DEVELOPMENT OF A PALM-SIZE ELECTRON PROBE X-RAY ANALYZER

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ABSTRACT
An electron probe microanalyzer (EPMA) with a palm-size chamber including the electron source and the sample stage was developed using a pyroelectric crystal. Energy of obtained continuous X-rays and lower limits of detection of transition metals (titanium, iron, and nickel) were evaluated. End point energy (Duane-Hunt limit) of obtained continuous X-rays was about 40 keV, but the palm-size EPMA can analyze characteristic X-rays with energies less than 20 keV due to the small amounts of electrons with energies above 20 keV. It is possible to measure thin metal wires of titanium, iron, and nickel with the palm-size EPMA. Their lower limits of detection were 0.081 mm$^2$ for titanium, 0.051 mm$^2$ for iron, and 0.057 mm$^2$ for nickel as surface areas, respectively.

INTRODUCTION
Brownridge (1992) first reported that it is possible to generate X-rays using pyroelectric crystals. After that, Brownridge and his co-workers developed the X-ray generator (Brownridge, 2004; Tornow et al., 2008), and then Amptek Inc. commercialized a portable X-ray generator using a pyroelectric crystal. The X-ray generator can produce X-rays with the Duane-Hunt limit of 35 keV. Geuther et al. (2005) reported that they fabricated an X-ray generator using a paired-crystal of lithium tantalate (LiTaO$_3$) and that X-rays with the Duane-Hunt limit of 215 keV were generated. Hiro et al. (2010) reported that they developed a portable X-ray tube which consisted of a paired-crystal of LiTaO$_3$ and that characteristic X-rays of copper and zinc were obtained by putting a brass plate on a LiTaO$_3$ crystal in the portable X-ray tube. This result implies that it is possible to develop a small size electron probe microanalyzer (EPMA) using a pyroelectric crystal if samples were placed instead of the brass plate. In the present study, we developed the small size EPMA with a palm-size chamber including the electron source and the sample stage based on Hiro’s idea and evaluated the performance of the palm-size EPMA.

EXPERIMENTAL
The apparatus we developed in the present study is shown in Figure 1 (a). As for an electron source of the apparatus, single crystal of LiTaO$_3$ (Shin-Etsu Chemical) was attached on a Peltier device with silver paste. The size of the LiTaO$_3$ crystal was 3 mm $\times$ 3 mm in the x-y plane and 5 mm in the z-axis, and the top face of the LiTaO$_3$ crystal was the $-z$ plane. The other face of the Peltier device was attached on a copper rod with silver paste, and a copper wire was connected between silver electrode on the top surface of the Peltier device and the copper rod (Figure 1 (b)). The center of the bottom of the copper rod was drilled in order to insert a wire of the Peltier device, and the exit of the hole was closed with low vapor pressure resin. The sample stage was attached on another copper rod, whose bottom had a hole in the center, with silver paste (Figure 1 (c)). The copper rod was connected to an oil-sealed rotary pump through a vacuum joint. The sample stage had 45$^\circ$ gradients and consisted of brass. Samples were placed on the sample stage.
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with carbon tape. Borosilicate glass tube with an outer diameter of 18 mm was placed between
the two copper rods, and the glass tube and copper rods were connected with detachable vacuum
joints. The two copper rods were connected with a copper wire in order to keep the electric
potential of the sample stage same as that at the bottom of the LiTaO₃ crystal. The center of the
borosilicate glass tube had a hole with a diameter of 10 mm and polyimide tape (Kapton tape)
was put on the hole. Si-PIN (X-123, Amptek Inc.) or CdTe detector (XR-100T-CdTe, Amptek
Inc.) was set towards the hole. The Peltier device was connected to 3V battery and heated the
LiTaO₃ crystal for two minutes. Then, the LiTaO₃ crystal was cooled by switching the connection
to the battery and measured X-ray spectra for 90 seconds. Pressure of the chamber including the
LiTaO₃ crystal was monitored with Pirani gauge and about 5 Pa during the measurement.
Titanium (99.8%), iron (99.5%), and nickel (99%) wires, whose diameters were 0.05, 0.1, and 0.1
mm, respectively, were used as samples. Also, silver (99.98%) and copper (99.96%) plates,
whose thickness were 0.05 and 0.1 mm, respectively, were used as samples.

RESULTS AND DISCUSSION
First, we measured silver and copper plates, whose sizes were 5 mm × 10 mm, and figure 2 (a)
shows the obtained EDX spectrum of the samples. Clear silver Lα and copper Kα lines were
detected during 90 seconds measurement, which shows that our apparatus works as an EPMA.
Duane-Hunt limit of continuous X-rays was about 40 keV. However, intensity of X-rays above
20 keV was low because silver Kα line (22.16 keV) was not detected. It is expected that the
palm-size EPMA can analyze characteristic X-rays with energies less than 20 keV. We also
measured the time dependence of total intensity of X-rays during the measurement and the result
is shown in figure 2 (b). Total intensity of X-rays was not constant during the measurement
because electric charges on the surface of the LiTaO₃ crystal were neutralized as time passed.
Elemental analysis was carried out using titanium, iron, and nickel wires with the palm-size
EPMA. Figure 3 (a) shows the EDX spectra of titanium, iron, and nickel wires with the lengths of
5 mm. Copper and zinc Kα lines were detected in addition to K lines of the elements of the metal
wires. These elements (Cu, Zn) came from the brass sample stage. Lower limits of detection
(LLD) of titanium, iron, and nickel were evaluated from the EDX spectra in figure 3 (a) and the
following equation:

\[
LLD = \frac{3W}{I_{Net}} \sqrt{\frac{I_{BG}}{t}}
\]  

(1)
where $W$, $I_{\text{Net}}$, $I_{\text{BG}}$, and $t$ are content (%), net intensity (cps), background intensity (cps), and measurement duration (sec), respectively. The calculated lower limits of detection of titanium, iron, and nickel were plotted in figure 3 (b). In this calculation, surface area was used instead of content ($W$). From figure 3 (b), it follows that iron had the lowest detection limit among metals we measured in this study and that it is possible to detect metals with total surface areas more than $250 \, \mu m \times 250 \, \mu m$ using the palm-size EPMA.

Figure 2. (a) EDX spectrum of silver and copper plates with CdTe detector. (b) Time dependence of total intensity of X-rays during the measurement of silver and copper plates with Si PIN detector.
CONCLUSIONS
The results obtained in the present study can be summarized as follows:

1. We developed a small size EPMA with a palm-size chamber including the electron source and the sample stage using a pyroelectric crystal. Clear peaks of metals were obtained in 90 seconds measurements. Duane-Hunt limit of the continuous X-rays was about 40 keV. However, the palm-size EPMA can analyze characteristic X-rays with energies less than 20 keV because of the small amounts of electrons with energies above 20 keV.

2. It is possible to measure thin metal wires of titanium, iron, and nickel with the palm-size EPMA. Their lower limits of detection were 0.081 mm$^2$ for titanium, 0.051 mm$^2$ for iron, and 0.057 mm$^2$ for nickel as surface areas, respectively.

It was confirmed that it is possible to perform elemental analysis of quite small amount of transition metals in 90 seconds measurement with the palm-size EPMA we developed.

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Figure 3. (a) EDX spectra of titanium, iron, and nickel wires with the lengths of 5 mm using the palm-size EPMA. (b) Lower limits of detection of titanium, iron and nickel evaluated from figure 3 (a) as a function of atomic number.
REFERENCES