Compton scattering internal standard correction extended by FP method and applied to metal element analysis of ore and concentrate samples

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Abstract

The Compton scattering internal standard correction technique, which is a matrix correction method conventionally used for geological powder sample analysis, has been improved by integration of a matrix correction term. The matrix correction coefficients are theoretically calculated by the fundamental parameter (FP) method. The improved method accurately extends the applicable range of calibrations to high concentrations.

The improved correction method can be applied to mining samples, such as iron ores, copper ore / concentrate and nickel oxide and sulfide ores analyzed by the pressed pellet method.

The theoretical alpha coefficients obtained by the FP calculation are smaller than conventional theoretical alphas without internal standards. This means the method can reduce the influence of analytical errors from coexisting components. The method has applications in the analysis of powdered ore samples in mining.

1. Introduction

The internal standard method is one technique used to correct matrix effects in geological samples. In X-ray fluorescence analysis, X-rays scattered by a sample can be used as an internal standard. The matrix correction method using Compton scattering X-rays as an internal standard is convenient because it does not require complex sample preparation, such as adding anything to the sample, and is a useful technique for correcting matrix effects in geological samples such as silicate rocks and ores.

Rigaku developed a unique advanced fundamental parameter (FP) program to extend the internal standard method using Compton scattering, which expanded the analysis range for valuable metal element analysis in ores and concentrates.

This report shows Rigaku's unique correction technique and some application examples.

2. Conventional Compton Scattering Internal Standard Correction Method and Extension

The matrix effects of on a peak and the background near the peak position can be considered to be the same owing to their similar 2θ angles. Therefore, the X-ray intensity ratio of the measurement line to the background can correct matrix effects. This is an internal standard method unique to X-ray fluorescence analysis.

The X-ray intensity of the Compton scattering line is inversely correlated to the bulk mass absorption coefficient of the sample. Therefore, like the background, the Compton scattering line can also be used as an internal standard. This Compton scattering internal standard method has been used as an easy, convenient and practical method to correct matrix effects because it is not necessary to know the details about other elements coexisting in the sample.

The equation for a calibration curve for the Compton scattering internal standard method is as follows (1).

$$\begin{aligned} W_i &= AI_R^2 + BI_R + C \\ I_R &= I_i / I_{\mathrm{Compton}} \end{aligned} \tag{1}$$

A, B, C: constant
I_i: X-ray intensity of element i
I_{Compton}: Intensity of Compton line

Applying the conventional Compton scattering internal standard method has some conditions. 1) There can be no large absorption edge by any major components between the Compton line and the analyte, 2) The applicable elemental range is restricted to heavy elements with wavelengths close to the Compton scattering line, which is empirically shorter than chromium, 3) It is more effective for analysis of trace-to-minor elements.

When the absorption edge of any major component exists between the Compton line and the measurement line of the analyte, the relationship of the mass absorption coefficients between the Compton line and the measurement line is not constant owing to variations in concentration of the major component.

In the case of silicate rock sample analysis, samples usually contain abundant Fe as a major component. In this case, the Compton scattering internal standard method can be applied to elements with shorter wavelengths than the absorption edge of the Fe-K line. Most trace heavy elements in silicate rock are within this wavelength range.

For the iron analysis of iron ores at mining sites,

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the Compton scattering internal standard correction method has been used. This conventional method was usually effective but does not give the best results, even though there are no major absorption edges between the Compton line and iron. The analyte is affected by absorption effects from lighter elements. Iron ore contains elements lighter than Fe as major components. In particular, Ca is a relatively abundant component in iron ores and is close to Fe in atomic number, which means it can have a large effect on the X-ray intensity of Fe in iron ores(1).

Potts(2) pointed out that analyses for elements with over several hundred ppm in concentration require further correction.

Arai(3) and Kataoka et. al.(4) have integrated a correction term for coexisting elements into the calibration formula of the Compton scattering internal standard method to extend its application to components with high concentrations such as iron in iron ores and copper in copper concentrates.

Rigaku has expanded the theoretical X-ray calculation program using the FP method to calculate theoretical alphas in Compton scattering internal standard calibration and integrated it with the ZSX Guidance software as the Quant. Scatter FP function(5). This function easily and conveniently produces matrix coefficients for the Compton scattering internal standard method using theoretical FP calculations with simple model compositions, which were conventionally obtained by empirical calculations using large number of standard samples. This function can be used to extend the application of the Compton scattering internal standard method.

This function is now an option available for Rigaku ZSX Primus series, Supermini200 and Simultix wavelength dispersive XRF spectrometer.

The equation of a calibration curve for the Compton scattering internal standard with theoretical matrix corrections is shown in equation (2). Note that the theoretical alpha coefficients in the Compton scattering internal standard method are presented as α^* to distinguish them from the normal calibration method.

$$W_i=(AI_R^2+BI_R+C)(1+\sum\alpha_j^*W_j)$$
$$I_R=I_i/I_{Compton} \qquad (2)$$

A, B, C: constant
I_i: X-ray intensity of element i
$I_{Compton}$: Intensity of Compton line
α_j^*: Theoretical alpha coefficient of element j
W_j: Weight fraction of element j

Figure 1 shows calibration curves for the Compton scattering internal standard correction with or without theoretical alphas for total iron in iron ores. The calibration line is usually represented as a quadratic in high concentration. The correction in this report improves the accuracy of the calibration curve.

Table 1 shows a comparison between theoretically calculated alphas from the Compton scattering internal standard correction and the normal alpha correction. Correction coefficients α^* in the Compton scattering internal standard correction are almost an order of magnitude smaller than those from the normal alpha correction.

This means that errors caused by coexisting elements in the calculation of the analytical values of the target component can be reduced.

There is an advantage in the analysis of powder samples by significantly reducing errors due to heterogeneity, such as particle size and mineralogical effects.

3. Application

3.1 Iron ore

There are many factors indicating the quality of iron ore such as the type of mineral, ore size, type and/or abundance of impurities and so on. The most important factor in ore grade is iron content (total iron, T.Fe). The grade of iron in iron ore controls the transaction price of

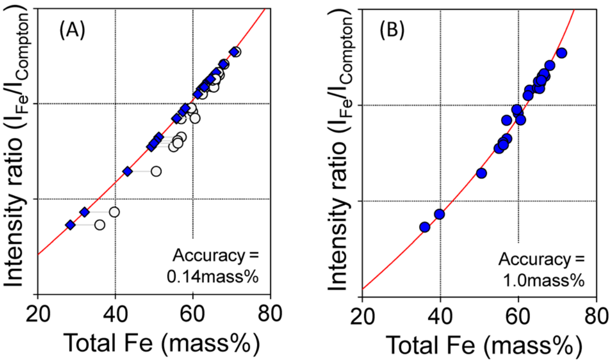

Fig. 1. Calibration curves of Compton scattering internal standard with / without theoretical alpha correction.
Total iron calibration curve of iron ores.
(A): Compton scattering internal standard with theoretical alphas.
(B): Conventional Compton scattering internal standard.

Table 1. Comparison of theoretical alpha coefficients (iron ore).

(mass%)

Component	Theoretical alpha coefficient	
	With internal standard correction	Without internal standard correction
T.Fe	—	0.0601
SiO_2	0.0023	0.0224
CaO	0.0099	0.1000
MnO	0.0165	0.1755
Al_2O_3	0.0017	0.0183
TiO_2	0.0093	0.0995
MgO	0.0016	0.0160
P	0.0056	0.0583
S	0.0071	0.0717
K_2O	0.0096	0.0992
V	0.0172	0.1840

iron ore trading.

At iron ore mining site, the analysis of over one thousand samples per day may be necessary to control mining and mineral processing. Therefore, in addition to accuracy, speed and cost-effectiveness of the analytical method are essential issues.

X-ray fluorescence analysis with the pressed powder method is the best option to meet the demands of speed and cost-efficiency. Currently, many mines use X-ray fluorescence spectrometers to control mining and mineral processing. There is an increased demand to improve accuracy in the determination of total iron in ores. The correction method in this report was applied to the analysis of total iron in iron ores by the pressed pellet method.

3.1.1 Reference standard samples and sample preparation

Commercially available standard samples, supplied by JSS, BAS, BCS, NBS, LKAB, CSMI and IMZ, were used for the calibration. These standards are composed of hematite ore, magnetite ore, limonite, iron sand, sinter, pellet and pure iron oxide, which cover almost all natural and processed iron ores as raw materials in steel making. Total iron content among these standards ranges from 29.0 to 69.8 mass%.

A standard sample is pressed in an aluminum ring at 250 kN after pulverization by a tungsten carbide grinder. No binding agent was used because the accuracy of calibration with the Compton scattering internal standard method becomes worse for pellets made with binder$^{(6)}$. Because iron ores have high density and there is a risk of sample falling in the sample chamber, using an XRF spectrometer equipped with tube-above optics is recommended.

3.1.2 Instrument

Measurements were performed using Rigaku's ZSX PrimusIV, a sequential wavelength dispersive X-ray fluorescence (WDXRF) spectrometer. Voltage and current for these measurements are 50 kV and 50 mA, respectively. As a comparison, the Simultix 15, a simultaneous WDXRF spectrometer with multiple channels, was also used, also with 50 kV and 50 mA of tube load.

3.1.3 Calibration curves and results

Calibration curves for 11 elements in iron ores, Mg, Al, Si, P, S, K, Ca, Ti, V, Mn and Fe, were created. Table 2 shows the calibration range and accuracy of calibration for each component.

Table 2. Accuracy of calibration for iron ore.

(mass%)

Component	Range	Accuracy
T.Fe	29.0 – 69.8	0.14
SiO_2	0 – 45	0.69
CaO	0 – 20	0.11
MnO	0 – 1.1	0.0057
Al_2O_3	0 – 6.8	0.27
TiO_2	0 – 6.3	0.0078
MgO	0 – 3.5	0.10
P	0 – 0.59	0.0065
S	0 – 0.85	0.0068
K_2O	0 – 0.69	0.0067
V	0 – 0.46	0.0020

Instrument: ZSX PrimusIV

Figure 2 show the calibration curves of total iron obtained by three correction methods: the conventional theoretical alpha correction, the conventional Compton scattering internal standard correction and the Compton scattering internal standard with theoretical alpha correction method (this report). Since these calibration curves are created using identical X-ray intensity data sets, differences in accuracy indicate effects from only differences in the correction method. Using identical intensity data sets obtained from nine CRMs of iron ore, total iron content was calculated by three correction methods (Table 3).

Figure 2 and Table 3 indicate that the Compton scattering internal standard correction method integrated with theoretical alphas can significantly improve accuracy in the calibration curve of pressed pellets. Validation samples in Table 3 are composed of iron ores with a variety of mineral assemblages in iron oxide, from hematite-abundant to goethite-abundant ore. Thus, despite different mineral assemblages, this correction method gives satisfactory results for total iron analysis, which means this technique is widely applicable independent of ore type, deposit and mine.

Figure 3 shows a calibration curve for total iron by Simultix 15. Results equivalent to the sequential type XRF are obtained in this fixed channel type XRF.

3.2 Copper ore

Run-of-mine ores of copper are processed to be concentrated and then shipped. Copper with 0.5–2 mass% contained in these ores is concentrated to 25–35 mass% at a processing plant.

The price of Cu concentrate is determined by three elements: Cu, Au and Ag. Cu ore generally contains numerous other elements, such as As, Sb, Bi, F, Cl, Hg, Zn, Ni and Pb. These elements are impurities that affect the price of concentrate$^{(8)}$. The nature of the impurity elements differs based on deposit type. Since it is necessary to monitor a number of elements in copper ores and concentrates, XRF, which can easily and promptly measure-multiple elements, is the optimal technique to determine elements in ore samples.

3.2.1 Reference standard samples and sample preparation

Standard samples used as calibration samples were commercially available CRMs. These standards are supplied by Geostats Pty Ltd, Mongolia Central Geological Laboratory, Ore Research & Exploration Pty Ltd. Calibration samples with a range of Cu content between 0.14–32 mass% contain five concentrates.

After pulverization to fine grained powder by a chrome steel vessel, each standard sample was pressed into an aluminum ring at 300 kN.

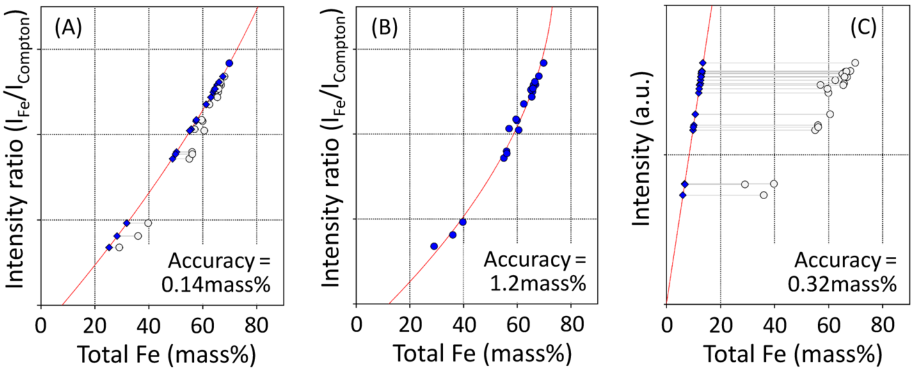

Fig. 2. Calibration curve of total Fe in iron ores with matrix correction.
Instrument: ZSX PrimusIV.
(A): Compton scattering internal standard with theoretical alphas.
(B): Conventional Compton scattering internal standard.
(C): Conventional theoretical alphas.

Table 3. Analytical results by each correction method for iron ore.

(mass%)

Sample	Ore type	Chemical value (T.Fe)	Correction method					
			This report	deviation	Method 2	deviation	Method 3	deviation
ECRM 677–1	—	51.54	51.34	−0.20	53.46	1.92	49.65	−1.89
JSS 821–1	Australian limonite	57.05	56.87	−0.18	59.76	2.71	57.73	0.68
JSS 806–1	Australian hematite	62.77	62.57	−0.20	63.86	1.09	63.86	1.09
ASCRM030	West Pilbara CID	56.76	56.64	−0.12	59.46	2.70	57.27	0.51
ASCRM031	Pilbara Marra Mamba	62.53	62.44	−0.09	63.94	1.41	64.11	1.58
ASCRM032	Pilbara hematite	63.53	63.58	0.05	64.50	0.97	64.35	0.82
ASCRM033	East Pilbara CID	58.45	58.05	−0.40	60.82	2.37	59.46	1.01
ASCRM034	Pilbara fines	61.59	61.53	−0.06	63.05	1.46	61.95	0.36
ASCRM035	Yilgarn hematite	62.35	62.37	0.02	63.59	1.24	62.39	0.04
Accuracy (N=9)		—	0.183		1.88		1.04	

Homma et al.(7) is modified.
Method 2: Conventional theoretical alphas.
Method 3: Conventional Compton scattering internal standard.

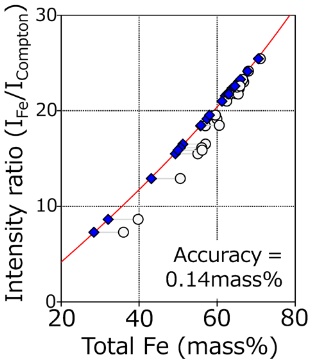

Fig. 3. Calibration curve of total Fe in iron ores
Instrument: Simultix 15.

3.2.2 Instruments

Rigaku's sequential WDXRF ZSX PrimusIV was used for measurements. The measurement condition was 50 kV and 50 mA.

3.2.3 Calibration curves and results

ZSX PrimusIV was calibrated for 21 components: Ni, Cu, Zn, Pb, Co, As, Ag, S, Fe, Mg, Al, Si, P, K, Ca, Ti, Mn, Mo, Sn, Se and Sb. Table 4 shows the concentration range and accuracy of calibrations.

The calibration curve of copper is shown in Fig. 4.

By applying the Compton scattering internal standard with theoretical alpha correction, the accuracy of the calibration improves from 0.51 to 0.14 mass%.

Figure 5 shows the calibration curve of Zn(9) derived from a different standard set from the one described above. These ore standards are polymetallic sulfide ores obtained from volcanogenic massive sulfide deposit, which is an important metal source of Cu, Zn, Pb, Ag and Au. Accuracy of calibration of Zn is also improved by the correction method in this report.

3.3 Nickel ore

There are two different types of nickel ore, oxide ore and sulfide ore, and the constituent minerals of each

Table 4. Accuracy of calibration for copper ore and concentrate.

(mass%)

Component	Range	Accuracy
Cu	0.14 – 32	0.12
Zn	0.0013 – 12	0.080
Ni	0.0021 – 0.13	0.0012
Pb	0.014 – 1.3	0.021
Co	0.0054 – 0.077	0.0055
As	0.0052 – 0.26	0.004
Ag	0.0019 – 0.016	0.0002
S	1.2 – 34	1.2
Fe	1.6 – 30	0.90
Mg	0.038 – 3.2	0.19
Al	0.043 – 7.5	0.34
Si	1.8 – 36	1.2
P	0.0055 – 0.080	0.0024
K	0.078 – 4.7	0.065
Ca	0.16 – 6.3	0.15
Ti	0.044 – 1.0	0.035
Mn	0.022 – 0.13	0.011
Mo	0.0006 – 0.14	0.0026
Sn	0.015 – 0.11	0.008
Se	0.0012 – 0.056	0.0004
Sb	0.0019 – 0.046	0.0011

Instrument: ZSX PrimusIV.

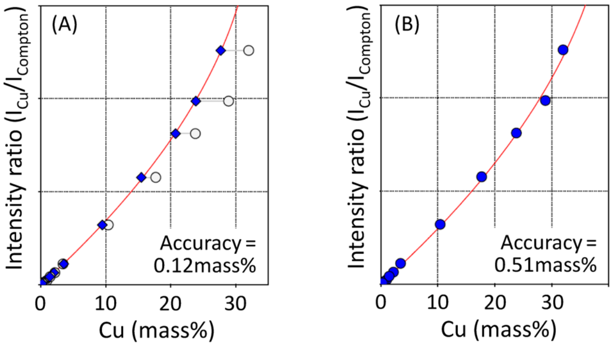

Fig. 4. Calibration curve of Cu in copper ore and concentrate.
Instrument: ZSX PrimusIV.
(A): Compton scattering internal standard with theoretical alpha correction.
(B): Conventional Compton scattering internal standard correction.

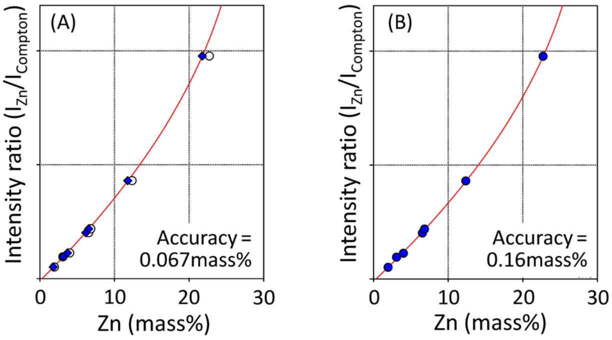

Fig. 5. Calibration curve of Zn in polymetallic sulfide ore.
Instrument: Supermini200.
(A): Compton scattering internal standard with theoretical alpha correction.
(B): Conventional Compton scattering internal standard correction.

are different. The average grade of nickel in sulfide and oxide ore is about 0.6 mass% and 1.3 mass%(10), respectively. Nickel oxide accounts for 70% of total Ni resources but the production volume is almost the same for nickel oxide and sulfide. Since sulfide ore can be concentrated by a floatation process and can smelt easily by existing pyrometallurgical methods, nickel sulfide provides high production volume in spite of its relatively low grade.

Because nickel oxide is difficult to concentrate by beneficiation, oxide ore is shipped as ore or intermediates (ferronickel, matte and mixed sulfide). For nickel oxide smelting, an economically feasible process has not been established. Recently, performance of a hydrometallurgical smelting process for nickel oxide has been improving(10)–(12). In the future, nickel oxide ores will expand nickel production.

Valuable metals in nickel ores are Ni, Co, Cu and platinum group metals (PGMs). Nickel sulfide often contains Cr, Mn, Fe, Zn, As, Pb and so forth as impurity elements(8). Since Mg, Al and Ca consume sulfuric acid in the hydrometallurgical process for nickel oxide, which can increase processing cost, it is essential to control these light elements. The analysis instrument needs to be highly sensitive for these light elements as well as capable of analyzing trace impurities.

In the case of XRF analysis, the wavelength of Co Kα is close to the Fe Kb1 line, so the Co Kα line from trace Co is overlapped by the abundant Fe in Ni ore. High spectral resolution is necessary for analysis by XRF. Owing to its sensitivity for light elements and spectral resolution, wavelength dispersive type XRF is suitable for nickel ore analysis.

3.3.1 Reference standard samples and sample preparation

Commercially available standard samples were used for making a calibration for Ni oxide ores. These are commercially available CRMs supplied by ECRM, Geostats Pty Ltd, Ore Research & Exploration Pty Ltd. These standards are typical nickel oxide ores, such as nickel laterite ores, including limonite, transitional type and saprolite. This implies that these standards cover nickel oxide ores for almost the entire stratigraphic profile from bottom to top in typical nickel laterite deposits. The concentration ranges of nickel and cobalt are 0.37–2.9 mass% and 0.021–0.090 mass%, respectively.

Each standard sample was pressed into an aluminum ring at 150 kN after pulverization by a chrome-steel vessel. Pressing was performed without any binding agent. The pelletized samples were covered with 4 μm thick prolene thin film during the measurement.

Calibration curves for Ni sulfide ores used standard samples supplied by Geostats Pty Ltd, IGS, Ore

Research & Exploration Pty Ltd. Nickel content in these standards, including nickel concentrate, is 0.41–11.7 mass%. After pulverizing in a chrome-steel vessel, these standards were pressed into aluminum ring at 150 kN. As with the oxide ores, no binding agent was used for pressing.

3.3.2 Instruments

The measurement of oxide ores was performed using a Rigaku Supermini200, WDXRF spectrometer. The measurement condition was 50 kV–4 mA. For the analysis for sulfide ores, the Simultix 15 simultaneous spectrometer, was used, running at 50 kV–50 mA.

Table 5. Accuracy of calibration for nickel oxide ore.

(mass%)

Component	Range	Accuracy
Ni	0.37 – 2.9	0.030
Co	0.002 – 0.090	0.0031
Fe	8.9 – 47	0.27
Mg	1.2 – 17	0.32
Na	0.006 – 0.47	0.016
Al	0.62 – 4.5	0.19
Si	3.2 – 33	0.71
P	0.002 – 0.017	0.0010
S	0.002 – 1.3	0.016
K	0.009 – 0.28	0.0018
Ca	0.095 – 9.0	0.021
Ti	0.012 – 0.21	0.0014
Cr	0.14 – 1.8	0.022
Mn	0.009 – 0.28	0.0067
Cu	0.085 – 0.58	0.0019
Zn	0.005 – 0.14	0.0017

Instrument: Supermini200.

3.3.3 Calibration curves and results

For nickel oxide ores, 16 elements, Ni, Co, Fe, Mg, Na, Al, Si, P, S, K, Ca, Ti, Cr, Mn, Cu and Zn were calibrated. Table 5 shows the calibration range and accuracy of calibration of each element. The Compton scattering internal standard with theoretical alpha correction was applied to Ni, Fe and Zn. Nickel oxide ore originates from deep weathering of ultramafic rocks, so it is abundant in Fe and Mg. The Fe content in nickel oxide varies from about 10 to 50 mass%. Figure 6 shows calibration curves of Fe(13). Calibration standards were analyzed using the obtained calibrations. The analytical results for Fe between the Compton scattering internal standard with/without theoretical alpha corrections are compared in Table 6. It shows that the correction method in this report improves the accuracy of Fe in nickel oxide ores.

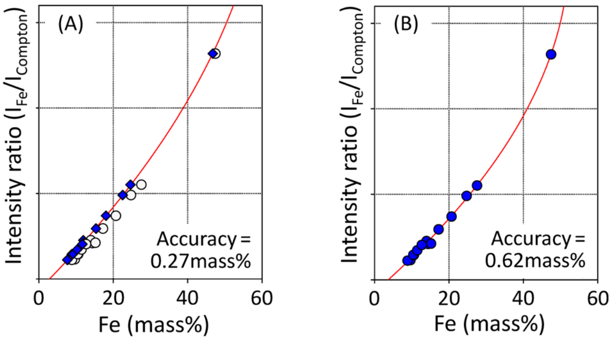

Fig. 6. Calibration curve of Fe in nickel oxide ore.
Instrument: Supermini200.
(A): Compton scattering internal standard with theoretical alpha correction.
(B): Conventional Compton scattering internal standard correction.

Table 6. Analysis results of total iron in nickel oxide ore by each correction method.

(mass%)

Sample	Chemical value (T.Fe)	Correction method					
		This report	deviation	Method 2	deviation	Method 3	deviation
1	47.46	47.49	0.03	47.73	0.27	47.45	−0.01
2	14.4	14.1	−0.3	14.3	−0.1	13.7	−0.7
3	9.68	9.66	−0.02	9.52	−0.16	9.33	−0.35
4	14	14.8	0.8	15.2	1.2	14.4	0.4
5	15.2	14.8	−0.4	14.9	−0.3	13.7	−1.5
6	10.6	10.9	0.3	10.8	0.2	10.7	0.1
7	20.72	20.66	−0.06	20.23	−0.49	20.48	−0.24
8	8.90	9.00	0.1	9.10	0.2	9.18	0.28
9	27.57	27.72	0.15	27.60	0.03	27.45	−0.12
10	10.45	10.44	−0.01	10.60	0.16	10.75	0.3
11	24.76	24.75	−0.01	24.16	−0.6	25.20	0.44
12	17.23	16.99	−0.24	17.17	−0.06	17.37	0.14
13	11.48	11.41	−0.07	11.69	0.21	11.98	0.5
14	12.70	12.54	−0.16	12.80	0.1	13.41	0.71
Accuracy (N=14)	—	0.28		0.49		0.55	

Create from Application Note(13).
Method 2: Conventional theoretical alphas.
Method 3: Conventional Compton scattering internal standard.

Table 7. Accuracy of calibration for nickel sulfide ore.

(mass%)

Component	Range	Accuracy
Ni	0.41 – 12	0.070
Cu	0.022 – 1.5	0.020
Co	0.013 – 0.27	0.0075
Zn	0.0067 – 2.7	0.0042
Pb	0.0011 – 0.21	0.0038
As	0.0005 – 0.21	0.0031
S	1.4 – 27	0.78
Cr	0.0096 – 0.22	0.018
Fe	6.8 – 45	0.79
Na	0.053 – 1.9	0.097
Mg	1.2 – 20	0.91
Al	0.55 – 6.8	0.20
Si	4.5 – 24	0.87
P	0.0075 – 0.077	0.0018
K	0.019 – 1.1	0.021
Ca	0.51 – 5.9	0.18
Ti	0.039 – 1.1	0.011
Mn	0.027 – 0.13	0.0026

Instrument: Simultix 15.

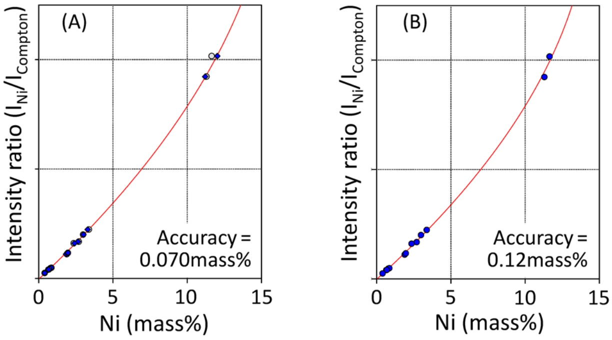

Fig. 7. Calibration curve of Ni in nickel sulfide ore and concentrate.
Instrument: Simultix 15.
(A): Compton scattering internal standard with theoretical alphas.
(B): Conventional Compton scattering internal standard.

For the nickel sulfide ores, 18 elements, Ni, Cu, Co, Zn, Pb, As, S, Cr, Fe, Na, Mg, Al, Si, P, K, Ca, Ti and Mn, were calibrated (Table 7). Figures 7 and 8 are calibration curves of Ni and Fe$^{(14)}$, respectively. Satisfactory calibration curves are obtained as with the oxide ores.

4. Summary

The Compton scattering internal standard integrated with theoretical alpha correction improves the accuracy of calibration curves of metal elements in ore and concentrate. Whereas the conventional Compton scattering internal standard method is intended for trace components, this correction method allows satisfactory results in the high-concentration range, such as total iron in iron ores, copper and iron in Cu concentrate.

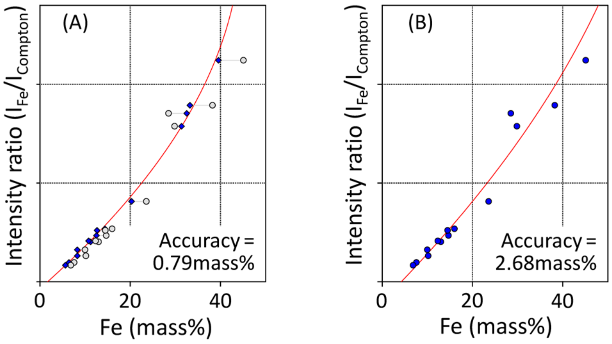

Fig. 8. Calibration curve of Fe in nickel sulfide ore and concentrate.
Instrument: Simultix 15.
(A): Compton scattering internal standard with theoretical alphas.
(B): Conventional Compton scattering internal standard.

This correction method has the advantage that the analytical result is less influenced by analytical errors from existing components because theoretical alphas obtained by this correction method are about one order of magnitude smaller than conventional standard theoretical alphas without an internal standards correction. In the XRF analysis by pressed pellet method for powder samples, it is difficult to eliminate errors caused by particle size and mineralogical effects. The fused bead technique can eliminate errors from the properties in powders mentioned above, but the method is generally expensive and time-consuming. That is a heavy burden for mine site requiring analysis of large quantities of ore sample to control their mineral processing processes.

There is a practical advantage in this method, because it enables results to be less influenced by analytical errors from coexisting components.

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