TXRF-NEXAFS study of nitrogen compounds in coastal Antarctic fine aerosol particles

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While compounds in the gas phase can be measured by high temporal and spatial resolution using optical and remote sensing methods it is crucial to have analytical methods that enable us to measure the aerosol samples collected in a short time whilst retaining the information on the size distribution of the particles. Although ion chromatography (IC) is a relatively simple analytical method for the determination of major ionic species in aerosols, its major disadvantages are the destructiveness and the relatively high detection limit that needs a relatively high sample volume for reliable analysis [1]. Total-reflection X-ray fluorescence (TXRF) spectrometry is sufficiently sensitive for a multielemental analysis of size-segregated aerosol samples of around 10^{-9} g [2]. Cascade impactors allow the collection of aerosols directly on the reflector surface. A near edge X-ray absorption fine structure (NEXAFS) investigation in conjunction with TXRF spectroscopy analysis of minute samples on wafer surfaces is a unique non-destructive method for the speciation of the atmospherically important low-Z elements (C, N and O) [3]. Due to the extremely high sensitivity of the technique, a nanoscopic amount of material is enough to carry out the measurement.

Coastal Antarctic aerosol particles were collected near the Italian base located at Terra Nova Bay (Ross Sea), on silicon wafers using a 7-stage May cascade impactor, from 14 to 19 February 2004. For comparative purposes, aerosol samples were also collected with the same instrument near the sea-shore in Alghero (Sardinia, Italy), from 6 to 11 June 2004. The May impactor has, at a 20 l/min sampling flow, aerodynamic cut-off diameters of 1, 0.5 and 0.25 μm for stages 5 to 7, respectively. The sampling duration varied between 1 to 10 (for stage 7), 5 to 50 (for stage 6) and 10 to 100 minutes (for stage 5), to obtain the best loading of particles in the impacted lines. The shorter collection times were applied in Alghero, while the lower concentration of aerosols in Antarctica required an order of magnitude longer sample collection duration.

The TXRF experiments were performed at the plane grating monochromator (PGM) beamline of Physikalisch-Technische Bundesanstalt (PTB), the German national institute for metrology, at the electron storage ring BESSY II using undulator radiation that provides a high photon flux of high spectral purity in the soft X-ray range. The K edge of nitrogen was examined on the wafer samples in the UHV irradiation chamber of PTB. The beam profile was 140 × 40 μm², which resulted in an illuminated area of 3.2 mm × 40 μm at an angle of incidence of 2.5°. For a typical energetic scan at the N-K edge, the incident photon energy was varied from 395 eV to 415 eV in steps of 125 meV. At each point of the scan a TXRF spectrum was recorded for 20 s and the detected N-Kα count rate was deduced. To determine the molar ratio of ammonium and nitrate in the aerosol samples, $(NH_4)_2SO_4$ and $NaNO_3$ standards prepared on silicon wafers were measured in identical conditions. Using a linear combination of the TXRF-NEXAFS spectra recorded for the two standards, a semi-quantitative ammonium/nitrate ratio was obtained [1].

TXRF-NEXAFS spectra collected at the K edge of nitrogen provide information on the chemical environment of nitrogen in the samples. Figure 1 shows N K-edge TXRF-NEXAFS spectra of fine aerosol samples (on May-impactor stages 7, 6 and 5) collected in Antarctica on 14 February 2004, and in Alghero on 11 June 2004. At Terra Nova Bay more than 90 % of

nitrogen was present as ammonium in submicrometer aerosol particles (0.25–1 µm) and the ammonium contribution in the 1–2 µm size fraction decreased to 40–50 %. The ammonium to nitrate ratio showed a decreasing trend with increasing particle sizes in the range of 0.25–2 µm. These results are in accordance with the IC results reported elsewhere [4, 5]. According to Teinilä et al. [4], the dominant mode containing ammonium had a peak at ~0.3 µm aerodynamic diameter, and the nitrate-containing particle mode peaked at slightly below 2 µm. The ammonium-to-nitrate molar ratio was found on average to be 40%/60% in the supermicrometer modes. However, our results were obtained from a 2 m^3 sampled air volume, which is one order of magnitude smaller than for the IC results of Teinilä et al. [4] (30 m^3). At Alghero, more than 90 % of nitrogen was present as nitrate at stage 5 on 6 June 2004, which decreased to 70 % on 11 June 2004. The higher nitrate content was expected due to the characteristics of aerosols throughout Europe [6]. Since both sampling sites were on coastal areas, nitrate was mostly present as $NaNO_3$, which was formed by heterogeneous reactions of sea salt aerosols with gaseous HNO_3 and other nitrous compounds [4]. The results obtained for Terra Nova Bay (Antarctica) show the applicability of the presented technique, supported by the fact that our observations on ammonium and nitrate species at the different size fractions fit in the trends expected from analyses of greater sample volumes [7].

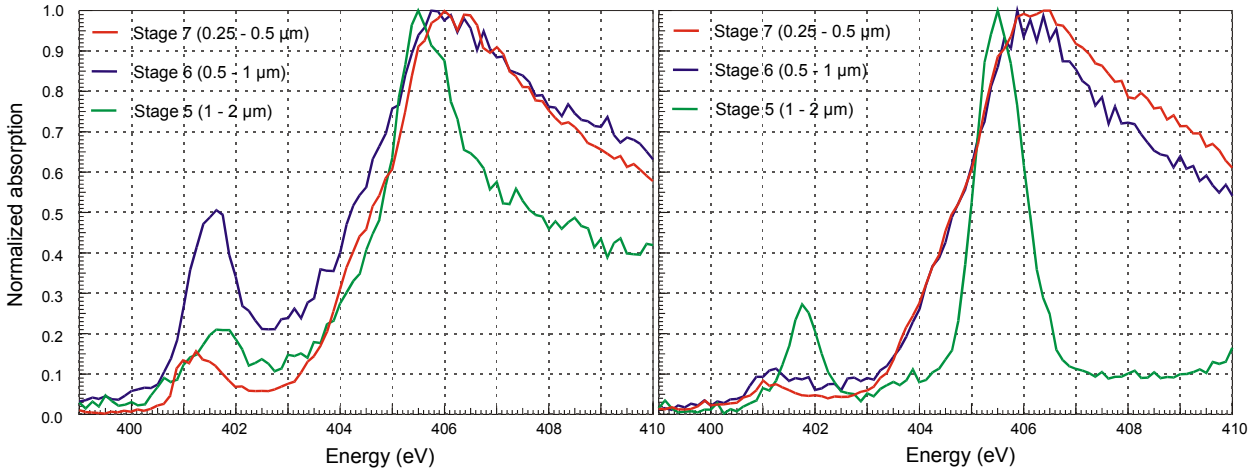

Fig. 1. N K-edge TXRF-NEXAFS spectra of fine aerosol samples collected in Antarctica (left) and in Alghero (right)

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