and time development in winter, and the composition and behaviour of the city’s pollution plume. The other field campaign took place in Pasadena, California, USA, in May/June 2010, within the framework of the CalNex-LA campaign. This campaign pursued the goal to better understand the aerosol impact on climate change in California, and – more relevant to the trace element samples – to identify sources of Mercury in the area. Although trace elements do not contribute substantially to the total mass of aerosols, they can contribute significantly to source identification [1].

Measurements of a broad range of heavier elements (Mn, Fe, Ni, Cu, Zn, Se, Sr, Zr, Cd, Sn, Sb, Ba) were done at HASYLAB with a polychromatic beam with an energy range from 5 keV to 80 keV. The beam spot size was set to 100x200 μm, providing sufficient photon flux to detect as small concentrations as a few μg per total sample area. Aluminium absorbers of different thicknesses were employed to shape the continuous spectrum. For the measurement of heavier elements up to the Ba Kα line at 32 keV, a Si(Li) detector with a large active volume (crystal area 80 mm², crystal depth 4 mm) and a 12.5 μm thick beryllium window was chosen (nitrogen cooled Sirius 80, Gresham). Lighter elements (Al, Si, P, S, Cl, K, Ca, Ti, V, Cr) of the same samples were measured at the Swiss Light Source (SLS) of the Paul Scherrer Institute, Switzerland. Preliminary results are shown in Figure 1.

Figure 1: Time series of Ni in three size fractions (PM₁₀–PM₂.₅, PM₂.₅–PM₁, PM₁–PM₀.₁) collected in downtown Paris, France, 12 January to 13 February 2010. Most of the Ni mass is found in the smallest size fraction.
While the method applied for the sample analyses has basically reached a state of maturity with the previous beamtimes, some effort was still necessary to improve the calibration procedure for the accurate quantitative determination of aerosol masses. The inkjet method proposed in [2] had been modified and adjusted to the setup used here [3]. Several tests with different carrier substrates and coatings have been performed with the result that a 25 µm polypropylene (PP) film proved to be best suited for the calibration method used here (Figure 2).

Figure 2: Comparison of SR-XRF spectra of two different calibration films. Count rates were normalized to photon flux and detector dead time (from [3]).

A quick look at individual spectra showed interesting differences between the different sampling sites. For example, the CalNex-LA spectra from Pasadena, California, revealed a remarkable contribution of Br, an element more or less absent in Swiss cities. Br correlates well with Cl and thus hints to sea salt as the source. Similar and more sophisticated source apportionment is the ultimate goal of these synchrotron-radiation-induced XRF analyses.

References