Application Brief

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Measuring controlled substances in brass using the SEA1000A

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1. Introduction

In response to the requirements of RoHS/ELV directives, there has been considerable attention focused on the presence Pb and Cd in metals. In order to improve the cutting characteristics of items such as brass, Pb has been often added to copper alloys. Furthermore, the permitted level of Pb in copper alloy is higher as an exemption, compared to general permitted levels. Due to these conditions, Pb in copper alloy must be measured accurately because concentrations from this application are close to the regulation limits. Cd is also an important since it is an impurity in raw Zn and its value may sometimes exceed regulations.

This application brief illustrates how to improve the detection range for Pb and Cd in brass when using the SEA1000A.

2. The characteristics and uses of measurement methods

Both FP and the calibration curve methods can be used to measure metals with X-ray fluorescence. However, each has its own advantages and disadvantages and they must be applied properly.

Both methods have the following conditions.

1. The constituent elements must be known
   The coexisting elements change the intensity of X-rays, and so this change must be corrected.
2. The measurement sample must be homogeneous
   The measurement sample is assumed to be homogeneous when calculations are performed. A film method shall be used for non- homogeneous samples, such as layered plating.
3. X-ray saturation thickness must be reached
   Metals with a thickness of around 100 μm are sufficiently saturated by X-rays, while light elements such as Al require a thickness of about 1 mm. Samples thinner than these values must be calculated as film.

Each measurement method also has its own characteristics.

1. Calibration curve method (Plastics and metals can be used)

1) Concentrations are calculated based on the intensity of standard sample
   An accurate analysis can be expected because measurement samples are compared to standard sample
2) Standard samples with the same matrix must be prepared
3) The X-ray fluorescence intensity changes depending on the measurement sample area, surface shape and thickness, even though the composition is the same.

2. FP method (Metals, etc.)

1) The concentration is calculated based on theoretical calculations
   Accuracy can be improved by correction using the standard samples.
2) Supports various measurement sample shapes (the shape does not affect this method greatly)
3) If measurement samples contain unknown composition of light elements, such as C or N, adjustment is difficult.

3. Measurement

The SEA1000A measured brass using the bulk calibration curve method and FP method. The following chart lists the measurement conditions.

Measurement condition

	Measurement condition 1	Measurement condition 2
Measurement time (seconds)	300	300
Collimator	φ5.0mm	φ5.0mm
Excitation voltage (Kv)	50	50
Tube current (μA)	30	850
Filter	For Pb	For Cd
Environment	Air	Air

4. Results

4-1 Accuracy

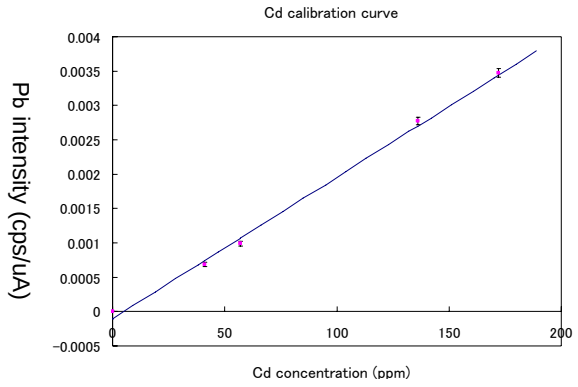
Pb and Cd were measured using the calibration curve and FP methods. A copper alloy measurement sample for X-ray fluorescence was used as a standard sample. This sample was manufactured by Sumitomo Metal Technology. As can be seen, good linearity was obtained. The calibration curve method has better precision than the FP method. Numerically, both the calibration curve and FP methods provided good values.

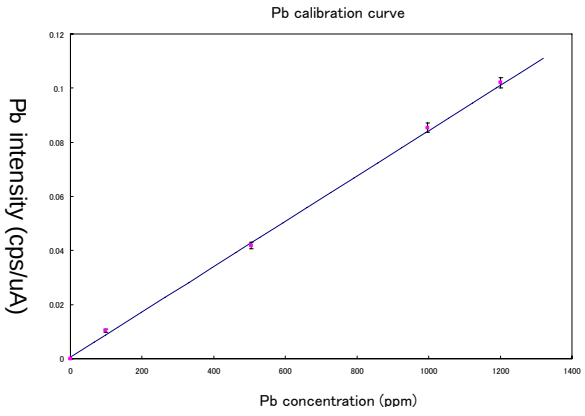
Measurement of brass (ppm)

	Calibration curve		FP	
	Pb	Cd	Pb	Cd
	991	57	1086	64
	999	53	1027	56
	953	49	982	51
	1064	61	937	83
	976	43	1003	44
Indicated value	997	57	997	57
Avg.	996.6	52.6	1007.0	59.6
Range	111.0	18.0	149.0	39.0
Standard deviation	41.5	7.0	55.2	15.0
Max.	1064.0	61.0	1086.0	83.0
Min.	953.0	43.0	937.0	44.0
CV value (%)	4.2	13.3	5.5	25.1

In these results, background subtraction was not used for calibration curve method, the measurement error is relatively small.

Note: If background is not subtracted, the surface must be flat and smooth.





4-2 The effect of shape

The effect of shape is dependant on the method used. When the calibration curve method is used, the X-ray fluorescence intensity changes depending on the surface shape and this change affects the concentration. This is true even when the composition is the same.

We studied this effect with measurement samples that had different irradiation areas, gradients (samples that rise up from the stage) and uneven surfaces.

The effect of shape on brass test samples (Calibration curve)

	Pb	(Indicated value)	Cd	(Indicated value)
CDA922	13485	(12300)	0	(—)
CDA485 gradient	4119	(16700)	0	(—)
CDA485 uneven	15122	(16700)	0	(—)
CDA485	16623	(16700)	4.36	(—)
CDA482	6222	(6500)	33.45	(—)
GBR5 gradient	864	(1200)	114.49	(172)
GBR5 small dimensions	699	(1200)	83.7	(172)

The effect of shape on brass test samples (FP)

	Pb	(Indicated value)	Cd	(Indicated value)	Other compositions
CDA922	12874	(12300)	0	(-)	Zn 4.29%,Sn29%
CDA485 gradient	16328	(16700)	0	(-)	Zn 38%
CDA485 uneven	15338	(16700)	2	(-)	Zn 38%
CDA485	16434	(16700)	3	(-)	Zn 38%
CDA482	6718	(6500)	55	(-)	Zr 40%
GBR5 gradient	1179	(1200)	162	(172)	Zn 38%
GBR5 small area	1272	(1200)	158	(172)	Zn 38%

The measurement sample shapes affected the calibration curves. Warped or inclined measurement samples had a lower X-ray intensity than flat and smooth measurement samples. Furthermore, the composition of CDA922 was different from the standard sample used to create the calibration curve so the values were higher than the actual values. Coexisting elements affected the gradient and curvature of the calibration curve. The measurement sample shape did not affect the results of the FP method very much. Additionally, the effect of the composition of coexisting elements was theoretically calculated.

5. Conclusion

Measurement samples come in various shapes and sizes so the FP method offers more flexibility in the measurement values and has a smaller margin of error.

Alternatively, when the measurement conditions are good, such as when the surface is flat, smooth and sufficiently large, the calibration curve method can provide improved repeatability.