Trace Characterization of Individual Aerosol Particles using an X-ray Microprobe

The elemental compositions of atmospheric aerosols are related both to their origin (source) and with physical and chemical processes during transportation. Therefore, the analysis of individual aerosol particles has been received great interest in terms of source apportionment and estimation of transformation reactions, etc . An electron probe micro-analyzer (EPMA) has been utilized for this purpose [1]. However, owing to the significant background beneath the signal, the detectable elements are limited to the major components. A combination of a newly installed X-ray microprobe and X-ray fluorescence (XRF) detection has realized trace quantification down to fg (femtogram) level and chemical state diagnosis using XANES (X-ray absorption near edge structure) spectra has become possible. Some new possibilities for discovering the history of individual aerosol particles are under discussion.

Figure 1 shows the experimental layout around the specimen. A pair of elliptical mirrors (Kirkpatrick and Baez mirror, KB mirror) were installed at beamline **BL39XU**. Its effective aperture is approximately 150 × 150 μm^2, and Rh coated mirrors cover X-rays up to 18 keV. The preliminary experimental results show a focal spot down to 2 μm(V) × 4 μm(H) with the photon flux more than 1× 10^{10} photons/s for monochromatized 10 keV X-rays [2]. A sample was mounted on the XY scanning stage, and XRF from the sample was detected with a conventional Si(Li) detector. To avoid an excessive counting rate, a sample-detector distance of 100 mm was used. The minimum detection limit (MDL) of the XRF analysis was evaluated with a series of thin metal films deposited onto the Kapton foils of 10 μm in thickness, and the evaluated MDL was 0.3 fg for Ni using 10 keV X-ray microbeam.

Coarse and fine fractions of aerosols were collected separately in two-stage filterpacks (8 and 0.4 μm Nuclepore filters) with a 50% effective cutoff diameter of 1 μm. Sampling was conducted at the Uji campus of Kyoto University during the Asian dust storm (Kosa) event. A coarse fraction of the

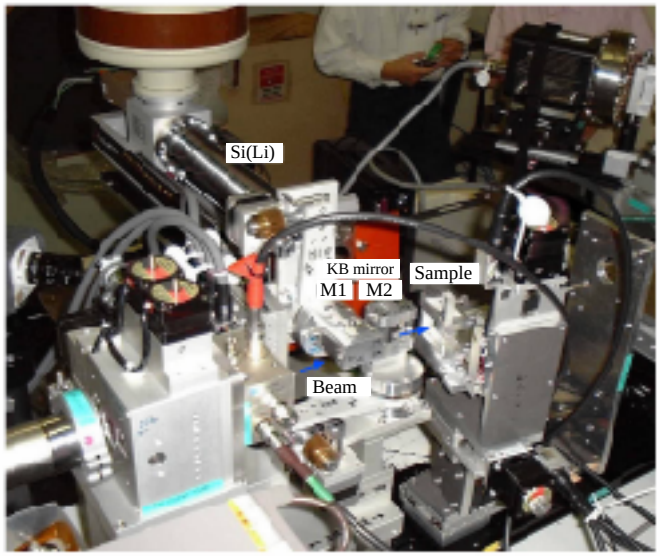

Fig. 1. Experimental setup for the X-ray microprobe.

collected aerosol particles was subjected to XRF measurement.

Figure 2 shows an Fe XRF image of the aerosol particles obtained with a 10 keV X-ray microbeam. Black points represent particles which give strong Fe signals. The sizes of the large particles were evaluated from a cross section of the Fe XRF image, and the sizes of the particles less than the beam size were estimated from the Fe signal on the assumption that the portion of the Fe composition was the same among the particles.

Figure 3 shows micro-XANES (X-ray absorption near edge structure) spectra of aerosol particles marked on an Fe image, (a) and (b) in Fig. 2. The XRF yield method was used to obtain these spectra. The XANES spectrum obtained for particle (b) is identical to that of hematite Fe_2O_3, and most of the other particles gave similar spectra. Chemical shifts in the absorption edge between the spectra of the aerosol particles and those of a reference, Fe thin film show the difference in valence state of Fe, and the Fe in the aerosol particle (a) might be in a divalent state.

Figure 4 shows XRF spectra measured from an individual aerosol particles. The diameter of the particle (a) is estimated to be 10 μm from the cross section of the Fe XRF image. Considering that the matrix of the particle is quartz, the mass of the particle can be estimated to be 1.2 ng from the density of the quartz (2.2 g/cm^3). Owing to the atmospheric environment and the rather poor excitation efficiencies for light elements, no peak was observed for S and Cl. However, Ca, Ti, Cr, Mn, Fe, Ni, Cu and Zn were detected. For small particles attenuation of XRF inside the sample can be neglected, and semi-quantitative information can be obtained from a comparison of the XRF signals between the sample and reference thin films previously measured. The absolute amounts of Ca, Ti, Mn and Ni in the particles were estimated to be 220, 120, 110, 17 fg for the particle (a) and 470, 100, 30, 3 fg for the particle (b), respectively [3]. Similarly, semi-quantitative analyses of the particles were carried out for 16 particles on this sample, and the difference of elemental compositions (elemental profiles) was

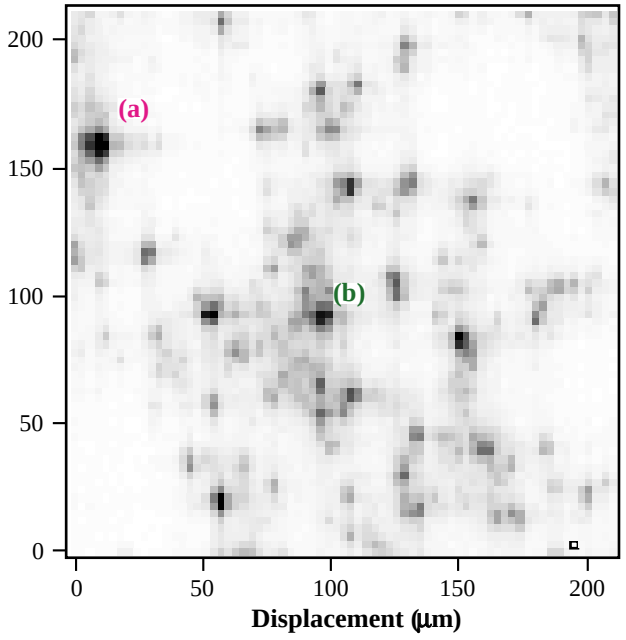

Fig. 2. Fe XRF image of aerosol particles on a Nuclepore filter. 10 keV X-rays were used for excitation.

found between the particles. Further interpretations of elemental profiles are being carried out to reveal the origin and the transportation process of individual aerosol particles. Utilizing this unique characteristics of the X-ray microprobe of ultra-high sensitivity, analyses of a single rain drop and a single fog droplet [4] are now in progress.

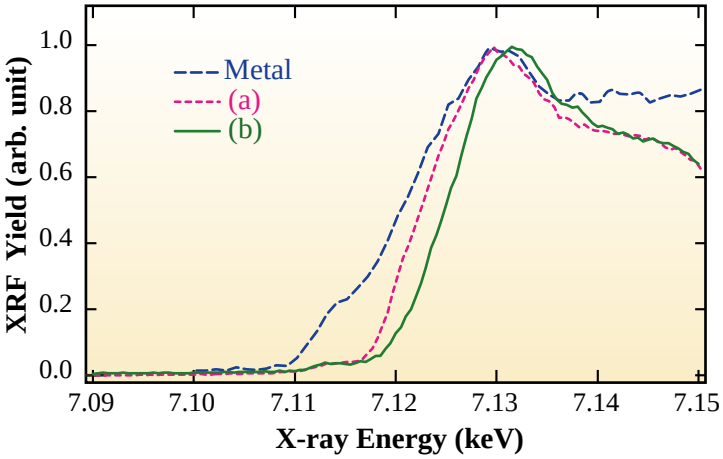

Fig. 3. Micro XANES spectra from individual aerosol particles marked on the Fe image (see Fig. 2). The reference metal spectrum is imposed in the figure.

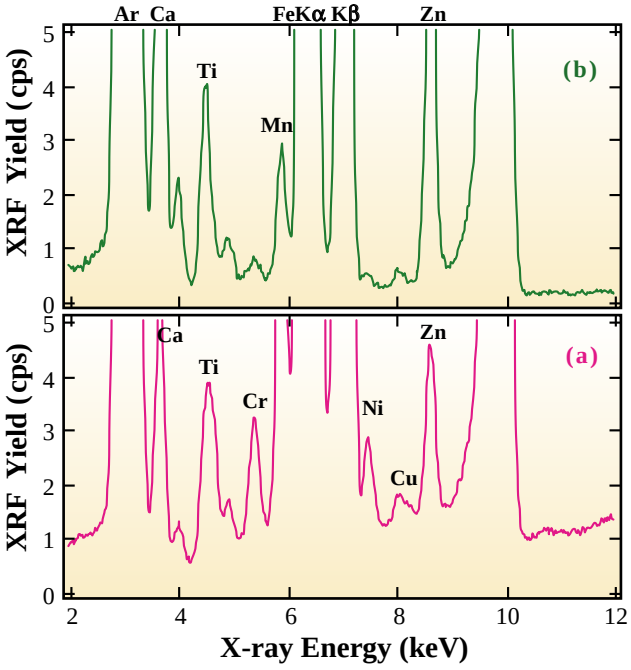

Fig. 4. XRF spectrum from individual aerosol particles (a) and (b) marked in Fig. 2.

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