Spatially Resolved X-ray Fluorescence Analysis with a Pyroelectric X-ray Emitter

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A portable instrument for two-dimensional X-ray fluorescence imaging was assembled with an X-ray source using a pyroelectric crystal, which was driven by a 9-V dry battery, a Si-PIN detector, a slit, and pulse motors. Line scanning for a mug and a knife-edge-scan of an iron sheet were carried out using this spectrometer. The sensitivity of the spectrometer was sufficient for elemental analysis of a mug using a 1 mm^2 slit, and several elements, such as Co, Ni, Zn, Pb and Zr, were detected. The estimated spatial resolution using a 0.8-mm pinhole was 3.5 mm.

Introduction

The development of a portable X-ray fluorescence spectrometer has been the subject of intensive study for on-site analysis for various samples, such as environmental samples, articles for sale, works of art, and archaeological artifacts. The analysis of micro areas has also been required. A pyroelectric-type X-ray emitter developed by Brownridge[1,2] is one of the prime candidates for the X-ray source of a portable analyzer. Brownridge and his colleague reported that changing the temperature of a pyroelectric crystal, such as $CsNO_3$,[1] $LiTaO_3$[2] or $LiNbO_3$,[2] at appropriate pressures caused charging on the surface, and that X-rays were emitted by the impact of electrons alternately on a metal target and the charged surface along with the z-axis. A miniature X-ray emitter, "Cool-X", with a pyroelectric crystal has been commercially available, which was developed based on their studies. The dimensions are as small as 15 mm in diameter and 10 mm in height. When it is installed in a controller box with a 9-V dry battery, which is utilized for the temperature control of a pyroelectric crystal, dimensions of the device are 125 mm in length, 45 mm in width, and 30 mm in height. The pyroelectric X-ray emitter is thus useful for a portable XRF spectrometer because of its small dimensions and low-power.

Our research group assembled this commercially available pyroelectric X-ray emitter and a Si-PIN detector, and applied it to the X-ray fluorescence spectrometer in 2004.[3] They have subsequently been utilized for the identification of paint and leather,[4] glass and ceramics,[5] steel,[6] daily necessaries, such as printing paper, business cards, cinnabar seal inks, aluminum foils and wrapping films.[3,7,8] Environmental reference samples,[9] rice and rice bran[10] were also analyzed. By using of an X-ray fluorescence setup with a pyroelectric X-ray emitter and a disk-shaped secondary target, Ida and Kawai succeeded in the quantitative analysis of Cr in steel (% level).[11] Trace quantitative analysis and detection at less than 1 mg l^{-1} were achieved using

a simple preconcentration procedure.[12] Except for our research group, however, the application of this X-ray source has been scarcely reported.

As the next step, we planned to apply this pyroelectric X-ray emitter to an X-ray source for a portable two-dimensional elemental analyzer. Although a portable X-ray fluorescence spectrometer accompanied by spatial resolution capability has been reported by several research groups,[13-18] the X-ray sources utilized were conventional X-ray tubes. In this study, we assembled an X-ray fluorescence spectrometer with a pyroelectric X-ray emitter, a Si-PIN X-ray detector, a slit and two position-controlled sample stages; elemental mapping of a mug and a knife-edge-scan of an iron sheet were carried out to assess the capability of this X-ray emitter for two-dimensional X-ray fluorescence analysis.

Experimental

Instrument

A two-dimensional X-ray fluorescence spectrometer was assembled with a pyroelectric X-ray source Cool-X (Amptek Inc., Bedford, MA), a Si-PIN detector, a slit made of Teflon or Cu sheet, a translation motorized stage, and a rotation motorized stage. Figure 1 shows a photograph of the instrument, and the geometry is illustrated in Fig. 2. The translation and rotation motorized pulse stage utilized were LTS-200 (Sigma Koki Co. Ltd., Japan) and MINI-60θz (Sigma Koki Co. Ltd.), respectively. The sample positions were computationally controlled by software programmed with LabVIEW (National Instruments Co., Austin, TX). Fluorescent X-rays were detected by using a Si-PIN detector XR-100CR (Amptek) containing a pre-amplifier. Voltage signals from the pre-amplifier were amplified by using an amplifier PX2CR (Amptek) and the amplified signals were taken into a Microsoft Windows computer through a multi-channel analyzer (MCA) MCA8000A (Amptek). The number of channels of the MCA was set to 512, and one channel corresponded to an X-ray energy of 41 eV at the setting.

The details of the X-ray source utilized were reported in a previous paper,[8,19] and are shortly summarized as follows: (1)

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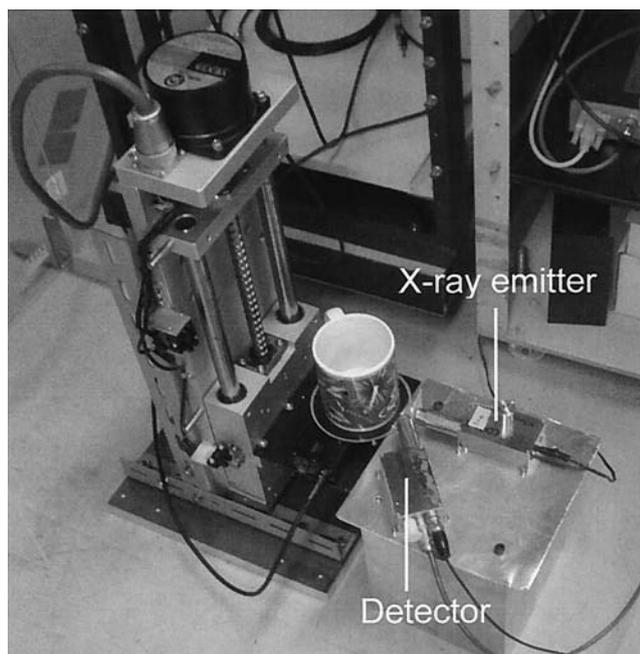E-mail: t.yamamoto@materials.mbox.media.kyoto-u.ac.jp
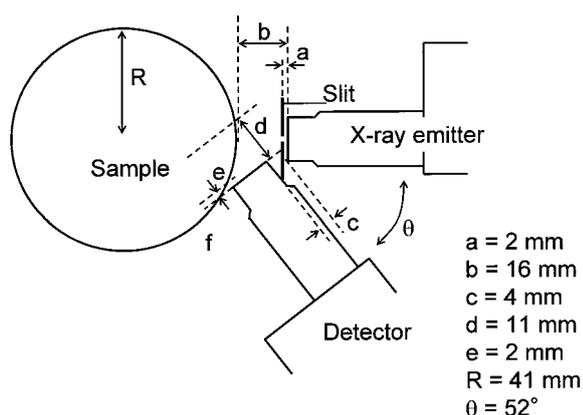
Fig. 1 Schematic view of the instrument.

Fig. 2 Geometry among the X-ray emitter, the detector, the slit and the sample.

a = 2 mm
b = 16 mm
c = 4 mm
d = 11 mm
e = 2 mm
R = 41 mm
θ = 52°

The X-ray source mainly consists of $LiTaO_3$ as a pyroelectric crystal and Cu as a target material, (2) the surface of the crystal becomes positively or negatively charged when it is heated or cooled, (3) X-rays are emitted by the cyclic charging, and (4) the X-ray emitted are Cu and Ta characteristic X-rays and continuous X-rays up to 35 kV. According to Amptek, Inc.,[20] the electric power for X-ray production is less than 300 mW, and is supplied by a 9-V dry battery. The X-ray output flux varies throughout the heating-cooling cycle (~2 min) and the maximum is less than 10^8 photons/s.

Measurements

The mug shown in Fig. 3 and an iron sheet were utilized for the present study. The surface of the mug was painted green, blue, red, or white. A Teflon® (poly-tetra-fluoroethylene, PTFE) sheet (0.5 mm thickness) with a 1-mm² aperture was placed between the X-ray source and the mug in order to restrict the size of the primary X-rays. An iron sheet with a thickness of 1.2 mm was measured in order to estimate the spatial resolution of
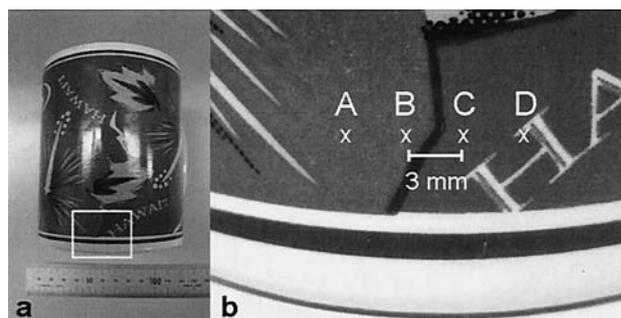

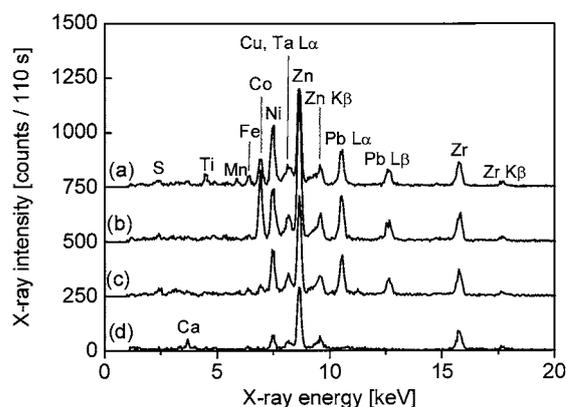Fig. 3 Measured mug (a) and four measured points (b). A, B, Red; C, D, blue areas.

Fig. 4 XRF spectra of the mug. (a) Green, (b) blue, (c) red, (d) white sections.

the instrument. In measurements of the iron sheet, a Cu sheet (1.5 mm thickness) with a pin hole (0.8 mm in diameter) was placed in front of the X-ray source. The measurements at each point were performed in air for 110 or 40 s. As described above, the X-ray output flux varies during the thermal cycle. The incident X-rays for the present 40 and 110 s measurements are for a single heating phase and a single heating-cooling phase, respectively. Prior to a measurement, the X-ray emitter had been switched off for at least 5 min to be sure that each total flux of the emitted X-ray was constant.

Results and Discussion

Figure 4 shows the XRF spectra of the mug measured in (a) green, (b) blue, (c), red, and (d) white sections. The Cu *K* and Ta *L* lines were due to the characteristic X-rays from the X-ray source. Emission lines due to the Zn and Zr species were detected at all of the spots. The S, Fe, Co, Ni, and Pb were detected at the red, blue and green areas. Most kinds of elements were detected in the green section; *i.e.*, emission lines for Ti and Mg were also detected accompanied by those for Co, Ni, Zn, Pb and Zr. It should be noted that the net intensity of the Co K_α line was the highest at the blue area, while it was negligible at the red area. This clearly shows that the sensitivity of the present spectrometer using a 1-mm² slit is sufficient to distinguish the elemental composition, and that the Co K_α line is useful to assess the spatial resolution.

Then, X-ray fluorescence spectra of the mug around the boundary between red and blue areas were recorded in 3 mm
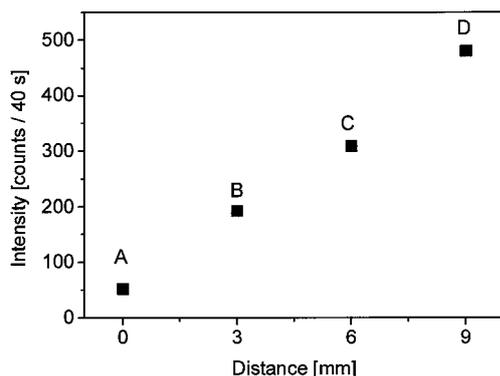
Fig. 5   Relationship between the measured points and the net intensities of the Co K_α peak.

Fig. 6   X-ray intensity of an Fe sheet and the 1st derivative of the X-ray intensity.

intervals; the measuring position is indicated in Fig. 3. Positions (A, B) are red and (C, D) are blue. The net intensities of the Pb L and Zr K lines did not change systematically, and were almost constant within 15% of the relative standard deviations. Figure 5 shows the net intensities of the Co K_α line for each position. In contrast to our assumption, the stepwise change of the net intensity was not confirmed when the measuring position varied from position A through D, but the intensity increased monotonously. This result indicates that the spatial resolution of this setting was less than the size of the Teflon slit (1 × 1 mm, 0.5 mm thickness), because of three possible reasons: (1) the transmission of the Teflon sheet utilized had a nonzero value of 0.24 at the energy for the Cu K_α line, which was calculated using the composition of Teflon, the density, and the mass-absorption coefficients[21] obtained by Victoreen's coefficients; (2) the blue area on the mug was overcoated with the red area; (3) the size of X-ray beam at the sample position was larger than 1 mm².

To evaluate the spatial resolution in more detail, a knife-edge-scan of an iron sheet was finally performed along with the horizontal direction. This measurement was carried out with the same geometry as shown in Fig. 2, and an iron sheet was placed perpendicular to the X-ray emitter. A Cu sheet (1.5 mm of thickness) with a hole of 0.8 mm diameter was placed in front of the X-ray emitter. The Cu sheet was selected because the transmittance for X-rays below 20 keV is less than 0.01, and Cu K_α line does not interfere with Fe K_α line if it is emitted. Note that an incident X-ray, itself, contains the characteristic X-ray of 8.1 keV due to Cu K_α and/or Ta L_α lines. Thus, Cu is the best element for a slit. Figure 6 shows the measured net intensity of the Fe K_α peak and the result of a fitting by a sigmoidal curve. The first derivative of the fitted curve is also shown, and the evaluated spatial resolution obtained by the full width at half maximum of the curve was 3.5 mm.

The preset X-ray emitter is driven by a dry battery that is used for the temperature control of an equipped pyroelectric crystal. Therefore, the all dimensions of the X-ray source and the weight are much less than those of a conventional X-ray tube. Regardless of the lower output power, the sensitivity for the present elemental analysis was sufficient, even when using a small 1 mm² slit, and a spatial resolution of mm level was achieved. The output angle for 50% intensity of the X-ray generator Cool-X is 140°.[20] Thus, the spread of an incident X-ray beam suppressed the spatial resolution as shown in Fig. 5. Because a pin hole was simply utilized in order to restrict the incident X-rays in the present study, the spatial resolution would be improved by using an appropriate slit. In conclusion, the
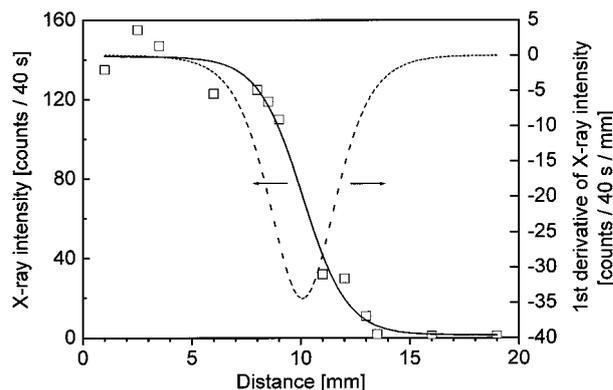
assembled X-ray fluorescence spectrometer using a pyroelectric X-ray source has a potential to be used as a portable X-ray imaging analyzer.

Conclusions

A portable analyzer for two dimensional X-ray fluorescence imaging was assembled with an X-ray source using a pyroelectric crystal, a Si-PIN detector, a slit and pulse motors. A line scan for a mug and a knife-edge-scan of an iron experiments were carried out. The S, Ca, Ti, Mn, Fe, Co, Ni, Zn, Pb and Zr were detected from the mug for 110 s measurements using a 1-mm² slit. Different kinds of elements were detected according to each color on the surface, and the Co K_α line was detected significantly at the blue section. The line scan of a mug with a Teflon slit did not give satisfactory spatial resolution of elemental imaging due to spreading of the incident X-ray beam and insufficient absorption coefficient of the Teflon sheet. The evaluated spatial resolution for this apparatus using an Fe sheet and a pin hole made of Cu was 3.5 mm.

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