SHIMADZU
Excellence in Science

Application News

No. X264

X-Ray Analysis

Quantitative Analysis of Lead in Bismuth Bronze

- Matrix Elements/Profile Correction and Comparison with AA -

Some copper alloys are added with lead (Pb), but with the regulation of environmentally hazardous substances such as RoHS, it has been replaced by bismuth (Bi) in recent years. In X-ray fluorescence analysis, Bi interferes with Pb, that is, spectra overlap, so the quantitative accuracy of low content Pb may not be sufficient. In such cases, calibration curve method applying overlap correction by coexisting elements is effective.

Metal samples are generally measured in the plane of cutting and polishing, but there are cases in which the samples are irregular shapes such as chips and wiring. For irregularly shaped samples with coexisting elements, shape correction is required in addition to the overlap correction described above.

This article introduces an examination of the quantitative analysis precision when applying these corrections to a flat-surface sample and chip sample through a comparison with atomic absorption (AA) analysis.

K. Hori, S. Ueno

Samples

1. Four samples of bismuth bronze (MBH: 32X SEB 1, 2, 4, 5) and one sample of pure copper
2. Content (certified value)

Table 1 Pb, Bi, and Se Content [wt%]

Sample No.	SEB No.	Pb		Bi		Se	
		Certified Value	Uncertainty	Certified Value	Uncertainty	Certified Value	Uncertainty
①	1	0.197	0.003	4.25	0.05	0.812	0.012
②	2	0.104	0.002	4.57	0.05	0.044	0.002
③	4	0.0357	0.0008	2.48	0.04	0.119	0.003
④	5	0.268	0.007	1.056	0.016	0.471	0.006

3. Shape: 40 mmφ × 18 mmH ingot

Elements

Pb : Microdetermination
Bi, Se : Matrix element correction (overlap correction) *
* Due to Bi and Se spectra overlapping the Pb spectrum
Rh : Internal standard correction

Quantitative Analysis Using the Calibration Curve Method on Flat-Surface Samples

Quantitative analysis using the calibration curve method was performed.

1. Sample preparation
A flat surface was cut on the samples using a lathe. The samples were measured after ultrasonic cleaning with ethanol. Fig. 1 shows a sample.

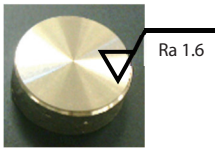

Fig. 1 Sample After Lathe Cutting

2. Calibration curves
Calibration curves were created using the five samples. Fig. 2 shows the calibration curves for Pb, Bi, and Se. Overlap correction (dj method) by coexisting elements of Bi and Se was applied to Pb. Table 2 shows the accuracies and the lower limits of detection calculated from the theoretical statistical changes in background intensity.
From the Pb calibration curve, it can be seen that the overlap of Bi is large. Accuracy is 0.0029 %, which is good in the calibration curve range 0 to 0.268 %.

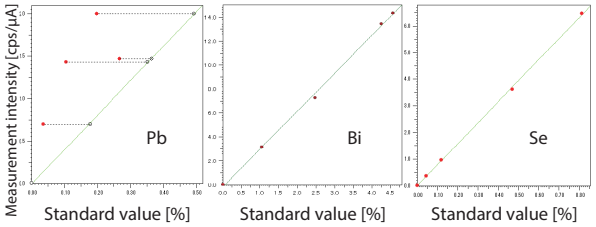

Fig. 2 Calibration Curves of Pb, Bi, and Se (Zero Point: Pure Copper)

Table 2 Calibration Curve Accuracy and Lower Limit of Detection [wt%]

	Pb	Bi	Se
Accuracy	0.0029	0.075	0.0079
Lower Limit of Detection	0.0015	--- (Due to high content)	0.00063

3. Quantitative analysis and repeatability test
The static repeatability testing was performed on sample ③ by repeating quantitative analysis 10 times using the calibration curves from section 2. Table 3 shows the results.

Table 3 Quantitative Analysis and Repeatability Test Results for Sample ③ [wt%]

	Pb	Bi	Se
Average	0.0368	2.35	0.122
Standard deviation	0.0012	0.043	0.0075
Coefficient of variation [%]	3.2	0.18	0.62

Quantitative Analysis with Profile Correction of Cutting Chips

In order to measure the samples in chip form, an internal standard correction effective for profile correction was applied to the calibration curves.[*1 *2] For the calibration curve sample, the flat-surface sample of the previous section was used.

1. Samples
Cutting chips of samples ① to ④ in Table 1
2. Preparation
Ultrasonic cleaning with ethanol
3. Setting
A sample container covered with 5 μm thick polypropylene film was used and the chips were evened out to cover an analysis diameter of 10 mmφ.

Fig. 3 Cutting Chips

4. Calibration curves
Curves were created in the same manner as Fig. 2 (figures omitted). The measurement amount (vertical axis) is an intensity ratio (internal standard correction)[*1 *2] which is the analytical line intensities of Pb, Bi, and Se divided by the RhKα scattered radiation intensity. Table 4 shows the accuracies and lower limits of detection. The values are approximately the same as those for the flat-surface samples.

Table 4 Calibration Curve Accuracy and Lower Limit of Detection [wt%]

	Pb	Bi	Se
Accuracy	0.0038	0.11	0.0057
Lower Limit of Detection	0.0018	--- (Due to high content)	0.00075

5. Quantitative analysis and repeatability test
The static repeatability testing was performed on four samples by repeating quantitative analysis 10 times. Table 5 shows the results for Pb.

Table 5 Quantitative Analysis and Repeatability Test Results for Pb [wt%]

Samples	①	②	③	④
Average	0.183	0.105	0.0375	0.242
Standard deviation	0.0020	0.0041	0.00073	0.0016
Coefficient of variation [%]	1.1	3.9	2.0	0.68

6. AA analysis
Chips were dissolved in acid and analyzed with AA.
(1) Preparation
Fig. 4 shows the acidic dissolution procedure.

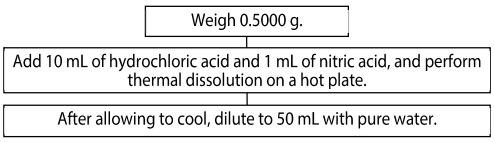

Fig. 4 Acidic Dissolution Procedure

(2) Measurement method
Frame measurement (calibration curve method)
(3) Calibration curve samples
Pb 5, 10, 20, 30 mg/L (HCl 20 %, HNO_3 2%)
(4) Measurement results

Table 6 Pb Measurement Results [wt%]

Samples	①	②	③	④
Concentration in solid	0.187	0.0995	0.0354	0.266

7. Comparison of EDX and AA
Table 7 shows the relative error of each instrument with respect to the certified values. Although the error of AA is about 5 %, the error of EDX is a little less than 10 % at the maximum, which is a slightly large value. However, since EDX is advantageous in that chip-form samples can be analyzed easily without disolving in acid, it can be used depending on the required precision for control reference judgment.
For example, if the standard for judging quantitative values with respect to management criteria of environmentally hazardous substances is set as 0.07 wt%, the sample ③ is less than the management criteria from the following formula (refer to Table 5).

Criterion formula (quantitative value + 3σ) $= 0.0375 + 3 \times 0.00073$
$= 0.040 < 0.07$ [wt%]

Table 7 Relative Error with Respect to Certified Values for EDX and AA [%]

Samples	①	②	③	④
EDX	-7.1	+1.0	+5.0	-9.7
AA	-5.1	-4.3	-0.8	-0.7

Measurement Conditions

EDX

Instrument	: EDX-8000/(7000)
Element - analytical line * *	: PbLβ$_1$, BiLα, SeKα, RhKα
Analysis method/profile correction	: Calibration curve method/BG internal standard correction[*1 *2]
Detector/X-ray tube	: SDD/Rh target
Tube voltage - current	: 50 [kV] - Auto [μA]
Collimator/primary filter	: 10 [mmφ]/#4
Measurement atmosphere	: Air
Integral time/dead time	: 600 [sec]/max. 30 [%]

AA

Instrument	: AA-7000
Analytical wavelength	: 283.3 nm
Slit width	: 0.7 nm
Current value	: 10 mA
Ignition mode	: BGC-D2

* * Analytical line
Since Pb and Bi have neighboring atomic numbers, the X-ray fluorescence X-ray spectrum of each element overlaps. In addition, when As and Se are coexisting elements, the AsKα line overlaps the PbLα line and the SeKβ line overlaps the PbLβ$_1$ line. Although the PbLβ$_1$ line was selected as the analytical line, overlap correction was applied using Se and Bi since the SeKβ line and BiLβ$_1$ line overlap. Fig. 5 shows the profiles neighboring the analytical line PbLβ$_1$ and Table 8 lists the energy values for reference.

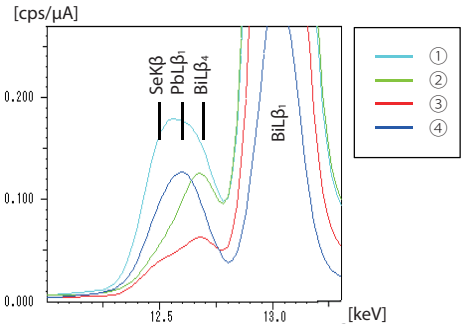

Fig. 5 Spectra of Analytical Lines

Table 8 Energy of Analytical Lines and Neighboring Lines (Reference)

Fluorescent X-Ray	Energy [keV]
AsKα	10.53
PbLα$_{1,2}$	**10.55**
BiLα$_{1,2}$	10.84
SeKβ	12.50
PbLβ$_{1,2}$	**12.61**
BiLβ$_4$	12.69
BiLβ$_{1,2}$	13.02

Conclusion

The effectiveness of overlap correction was confirmed in regard to the quantitation of low contents of lead coexisting with bismuth. Since sufficient precision was obtained by using overlap correction in conjunction with profile correction even in the analysis of cutting chips, these methods are usable in the management of RoHS analysis that tends to involve many samples with irregular shapes. These methods can be utilized for application to other elements and materials according to purpose and use (precision, sample shape, time, preparation, etc.).

*1 Shimadzu Application News No. X246
*2 Hirotomo Ochi, Hideki Nakamura, Shinji Watanabe: Advances in X-Ray Chemical Analysis, Japan, Vol. 38, p191 (2007)

First Edition: Nov. 2017

SHIMADZU
Shimadzu Corporation
www.shimadzu.com/an/