

## SEA no.33

## Correcting calibration curves for the X-ray fluorescence analysis of metals

2007.9

### 1. Introduction

It is possible to perform X-ray fluorescence analysis without standard samples because theoretical calculations known as the FP method can be used. This simple measurement method is widely used to perform easy and quick measurements.

On the other hand, if standard samples are available, a more accurate analysis is possible with the calibration curve method. It has been relatively easy to obtain standard samples for metal analysis in recent years.

However, to obtain accurate measurements with calibration curves, there are many important factors to consider. It is also necessary to implement a range of measures to support all measurement sample types. This application brief explains the cautions and measures necessary when analyzing metals.

### 2. Cautions when using calibration curves

Calibration curves are expressions of the relation between X-ray intensity and concentration. Because X-ray intensity is converted to concentration, changes in intensity may cause errors in the following cases.

- (1) The measurement sample is smaller than the diameter of the X-ray beam.
- (2) The surface of the measurement sample is uneven.
- (3) The position of the measurement sample is different.

Negative errors tend to occur in such cases because the X-ray intensity is reduced, which in turn lowers the concentration.

### 3. Correcting calibration curves

There are two correction methods to reduce errors.

- (1) Correction using Rh Scattered X-rays.
- (2) Correction using the X-ray intensity of the main elements.

When the primary X-rays contact the measurement sample surface, scattered X-rays are produced. Since the scattered X-ray intensity is correlated with the target fluorescent X-ray intensity, the influence of the measurement sample shape can be reduced by using this correlation.

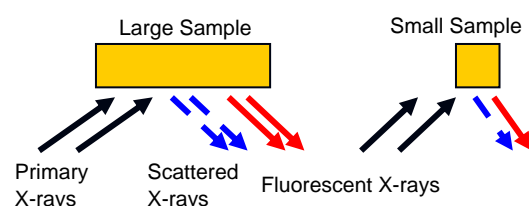


Figure 1 – Overview of scattered X-ray correction

Figure 2 shows that the shape of the measurement sample has reduced the fluorescent X-ray intensity. However, we can see that the Rh scattered X-rays are also lowered in the same manner as the X-ray intensity as shown in Figure 2. As a result, we know that the fluorescent X-ray intensity of the target element and the intensity of the Rh scattered X-rays are correlated. By using this ratio, we can offset the influence of the measurement sample shape.

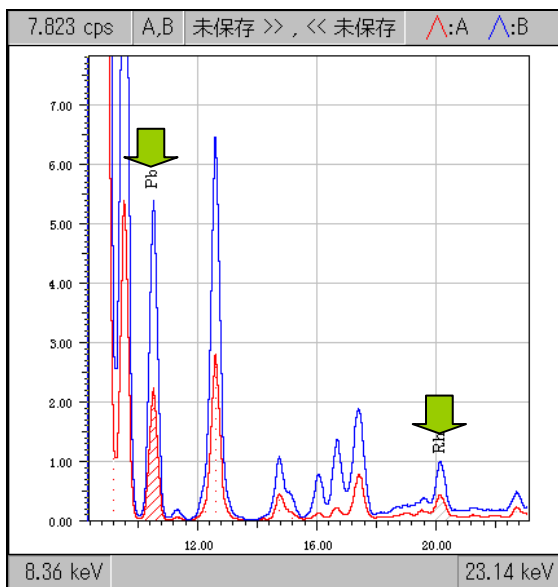


Figure 2 – Fluorescent X-rays and scattered X-rays

In addition, the increases and decreases of the fluorescent X-rays of the main elements can be used to make corrections for changes, such as changes in measurement sample size, in a way similar to correction using scattered X-rays.

## 4. Measurement

A brass measurement sample was measured using the calibration curve method. The results listed below show the measurements after scattered X-ray correction.

Corrected results for the measurement of Pb and Cd in brass (ppm)

Measurement sample direction	No correction	Correction by Rh scattered X-rays	Correction by Cu fluorescent X-rays
ICP-OES Certified value	Pb 38000.0		
	Cd 74.0		
Standard position	Pb 36137.6	37027.8	37323.6
	Cd 66.3	69.1	69.6
Elevated 2 mm	Pb 15210.5	33701.1	39187.1
	Cd 30.1	62.4	72.0
Inclined	Pb 23764.4	33718.8	36638.4
	Cd 50.7	71.5	77.2
1/2 surface area	Pb 15408.3	33039.8	37927.9
	Cd 25.5	50.0	57.2

As can be seen from these results, when values are not corrected, the shape and size of the material affect the calculation of the concentration greatly.

Corrected concentrations can be obtained by performing corrections. However, these correction methods have advantages and disadvantages.

### (1) Correction using Rh scattering

- This method is widely used.
- With metals, correction causes variations because the intensity of the scattered X-rays themselves is not very high.
- As a result, repeatability is somewhat hindered.
- When measurement samples are a mixture of plastic and metals, scattered X-rays from plastic are detected and the results are over-corrected.

## (2) Correction by the main elements

- If the composition of the main elements is different, error is introduced to the correction. As a result, this method generally cannot be used.
- It may be possible to correct measurement samples that include plastic.

Actual measurements showed repeatability when using no correction and Rh correction.

Measurement conditions (SEA1000A)

	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

Repeated measurements of GBR5

	No correction		Rh correction	
	Pb	Cd	Pb	Cd
1	1145	170	1081	160
2	1265	189	1171	174
3	1281	173	1177	158
4	1297	197	1270	192
5	1289	191	1265	187
6	1273	166	1199	156
7	1273	166	1160	162
8	1248	173	1226	169
9	1180	163	1107	152
10	1154	170	1116	164
Avg.	1241	176	1177	167
STD	58	12	65	13
CV	4.7%	6.8%	5.5%	7.9%

The same calibration curve correction can be used with the measurements of other metals. An example with aluminum alloy is listed below.

Corrected results for the measurement of Pb and Cd in aluminum alloy (ppm)

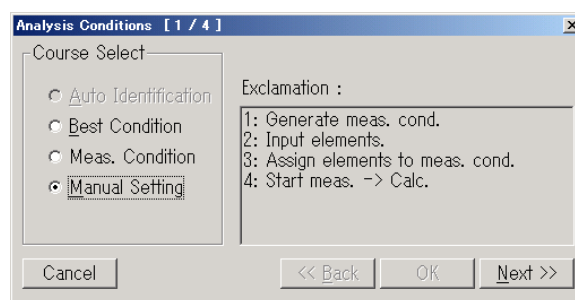
Measurement sample direction		No correction	Rh scattered X-ray correction
Standard position	Pb	401.0	376.0
	Cd	8.0	7.0
1/2 surface area 1	Pb	174.0	454.0
	Cd	2.0	5.0
1/2 surface area 2 (Current setting changed)	Pb	158.0	401.0
	Cd	2.0	5.0
With gradient	Pb	357.0	341.0
	Cd	5.0	5.0

## 5. Setting the Conditions

This section shows how to set the analysis conditions.

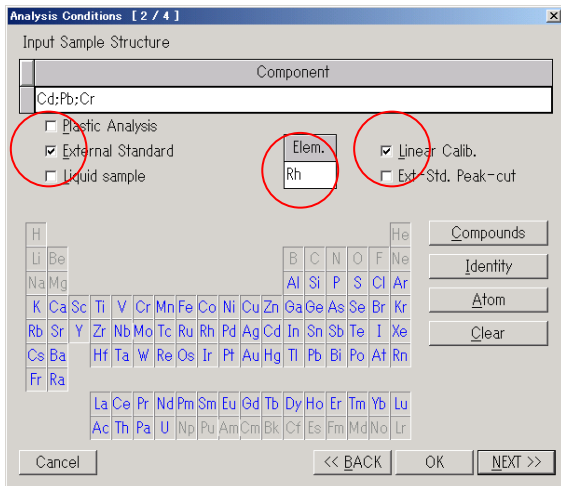
- (1) Select Bulk Analysis (CAL) mode.
- (2) Analysis Parameters.

In the **Analysis Parameter [1/4]** dialog box, select the course. Select either **Meas. condition** or **Best Condition**. Select the latter to reduce the filter conditions and simplify the measurement conditions.



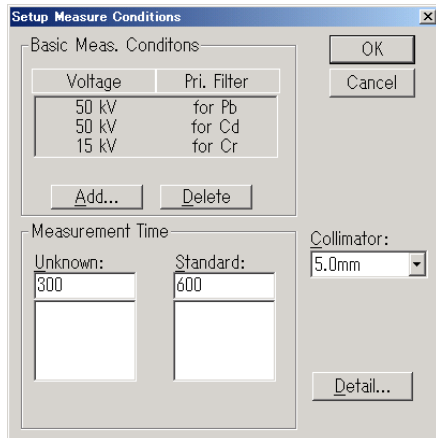
### Analysis Parameter [2/4] dialog box

- Enter the target elements to be measured.
- Select the External Standard check box.
- Select the Linear Calib. check box.
- Enter Rh under Elem.



### (3) Measurement conditions

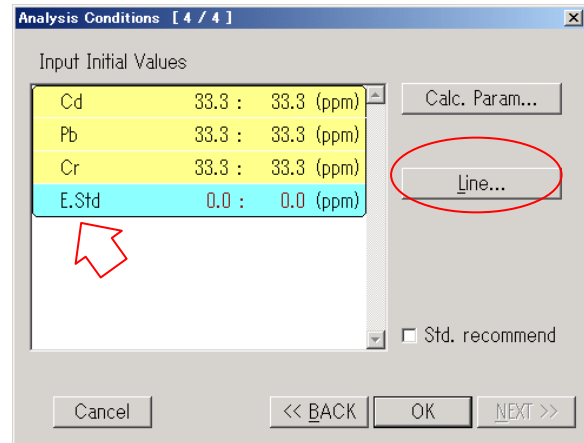
- As necessary, set the conditions of primary filter, such as For Pb, For Cd or 15 kV. (Setup Measure Conditions)
- When **Best Condition** is selected, the values cannot be changed because the optimal conditions are specified automatically.



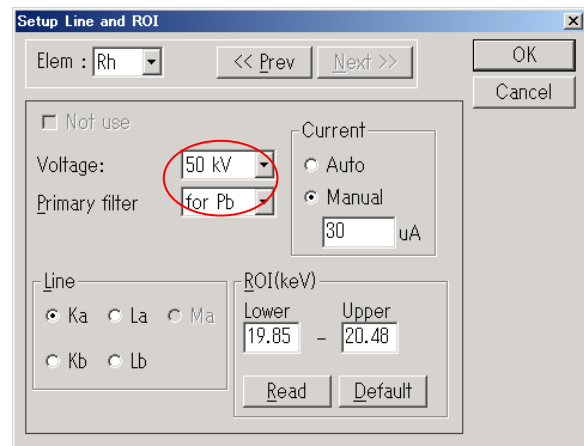
### (4) Re-edit analysis conditions (Rh settings)

Select **Manual** for the course.

At the **Analysis Parameter [4/4]** dialog box, select **E.Std (Rh)** and click **Line**.



Set the conditions such as 50kV or a For Pb filters as conditions for acquiring Rh scattered X-rays.



(5) Set the tube current.

From the **Measurement** menu, click **Current Adjust Start**. Measure the standard sample to be registered and use the lowest voltage.

## 6. Conclusion

The calibration curve method measures metals precisely and accurately.

However, two facts must be considered before using this method: it is difficult to apply to metals with different compositions and it is influenced by the shape of the measurement sample. This document introduced methods to correct measurement results using the scattered X-rays of Rh and main elements. It is important to select measurement methods based on the composition of measurement samples because this method cannot be used with measurement samples that contain plastics.