SHIMADZU
Excellence in Science

Application News

Shimadzu Energy Dispersive X-Ray Fluorescence Spectrometer EDX-7200

Quantitative Analysis of Amount of Deposition and Plating Thickness: Multilayer and Irregular Shaped Samples

H. Moriya and A. Urushizaki

User Benefits

- The EDX-7200 has greater sensitivity as a result of its improved counting rate.
- Multilayer platings can be analyzed as is, non-destructively.
- Even irregular shaped samples can be quantified with good accuracy using the background FP (BG-FP) method.

■ Introduction

X-ray fluorescence spectrometers are widely used for analyzing amount of deposition and plating thickness because they can easily analyze without complex pretreatment and destruction.

The new EDX-7200 enables more sensitive, faster, and higher accuracy analysis than with previous models. The performance improvements contribute to analytical throughput and faster examination. In addition, the background FP (hereinafter the BG-FP) method using Shimadzu's proprietary scattered X-ray intensity can measure a sample such as a screw whose plated surface is not flat with the same accuracy as a flat surface.

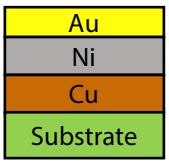
This article introduces the following.

1. Quantitative analysis of amount of deposition and plating thickness and measurement accuracy for a 3-layer sample comprised as follows: Layer 1: Gold (Au), Layer 2: Nickel (Ni), Layer 3: Copper (Cu).
2. Application to irregular shaped samples using the BG-FP method, and its measurement accuracy.

1. Analysis of a 3-Layer Au/Ni/Cu Plating

■ Sample

Reference Substance: NMIJ CRM 5208-a (20 mm × 20 mm)



Standard Value
Layer 1: 184 μg/cm²
Layer 2: 869 μg/cm²
Layer 3: 880 μg/cm²
Substrate

Fig. 1 Layered Plating Configuration of NMIJ CRM 5208-a

■ Element

The plating layers were configured as follows, and the amount of deposition for each layer was quantitatively determined.

Layer 1: Au, Layer 2: Ni, Layer 3: Cu

■ Results for the Quantitative Analysis of Amount of Deposition and Plating Thickness

(1) Amount of Deposition

Table 1 shows the results of the quantitative analysis of amount of deposition by the thin film FP method. In addition, Fig. 2 shows the profiles for each element, overlapped on the profiles from the previous model, the EDX-7000. The sensitivity has improved compared with the previous model.

Table 1 Results for the Quantitative Analysis of NMIJ CRM 5208-a
[μg/cm²]

Element	Au	Ni	Cu
Quantitative Value	176	861	861
Standard Value	184	869	880

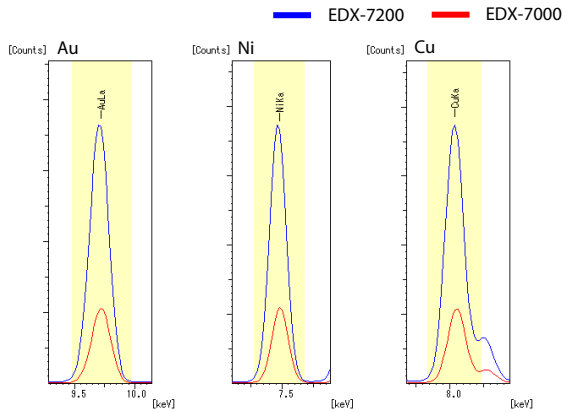


Fig. 2 Overlay of Profiles

(2) Plating Thickness

With the thin film FP method, the result is obtained as the amount of deposition (weight per unit area). This amount of deposition can be converted to plating thickness by dividing by the density (formula shown below). Both the amount of deposition and the plating thickness can be quantitatively determined with Shimadzu EDXRF.

$$Plating\ thickness\ [nm] = \frac{Plating\ weight\ [\mu g/cm^2]}{Density\ [g/cm^3]} \times 10$$

Table 2 shows the results of converting the amount of deposition from Table 1 into plating thickness.

Table 2 Results of the Quantitative Analysis of Plating Thickness for NMIJ CRM 5208-a
[nm]

Element	Au	Ni	Cu
Quantitative Value	91.1	1041	937

■ Repeatability

Table 3 shows the results of a simple 10-cycle repeatability test. The improved counting rate increased sensitivity, and the coefficient of variation, which indicates variance, was favorable at less than 1 % max.

Table 3 Summary of Repeatability Test Results
[μg/cm²]

Element	Au	Ni	Cu
Average Value	176	862	859
Standard Deviation	0.29	0.70	4.96
Coefficient of Variation [%]	0.2	0.08	0.6

2. Analysis of Irregular Shaped Samples

Since the thin film FP method used in plating analysis assumes a smooth and uniform sample, there is a problem that the quantitative error becomes large for irregular shaped samples.

Such samples can be measured by applying the BG-FP method, which corrects for the effect of shape (or material properties) using scattered X-rays, and quantitative accuracy comparable to that for flat samples can be obtained.

■ Sample

An iron screw with zinc plating was analyzed (Fig. 3).

Fig. 3 Appearance of Sample

■ Element

The configuration of the plating layers was set as follows.

Layer 1: Zn

Base: Fe

■ Results of the Quantitative Analysis of Plating Thickness

The plating thickness was quantified separately for the screw head and the shaft; the head has a smooth surface and the shaft has an irregular shape. Fig. 4 shows the respective sample measurement positions, and Table 4 shows a summary of the quantitative analysis results. In addition, Fig. 5 shows the qualitative profile.

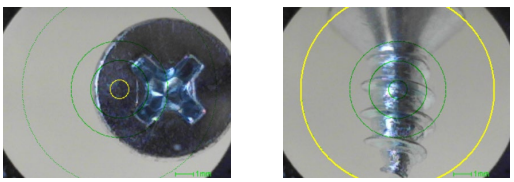


Fig. 4 Sample Measurement Positions (Parts Circled in Yellow)
Left: Screw head 1 mm dia. ; Right: Screw shaft : 10 mm dia.

Table 4 Summary of Quantitative Analysis Results

Measurement Position	Screw Head	Screw Shaft	Screw Shaft
Analysis Diameter	1 mm φ	10 mm φ	10 mm φ
Quantitative Method	Thin Film FP Method	Thin Film FP Method	BG-FP Method
Quantitative Value	4.08 µm	0.96 µm	4.29 µm

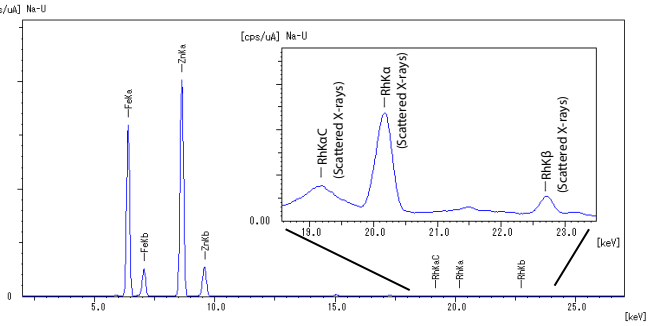


Fig. 5 Qualitative Profile

■ Conclusion

The features of plating analysis using EDX-7200 are shown below.

1. Accuracy
   Both the quantitative analysis accuracy and repeatability were favorable.
2. Irregular Shaped Samples
   For the screw shaft, an accuracy equivalent to that for flat surfaces was obtained by applying the BG-FP method. This can also be applied to springs and curved surfaces.
3. Quantitative Range for Plating Thickness
   Platings on the order of nanometers to micrometers can be quantified.
4. Operability
   The instrument is easy to operate, and analysis can be quickly performed by anyone.

■ Measurement Conditions

1. Measurement Conditions for the Analysis of a 3-Layer Au/Ni/Cu Plating

Instrument	: EDX-7200
Elements	: $_{79}$Au, $_{28}$Ni, $_{29}$Cu
Analysis Group	: Quantitative Determination
Analysis Method	: 1. Thin Film FP
Detector	: SDD
X-Ray Tube	: Rh Target
Tube Voltage - Tube Current	: 50 [kV] – Auto [µA]
Collimator	: 10 [mm φ]
Primary Filter	: None [Ni, Cu], #4[Au]
Atmosphere	: Air
Integration Time	: 100 [sec]
Dead Time	: Maximum 30 [%]

2. Analysis of Atypical Platings

Instrument	: EDX-7200
Elements	: $_{30}$Zn
Analysis Group:	: Quantitative Determination
Analysis Method	: Thin Film FP Method, BG-FP Method
Detector	: SDD
X-Ray Tube	: Rh Target
Tube Voltage - Tube Current	: 50 [kV] – Auto [µA]
Collimator	: 1, 10 [mm φ]
Primary Filter	: None
Atmosphere	: Air
Integration Time	: 100 [sec]
Dead Time	: Maximum 30 [%]

01-00208-EN First Edition: Dec. 2021

SHIMADZU
Shimadzu Corporation
Analytical & Measuring Instruments Division
Global Application Development Center

www.shimadzu.com/an/