ULTRA-TRACE SPECIATION OF NITROGEN COMPOUNDS IN AEROSOLS COLLECTED ON SILICON WAFER SURFACES BY MEANS OF TXRF-NEXAFS

S. Török¹, J. Osán¹, B. Beckhoff² and G. Ulm²

¹KFKI Atomic Energy Research Institute, Budapest, Hungary
²Physikalisch-Technische Bundesanstalt, Berlin, Germany

ABSTRACT

Total reflection X-ray fluorescence analysis (TXRF) using monochromatized undulator radiation in the PTB radiometry laboratory at the synchrotron radiation facility BESSY II has been employed to investigate the chemical state of nitrogen compounds in aerosols. The aerosol samples of different size fractions were deposited on silicon wafer surfaces in a May impactor. Using a thin window Si(Li) detector, TXRF detection limits for nitrogen are in the upper fg and lower pg range. Taking advantage of the tunability of monochromatized undulator radiation, the near edge X-ray absorption fine structure (NEXAFS) could be combined with TXRF analysis allowing for the speciation of the aerosols at the nitrogen K absorption edge. Such low detection limits enable analysis of aerosol samples taken in 10 minutes with acceptable accuracy. Applicability of the technique to real aerosol samples has been used to compare nitrogen oxidation state in suburban and rural aerosols.

INTRODUCTION

Air quality monitoring and assurance is a transboundary issue involving co-ordinated environmental action and policies among neighboring countries. This is especially valid for aerosols that can be strongly related to the health of the citizens. Nitrogen compounds play a very important role in the atmosphere’s chemical conversion processes. Most of them are heterogeneous gas-solid phase reactions and depend on many parameters among them the intensity of solar radiation, the vapor content or VOC concentration [1]. Most oxidized nitrous compounds have a relatively short residence time in the atmosphere and interact with the available radicals or aerosols. Compounds in the gas phase can be measured by high temporal and spatial resolution using optical and remote sensing methods [2]. It is crucial therefore 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 [3]. Atmospheric turbidity shows the particulate matter load but it does not provide information on the chemical nature of the substances present in the atmosphere. However, particulate matter is a tracer for pollutant dispersion, and turbidity is an appropriate pollution indicator due to its strong correlation with the concentration of small particles, that have recently been proven to be most harmful to human health. In order to validate aerosol optical thickness values obtained from satellite images highly sensitive analytical method is
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needed that is capable to carry out analyses from aerosols sample taken during the short period of the satellite passage.

A near edge X-ray absorption fine structure (NEXAFS) investigation in conjunction with total reflection X-ray fluorescence (TXRF) spectroscopy analysis of the wafer surfaces is able to contribute to the speciation of the atmospherically important low-Z elements (C, N and O). Due to the extremely high sensitivity of the technique, a nanoscopic amount of material is enough to carry out the measurement.

TXRF using high flux synchrotron radiation (SR) for the specimen excitation is a powerful technique for the non-destructive analysis of very small (nanoscopic, $10^{-9}$ g) amounts of solid material collected on silicon wafer surfaces [4, 5, 6]. Several different TXRF experiments [7, 8] were conducted at the plane grating monochromator (PGM) beamline [9] for undulator radiation within the radiometry laboratory [10] of the Physikalisch-Technische Bundesanstalt (PTB), the German national institute for metrology, at the electron storage ring BESSY II (Berlin, Germany), which provides photon energies between 0.1 keV and 1.9 keV for the specimen excitation. Involving exciation energies from 0.1 keV to 10.5 keV the PGM and the four-crystal monochromator (FCM) beamlines [11] of the PTB are very well suitable for standard-free XRF analysis both of classical bulk samples to thin multi-elemental, multi-layered structures deposited on silicon surfaces.

This paper aims to find adequate sampling, standard preparation and spectrum processing for TXRF-NEXAFS analysis of nanoscopic samples like size fractionated atmospheric aerosol particles collected during a short sampling time. The technique is applied for the analysis of rural and suburban aerosol samples, and compared to single-particle electron-probe X-ray microanalysis (EPMA).

**MATERIALS AND METHODS**

**Samples**

Standard samples of known nitrogen speciation were prepared on silicon wafer substrates from pro analysis grade NaNO$_3$ and (NH$_4$)$_2$SO$_4$. In order to obtain a thin layer of submicrometer particles, suspensions prepared from the selected chemicals were sprayed onto the silicon substrate and dried under vacuum. Suspensions were made in 70 % acetone and 30 % water to obtain rapid drying of the particles. The concentration of the materials in the suspension was approximately 0.05 M. The water content (30 %) was chosen as an optimum to solve (NH$_4$)$_2$SO$_4$ and NaNO$_3$ that are not soluble in acetone.

Aerosol samples were collected at two locations in Hungary, a rural (Szatmárcseke, close to Ukrainian border) and a suburban (KFKI campus, Budapest) site. The Budapest sample was taken at 10 m height and the one in Szatmárcseke at 5 m. Particles were sampled on silicon wafers using a seven-stage May cascade impactor [12]. The May impactor has, at a 20 l/min sampling flow, aerodynamic cut-off diameters of 16, 8, 4, 2, 1, 0.5 and 0.25 µm for stages 1, 2, 3, 4, 5, 6 and 7, respectively. Since the present study aimed to investigate the fine aerosol fraction only, aerosol collection was performed only at stages 5, 6 and 7. The May impactor has
an impacting slit at each stage and thus the aerosols collected on the silicon substrate show a pattern of a thin line. The widths of the impacted lines were between 100 and 300 µm. The background aerosol sampling duration to obtain optimal loading for single-particle EPMA was 1, 5 and 10 minutes for stages 7, 6 and 5, respectively [13]. However, in order to test the optimal material load for the TXRF-NEXAFS measurements at the K absorption edge of nitrogen, aerosol particles were also collected using longer sampling duration, i.e. 2-5, 10-20 and 20-40 minutes for stages 7, 6 and 5, respectively.

**TXRF**

The PGM monochromator beamline at the electron storage ring BESSY II using undulator radiation provides high photon flux of high spectral purity in the soft X-ray range. At a typical stored electron current of 200 mA, the photon flux at the PGM ranges from $6.0 \times 10^{11} \text{ s}^{-1}$ at about 400 eV to $6.0 \times 10^9 \text{ s}^{-1}$ at 1700 eV using the first PTB insertion device, the U180 undulator. Depending both on the exit slit size and on the trigonometric ratio of the incident and of the exit angle at the 1200 mm$^{-1}$ grating, the PGM resolving power $E/\Delta E$ ranges from about 1000 to 9000. In the current investigation the new U49 undulator was employed offering a slightly higher flux of about $8 \times 10^{11} \text{ s}^{-1}$ at the photon energy of 400 eV in conjunction with the PGM beamline.

The UHV irradiation chamber for TXRF of the PTB can accommodate three wafer samples having a respective area of up to 30×30 mm$^2$. Each of the three wafer samples can be fully scanned horizontally and vertically. With respect to the incident radiation the possible angles of incidence range from 0.01° to 5°. In the current investigation the beam profile was $140 \times 40 \mu\text{m}^2$ resulting in an illuminated area of $3.2 \text{ mm} \times 40 \mu\text{m}$ at an angle of incidence of 2.5°. The solid angle of detection was defined by the distance of the Si(Li) detector having a 4.4 mm large diameter of its silicon entrance diaphragm and the silicon wafer. This distance could be varied between a few mm up to several cm adopting to the photon rate emitted by the sample.

**TXRF-NEXAFS**

The PGM beamline is an appropriate source for TXRF-NEXAFS experiments, which require the tunability of the excitation radiation and a relatively high resolving power while ensuring both a sufficient photon flux to allow for trace analysis of low Z elements and a high spectral purity.

The K edge of N has been examined using the TXRF chamber of the PTB. Apart from the N-Kα fluorescence count rates also the incident radiant power was recorded by means of a reference measurement employing a calibrated photo diode allowing for a normalization procedure. During the TXRF spectrum acquisition, the incident radiant power can be monitored by both the measurement of the stored electron beam current as well as the measurement of the radiant power of the beam reflected at the wafer sample. 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 and the detected N-Kα,β count rate deduced.
EPMA measurements

The visualization and low-Z EPMA measurements of the particles collected on silicon wafers were carried out on a JEOL 733 electron probe micro-analyser equipped with an OXFORD energy-dispersive X-ray detector with a super atmospheric thin window (SATW). The resolution of the detector was 133 eV for Mn-Kα X-rays. To achieve optimal experimental conditions, such as low background levels in the spectra and high sensitivity for light element analysis, a 10 kV accelerating voltage and a beam current of 1 nA were chosen [14]. Measurements on individual particles were carried out manually in the point analysis mode, collecting around 50 X-ray spectra of typical aerosol particles using a 30 s measuring live time for each spectrum. The spectra were evaluated by non-linear least-squares fitting using the AXIL program [15].

RESULTS AND DISCUSSION

Previous studies of Hungarian background aerosol have revealed that the ammonium and the oxidized nitrogen compounds are present in different concentration in the same size fraction depending on the season [16]. The samples were taken by a high volume impactor that was sampling 24 hours. Better temporal resolution (shorter sampling period) of size fractionated aerosol samples was only achieved by Laskin et al. [17] using single particle EPMA after sampling.

Different analytical methods can be applied to determine the ammonium and nitrate concentration in atmospheric aerosol samples. Table 1 contains a comparison of minimum detection limits (MDL) and the corresponding minimum sampling volumes (MDLV) for the widely used ion chromatography, ESCA and the TXRF-NEXAFS method presented below. The latter two techniques are non-destructive but can be carried out only in vacuum environment. The relatively narrow (100 µm to 300 µm) line where the aerosols are deposited on the silicon wafers in the May impactor makes it rather inefficient to analyze since the X-ray beam has an oval shape.

Table 1. Minimum detection limits (MDL) for ammonium and nitrate achievable by different analytical methods, and the corresponding minimum air sampling volumes

<table>
<thead>
<tr>
<th>Analytical method</th>
<th>MDL/sample</th>
<th>MDLV for air sampling</th>
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<tbody>
<tr>
<td>Ion chromatography</td>
<td>~0.1 mg/l</td>
<td>~5 m³</td>
</tr>
<tr>
<td>ESCA</td>
<td>0.1 percent in 20 nm</td>
<td>0.5 m³</td>
</tr>
<tr>
<td>TXRF-NEXAFS</td>
<td>500 fg for the PGM-U49</td>
<td>10 L</td>
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Optimization of aerosol sampling for TXRF-NEXAFS

Because of the geometry used for the TXRF-NEXAFS measurements, the on-line visualization of the sample using a microscope was not possible. The samples collected using a May-type cascade impactor, however, had the advantage that the impacted particles formed a pattern of a thin line with a width of 100 µm to 300 µm. Therefore the position of the particles could be located relatively easily by monitoring the intensity of the nitrogen Kα X-ray line during X–Y translation of the sample. At the position of the maximum nitrogen Kα intensity, the dead time
was more than 60% using a 415 eV excitation energy for samples collected for longer duration than the optimal for single-particle EPMA, even when the detector was moved to the furthest possible distance from the sample. For these samples, the intensity of the exciting beam had to be decreased using either thin absorbers or a very small exit slit. The particle load of the impactor samples optimal for single-particle EPMA was found to be optimal also for TXRF-NEXAFS at the nitrogen K-edge, resulting in that both methods can be applied to exactly the same samples. For larger particles ($d > 1 \, \mu m$), the nitrogen speciation analysis can also be performed on individual particles. Due to the destructiveness of EPMA for ammonium and nitrate particles, TXRF-NEXAFS measurements should be applied first.

**TXRF-NEXAFS at the N K edge**

Nitrogen K-edge NEXAFS was mostly applied hitherto for speciation of nitrogen-containing organic compounds [18, 19]. The only paper dealing with inorganic compounds contains a detailed description of N-NEXAFS spectrum of sodium nitrate [20]. Literature data for ammonium could not be found.

The nitrogen K-edge TXRF-NEXAFS spectrum of ammonium sulfate (Figure 1) contains a typical multiplet of $\pi^*$ resonances, five peaks between 400.0 and 401.5 eV. The intensity of the resonances decreases with increasing energy. The spectrum contains also a broad and intense $\sigma^*$ resonance, with a shoulder at 403.5 eV and a maximum at 405.3 eV. The fine structure of the sodium nitrate standard spectrum is similar to that reported by Preobrajenski et al. [20], with the difference that the peak appearing at 401.1 eV is much more intense in the present TXRF-NEXAFS spectrum (Figure 1). According to Preobrajenski et al. [20], this peak in the N K-edge spectrum indicates the energy position of the $\pi^*$ resonance of the NO$_2$ species resulting from slight decomposition of NaNO$_3$.

![Figure 1. N K-edge TXRF-NEXAFS spectra of ammonium sulfate and sodium nitrate standards prepared on silicon wafers](image-url)
The N K-edge NEXAFS spectra of the submicrometer aerosol fractions showed multiplet $\pi^*$ resonances similar to that of ammonium sulfate (Figure 2). No significant difference was found in the spectra of the suburban and rural aerosol samples. The N K-edge NEXAFS spectra of the aerosol samples also show minor $\pi^*$ resonances at 398.3 and 399.3 eV, indicating the presence of other nitrogen compounds. The spectra of the 1 µm to 2 µm aerosol fraction were more
similar to that of nitrate, but the $\pi^*$ resonance peaks at 400.3 and 400.5 eV indicate the presence of ammonium in significant amount. For this reason, semi-quantitative evaluation of a spectrum of this size fraction was performed using linear combination of the ammonium sulfate and sodium nitrate standard spectra. The result of the fitting is shown in Figure 3, resulting in a nitrate/ammonium ratio of 70%/30%. These results were also expected from wet chemical analyses of size-fractionated bulk samples, since ammonium preferred to be present in smaller particle size fraction than nitrate [16]. Looking at the residuals in Figure 3, minor $\pi^*$ 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 lowest energy of dominant $\pi^*$ resonance peak was found for pyridinic nitrogen at 399.8 eV and 399.0 eV for porphyrines [19]. According to Hennig et al. [18], amine type nitrogen shows resonance at 399.3 eV, while imine type between 397.9 and 398.3 eV. For this reason, a wide variety of organic-bound nitrogen species can be present in the samples either attached to the nitrates or ammonium particles or as biogenic particles containing significant amount of nitrogen.

**EPMA RESULTS**

After the TXRF-NEXAFS measurements, the standard and aerosol samples were visualized by scanning electron microscope (SEM) and analyzed by EPMA. As a demonstration of the quality of the prepared standards, Figure 4a shows a secondary electron image of the ammonium sulfate standard. The diameter of the resulted particles was around 2 µm. Due to the specimen damage caused by the electron beam [21], a spectrum of ammonium sulfate where the N K\(\alpha\) peak is clearly visible, could only be collected when a relatively large area was scanned (see Fig. 4b). When the scanning was limited to an area of 10×10 µm², the intensity of N, O and S K\(\alpha\) lines decreased dramatically (Fig 4c).

As an example of the rural aerosol particles, SEM and EPMA results of the aerosol fraction of 1 µm to 2 µm collected at Szatmárcseke are shown in Figure 5. Due to the drastic specimen damage of ammonium and nitrate containing particles, single-particle analysis was not possible on the smaller size fractions at room temperature. Typical nitrogen containing particles show low contrast in the secondary electron image, and they seem to be of hemispherical shape. Sodium nitrate as well as nitrogen containing organic particles were found in the sample at a high abundance (X-ray spectra are shown in Fig. 5b,c). Sodium nitrate particles were formed during long-range transport of sea salt particles, by reaction with atmospheric gaseous pollutants [13]. The presence of nitrogen containing organic particles also supports the suggestion of TXRF-NEXAFS, that organic-bound nitrogen is also present in the sample.

**CONCLUSIONS**

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 the identification and speciatation of nitrogen rich particles TXRF-NEXAFS was highly superior to EPMA. For atmospheric research this implies that very short time sampling with size fractionation can result in useful samples and as a consequence the analytical method enables very high time resolution (eg. the time of satellite passage) or sampling in very remote areas (like Antarctica).
Figure 4. Electron microscope analysis of the ammonium sulfate standard, (a) secondary electron image, (b) X-ray spectrum collected while scanning the whole image area, (c) X-ray spectrum collected from a smaller area indicated by white square.
Figure 5. (a) Secondary electron image of the aerosol sample collected at Szatmárcseke, size fraction 1-2 µm, (b) X-ray spectrum of a nitrogen containing organic particle (left circle), (c) X-ray spectrum of a sodium nitrate particle (right circle).
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