
Example of a Pb-Free Coating Measurement Sn-Bi-Ag-Cu System

1. Overview

From the standpoint of protecting the environment, the practical use of lead-free solder has progressed in recent years. This application brief provides an example of measuring Sn-Bi-Ag-Cu system lead-free solder.

2. Analysis Conditions

Analysis conditions are listed in Table 1.

Table 1

Item	Settings
Model	SEA5120
Collimator	1.0 mm
Tube Voltage	50 kV
Tube Current	Auto Set
Quantitative Method	Fundamental Parameter (FP)
Measurement Time	100 seconds

3. Analysis Results

3-1 Ingot Analysis

3-1-1 Qualitative Analysis

A spectrum of the ingot sample is displayed in Figure 1. Here Sn, Bi, Ag, and Cu peaks are confirmed.

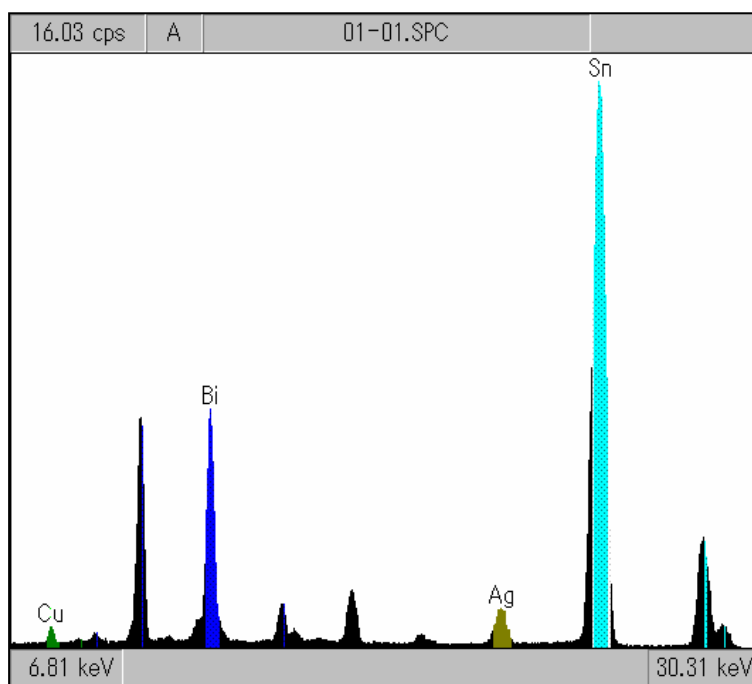


Figure 1 Ingot Sample Spectrum

3-1-2 Quantitative Method

Quantitative analysis results are shown in Table 2. Three measurements were taken at different points of analysis.

Table 2 Results of Analysis

Element	Sn (%)	Bi (%)	Ag (%)	Cu (%)
Standard	86.80	10.0	2.80	0.60
Location 1	87.05	9.83	2.60	0.52
Location 2	86.09	10.54	2.79	0.57
Location 3	87.91	9.14	2.50	0.45

Uneven distribution of sample components can be seen from this analysis result. Quantitative values were calculated based on pure element standard samples using the FP method. The values, therefore, can be thought of as semi-quantitative values. Accuracy can be improved by calculating with the intensity corrected FP method and by using a minimum one-point known density standard sample. Table 3 shows the results of 10 measurement repetitions.

Table 3 Measurement Results of 10 Repetitions

Element	Sn (%)	Bi (%)	Ag (%)	Cu (%)
Average	86.93	9.88	2.56	0.63
Stand Deviation	0.152	0.147	0.063	0.033
Maximum	87.22	10.09	2.64	0.69
Minimum	86.70	9.66	2.46	0.58
Range	0.52	0.43	0.18	0.11
CV (%)	0.17	1.48	2.47	5.32

Clearly, measuring with Bi quantitative values can be done at a repeatability of a 1.5% CV value. X-ray fluorescent analysis shows that statistical variation from fluctuation of fluorescent X-rays is reflected in the dispersion of quantitative values. Consequently, increasing measurement time can decrease dispersion.

3-2 Coating Line Analysis

3-2-1 Qualitative Analysis

Figure 2 shows the spectrum of a coating sample.

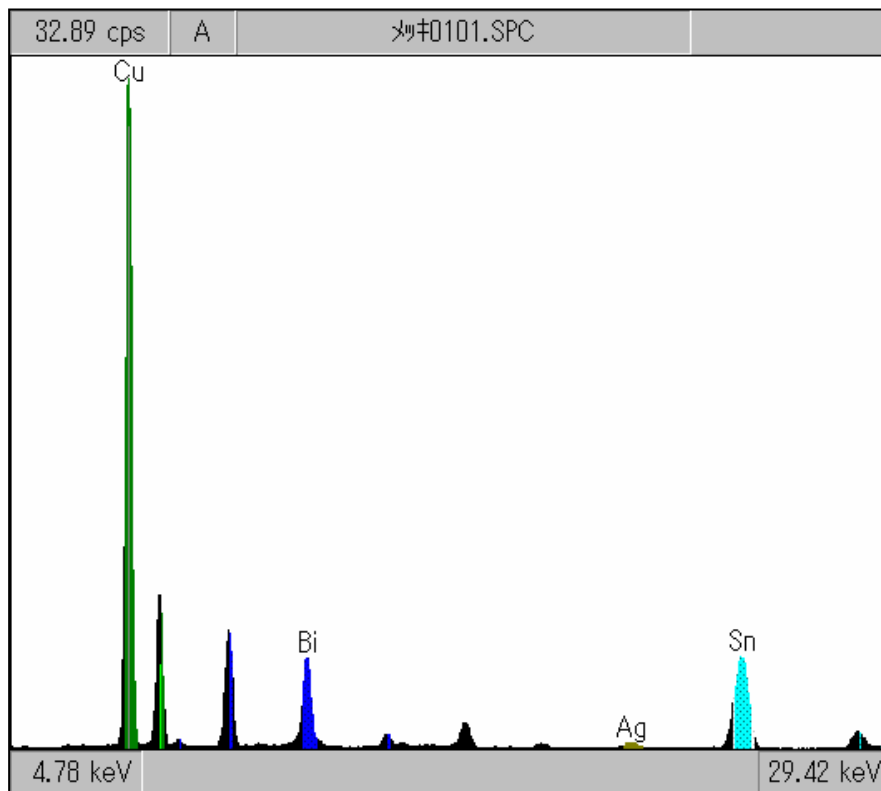


Figure 2 Coating Sample Spectrum

Sn, Bi, Ag, and Cu peaks are verified. The Cu here comes from both the coating and the base, but we were unable to selectively detect only the Cu in the coating.

3-2-2 Quantitative Analysis

Table 4 shows the quantitative results. Three measurements were performed at different analysis points. Cu within the coating and base are identical elements and cannot be distinguished. As a result, we ignored the Cu within the coating and analyzed by Sn, Bi, and Ag.

Table 4 Quantitative Results

Element	Sn (%)	Bi (%)	Ag (%)	Th. (um)
Point 1	87.47	10.03	2.50	7.46
Point 2	86.04	10.98	2.98	5.40
Point 3	85.34	11.73	2.93	6.86

This analysis clearly shows that simultaneous quantitative analysis of thickness and composition of lead-free solder is possible. Since these quantitative values were calculated by the FP method based on pure material standards, they can be thought of as semi-quantitative. Calculating with the intensity corrected FP method by using a minimum one-point known density standard sample can increase accuracy

Table 5 shows the results of 10 measurement repetitions.

Table 5 Ten Repetition Measurement Results

Element	Sn (%)	Bi (%)	Ag (%)	Th. (um)
Average	88.68	8.74	2.58	7.49
Stan. Deviation	0.39	0.201	0.272	0.031
Maximum	89.21	9.16	2.95	7.53
Minimum	88.11	8.46	2.15	7.44
Range	1.10	0.70	0.80	0.09
CV value (%)	0.44	2.23	10.5	0.41

Clearly, measuring can be done at a repeatability of a 1.5% CV value with Bi quantitative values. In the case of X-ray fluorescent analysis, statistical deviation from fluctuation of fluorescent X-rays is reflected in the dispersion of the quantitative values. Consequently, increasing measurement time can decrease dispersion.