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Energy Dispersive X-ray Fluorescence Spectrometer EDX-7200

Application News

Quantitative Analysis of Copper Alloys and Differentiation of Sample Types by Matching Function

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User Benefits

- The EDXRF has a smaller footprint than the WDXRF, and does not require cooling water or other auxiliary equipment.
- Analyses can be carried out simply without tedious and time-consuming sample preparation because there are few limitations on the sample shape.
- Sample types can be differentiated by using the matching search function provided as a standard feature.

■ Introduction

Copper alloys are copper-based alloys which are produced by adding zinc, lead, tin, or other alloying elements to copper to improve machinability, wear resistance, corrosion resistance, or other properties. By composition, copper alloys are classified as the 1000 series to the 7000 series.

Energy dispersive X-ray fluorescence spectrometers (EDXRF) are widely used in applications such as receiving inspections of recycled materials, taking advantage of their excellent operability and simple sample handling, but high-accuracy wavelength dispersive X-ray fluorescence spectrometers (WDXRF) are used mainly in metal manufacturing processes. However, as a result of improvement in the quantitative accuracy of EDXRF in recent years, a wider range of applications, such as use in manufacturing processes, is expected in the future.

This article introduces an evaluation of the analytical performance of the Shimadzu EDX-7200 in an analysis of copper alloys, focusing on the following items.

1. Quantitative analysis by the calibration curve method (accuracy of calibration curves, lower limit of quantitation, repeatability)
2. FP (fundamental parameter) qualitative/quantitative analysis and matching function

1. Quantitative Analysis by Calibration Curve Method

■ Samples

This section lists the standard samples and unknown samples used in the evaluation.

(1) Standard samples: Copper alloy standard samples produced by LGC Standards (Table 1)

(2) Unknown samples: Copper alloy sample, 1 sample

Table 1 List of Standard Samples

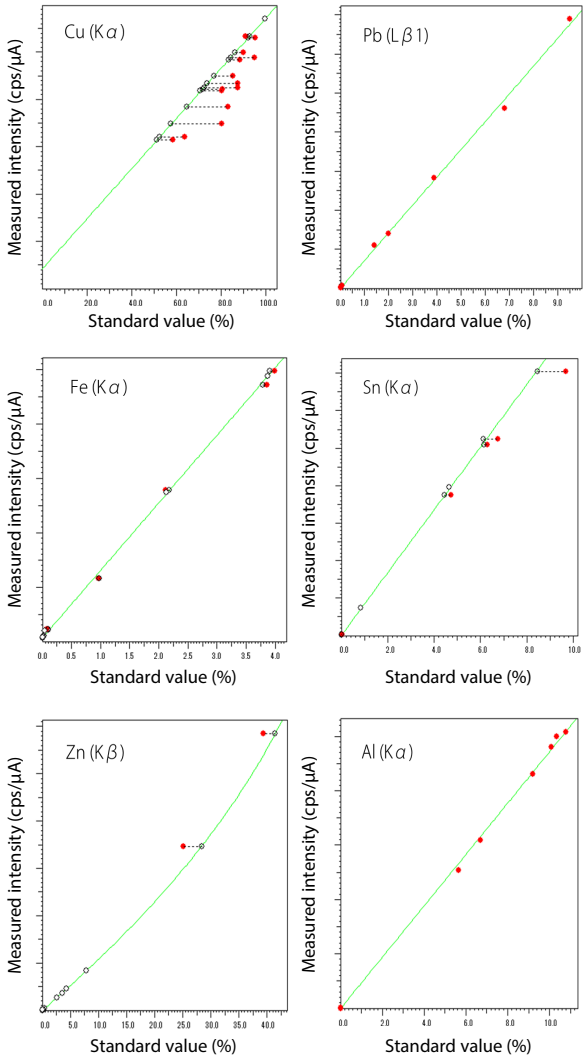
#	Designation of standard sample	Classification
1	CDA110	Pure copper
2	CDA314	Lead bronze
3	CDA510	Phosphor bronze
4	CDA544	Phosphor bronze
5	CDA623	Forged aluminum bronze
6	CDA630	Nickel aluminum bronze
7	CDA642	Aluminum bronze
8	CDA655	Silicon bronze
9	CDA675	Manganese bronze
10	CDA863	Manganese bronze
11	CDA922	Lead tin bronze
12	CDA932	Lead tin bronze
13	CDA937	Lead tin bronze
14	CDA954	Aluminum bronze
15	CDA955	Nickel aluminum bronze

■ Measument Elements

Cu, Pb, Fe, Sn, Zn, Al, Mn, Ni, P, Si

■ Calibration Curves

Calibration curves of the 10 elements (Cu, Pb, Fe, Sn, Zn, Al, Mn, Ni, P, Si) were prepared using the standard samples. Fig. 1 shows the prepared calibration curves. When it was necessary to correct for the influence of coexisting elements, absorption excitation correction by the dj method or overlap correction by the lj method was carried out for each element. Table 2 shows the details of these coexisting element corrections, and Table 3 shows the calibration curve range and accuracy, and limit of detection and limit of quantitation calculated from the theoretical statistical changes.



x-axis: Standard value (%)
y-axis: Measured intensity (cps/μA)

Fig. 1 Calibration Curves (Cont'd on Next Page)

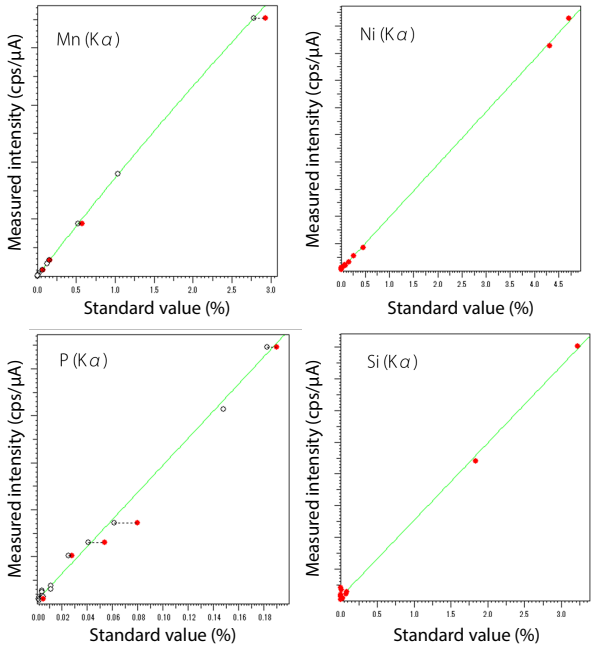


Fig. 1 Calibration Curves (Cont'd from Previous Page)

Table 2 Correction for Coexisting Elements

Corrected element \ Measurement element	Cu	Pb	Fe	Sn	Zn	Al	Mn	Ni	P	Si
Cu										
Pb	○			○					×	
Fe	○				○		○			
Sn	○									
Zn	○									
Al	○									
Mn	○		×							
Ni	○		○				○			
P										
Si	○									

○ : Correction for absorption excitation (dj)
× : Correction for overlap (lj)

Table 3 Calibration Curve Range, Accuracy, and Limit of Detection and Limit of Quantitation

Unit [wt%]

Element (analysis line)	Cu (Kα)	Pb (Lβ1)	Fe (Kα)	Sn (Kα)	Zn (Kβ)
Calibration curve range	58.7 to 99.9	0.0003 to 9.50	0.0005 to 3.99	0.0002 to 9.70	0.001 to 39.3
Accuracy *1	0.1796	0.1145	0.0357	0.0499	0.0517
Limit of detection*2	-*4	0.0018	0.0022	0.0010	0.0121
Limit of quantitation*3	-*4	0.0061	0.0074	0.0033	0.0405
Element	**Al (Kα)**	**Mn (Kα)**	**Ni (Kα)**	**P (Kα)**	**Si (Kα)**
Calibration curve range	0.001 to 10.8	0.0002 to 2.93	0.0001 to 4.71	0.002 to 0.19	0.0003 to 3.22
Accuracy	0.1158	0.0030	0.0299	0.0036	0.0510
Limit of detection	0.0085	0.0018	0.0037	0.0025	0.0059
Limit of quantitation	0.0284	0.0060	0.0123	0.0084	0.0196

*1 Accuracy: Standard deviation of error (quantitative value – standard value).
*2 Limit of Detection: 3 times the theoretical reproducibility accuracy obtained from the calibration curve.
*3 Limit of Quantitation: 10 times the theoretical reproducibility accuracy obtained from the calibration curve.
*4 Since Cu is the main component, limit of detection and limit of quantitation are not given.

■ Quantitative Analysis and Repeatability

Table 4 shows the results of a simple 10-time repeatability test of the unknown sample.

The coefficient of variation is approximately 1 to 5 % for elements with trace contents (no more than 1 %) and approximately 0.05 to 0.5 % for elements with larger contents, demonstrating that highly accurate analysis is possible.

Table 4 Results of Simple Repeatability Test of Unknown Sample

Unit [wt%]

Element	Cu	Pb	Fe	Sn	Zn
Average value	87.5	1.52	0.119	6.20	4.37
Standard deviation	0.043	0.004	0.001	0.009	0.020
Coefficient of variation [%]	0.05	0.3	1.0	0.14	0.5
Element	**Al**	**Mn**	**Ni**	**P**	**Si**
Average value	ND*1	ND*1	0.261	0.035	ND*1
Standard deviation	-	-	0.003	0.002	-
Coefficient of variation [%]	-	-	1.2	5.2	-

*1 ND (not detected): Below the lower limit of detection.

2. FP Qualitative/Quantitative Analysis and Matching Function

■ Outline

The matching function makes it possible to search for substances that are close to the sample by comparing the analysis results and preregistered library data. Matching results are shown in order from those with low calculated degrees of difference (high similarity).

■ Samples

The following three copper alloy samples were tested. Fig. 2 shows an image of the samples.

- Sample ① Phosphor bronze
- Sample ② Brass
- Sample ③ Nickel silver

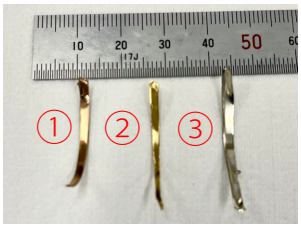


Fig. 2 Image of Samples

■ FP Qualitative/Quantitative Analysis Results and Matching Results

Fig. 3 to Fig. 5 show the FP qualitative/quantitative analysis results and the matching results of samples ① to ③, respectively.

The matching search results showed that sample ① was C5191, sample ② was C2801, and sample ③ was C7521.

Even small samples with a width of about 2 mm can be differentiated.

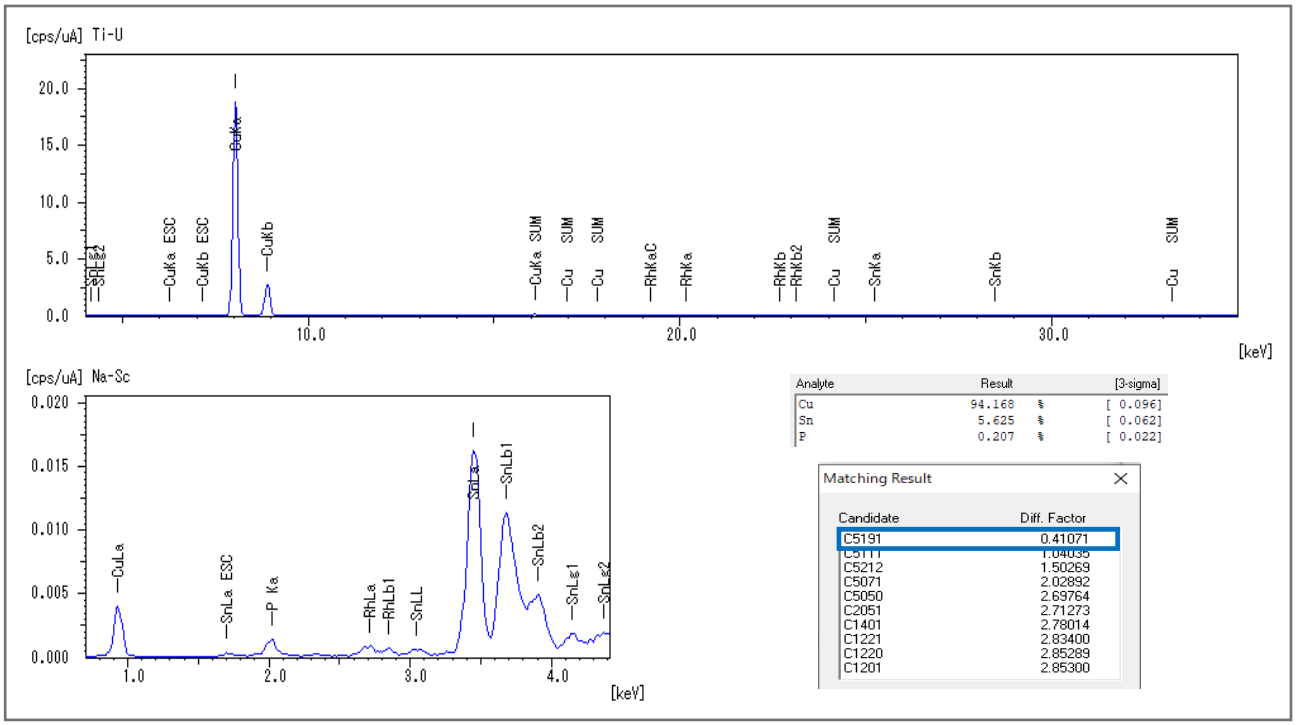


Fig. 3 FP Qualitative/Quantitative Analysis Results and Matching Search Results of Sample ① Phosphor Bronze

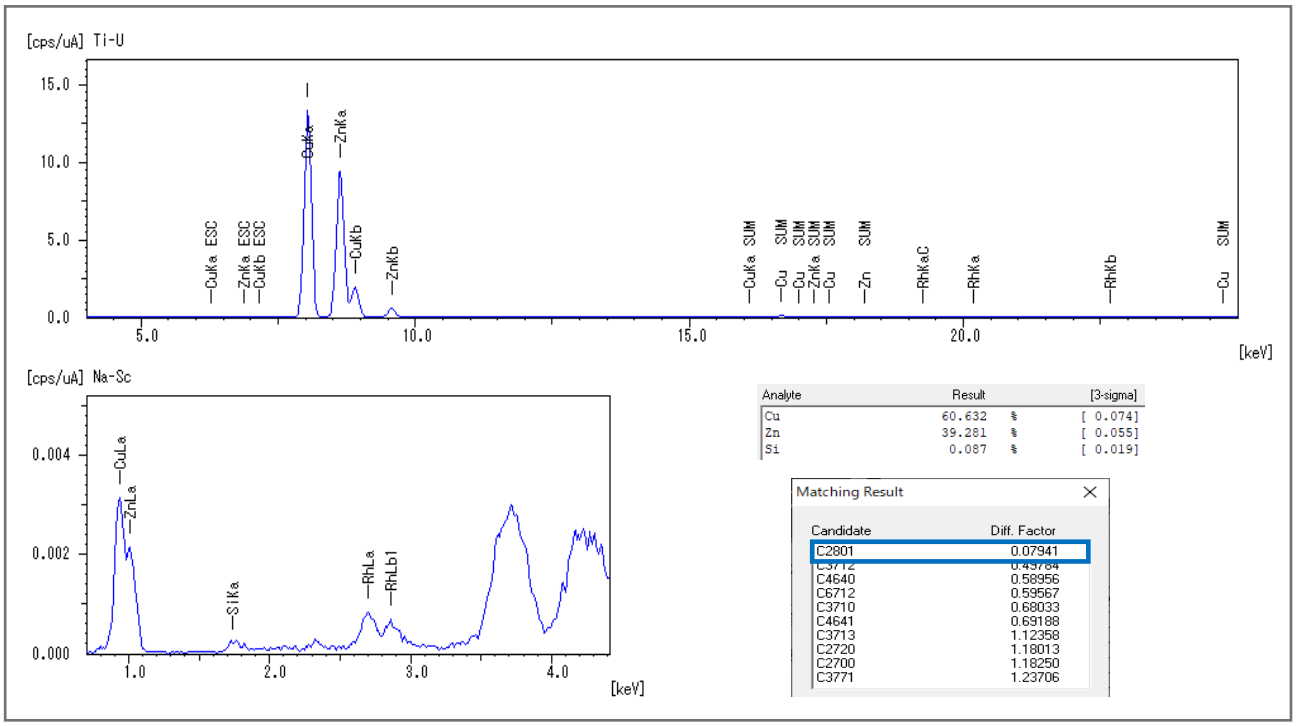


Fig. 4 FP Qualitative/Quantitative Analysis Results and Matching Search Results of Sample ② Brass

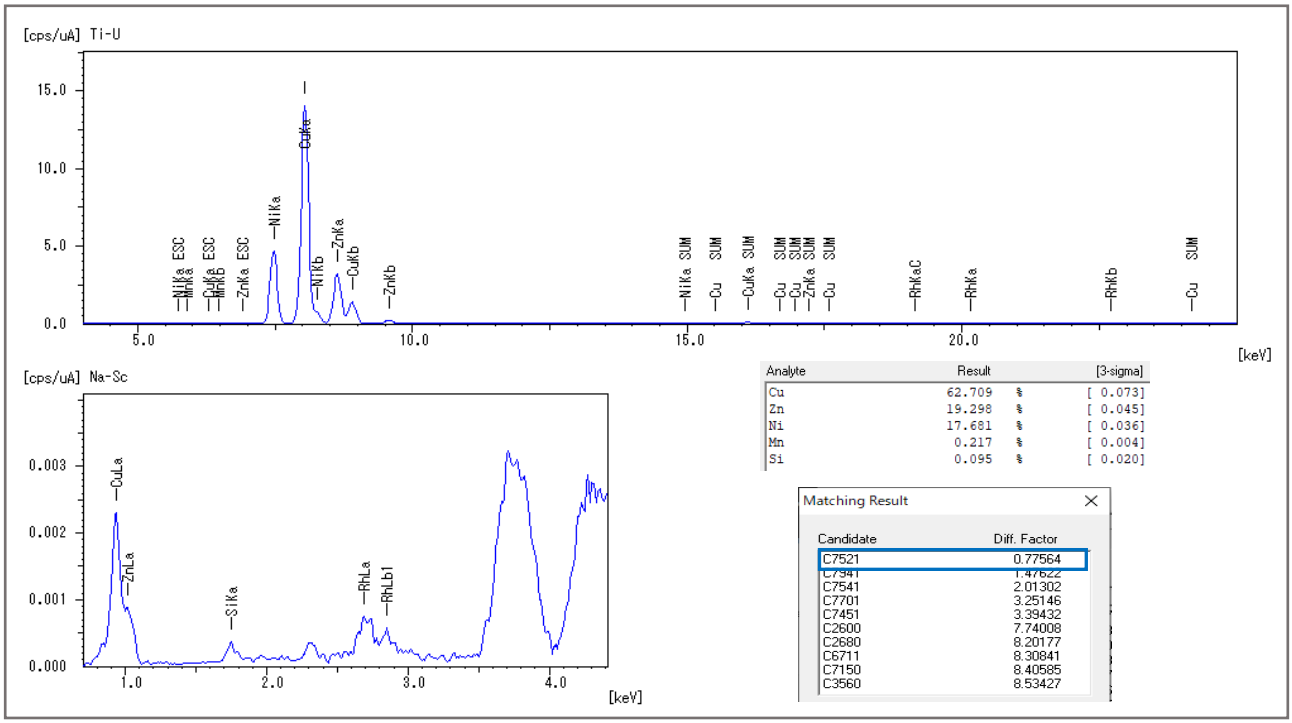


Fig. 5 FP Qualitative/Quantitative Analysis Results and Matching Search Results of Sample ③ Nickel Silver

■ Analysis Conditions ①: Calibration Curve Method

Table 5 Analysis Conditions (Calibration Curve Method)

Instrument	EDX-7200
Elements	Cu, Pb, Fe, Sn, Zn, Al, Mn, Ni, P, Si
Analysis group	Calibration curve method
Detector	SDD
X-ray tube	Rh target
Tube voltage	15 [kV] (Al, P, Si) 50 [kV] (Cu, Pb, Fe, Sn, Zn, Mn, Ni)
Tube current	Auto [µA]
Collimator	10 [mmφ]
Primary filter	None (Al, P, Si), #3 (Fe, Mn, Ni), #4 (Cu, Pb, Zn), #1 (Sn)
Atmosphere	Vacuum
Integration time	100 [s] × 4 Ch
Dead time	Max. 30 [%]

■ Analysis Conditions ②: FP Qualitative/Quantitative Analysis

Table 6 Analysis Conditions (FP Quantitative/Qualitative Analysis)

Instrument	EDX-7200
Elements	Na-U
Analysis group	Qualitative/quantitative analysis
Detector	SDD
X-ray tube	Rh target
Tube voltage	15 [kV] (Na-Sc) 50 [kV] (Ti-U)
Tube current	Auto [µA]
Collimator	1 [mmφ]
Primary filter	None
Atmosphere	Vacuum
Integration time	60 [s] × 2 Ch
Dead time	Max. 30 [%]

■ Conclusion

This article has introduced an evaluation of the analytical performance of the EDX-7200, using copper alloys as an example.

In the quantitative analysis by the calibration curve method, repeatability was evaluated, showing that results with high reliability can be obtained.

The qualitative/quantitative analysis by the FP method also showed that samples can be differentiated easily by using the matching search function of the EDX-7200.

Thus, the EDX-7200 offers a combination of merits. In addition to excellent analytical performance and a small installation footprint, there is no need cooling water or other auxiliary equipment, there are few limitations on the sample shape, and highly accurate analysis of samples even in their original shape is possible.

Based on these advantages, It is expected that EDX-7200 will be widely used to replace analysis using WDXRF.

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01-00721-EN First Edition: Nov. 2024