Improvement of SAXS Measurement near the Sulfur $K$-edge

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Abstract. We have made feasibility study of anomalous small-angle X-ray scattering (ASAXS) near the sulfur $K$-edge (2.472 keV). In the present study, we report the improvement of SAXS measurement with the use of Si (111) channel-cut monochromator and Kratky camera at BL27SU, SPring-8. The photon flux and the energy resolution of the incident X-ray beam increased by 10 times and 2.5 times, respectively. SAXS intensity also increased by about 10 times with the improved low-q and high-q limits, enabling us to measure SAXS with a better S/N ratio over a wider q range.

1. Introduction

Small-angle X-ray scattering (SAXS) is greatly effective in analyzing the structure of soft matter (for example [1]). The contrast of scattering length density, which causes SAXS, can be varied with anomalous dispersion. The scattering length of a constituent element, $f$, has a dependence on the energy of incident X-rays near its absorption edge as

$$ f(E) = f_0 + f'(E) + if''(E) $$

where $f'$ and $f''$ represent the real and imaginary parts of the dispersion corrections, respectively. By using the anomalous dispersion one can get the structural information related to the specific element. SAXS using this dispersion is called as anomalous SAXS (ASAXS). ASAXS has been widely applied to the systems containing high-Z elements whose $K$-edges are located in a hard X-ray region ($E > 4$ keV), while it has been poorly explored in a soft X-ray region ($E < 4$ keV). There are, however, some buried treasures of $K$-edges of important elements in biological and synthetic macromolecules such as silicon, phosphorus, and sulfur [2]. The $K$-edge of sulfur, the main target of the present study, is located at $E = 2.472$ keV.

Recently, we have made feasibility study of SAXS and ASAXS near the sulfur $K$-edge [3]. In the previous study, we used a varied-line-spacing plane grating monochromator (VLS-PGM), which had been originally equipped at BL27SU, SPring-8 [4, 5]. The flux available with this monochromator was in the order of $10^{13}$ photons/s/100mA/0.03%B.W. in an energy range of 0.10 - 2.0 keV, but it decreased by two orders of magnitude in an energy range above 2.0 keV [6]. This is mainly because the four mirrors and grating in the previous setting were all coated with gold having its $M$-edges at 2.21 and 2.29 keV, and X-ray beam was greatly absorbed by these optical elements.
In the present study, we have arranged a new experimental setting at BL27SU that is equipped with Si channel-cut monochromator and mirrors coated with Ni so as to increase the photon flux and the energy resolution. The characteristics of the X-ray beam and SAXS intensity profiles with the new setting were examined and compared to those in the previous study.

2. Experimental
We performed the experiment at B-branch of BL27SU, SPring-8 (Hyogo, Japan). All optical elements were arranged as shown in Fig. 1. In this layout, an X-ray beam was diverted into the experimental station by pre-mirror (M0). Three slits (S1, S2, and S3) were used to collimate the X-ray beam. Kirkpatrick-Baez (KB) mirrors were temporarily adopted to focus the X-ray beam at the sample position where the beam size was about 10\(\mu\)m \(\times\) 10\(\mu\)m. These mirrors were coated with Ni. Between horizontal and vertical mirrors, Si (111) channel-cut monochromator was placed to monochromatize the X-ray beam. By the use of this monochromator, the X-ray beam position shifted in the vertical direction when the energy was changed. We set a photodiode (AXUVPSV, International Radiation Detectors Inc.) adjustable in the vertical direction just downstream of the sample to measure the photon flux. This photodiode also played an important role as a beamstop. The combination of S2, S3 and the photodiode was arranged in the manner of Kratky camera [7], which efficiently blocked parasitic scatterings in a low-q range. All these elements were placed in a vacuum chamber. It had a small aperture of 2 mm in diameter between the vertical mirror and the third slit, and the X-ray beam passed through the aperture. This aperture limited the range of available energy to about 200 eV. The installation of a fixed-exit X-ray monochromator is now planned to overcome this problem.

An indirectly illuminated X-ray area detector was used for SAXS measurement. This area detector was composed of a phosphor screen (P43, Gd\(_2\)O\(_2\)S:Tb), an optical relay lens, and a full-frame back-illuminated CCD detector (C4742-98-KAG, Hamamatsu Photonics Co. Ltd.). The details of the detector were described in the previous report [4].

For SAXS measurement, we used a nanocomposite as a model sample. The matrix was thiokol (LP-2, Toray Fine Chemicals Co. Ltd.) whose chemical formula was \(-\text{C}_2\text{H}_4\text{O-CH}_2\text{-O-C}_2\text{H}_4\text{-S-S-}\). Monodispersive spherical silica particles (Seahoster, Nippon Shokubai Co. Ltd.) of 130 nm in diameter were added to thiokol. The volume fraction of the particles was 6.0 %. After the particles were added to thiokol, the sample was stirred and kept at 120\(^\circ\)C for 72 hours so that it stiffened. Then it was sliced into a piece of 30 \(\mu\)m in thickness by using a microtome.

3. Results and Discussion
3.1 Measurement of photon flux
We measured the photon flux by using the photodiode under the condition that the sample and all slits were removed; the result was shown in Fig. 2. We can see that the flux measured with the present setting (solid line) is more than 10\(^{10}\) photons/s/100mA/0.03%B.W. near the sulfur K-edge (2.472 keV), which is favorably compared to that with the previous setting (dotted line). The available energy range was limited to about 200 eV by the aperture of the vacuum chamber. It should be noted that in this
experiment a front-end slit was not fully opened. Accordingly there is still room for obtaining a higher flux by fully opening the front-end slit. In this setting, the energy resolution $\Delta E/E$ has also improved, which is calculated as

$$\Delta E / E = \sqrt{\omega^2 + \phi^2 \cot \theta_B}$$

where $\omega$ is a full width at half maximum (FWHM) of the rocking curve of Si 111 reflection, $\phi$ is the angular divergence of the incident X-ray beam, and $\theta_B$ is the Bragg angle. According to the data of BL27SU, $\phi$ is 0.0108 mrad. Assuming that $E = 2.5$ keV and Debye-Waller factor is vanishingly small, $\omega$ is calculated to be 0.1724 mrad [9]. Thus, $\Delta E/E$ with this setting is calculated to be $1.3 \times 10^{-4}$. This is 2.5 times higher than that with the previous setting.

![Figure 2. Photon flux with the two different settings. Solid line shows the flux with the improved setting (Si channel-cut monochromator) and dotted line shows that with the previous setting (the combination of grating, slits, and mirrors, VLS-PGM). They are normalized to a ring current of 100 mA and $E/\Delta E = 3000$.](image)

### 3.2 SAXS measurement.

We performed SAXS measurement in a transmission mode under the condition that all slits were set to collimate the X-ray beam. SAXS pattern was taken at $E = 2460$ eV. From the two-dimentional SAXS pattern, we calculated one-dimentional intensity profile by circularly averaging the intensities of corresponding pixels, and the result is shown together with the previous result in Fig. 3. The profiles need to be normalized with some factors because of the different experimental and sample conditions; the exposure time in the present study was 200 s, whereas 300 s in the previous study. In addition, the sample used in the present study differed in the thickness and the volume fraction of nanoparticles. Then the obtained profiles were normalized in terms of thickness of the sample, volume fraction of the particles, and exposure time [10]. We can see that the scattering intensity measured in the present study is, as a whole, 10 times higher than that in the previous study because of the improvement of the monochromator and collimating optics. In particular, the intensity profile in the high-$q$ range is clear, while that with the previous setting fluctuates considerably due to the readout noise of the CCD detector. We can also see the low-$q$ limit of the profile is greatly improved. This is because the appropriate arrangement as Kratky camera consisting of S2, S3 and the photodiode results in reduced parasitic scattering.
4. Summary
With the use of Si (111) channel-cut monochromator, the photon flux and the energy resolution increased by 10 times and 2.5 times, respectively, compared to those with the previous setting. In addition, collimating optics so-called Kratky camera was introduced to improve a low-q limit. Thus, SAXS intensity increased by about 10 times with the improved low-q limit. The meaningful high-q limit also extended to 0.02 nm\(^{-1}\) owing to the improved S/N ratio in SAXS intensity profile.

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