HIGH TIME RESOLUTION NITROGEN SPECIATION IN SIZE FRACTIONATED ATMOSPHERIC AEROSOLS

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INTRODUCTION

Nitrogen compounds play a very important role in the atmosphere's chemical conversion processes (Harrison & Van Grieken, 1998). Most oxidized nitrous compounds have a relatively short residence time in the atmosphere and interact with the available radicals or aerosols. 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 to measure the aerosols from a short sampling period while retaining the information on the size distribution of the particles. Satellite-borne sensors provide a synoptic view of environmental condition and this objective information is an ideal support for transboundary pollution because there is no legal limitation on the data. From the processed images the estimation of the rate of atmospheric turbidity due to aerosols, namely particulate optical thickness is possible (Masuda *et al.*, 2003). A near edge X-ray absorption fine structure (NEXAFS) investigation in conjunction with total reflection X-ray fluorescence (TXRF) analysis of the wafer surfaces is able to contribute to the speciation of the atmospherically important low-*Z* elements (C, N and O). TXRF using high flux synchrotron radiation (SR) for the specimen excitation is a powerful technique for the non-destructive analysis of nanoscopic (10^{-9} g) amounts of solid material collected on silicon wafer surfaces (Streli *et al.*, 2001).

METHODS

Aerosol samples were collected at two locations in Hungary, a rural (Szatmárcseke, close to Ukrainian border) and a suburban (KFKI campus, Budapest) site. Particles were sampled on silicon wafers using a seven-stage May cascade impactor. Aerosol collection was performed only at stages 5, 6 and 7, with aerodynamic cut-off diameters of 1, 0.5 and 0.25 µm, respectively. As standards of known nitrogen speciation, thin layers of submicrometer particles were prepared on silicon wafer substrates from suspensions containing pro analysis grade $NaNO_3$ and $(NH_4)_2SO_4$. The TXRF-NEXAFS measurements were carried out at the PGM monochromator beamline at the electron storage ring BESSY II using undulator radiation. The samples were investigated under UHV conditions. The beam profile was 140×40 µm² resulting in an illuminated area of 3.2 mm × 40 µm at an angle of incidence of 2.5°. N-Kα fluorescence count rates were recorded by a Si(Li) detector equipped with an ultra-thin polymer window. The incident radiant power was recorded by means of a reference measurement employing a calibrated photo diode allowing for a normalization procedure. 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 during 20 s.

RESULTS

The N K-edge NEXAFS spectra of the submicrometer aerosol fractions showed multiplet π^* resonances similar to that of ammonium sulfate. No significant difference was found in the spectra of the suburban and rural aerosol samples (Török et al., 2004). The spectra of the 1–2 µm aerosol fraction were more similar to that of nitrate, but the π* resonance peaks at 400.3 and 400.5 eV indicate the presence of ammonium in significant amount. Similar results were obtained by Mészáros *et al.* (1997) from wet chemical analyses of size-fractionated high volume samples where ammonium was dominating the smaller particle size fractions. Semi-quantitative evaluation of a spectrum of the 1–2 µm fraction was performed using linear combination of the ammonium sulfate and sodium nitrate standard spectra. The result of the fitting is shown in Fig. 1, giving a nitrate–ammonium ratio of 70%/30%. Looking at the fitting residuals in Fig. 1, minor π* resonances at 399.3 eV could not be described with ammonium and nitrate, that can be due to the presence of organic nitrogen compounds. The presence of biogenic particles containing significant amount of nitrogen was verified using electron-probe microanalysis (EPMA).

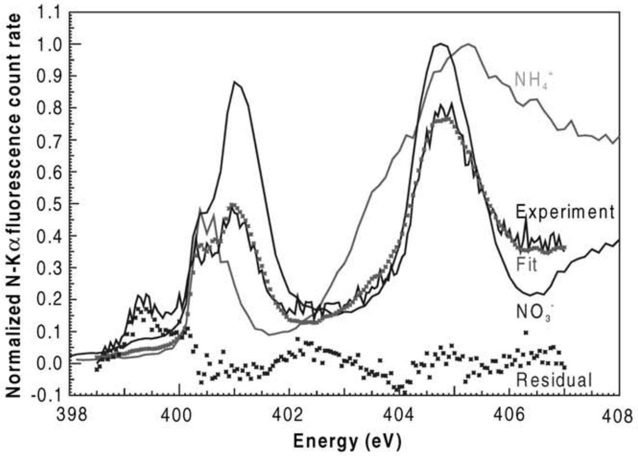

Figure 1. Evaluation of the N K-edge TXRF-NEXAFS spectrum of the 1–2 µm aerosol fraction collected at Szatmárcseke, using linear combination of standard spectra of ammonium and nitrate

CONCLUSION

The TXRF-NEXAFS experiments showed that the sensitivity of the technique enables to carry out nitrogen speciation studies on nanoscopic amounts of aerosols, or potentially even of an individual nanoscaled particle. For atmospheric research this implies that the analytical method enables very high time resolution (1–10 min) or sampling in areas with very low aerosol mass concentration.

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