Analysis of atmospheric aerosols with SR-TXRF: new direct calibration using pico droplets (pL) generated by ink-jet printers and speciation of Iron with SR-TXRF-XANES


Institut für Anorganische und Angewandte Chemie, Universität Hamburg, Germany
1 ITC-irst, via Sommarive 18, 38050 POVO, Trento, Italy
2 Atominstitut der Österreichischen Universitäten, TU Wien, Stadionallee 2, A 1020 Vienna, Austria
3 Hamburger Synchrotronstrahlungslabor at DESY, Notkestrasse 85, D 22607 Hamburg, Germany

In SR-TXRF the outstanding features of synchrotron radiation such as natural collimation, high intensity and low background allow for the detection of trace and ultra trace absolute amounts (pg, fg) of most medium Z elements.

However, an accurate and reliable calibration of SR-TXRF analysis of particulate samples until now is often problematic. As calibration with nano-droplets (10-50 nL) was found to give excellent results in the determination of trace impurities with TXRF in semiconductor material [1, 2], we developed a calibration suitable for atmospheric aerosol analysis with SR-TXRF by decrease in volume to the pico-droplet (pL) range [3,4]. Ink-jet printers are used to generate 5 to 130 pL droplets.

This new calibration technique was applied to elemental determination in atmospheric aerosol samples as characterization of aerosols representative for short time scales (1h and less) still remains a challenging analytical aim. Size classification of aerosols is a very important feature to determine toxicity and atmospheric behaviour of atmospheric aerosols. Especially small particles, fine dust (PM10, Particulate matter < 10 µm, aerodynamic particle size) and ultra fine dust (PM2.5) are subject of many studies and have been related to sever health damage [5]. For size fractionized aerosol sampling impaction devices with different specification varying in the number of stages and air throughput are in use. In this study a 12-stage Berner impactor which enables sampling particles of 60 nm in aerodynamic particle size was used.

Atmospheric aerosols were collected with the aid of a berner impactor on Si-wafer reflectors for 20 min and 60 min at the University of Hamburg. One droplet of a cobalt standard solution (1 g/L) containing 160 pg cobalt was spotted on the aerosol with an ink-jet printer. The element amounts were estimated with SR-TXRF at the HASYLAB beamline L (Fig. 1) from a calibration with the spotted standard and fundamental parameters.

Figure 1: Amount of elements determined in atmospheric aerosol displayed from 0 to 200.000 pg/m³ for three different sampling: 60 min day time (a) 10 min day time (b) and 60 min night time (c) in four size ranges 10.0-8.0 µm, 8.0-2.0 µm, 2.0-0.13µm, 0.13-0.015µm (I) and amounts displayed from 0 to 2000 pg/m³ (II)
In atmospheric aerosol research, element speciation is important to assess their origin, toxicity and potential to influence climate processes. A major challenge in element speciation is to avoid chemical transformation during analyses. This easily occurs during sample preparation as used e.g. in fractionated solvent extraction or in applying chromatographic techniques. XANES measurements allow element speciation without dissolving the samples. As Si-wafers can be used as aerosol collection plates in an impaction device and as sample carrier for XANES measurements, no additional step is necessary for sample preparation.

The same aerosol samples described above were analysed by TXRF-XANES to determine the oxidation states of iron before the internal standard was added.

![Figure 2: Iron K-Edge XANES spectra from aerosol samples (60 min sampling time) first scan of a series in three size ranges 10.0-8.0 µm (green), 8.0-2.0 µm (red), 2.0-0.13µm (blue) (a) and last scan of a series for the same size fractions (b)](image)

The TXRF-XANES measurements at the Fe K edge revealed that the oxidation state of iron was varying depending on the particle size fraction. A change in the oxidation state was observed between the first and the last scan of repetitive measurements for particle sizes from 10-8.0 µm and 8-2 µm but not for 2-0.13 µm.

**References**