Effect of electrical charging on scanning electron microscopy-energy dispersive X-ray spectroscopy analysis of insulating materials

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Abstract

We investigated the conditions under which we can obtain reasonable qualitative results in scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDX) analysis of trace elements in insulating materials using a diluted ionic liquid (EMI-CH$_3$COO) and changing probe current. Below 100 nA, electrical charging of insulating materials was prevented. The probe current of 10 nA was suitable for qualitative analysis because the intensities of peaks from these materials were strong enough to detect trace elements at the concentration of 0.1 wt% in the sample without interference by sum peaks. Diluted EMI-CH$_3$COO can also be used for SEM-EDX quantitative analysis of insulating materials as discharging agents. In contrast, when insulating materials were electrically charged, the obtained spectra contained characteristic X-rays of the insulating materials with low energies and of materials other than the samples such as the sample stage and the collimator in the X-ray detector. This is because electrons from the electron beam were decelerated by and deflected from the insulating materials. By coating the insulating materials with the diluted EMI-CH$_3$COO, the deceleration and deflection of the electron beam were prevented.

Key words: SEM-EDX analysis; electrical charging; insulating material; steelmaking slag; diluted ionic liquid

1. Introduction

Before scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDX) analysis of insulating materials, excepting very fine particles, they must be coated with a thin carbon layer by vacuum deposition to prevent electrical charging. We recently obtained EDX spectra of insulating materials without electrical charging by dropping a few microliters of 1 wt% 1-ethyl-3-methylimidazolium acetate (EMI-CH$_3$COO) diluted with ethanol onto their surface [1].

Ionic liquids consist solely of ions and have unique physical and chemical properties such as a relatively low vapor pressure, nonflammability, and high ionic conductivity. Among these properties, the feature of low vapor pressure (2.8×10^{-10} Pa for EMI-Tf$_2$N at 25 °C [2]) is suitable for their use in preventing electrical charging during SEM-EDX analysis. Kuwabata and coworkers first successfully obtained SEM images of insulating materials without electrical charging by dipping them into 100 wt% ionic liquids [3,4]. However, it is difficult to apply this method to the SEM-EDX analysis of samples containing fluorine, phosphorus, or sulfur because the ionic liquids they used also contained these elements. In addition, it is not possible to observe or analyze insulating materials in micrometer-scale area by the same method because a thick ionic liquid layer forms on the insulating materials and prevents the electron beam from reaching the surface. We resolved these difficulties by dripping several micro-liters of 1 wt% EMI-CH$_3$COO onto the insulating materials [1,5]. Clear SEM images of these materials in micrometer-scale area were obtained because a thin ionic liquid layer was formed on the samples. We also succeeded in the SEM-EDX analysis of insulating materials containing fluorine, phosphorus, and sulfur because EMI-CH$_3$COO consists only of hydrogen, carbon, nitrogen, and oxygen. In the SEM-EDX analysis of a fossil (*Baculogypsina* sp.) using 1 wt% EMI-CH$_3$COO, the following cations were detected: 75 wt% calcium, 20 wt% magnesium, and 5 wt% aluminum [5]. We can thus use diluted EMI-

CH_3COO in SEM-EDX analysis, except for the analyses of hydrogen, carbon, nitrogen, and oxygen.

In the present study, we investigated the conditions required to obtain qualitative or quantitative results in SEM-EDX analysis of trace elements in insulating materials using the diluted EMI-CH_3COO. Slag produced in the steelmaking process (steelmaking slag) was selected as the insulating material in the present study. Some steelmaking slags contain hazardous metals such as chromium in trace amounts, which may be dangerous to the environment if dissolved into water as hexavalent chromium [6-10]. If electrical charging of insulating materials is not prevented, we cannot obtain an accurate qualitative or quantitative result because electrical charging affects the shape of the EDX spectrum. Thus, before examining the conditions needed to obtain reasonable qualitative or quantitative results in SEM-EDX analysis, we investigated the effect of electrical charging on EDX spectra of insulating materials by examining the pathway of electrons from the electron beam.

2. Experimental

The sample analyzed in the present study was steelmaking slag produced in a secondary steelmaking process at JFE Steel Corporation. The size of the steelmaking slag sample was approximately 20 mm in length, 20 mm in width, and 2 mm in thickness. Compositional analysis of the steelmaking slag was carried out with an EDX spectrometer equipped with an SEM system (JEOL, JSM-5610LVS). A silicon drift detector (OURSTEX Corporation, SDD System) was used as the EDX spectrometer. The thickness of the beryllium window of the silicon drift detector was 8 µm [11]. The energy resolution was 200 eV measured as a full-width at half-maximum (FWHM) of the Fe Kα line. Before SEM-EDX analysis, carbon tape was attached on the sample stage and the steelmaking slag was placed on the carbon tape. About 10 µL of EMI-CH_3COO diluted with ethanol to 1 wt% was dripped

on the steelmaking slag and dried in air for a few minutes. The pressure of the SEM chamber was about 10^{-3} Pa during the analysis. The accelerating voltage and probe current of the SEM were set to 15 kV and 10 nA, respectively. The exposed area analyzed was 2×2 mm^2. The measurement duration of SEM-EDX analysis was set to 300 s. The energies of the obtained EDX spectra were calibrated by Cu Lα and Kα lines of a copper (99.96 %) plate. A mixed powder of magnesium oxide (MgO, 99.99 %), aluminum oxide (Al$_2$O$_3$, 99.99 %), silicon dioxide (SiO$_2$, 98.3 %), calcium oxide (CaO, 98.0 %), manganese (III) oxide (Mn$_2$O$_3$, 99.9 %), and iron (III) oxide (Fe$_2$O$_3$, 95.0 %) was used as a standard sample for quantitative analysis of the steelmaking slag. The powders of metal oxides were mixed with an agate motor for more than 20 min. The concentrations of MgO, Al$_2$O$_3$, SiO$_2$, CaO, Mn$_2$O$_3$, and Fe$_2$O$_3$ in the mixed powder were 7.1, 41.7, 2.7, 30.7, 7.1, and 10.2 wt%, respectively. The standard sample was measured in the form of powder. The quantitative result of the steelmaking slag was calibrated by ZAF correction [12].

3. Results and discussion

3.1 Effect of electrical charging on EDX spectrum

Figure 1 shows EDX spectra of the steelmaking slag with the diluted EMI-CH$_3$COO and the electrically charged steelmaking slag. K lines of Mg, Al, Si, P, Ca, Ti, Cr, Mn, and Fe were detected in the EDX spectrum of the sample with the diluted EMI-CH$_3$COO (Spectrum A). We identified the small peaks at 2.0, 4.5, and 5.4 keV as P, Ti, and Cr, respectively. This is because the intensities of P, Ti, and Cr peaks were above their detection limits, which were defined as the value of the background intensity plus three times the standard deviation of the background intensity. The detected K lines came from the steelmaking slag. Electrical charging of the steelmaking slag did not occur because the end-point energy (Duane-Hunt limit [13]) of the EDX spectrum coincided with the accelerating voltage of 15 kV. In contrast,

when steelmaking slag was electrically charged (Spectrum B), K lines of Ti, Cr, Mn, and Fe were not detected and the intensity of the Ca Kα line was about 100 times lower than that of the non-electrically charged steelmaking slag. A peak at 2 keV and Cu K lines were additionally detected. The peak at 2 keV was Zr Lα because a Zr Lγ line (2.30 keV) was detected in the electrically charged steelmaking slag by increasing the probe current to 800 nA. When a piece of a natural rubber glove used in experiments was electrically charged, Zr Lα and Cu K lines were also detected although the natural rubber contained neither zirconium nor copper. After dripping diluted EMI-CH$_3$COO on the natural rubber, Zr Lα and Cu K lines were not detected, and the intensity of the characteristic X-rays of calcium contained in the natural rubber as a strengthening agent increased. From these results, we consider that electrons from the electron beam are deflected from the insulating materials and that the deflected electrons then bombard the sample stage, as shown in Fig. 2(a). Thus, characteristic X-rays of copper contained in the sample stage (brass) were detected when the steelmaking slag and natural rubber were electrically charged. Zirconium is used in the collimator of the X-ray detector we used in this study [11, 14]. We also assume that the zirconium of the collimator is excited by X-rays from the sample stage since a large number of X-rays from the sample stage are not parallel to the collimator, as shown in Fig. 2(b). In addition, electrons from the electron beam are assumed to be decelerated by the insulating materials because of the electrical charging. As a result, the number of electrons with high energy decreases. Electrons from the electron beam are expected to be decelerated to approximately 5 keV on the electrically charged steelmaking slag because Ti, Cr, Mn, and Fe K lines were not detected. Thus, as drawn with the broken lines in Fig. 1, it is expected that the spectrum with the Duane-Hunt limit of approximately 5 keV (Background I) is that from the steelmaking slag and that the spectrum with the Duane-Hunt limit of approximately 11 keV (Background II) is that from the sample stage.

We then verified the assumptions that electrons from the electron beam behave as shown in Figs. 2(a) and (b) when insulating materials were electrically charged. First, SEM-EDX analysis of the steelmaking slag was carried out by preventing electrical charging at an accelerating voltage of 5 kV. The obtained EDX spectra are shown in Fig. 3(a). Ti, Cr, Mn, and Fe Kα lines were not detected. The intensities of Mg, Al, Si, and Ca Kα lines were lower than those of the non-electrically charged steelmaking slag at the accelerating voltage of 15 kV (Spectrum A). The shape of the EDX spectrum (Spectrum C) was similar to that of the electrically charged steelmaking slag below 5 keV at the accelerating voltage of 15 kV shown in Fig. 1 (Background I). Thus, we conclude that electrons from the electron beam are decelerated to approximately 5 keV on the steelmaking slag at the accelerating voltage of 15 kV when the steelmaking slag was electrically charged. Next, Spectrum C in Fig. 3(a) was combined with an EDX spectrum of copper and zirconium plates at an accelerating voltage of 11 kV, as shown in Fig. 3(b) (Spectrum D). The combined EDX spectrum is shown in Fig. 3(c). No Cu Lα line was detected in Spectrum B but it was detected in Spectrum D. This is because the detection efficiency for X-rays with energy less than 1.0 keV was less than 30% in the EDX detector adopted and the background intensity of approximately 1 keV in Spectrum B was more than 10 times higher than that in Spectrum D. The shape of the combined EDX spectrum was almost the same as that of the electrically charged steelmaking slag shown in Fig. 1 (Spectrum B). Thus, this result is consistent with our assumptions that electrons from the electron beam behave as shown in Figs. 2(a) and (b) when insulating materials are electrically charged. In contrast, electrical charging of the insulating materials was prevented when coated with diluted EMI-CH$_3$COO. In this case, electrons from the electron beam were drained to the ground through the ionic liquid layer, the sample stage, and cables connected to the SEM, as shown in Fig. 2(c). Thus, elements contained in the steelmaking slag were only detected when the steelmaking slag was not electrically charged.

3.2 EDX spectra at higher probe currents

The surfaces of insulating materials can be electrically charged easily by increasing the probe current. We thus carried out SEM-EDX analysis of the steelmaking slag with the diluted EMI-CH$_3$COO while changing the probe current. Figure 4 shows the EDX spectra at probe currents of 1, 10, 100, and 800 nA. Below 100 nA, electrical charging of the steelmaking slag did not occur because Zr Lα and Cu K lines were not detected. A small peak at 2 keV was detected when the probe current was 10 and 100 nA. This peak was the P Kα line because the X-ray fluorescence (XRF) spectrometer also detected a small amount of phosphorus in the steelmaking slag (see Table 1). The probe current of 10 nA was appropriate for SEM-EDX analysis in this study because the intensities of peaks from the steelmaking slag were strong enough to detect and no sum peaks prevented the detection of individual peaks. At the probe current of 1 nA (Spectrum E), the total intensities were 10 times lower than those at the probe current of 10 nA (Spectrum F). It was difficult to detect Ti and Cr Kα lines owing to the low total intensities. When the probe current was increased to 100 nA (Spectrum G), sum peaks were detected in addition to the K lines of elements contained in the steelmaking slag. In particular, the sum peak of Al and Ca Kα (5.18 keV) made detection of the Cr Kα line difficult. At the probe current of 800 nA (Spectrum H), the surface of the steelmaking slag was electrically charged because Zr Lα and Cu Kα lines were detected.

We then investigated the availability of the diluted EMI-CH$_3$COO for quantitative analysis. We used EDX spectra of the steelmaking slag and a powder mixture of MgO, Al$_2$O$_3$, SiO$_2$, CaO, Mn$_2$O$_3$, and Fe$_2$O$_3$ measured at the probe current of 10 nA with the diluted EMI-CH$_3$COO. In the quantitative analysis, the concentrations of Si, P, Ti, and Cr were not evaluated because the intensities of P, Ti, and Cr were below their respective determination limits. In the present study, we applied the definition of the determination limit as the value of

the background intensity plus ten times the standard deviation of the background intensity. The obtained results are summarized in Table 1 with the results of XRF analysis. The concentrations determined by SEM-EDX analysis were averages of values at five different areas in the steelmaking slag, and the precision of the measurement concentration [15] was less than 1 wt%. The calculated precision of the measurement concentration was about 5 times higher than those of minerals obtained with a polished standard [12]. Comparing the results of SEM-EDX and XRF analyses, we conclude that it is possible to use the diluted EMI-CH$_3$COO as a discharging agent in SEM-EDX quantitative analysis of insulating materials.

4. Conclusions

We investigated the effect of electrical charging on spectra during SEM-EDX analysis of insulating materials by examining the pathway of electrons from the electron beam. We then investigated the conditions required to obtain reasonable qualitative results in SEM-EDX analysis of insulating materials using diluted EMI-CH$_3$COO. The results obtained in the present study are summarized as follows.

1. When SEM-EDX analysis of insulating samples (20 mm in length, 20 mm in width, and 2 mm in thickness) was performed without preventing electrical charging, characteristic X-rays of the insulating materials with energies of more than 4.5 keV were not detected owing to the deceleration of electrons from the electron beam by the insulating materials. Cu and Zr were additionally detected even if the insulating materials did not contain Cu or Zr. Cu and Zr came from the sample stage of the SEM (brass) and collimator in the X-ray detector, respectively. Electrons from the electron beam were deflected from the insulating materials owing to the electrical charging of the insulating materials, and then bombarded the sample stage. X-rays from the sample stage excited zirconium of the

collimator because a large number of X-rays from the sample stage were not parallel to the collimator.

2. When electrical charging of insulating materials was prevented, characteristic X-rays of the insulating materials were detected while the characteristic X-rays of Cu and Zr were not.

3. Dripping diluted EMI-CH$_3$COO onto steelmaking slag prevented electrical charging at probe currents below 100 nA. The probe current of 10 nA was appropriate for quantitative analysis for major components (Mg, Al, Si, Ca, Mn, Fe) and qualitative analysis for trace elements (P, Ti, Cr) in this study. This is because the intensities of peaks from the steelmaking slag were strong enough to detect trace elements and there were no sum peaks that prevented the detection of the Cr Kα line. The diluted EMI-CH$_3$COO is also applicable in quantitative analysis even if the standard sample to be measured is in powder form.

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Figure captions

Fig. 1   EDX spectra of (A) steelmaking slag with diluted EMI-CH$_3$COO (black dots) and (B) electrically charged steelmaking slag (gray dots). The accelerating voltage and probe current were 15 kV and 10 nA, respectively. I and II in the figure show the background spectra from the steelmaking slag and the sample stage, respectively.

Fig. 2   Schematic illustrations of electron beam and X-rays (a) (b) when a sample is electrically charged and (c) when a diluted ionic liquid is dripped on a sample. (b) Enlarged schematic illustration of X-rays around the X-ray detector.

Fig. 3   (a) EDX spectra of the non-electrically charged steelmaking slag at the accelerating voltage of 5 kV. (b) EDX spectrum of copper and zirconium plates at the accelerating voltage of 11 kV. (c) EDX summed spectrum of (C) and (D) spectra. The probe current was 10 nA during the measurements.

Fig. 4   EDX spectra of steelmaking slag with diluted ionic liquid at the probe current of (E) 1 (gray dots in (a)), (F) 10 (black dots in (a)), (G) 100 (black dots in (b)), and (H) 800 (gray dots in (b)) nA. The accelerating voltage was 15 kV during the measurements.
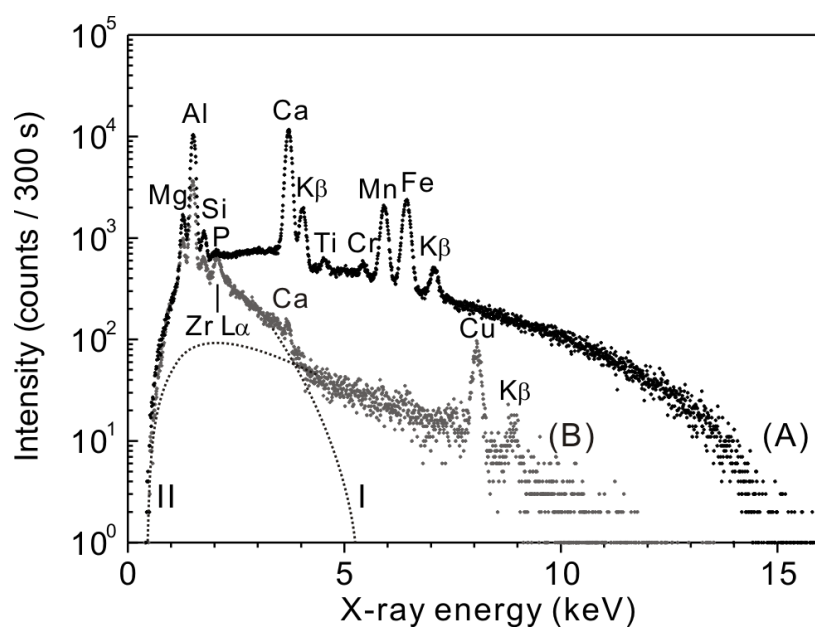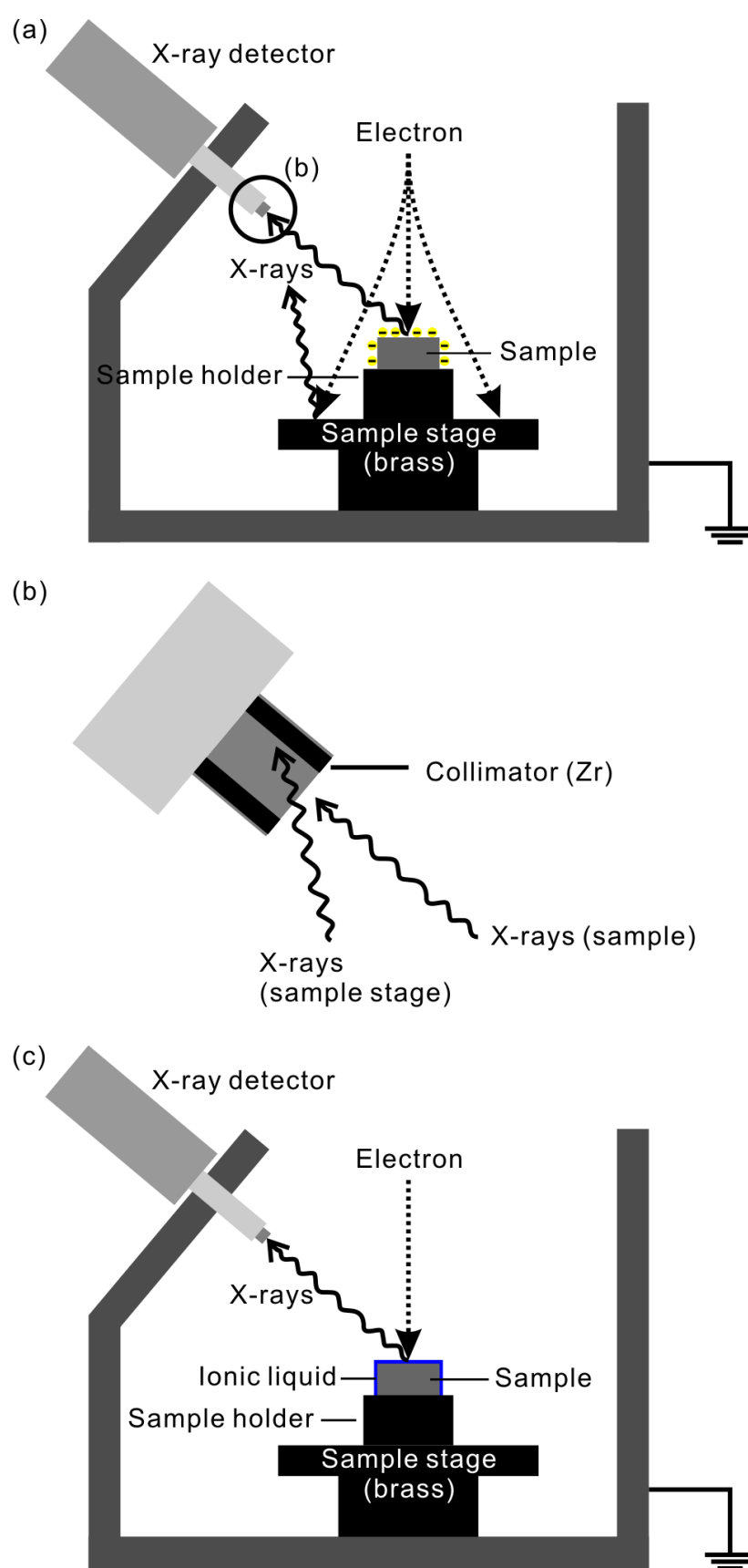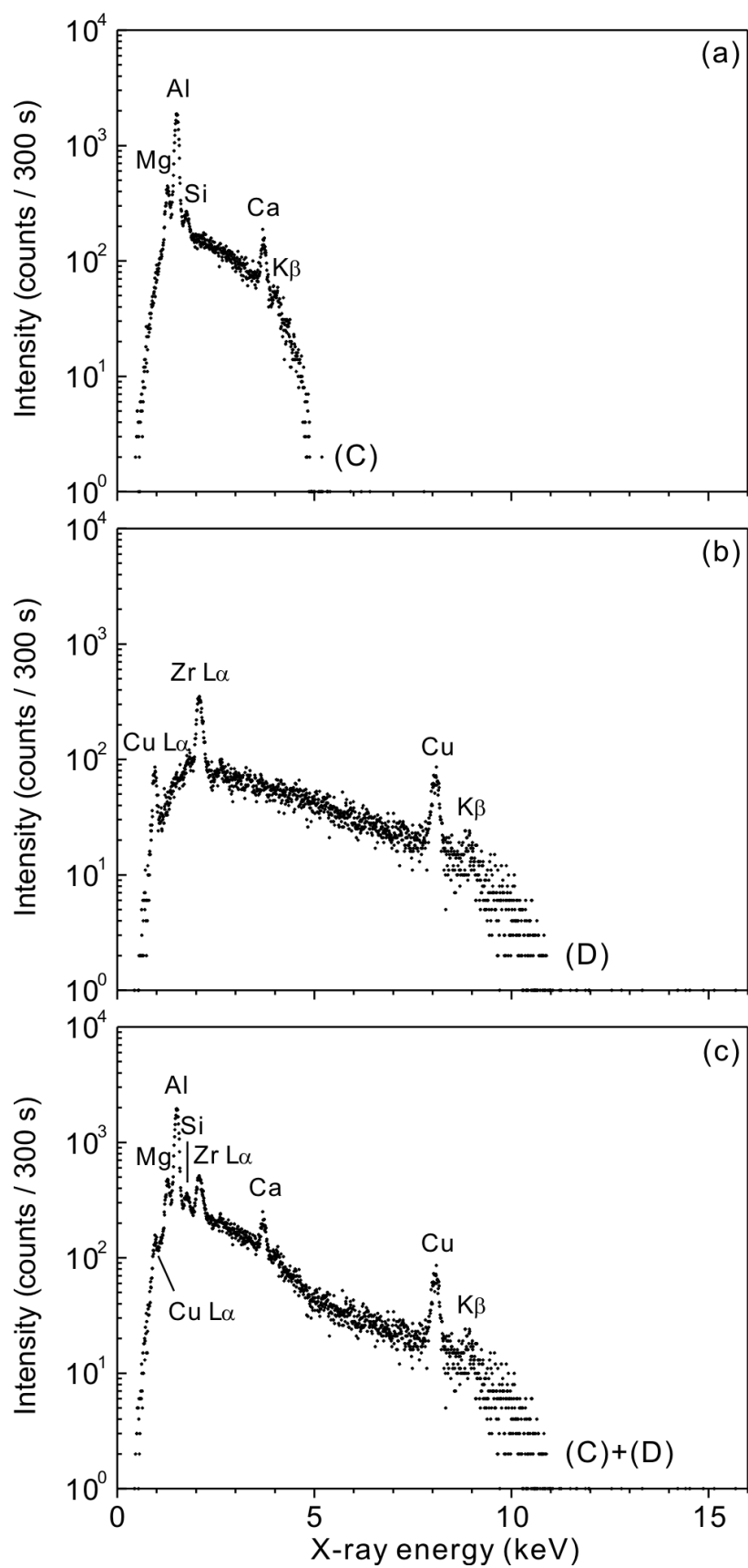
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