

Broad-band high-energy-resolution hard X-ray spectroscopy using transition edge sensors (TESs) and its application to environmental samples

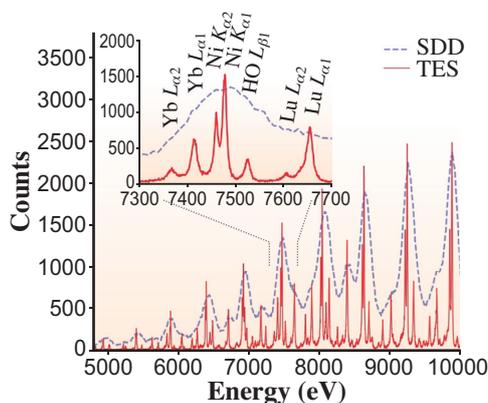
Speciation, the identification of chemical species of any elements in environmental samples, is basic information necessary to understand and predict the environmental behaviors of elements [1]. For example, the redox state and chemical bonding to neighboring atoms of an element of interest are essential for characterizing the element, such as its water solubility, toxicity to biota, and effect on climate change. X-ray absorption fine structure (XAFS) spectroscopy including X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) have been used as one of most powerful techniques for clarifying such information. In particular, XAFS measurement in the fluorescence mode by detecting X-ray fluorescence (XRF) has been widely used for trace elements in environmental and geochemical samples. However, there have been many cases where we cannot measure XAFS because of interference from the XRF of other elements and scattered X-rays even when using an energy-dispersive detector such as a silicon drift detector (SDD) with an energy resolution of around 130 eV.

Here, we have succeeded in operating a transition-edge sensor (TES) spectrometer to overcome the difficulties of interference at SPring-8 BL37XU [2]. The TES spectrometer consists of a 240-pixel NIST TES system with an energy resolution of 5 eV at 6 keV [3], which is an energy resolution that is more than 20 times higher than that of SDD. On the other hand, the count rate of X-ray allowed for the TES is generally around 1 count/s/pixel. The performance of the TES is studied over the energy range of 4–13 keV using a Mn target with different count rates and a Pb target with various beam energies. The energy resolution, which

could depend on the template and its calibration lines, is approximately 6 eV at 6 keV at the total count rate of <2000 c/s, while it becomes a few 10 eV above 10 keV.

To demonstrate the capabilities of TES at BL37XU, a NIST standard silicate glass (NIST610) spiked with 61 trace elements was used as a target. The XRF spectra of NIST610 measured with the TES (sum of 220 pixels) and SDD are shown in Fig. 1. The spectrum obtained with the SDD is composed of some sharp peaks corresponding to K lines, for example, Fe (6.4 keV), Co (6.9 keV), and Ni (7.5 keV), but the spectrum obtained with the TES revealed that each peak actually consists of L lines of various lanthanides, which shows that the use of the TES enables us to detect L lines of heavier elements, which are usually hidden by K lines of transition elements when measured with the SDD.

Fluorescence XANES analysis using the TES spectrometer was conducted for a synthetic sample (NIST610) and natural materials that contained various elements. Among the elements of interest in environmental sciences, arsenic (As) and lead (Pb) are the most important in terms of their health risk and wide occurrence in the earth's crust. The two elements frequently coexist in specific environments such as sulfide mine tailing and coal [4], which warrants the study of the environmental chemistry of the two elements in the same system. However, the determination and speciation of the two elements in the same sample can sometimes be troublesome when using XRF and XAFS because of the difficulty in separating the As $K\alpha$ and Pb $L\alpha$ emissions, since the energy resolution of the SDD is insufficient for adequately resolving the lines. Thus, the Pb L_{III} edge



TES & cryostats Readout System



Fig.1. (a) Spectra of SRM610 taken with TES (red) and SDD (blue). (b) Experimental setup of TES system in BL37XU.

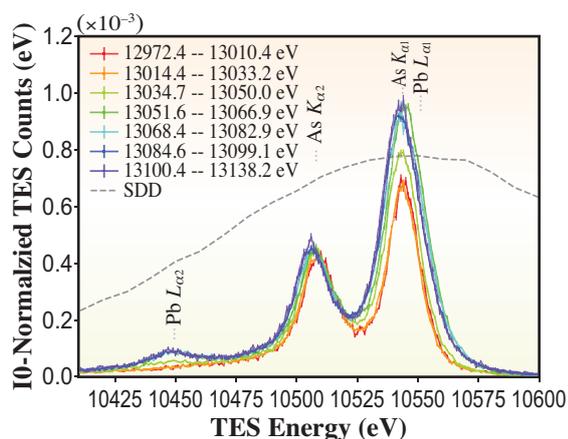


Fig. 2. X-ray emission spectra of TES spectrometer with seven different X-ray energies illuminating a sample of SRM 610 across the Pb L_{3} -edge (13035 eV). The SDD spectrum is overlaid as the dashed line.

XANES was measured using the TES to evaluate its potential for the chemical diagnosis of the heavy elements in complicated materials. As shown in Fig. 2, Pb L_{α} and As K_{α} severely interfere with each other and they cannot be resolved even by using the TES. In this case, it is effective to focus on Pb $L_{\alpha 2}$, which is free from the interference of As K lines, to measure the Pb L_{III} -edge (Fig. 3). Note that the speciation of As using its K-edge XAFS does not interfere with Pb, since the absorption edges of Pb are higher than the As K-edge. However, there is a huge demand for the speciation of Pb in the presence of As. Thus, fluorescence XAFS using the TES is worth considering as an option for samples containing both As and Pb.

Another application of the TES is to measure a small quantity of material. Its high resolution can help to resolve the elements from the background and mitigate the risk of misinterpreting the spectra. Here, we chose iron (Fe) in aerosols sampled above the sea, since Fe at the sea surface supplied from marine aerosols affects marine bioproductivity, which is linked to the absorption of carbon dioxide by seawater and, in turn, to climate change. Moreover, the dissolution rate of Fe in marine aerosols in seawater is important in the quantification of the amount of Fe available to biota, which can be assessed by the speciation of Fe [5]. However, the amount of Fe in aerosols collected on aerosol filters is very small, as interfered from the scattered X-rays. The fluorescence XANES spectrum of Fe in marine aerosols collected on the filter was obtained using the SDD and TES. The TES XRF spectra showed a better signal-to-background ratio (the ratio of 10-normalized counts at the peak and pre-edge energies; ~ 5.2) than the SDD spectra (~ 1.1) because of the low interference of scattered X-rays and contamination. As a result, a fluorescence XANES

at the Fe K-edge was successfully obtained, which will enable us to discuss the water solubility of Fe in the aerosol samples.

This study is the first important step toward the application of high-resolution spectroscopy for XRF and XAFS analyses in hard X-ray synchrotron facilities. The development of the TES is rapidly progressing; thus, its performance will improve in terms of the number of pixels, the effective area, and the energy range. In particular, further improvement of the energy resolution of TES technology approaching 1 eV as well as increasing the total count rate will make it a practical instrument for a high-energy-resolution fluorescence-detected XANES, which is a distinctive spectroscopy tool that can provide more information on electronic states than a normal XANES, in the future.

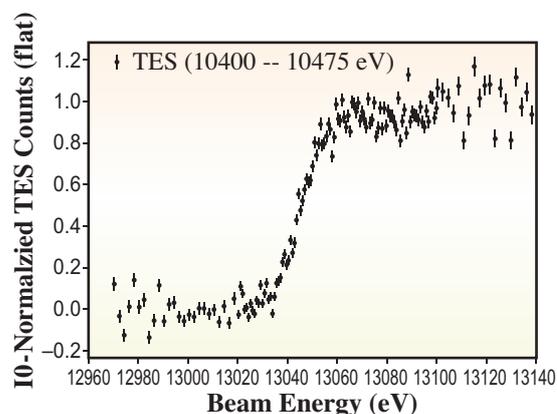


Fig. 3. XANES of Pb $L_{\alpha 2}$ obtained using TES with 10400 eV–10475 eV.

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