

Speciation of sulfate in size-fractionated aerosol particles using sulfur K-edge XANES

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Sulfate ions are a main constituent of aerosols, which can cause various environmental problems. In the evaluation of the influence of sulfate aerosols, it is necessary to determine what sulfate ions are contained in these aerosols. In this study, sulfur K-edge XANES was used to determine sulfate species present in size-fractionated aerosol particles based on the post-edge structure after the main absorption peak in the XANES region.

The aerosol samples were collected various sites in China and Japan as part of the Japan-China joint project, "Asian Dust Experiment on Climate Impact". The aerosol samples were collected using a low-volume Andersen-type air sampler (AN-200, Shibata) to obtain sulfur species in the aerosol particles with various diameters. Sulfur K-edge XANES was measured at Beamline BL-9A at Photon Factory, Japan.

A comparison of the XAES spectra of reference sulfate materials and aerosol samples collected in Tsukuba in Japan clearly showed that $(\text{NH}_4)_2\text{SO}_4$ was the main sulfur species in particles with a smaller diameter and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (gypsum) was the main sulfur species in particles with a larger diameter. A simulation of the XANES spectra by reference materials allows us to obtain the quantitative mixing ratios of the different sulfate species present in the aerosol samples. The presence of minor sulfur species other than $(\text{NH}_4)_2\text{SO}_4$ and gypsum at the surface of mineral aerosols is suggested in our simulations and by a surface-sensitive conversion electron/He-ion yield XANES. In the absence of a contribution from a large dust event, the mole concentration of gypsum in the mineral aerosol fraction (particle diameter $> 1 \mu\text{m}$) determined by XANES is similar to that of Ca which is determined independently using ion chromatography. This shows that the Ca and sulfate in the mineral aerosols are present only as gypsum. Considering that calcite is the main Ca minerals in the original material arising from an arid and semi-arid area in China, it is strongly suggested that gypsum is formed in aerosol during its long-range transportation by a reaction between calcite and sulfate ions.

This study has shown that sulfur K-edge XANES is a powerful tool to identify sulfur species in aerosol samples. The method has various merits in the chemical speciation of sulfur, or sulfate, in aerosol samples: (i) it is applicable to the small amount of size-fractionated samples collected by an Andersen-type sampler, (ii) the spectra can be measured under ambient conditions, even in the presence

of a variety of other minerals and elements in aerosols, (iii) the mixing ratio of several sulfur species can be extracted through the simulation of the spectra, and (iv) by coupling fluorescence XANES and CEY-XANES, sulfur species in the bulk and at the surface of the particles can be distinguished. It is expected that the coupling of bulk chemical analysis using ion chromatography and sulfur speciation using XANES for more samples will provide information on the precise characterization of sulfate aerosols.

References

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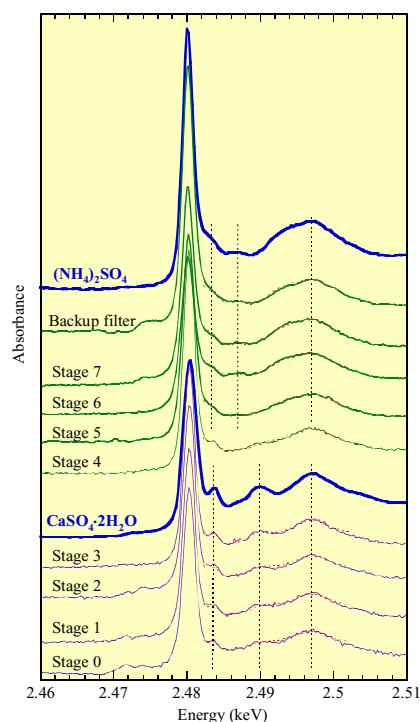


Fig. 1. Sulfur K-edge XANES for the sulfur species in aerosol sample collected at Tsukuba in April 2002 for different particle sizes. The particle diameters corresponding to each stages are as follows: Stage 0 ($>11 \mu\text{m}$), Stage 1 ($7\text{--}11 \mu\text{m}$), Stage 2 ($4.7\text{--}7 \mu\text{m}$), Stage 3 ($3.3\text{--}4.7 \mu\text{m}$), Stage 4 ($2.1\text{--}3.3 \mu\text{m}$), Stage 5 ($1.1\text{--}2.1 \mu\text{m}$), Stage 6 ($0.65\text{--}1.1 \mu\text{m}$), Stage 7 ($0.43\text{--}0.65 \mu\text{m}$), and the Backup filter ($< 0.43 \mu\text{m}$). The spectra for gypsum and $(\text{NH}_4)_2\text{SO}_4$ are also shown for comparison. The dotted red line curves show the simulated spectra assuming that gypsum and $(\text{NH}_4)_2\text{SO}_4$ were the main sulfur species in the samples.