Individual Micrometer-size Aerosol Particle Analysis with On-site Combination of Electron Microscope and Synchrotron X-ray Microscope

Aerosol particles, absorbing atmospheric toxic elements during flight, adversely affect human health upon reaching the lower respiratory tract. Global environmental factors, including climate, are also vulnerable to the simultaneous mass transfer of atmospheric elements, which also disturbs the global radiative energy transfer (albedo). Recent desertification and air pollution accompanying Asian industrialization are deteriorating the situation.

A scanning electron microscope with an energy-dispersive X-ray spectrometer (SEM-EDX) has been commonly used for the topographic image observation of materials down to the nanometer scale. A secondary electron image provides a detailed 3D-like surface morphology, while information on elemental composition is obtained by detecting the characteristic X-rays from B to U with a detection limit of *ca*. 0.5 wt.% for most elements, together with the sub-micrometer area image observation. SEM-EDX is (i) sensitive to light elements, (ii) capable of performing qualitative and quantitative analyses within a few minutes for most samples, and (iii) inapplicable under atmospheric pressure, but an ultrahigh vacuum is not necessary. On the other hand, a low excitation efficiency induced by an electron beam for heavy elements, as well as bremsstrahlung that leads to strong continuous X-ray backgrounds, has been a concern when detecting trace and microamounts of elements.

A synchrotron radiation X-ray fluorescence (SR-XRF) spectromicroscope, the minimum detection limit of which is less than one femtogram, is another elemental analysis instrument used in detecting the characteristic X-rays. SR-XRF is (i) appropriate for detecting trace and microamounts of elements, (ii) a tunable beam size down to a sub-micrometer scale for local measurement, and (iii) applicable under atmospheric pressure. However, one critical problem of SR-XRF application to individual aerosol particles despite its higher sensitivity than SEM-EDX is that optical microscopes, often used for beam position alignment in SR-XRF, are inappropriate for micrometer-size sample observation due to the limited resolution and very small depth of focus. It has been a problem that the exclusiveness of SEM measurement due to the vacuum seal requirement obliges SR-XRF and SEM to be performed separately.

In the present research, we succeeded in simultaneously performing SR-XRF and SEM-EDX measurements for a micrometer-size single Kosa aerosol particle without changing the sample position, by introducing a synchrotron radiation beam into a SEM chamber [1-3]. Sensitive multielement determination by SR-XRF and detailed surface topography observation by SEM, both crucial for the investigation of the state of an individual particle, have been simultaneously applied to individual particles in the SEM chamber by aligning the X-ray and electron beam positions.

A low-vacuum SEM (JEOL JSM-5600LVS) mounted with a silicon drift detector (SDD), Röntec

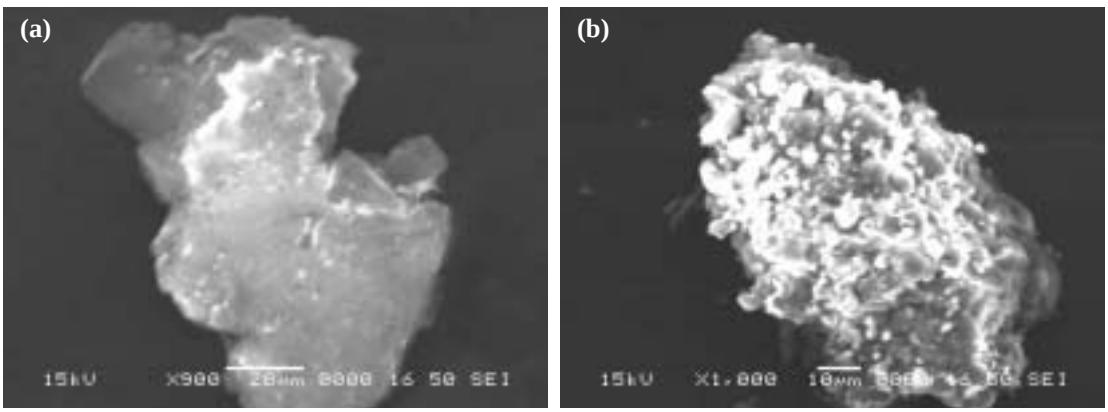

Fig. 1. Secondary electron images of single Kosa aerosol particles sampled in **(a)** Shenyang, China, in March 2004, and **(b)** Harbin, China, in September 2003.

Xflash 2000, was installed at beamline **BL37XU**. This SEM was equipped with a beryllium window (10 μm in thickness and 20 mm in diameter) to introduce a monochromatic synchrotron radiation microbeam inside the SEM chamber. The position of SEM was adjustable both vertically (by a pulse motor) and horizontally in such a manner that the synchrotron radiation beam and the electron beam can cross on the SEM sample stage.

The SEM images of two representative Kosa aerosol particles (*ca.* 50 μm in diameter) are shown in Fig. 1; one sampled at a building rooftop in Shenyang in March 2004, when severe Kosa aerosol outbreak was recorded, and the other sampled at a rooftop of a building in Harbin University of Science and Technology in September 2003, when Kosa was moderate (Shenyang and Harbin are major industrial cities located in northeastern China). Standard Kosa samples, CJ-1 and CJ-2, National Institute for Environmental Studies, Tsukuba, Japan, were also measured as typical Kosa particles before being contaminated.

The results have proved that the sensitivity of detecting constituent elements of individual Kosa aerosol particles is higher using this combination, as shown in Fig. 2, than solely using conventional SEM-EDX. It should be noted that elements from Mg to Fe, including major constituents of both soil and atmospheric pollutants, in a single particle were satisfactorily measured. We observed that the individual aerosol particles were contaminated with atmospheric sulfur and chlorine, by successfully detecting the deviation in elemental composition from the standard Kosa samples. Detailed SEM images were utilized in conjunction with the elemental analysis result, and it was implied that atmospheric sulfur primarily adheres to calcium intrinsic to Kosa aerosol and that the surface roughens as a consequence of the chemical reaction between the two elements ($CaSO_4$). The coexistence of sulfur and calcium was verified for tens of other aerosol particles by elemental distribution analysis.

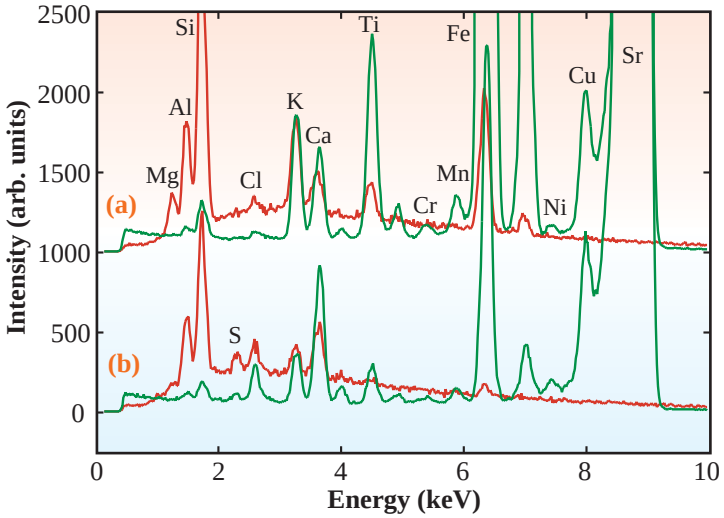

Fig. 2. SEM-EDX (red) and SR-XRF (green) spectra of **(a)** Shenyang and **(b)** Harbin particles, which are identical to those shown in Fig. 1.

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