# Two-dimensional approach to fluorescence yield XANES measurement using silicon drift detector

Since the pioneering work by Jaklevic *et al.*, in 1977 [1], fluorescence yield (FY) detection has been widely performed to measure the X-ray absorption near-edge spectroscopy (XANES) spectrum in the hard X-ray region. On the other hand, FY detection is not a mainstream technique in the soft X-ray region because fluorescence decay is a minor channel for low-Z elements. For example, the fluorescence decay probability for an oxygen 1*s* core hole is less than 1%, in which case an electron yield measurement is a common technique used to obtain the XANES spectrum in the soft X-ray region. Although the yield of fluorescence decay is low, FY detection has a notable advantage, that is, a higher signal-to-background ratio than the transmission method and the electron yield detection method [2]. In particular, selective X-ray fluorescence detection using an energy-dispersive detector, which is called partial fluorescence detection (PFY), allows us to obtain XANES spectra for trace elements with concentrations lower than 100 ppm.

A recent progress in the case of soft X-ray detector and the highly brilliant soft X-ray beamline make up for the low fluorescence yield of light elements, and the application of FY is spreading greatly even in the soft X-ray XANES measurement. In the present research, we demonstrated the capabilities of a two-dimensional (2D) fluorescence yield measurement in the X-ray absorption near-edge spectroscopy in the soft X-ray region [3]. The 2D measurement is a correlation plot between the excitation energy and the spectrum obtained by a secondary spectrometer. The noteworthy advantage of 2D data collection is that it allows us to carry out a full survey of XRF spectra and to determine the extracting area after the XANES measurement. In conventional procedures of PFY measurement, the XRF information was lost because the PFY was determined by selecting a region of interest (ROI) prior to the XANES data collection. Only a signal corresponding to the ROI is recorded. This is problematic for the PFY measurement of complex samples in which overlaid peaks obscure the fluorescence. This issue is more serious in the soft X-ray region where absorption edges of different elements are close to each other and where fluorescence lines overlap. In such cases, it is indispensable to store the entire fluorescence spectrum at every single point of the XAFS scan, and to validate the obtained spectrum after the XAFS measurement. In current procedures, the highly brilliant soft X-ray beam and high-count-rate performance of an X-ray detector allow us to collect complete "X-ray fluorescence yield maps" instead of ROI data, even for low-concentration samples of less than 0.1 wt%.

Experiments were carried out at the c-branch of soft X-ray photochemistry beamline **BL27SU**. The XANES spectra were measured by undulator gap scanning as well as monochromator scanning to maintain the maximum intensity of the incident soft X-rays, and by scanning the widths of the entrance and exit slits to maintain a constant resolving power.

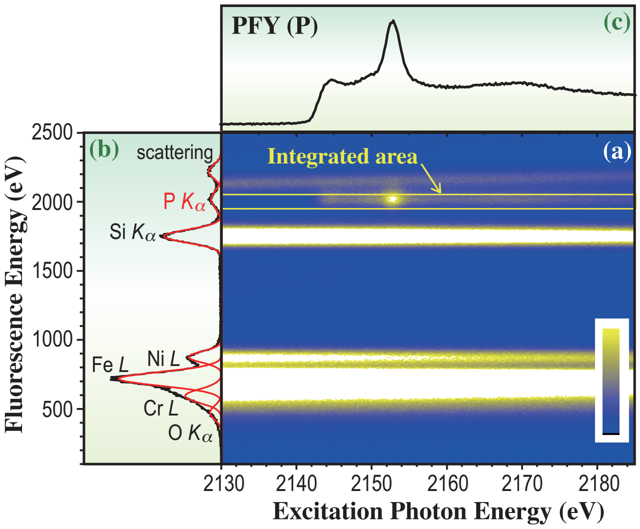

Fig. 1. **(a)** Two-dimensional fluorescence spectrum for SS304 obtained in the P *K*-edge region, **(b)** XRF spectrum obtained at 2190 eV, and **(c)** PFY spectrum of phosphorus extracted from an integration of fluorescence counts in the range of 1940–2020 eV.

The fluorescence signal was detected using a single-element silicon drift detector (SDD). The entrance window mounted in front of the detector is a MOXTEK AP3.3 window consisting of an ultrathin polymer film. The SDD module equipped with the AP3.3 window enables an X-ray transmission to the detector with an energy as low as the B $K_\alpha$ X-ray energy (170 eV), i.e., our detector is applicable to the XANES experiment at a boron *K*-edge.

The XANES spectrum of phosphorus in stainless steel (SS) 304 was measured using the 2D map approach. Generally, in SS304 samples, C (<0.08%), Mn (<2.0%), Si (<1.0%), P (<0.045%), and so forth, are present as minor components, while Cr (18~20%), Ni (8~10.5%) and Fe are present as major components. Figure 1 shows (a) the 2D spectrum, (b) the XRF spectrum obtained at 2190 eV, and (c) the PFY spectrum extracted from the 2D spectrum. The XRF spectrum can be fitted well to seven Gaussian peaks, as indicated by red lines in Fig. 1(b). The four peaks observed in the range of 400–1000 eV originate from the *K*-shell ionization of oxygen and the $L_{23}$-shell ionization of the main elements, Cr, Fe, and Ni. On the other hand, the fluorescences from Si and P *K*-shell ionizations can be observed at approximately 1720 and 2000 eV, respectively.

The FYs from the main elements and Si form horizontal stripes in Fig. 1(a), because these elements have no absorption edges in this energy region. On the other hand, only the FY of phosphorous changes drastically. Figure 1(c) shows the PFY spectrum extracted from the integration in the range of 1940–2020 eV. The obtained PFY spectrum closely resembles the XANES spectra of iron phosphate. Although the XANES spectrum is clearly observed in the PFY mode, it cannot be found in the TEY spectrum (data not shown). In the TEY mode, the imperceptible signals from the minor components are buried in the higher background signals originating from the excitation of major components, because Auger decay is the dominant decay channel following the *L*-shell ionization of 3*d*-transition metals.

The patterns formed by elastic scattering appear as diagonal stripes in the 2D map. The energy of the phosphorus $K_\alpha$ (2013.7 eV) is about 30 eV lower than the binding energy of the phosphorus 1*s* electron (2045.5 eV). Therefore, the diagonal line does not directly intersect with the phosphorus $K_\alpha$ line in the XANES region. However, elastic scattering contributes to the baseline of the XANES spectrum. Figure 2 shows the PFY spectra extracted from varying integration regions. This procedure corresponds to the PFY measurement with different ROI window selections. In principle, the baseline of the PFY spectrum should be flat in the pre-edge region, because the photon energy is insufficient to excite or ionize the P 1*s* electron and therefore cannot eliminate the $K_\alpha$ fluorescence from phosphorus. However, Fig. 2 indicates that the baseline shape depends on the integrated area owing to the contamination of elastic scattering. The contamination is especially apparent when the higher fluorescence energy region is included in the PFY spectrum extraction as exhibited by its effects on the baseline in the pre-edge region and the tilt of the PFY baseline. This phenomenon could be a significant issue for subtraction of the baseline in the data analysis procedures of the EXAFS measurement. The recording of the full XRF is necessary for a correct data treatment. The present research indicates that the selective fluorescence detection improves sensitivity to the imperceptible signal from phosphorus.

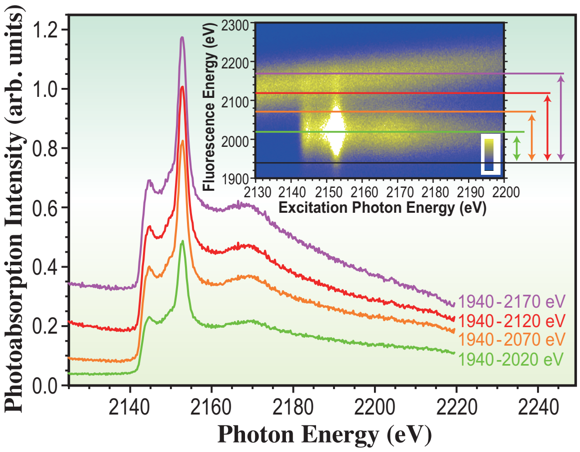

Fig. 2. Extraction region dependence of the PFY spectrum of SS304 in the P *K*-edge region. The inset shows the expanded 2D-XANES spectrum of SS304 in the P *K*-edge region and anintegrated region for each extracted PFY spectrum.

Yusuke Tamenori* and Tetsuya Nakamura

SPring-8/JASRI

*E-mail: tamenori@spring8.or.jp>

## References

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