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# Application News

EDX-7000 Energy Dispersive X-Ray Fluorescence Spectrometer

# Nondestructive Elemental Analysis of Historical Materials (Old Metal Specimens) by X-Ray Fluorescence Spectrometer

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## User Benefits

- ◆ Precious materials can be analyzed nondestructively without damage.
- ◆ Quick analysis of elements contained in samples in various forms is possible.
- ◆ The fundamental parameters method (FP method) enables quantitative analysis without using standard samples.

## ■ Introduction

The energy dispersive X-ray fluorescence spectrometer (EDX) enables quick and nondestructive elemental analysis of analysis targets. Nondestructive analysis, as its name implies, is a class of analysis techniques which are used to analyze the properties of analysis targets without decomposition or destruction of the sample. Needs for this type of analysis exist in all fields, including foods, materials, and medicinal drugs. Among fields of analysis, nondestructive analysis by X-ray fluorescence is used in research on cultural and historical materials, in which precious materials are handled.

Here, a composition analysis of four metal specimens from Japan's early Meiji Era (late 19$^{th}$ century) provided by the International Research Center for Japanese Studies was carried out using an EDX-7000 to investigate the scientific level in that period. In spite of remarkable surface corrosion of the metal specimens used in the analysis, the main component metals were clarified and their purity levels were determined.

## ■ Samples

Fig. 1 shows photograph of the four pure metal specimens.

The names used for the samples in this article are the names written on the wrapping paper stored with the samples. The element symbols of metals inferred from those names are shown in parentheses. The "plumbum" of the "Bar-shaped plumbum" sample is thought to originate from the Latin word for lead (Pb).

Sheet-shaped cadmium (Cd) 1.2 × 11.8 cm

Pure tin (Sn) 1.1 × 1.1 × 6.7 cm

Tin (Sn) 0.8 × 1.0 × 1.5 cm

Bar-shaped plumbum (Pb) Total length 12.6 cm

Fig. 1 Metal Samples

## ■ Instrument

Fig. 2 shows the external appearance of the EDX-7000.

Fig. 2 External Appearance of EDX-7000

## ■ Elements

The measurement targets were the elements $_{11}$Na to $_{92}$U.

## ■ Sample Preparation

The sample surface was analyzed in the as-received condition without sample preparation.

In the measurement of "Tin," the sample was placed in a sample container lined with a polypropylene film (thickness: 5 µm) because the diameter was smaller than the sample measurement window (1.3 cm φ) of the instrument.

## ■ Qualitative-Quantitative Analysis

A qualitative analysis of the four samples was conducted for the elements Na to U. Measurements from the main components to trace channels were carried out using six channels, as listed in Table 1.

Table 1 List of Measurement Channels

| | |
|---|---|
| Ti-U | : For main component of heavy elements |
| Na-Sc | : For high sensitivity analysis of light elements |
| S-Ca | : For high sensitivity analysis of trace Cl, etc., used as primary filter |
| Cr-Fe | : For high sensitivity analysis of trace elements, used as primary filter |
| Zn-As,Pb | : For high sensitivity analysis of trace elements, used as primary filter |
| Ru-Sb | : For high sensitivity analysis of trace elements, used as primary filter |

Although it is possible that the compound forms of the detected elements may include oxides formed by corrosion, the quantitative analysis was carried out by the fundamental parameters method (FP method) assuming the metallic form.

## 1. Sheet-Shaped Cadmium (Cd)

The surface of the sample was measured. Fig. 3 shows the image of sample observation, and Fig. 4 shows the results of the qualitative-quantitative analysis.

The quantitative value of cadmium (Cd), which is the main component, was 98.4 %.

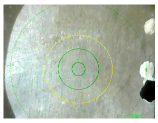
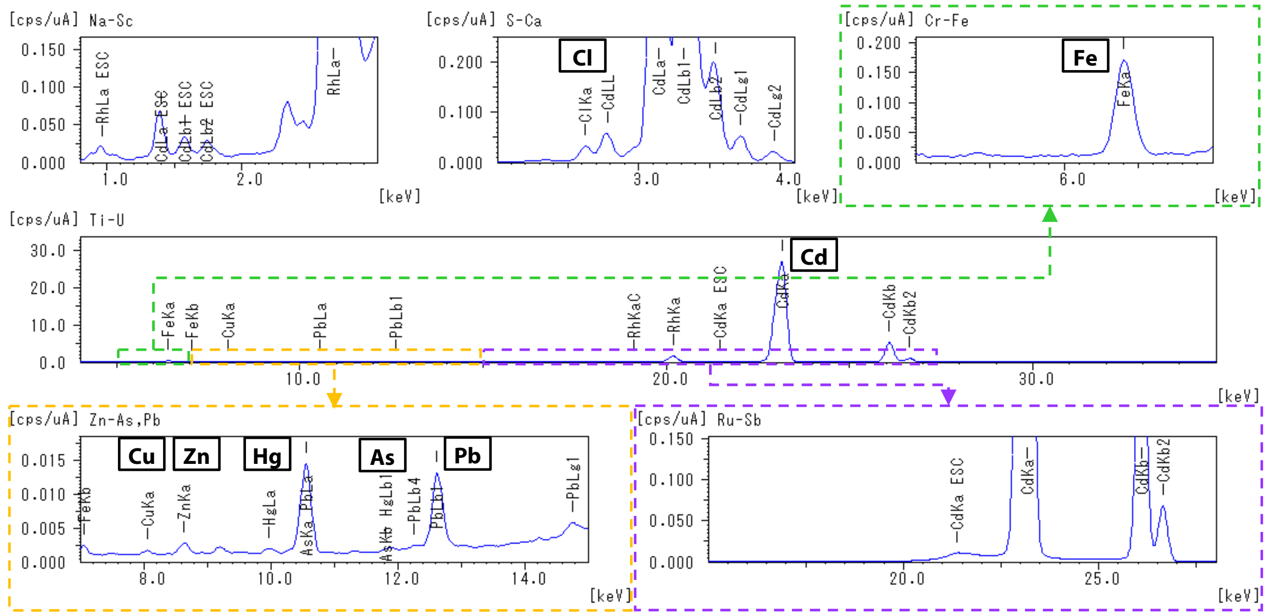


Fig. 3 Image of Sample Observation of “Sheet-Shaped Cadmium”




[wt%]

| Element | Cd | Cl | Fe | Pb | Zn | Cu | Hg | As |
|---|---|---|---|---|---|---|---|---|
| Surface | 98.4 | 1.3 | 0.24 | 0.062 | 0.013 | 0.0055 | 0.0047 | 0.0041 |

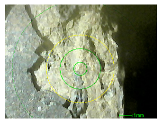
Fig. 4 Results of Qualitative-Quantitative Analysis of “Sheet-Shaped Cadmium”

## 2. Pure Tin (Sn)

Two areas were measured, one being an original surface, which was thought to be affected by corrosion, deposits, and segregation, and the other, a peeled portion where the surface was peeled off. Fig. 5 shows the images of sample observation, and Fig. 6 shows the qualitative-quantitative analysis results.

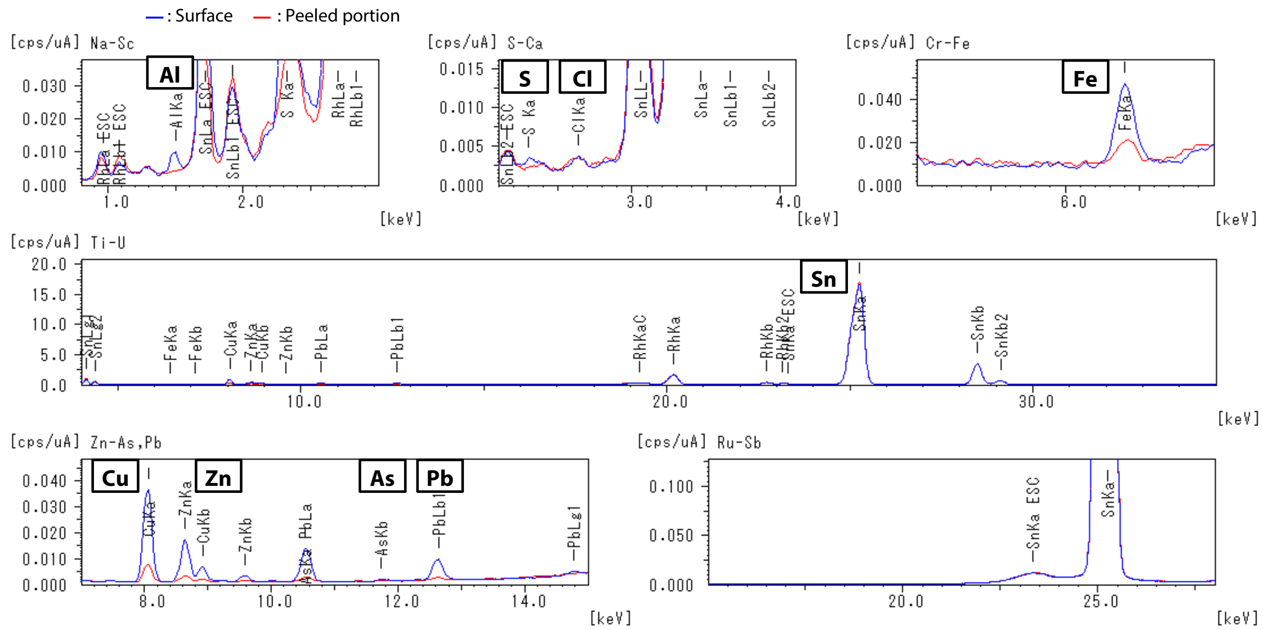
The quantitative value of tin (Sn), which is the main component, was 99.0 % for the surface and 99.9 % for the peeled portion.

Surface



Peeled portion

Fig. 5 Images of Sample Observation of “Pure Tin”




[wt%]

| Element | Sn | Cu | S | Al | Zn | Cl | Fe | Pb | As |
|---|---|---|---|---|---|---|---|---|---|
| Surface | 99.0 | 0.39 | 0.15 | 0.15 | 0.13 | 0.077 | 0.063 | 0.050 | 0.012 |
| Peeled portion | 99.9 | 0.070 | – | – | 0.018 | – | 0.016 | 0.0075 | – |

* – : Not detected.

Fig. 6 Results of Qualitative-Quantitative Analysis of “Pure Tin”

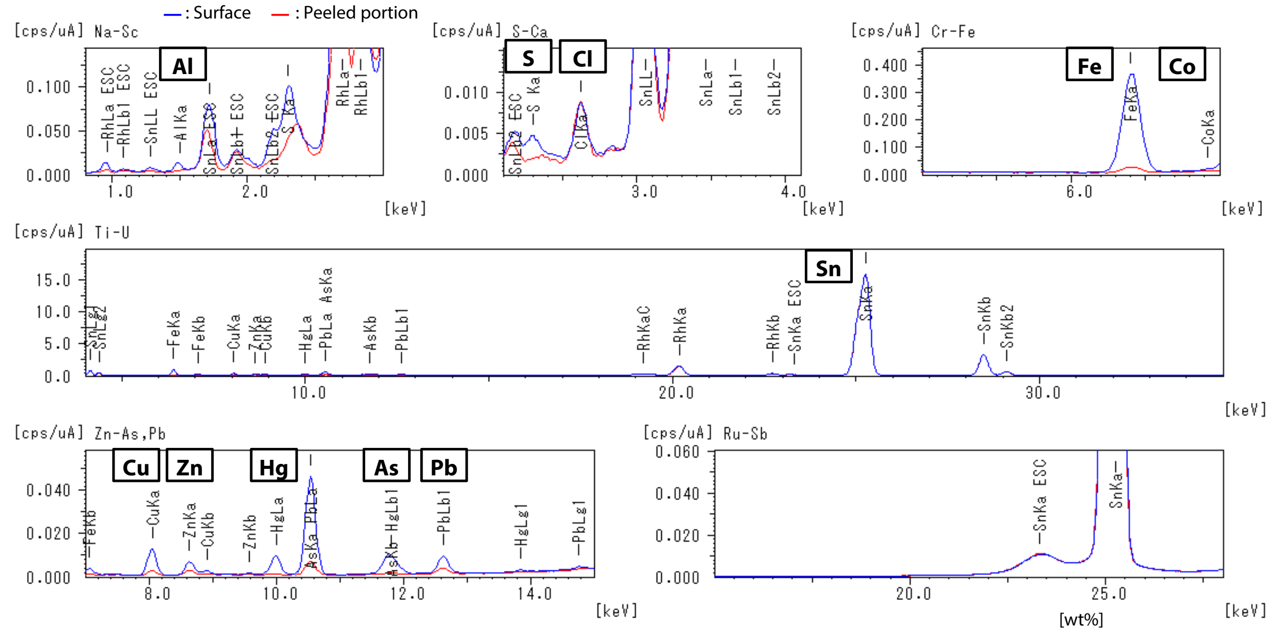
## 3. Tin (Sn)

As in 2. Pure Tin (Sn), two areas were measured, the surface and a peeled portion where the surface was peeled off. Fig. 7 shows the images of sample observation, and Fig. 8 shows the qualitative-quantitative analysis results.

The quantitative value of tin (Sn), which is the main component, was 97.9 % for the surface and 99.5 % for the peeled portion.

Surface Peeled portion

Fig. 7 Images of Sample Observation of "Tin"




[wt%]

| Element | Sn | Fe | Cl | S | Al | Cu | As | Hg | Zn | Pb | Co |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Surface | 97.9 | 0.59 | 0.39 | 0.31 | 0.34 | 0.14 | 0.098 | 0.079 | 0.053 | 0.048 | – |
| Peeled portion | 99.5 | 0.033 | 0.39 | – | – | 0.022 | 0.016 | 0.0054 | 0.022 | 0.018 | 0.0064 |

* – : Not detected.

Fig. 8 Results of Qualitative-Quantitative Analysis of "Tin"

## 4. Bar-Shaped Plumbum (Pb)

Five different points in the sample were measured. Fig. 9 shows the sample measurement positions, Fig. 10 shows the image of sample observation, and Fig. 11 shows the qualitative-quantitative analysis results.

The quantitative values of the main component lead (Pb) differed by several %, ranging from 93.1 to 97.9 %, depending on the measurement position.

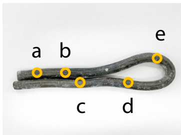



Fig. 9 Sample Measurement Positions

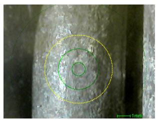
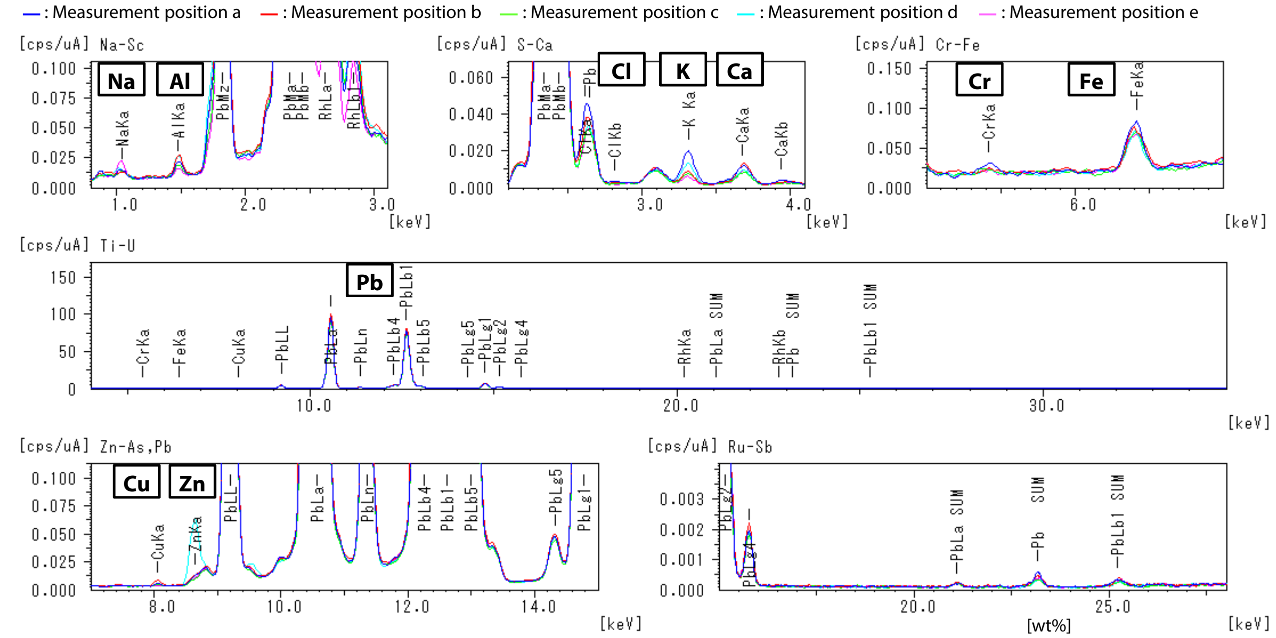


Fig. 10 Image of Sample Observation of "Bar-Shaped Plumbum" at Measurement Position a




[wt%]

| Element | Pb | Na | Ca | K | Al | Fe | Zn | Cu | Cl | Cr |
|---|---|---|---|---|---|---|---|---|---|---|
| Measurement position a | 93.1 | 2.6 | 0.31 | 0.76 | 0.22 | 0.063 | – | 0.012 | 2.9 | 0.031 |
| Measurement position b | 94.9 | 0.8 | 0.38 | 0.33 | 0.30 | 0.060 | – | 0.025 | 3.1 | – |
| Measurement position c | 97.9 | 1.3 | 0.23 | 0.29 | 0.17 | 0.057 | – | 0.006 | – | – |
| Measurement position d | 96.8 | 1.6 | 0.29 | 0.60 | 0.36 | 0.055 | 0.29 | 0.064 | – | – |
| Measurement position e | 94.8 | 4.5 | 0.27 | 0.20 | 0.13 | 0.057 | – | – | – | – |

* – : Not detected.

Fig. 11 Results of Qualitative-Quantitative Analysis of "Bar-Shaped Plumbum"

## ■ Evaluation of Differences in Analysis Results by Measurement Position

In the FP method used in the quantitative analysis, quantitative values are calculated on the assumption that the detected element exists homogeneously in the sample. For this reason, the quantitative values may be affected by the presence of corrosion, soiling, or segregation at the sample surface.

As confirmation of the homogeneity of the samples, the surface and delaminated portions of the "Pure Tin" and "Tin" samples were compared, and in the case of "Bar-Shaped Plumbum," the differences at five different positions were evaluated. As a result, differences in the detected elements and quantitative values could be seen depending on the surface condition and differences in the measurement position, as shown in Figs. 6, 8, and 11, suggesting the existence of soiling or segregation of the surface.

In particular, in the case of "Pure Tin," the S, Al, Cl, and As detected on the sample surface were not detected in the peeled portion. Thus, it was found that the peeled portion, which was not affected by elements originating from this corrosion, soiling, or segregation is a high purity metal with purity of close to 100 %.

## ■ Conclusion

A nondestructive analysis by EDX clarified the main component metals of the four metal samples, and also revealed that these are high purity metal samples, reflecting the high level of refining technology in the early Meiji era.

EDX is an extremely useful tool for composition analysis of precious historical materials, as it enables nondestructive analysis and does not require sample preparation.

## ■ Measurement Conditions

Table 2 Measurement Conditions

| | |
|---|---|
| Instrument | : EDX-7000 |
| Elements | : Na - U |
| Analysis group | : Qualitative-quantitative analysis |
| Detector | : SDD |
| X-ray tube | : Rh target |
| Tube voltage | : 50 [kV] (Ti-U), (Cr-Fe), (Zn-As, Pb), (Ru-Sb)<br>15 [kV] (Na-Sc), (S-Ca) |
| Tube current | : Auto [µA] |
| Collimator | : 3, 5 [mm φ] |
| Primary filter | : Non (Ti-U), (Na-Sc), #2 (S-Ca),<br>#3 (Cr-Fe), #4 (Zn-As, Pb), #1 (Ru-Sb) |
| Atmosphere | : Vacuum |
| Integral time | : 60 [s] (Ti-U), (Na-Sc), (S-Ca)<br>100 [s] (Cr-Fe), (Zn-As, Pb), (Ru-Sb) |
| Dead time | : Max. 30 [%] |

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