Simultaneous Detection of X-Ray Fluorescence and Conversion Electrons for Depth Selective XAFS Analysis

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Abstract. An apparatus has been developed, which enables us to monitor both x-ray fluorescence yield (XFY) and conversion electron yield (CEY) from a sample. The apparatus has been installed to the BL11 of HSRC, and its basic performance has been evaluated. The detection limit of X-ray fluorescence analysis is 1.5 ppm for Ca and 6.6 ppm for S when the incident x-ray energy is optimized just above the absorption edge energy. The probing depth of the CEY method is estimated to be 4.0 nm for Ag thin films around Ag L_{III} edge while the escape depth of the x-ray fluorescence is more than 1 μm. The near surface sensitivity of the CEY is advantageous for XAFS measurements because x-ray fluorescence mode may suffer self-absorption-effects.

Keywords: XAFS, x-ray fluorescence, conversion electron, detection limit
PACS: 61.10.Ht X-ray absorption spectroscopy: EXAFS, NEXAFS, XANES

INTRODUCTION

Comparisons between the surface and bulk properties of small particles have become important, and x-ray absorption fine structure (XAFS) analysis with depth selectivity has received great interest. One of the promising ways of the depth selective XAFS measurements is to utilize the difference of the probing depth between the x-ray fluorescence (XRF) yield and the electron yield. The difference of sulfur (S) chemical states of the coal fly ash has been discussed in terms of the S K edge XAFS spectra obtained with the total electron yield and with the XRF yield [1].

The yield (Y) of the XRF and the electron can be generally expressed as the following general equation as a function of the sample thickness *t*

$$Y = k\tau(1-e^{-\frac{t}{\tau}}) \qquad (1)$$

where τ is the probing depth, and k is constant. The probing depth, τ can be expressed as

$$\frac{1}{\tau} = \frac{1}{\tau_x} + \frac{1}{\tau_s} \qquad (2)$$

where τ_x is the penetration depth of the incident x-rays and τ_s is the escape depth of the XRF or the electrons, In the case of electron yield τ_s is much smaller than τ_x, and the probing depth is mainly determined by the averaged escape depth of the electrons. On the other hand the probing depth of XRF can be affected both with the penetration depth and the escape depth of x-rays.

We have developed a new apparatus to realize depth selective XAFS measurements under He environment, and its basic performance was evaluated.

EXPERIMENTAL

Experiments were carried out on the BL11 of the Hiroshima Synchrotron Research Center (HSRC)[2]. The beamline is equipped with a Ni coated bent-cylindrical mirror (glancing angle=0.5 deg) and a Si(111) double crystal monochromator. The storage ring is operated at 700MeV, and the monochromatized x-rays between 2.100 and 5.400 keV are available from the bending magnet source. A small ionization chamber and a sample chamber are placed at the end

of the beamline. The ionization chamber has the path-length of 12 mm, and. is operated under atmospheric condition. The transmittance of the x-rays ranges from 52 % (2.1 keV) to 96 % (5.4 keV), and the signal is utilized for the normalization. The beam size (FWHM) at the sample position is approximately 3 mm (H) ∗1 mm (V), and the typical photon flux is $1*10^{10}$ photons/s for 4 keV x-rays.

The sample chamber is filled with He, and the energetic Auger electrons from the sample ionize surrounding He molecules. The sample is mounted on the copper holder connected to the current amplifier, and a biased plane electrode is placed 3 mm apart from the sample surface. The electrode is a copper film of 100 nm deposited onto the poly-carbonate film of 6 μm. The electrode prevents created electron-ion pairs from the recombination, and the signal can be measured as the conversion electron yield (CEY). The angle between the incident x-rays and the sample surface is 45 deg, and the incident x-rays go through the film electrode. A commercial Si detector (Amptek, XR-100T) is placed normal to the beam in the plane of the orbit, and the XRF yield (XFY) can be monitored simultaneously through the film.

RESULTS AND DISCUSSION

Detection Limit of XRF Analysis

To evaluate the detection limit of the XRF analysis mixtures of boron nitride (BN) and calcium sulfate ($CaSO_4$) were prepared, and 200mg of each mixture was pelletized into disks of 8 mm in diameter. The concentrations of Ca were 600, 300, 200, 100 and 0 ppm, and the concentrations of S were 480, 240,160,80,0, respectively. XRF spectra measured with the incident x-ray energies of 4.500 keV and 3.000 keV are shown in Figures1. The gross counts of Ca Kα and S Kα regions are plotted as a function of the concentration. The detection limit (*DL*) was calculated from the standard deviation of the background σ and the slope of the analytical curve *m*.

$$(DL) = \frac{3\sigma}{m}. \qquad (3)$$

The evaluated *DL* for Ca is 1.5 ppm with 4.5 keV x-rays while that for S is 10.3 ppm. The DL for S can be improved by choosing the x-ray energy just above the absorption edge and the DL is 6.6 ppm.

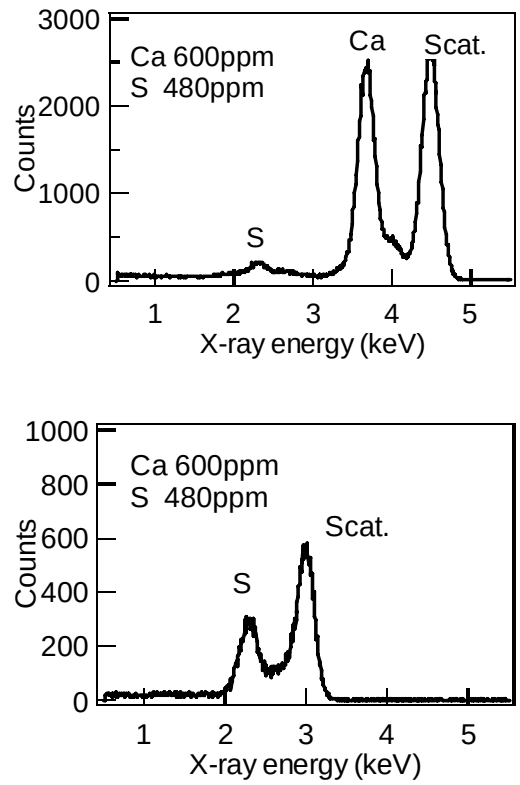

FIGURE 1. Synchrotron radiation excited XRF spectra of a mixture of $CaSO_4$ and BN. The incident x-ray energies are 4.5 keV (upper) and 3.0 keV (lower), respectively. The accumulation time was 300s.

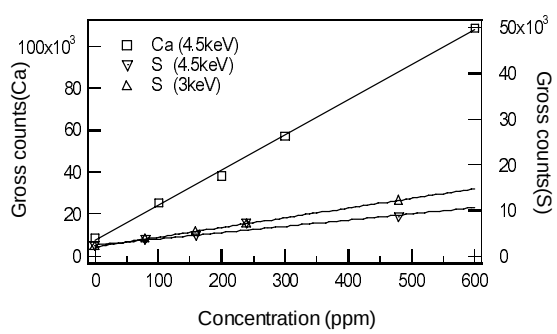

FIGURE 2. Analytical curves of Ca and S XRF signals (gross counts) as a function of the concentration.

Probing Depth of XFY and CEY

To evaluate the probing depth with the CEY method a series of silver (Ag) thin films (0.5, 2.1, 3.1, 20.5 nm) were evaporated onto the polypropylene substrates of 6 μm in thickness. As was expected from the linear absorption coefficient of Ag (5600 cm^{-1}) for

Ag Lα line (2.984 keV) the XFY was proportional to the film thickness, and the calculated probing depth is more than 1 μm with the takeoff angle of 45 deg.

Figure 3 shows thickness-dependence of the CEY from the Ag films. The signal was evaluated as a difference of CEY around the Ag L_{III} edge (ΔE=10eV). The obtained data were fitted to the equation (1) , and the evaluated probing depth is 4.0 nm.

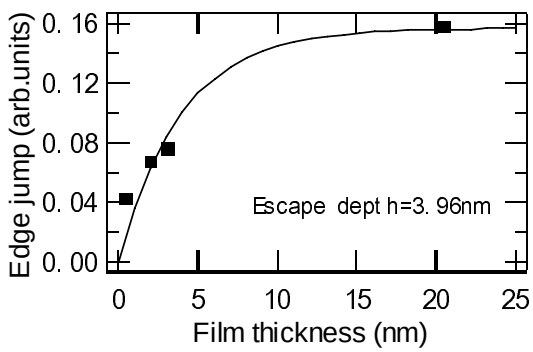

FIGURE 3. The thickness-dependence of the CEY (square) from the Ag films around Ag L_{III} edge. The solid line shows fitted theoretical curve.

XAFS Spectra with XFY and CEY

As mentioned previously the probing depth with the XFY method is much greater than that of the CEY method, and the depth selective XAFS measurements can be expected with this technique. However, one should be aware of the self-absorption effect in XAFS spectra obtained with the XFY method [4,5].

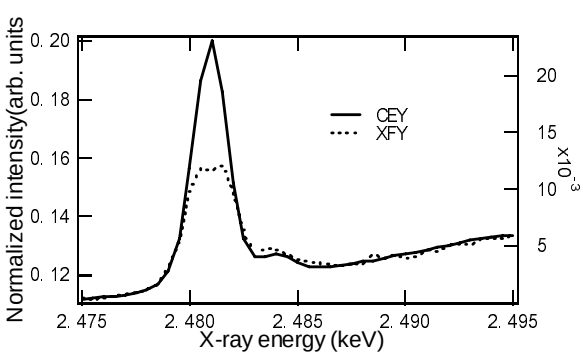

FIGURE 4. S K edge XAFS spectra of $CaSO_4$ obtained with the XFY (dotted line) and the CEY (solid line) methods. The x-ray energy was not calibrated.

Figure 4 shows S K edge XAFS spectra of $CaSO_4$ powder fixed onto the adhesive tape. The spectrum with the CEY method shows characteristic features of sulfate spectrum. Though $CaSO_4$ is stable and the spectral difference is not expected between the near surface region and the bulk, the spectrum with the XFY method shows weakened resonance peak. The spectral deformation was attributed to the change of the probing depth around the absorption edge, and the effect was negligible with the CEY method.

It should be noted that even with the sample of weak XRF signal (less areal density) the self-absorption-effect should be considered for XAFS spectra with the XFY method.

CONCLUSIONS

An apparatus has been developed, which enables us to monitor both the XFY and the CEY simultaneously from a sample, and the basic performance of the apparatus has been evaluated. The detection limit of the XRF analysis is 1.5 ppm for Ca and 6.6 ppm for S when the incident x-ray energy is optimized just above the absorption edge energy. The probing depth of the CEY method is estimated to be 4.0 nm for Ag thin films around Ag L_{III} edge while the escape depth of the x-ray fluorescence is more than 1 μm. It should be noted that the spectral difference should be carefully considered because the spectrum obtained with the XFY method may suffer from the self-absorption-effect that cannot be neglected when measuring the major element in the fine particles.

ACKNOWLEDGMENTS

Authors are grateful to Dr. Shunji Goto of SPring-8 for providing us a small ionization chamber. This work was supported by a Grant-in-Aid for Scientific Research on Priority Areas under Grant No. 14048212 from the Ministry of Education, Culture, Sports, Science and Technology (MEXT). One of the authors (S. H.) is financially supported from Shimadzu Science Foundation.

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