Comparison of analysis results between the fusion method and the pressed powder method for powder sample analysis

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1. Introduction

The fusion method and the pressed powder method are well-known and typical sample preparation techniques in X-ray fluorescence analysis of powder samples(1), (2). In the fusion method, a sample is fused with some alkali borate flux at high temperature to make a glass bead. The method allows more accurate analysis because it provides a substantially homogeneous sample specimen for analysis. It is, however, a costly and time-consuming technique. For highly precise analysis, a fusion machine is essential for making fused beads under identical conditions.

In the pressed powder method, a briquette is formed by pressing a ground powder sample with a ring or cup using a pressing machine. The pressed powder method is a very simple technique that requires no skills or experience. Therefore, this method is suited for rapid analysis or analysis of large quantities of sample. The pressed powder method, however, can create some errors due to grain size and mineralogical heterogeneity effects during sample measurement. It is nearly impossible to eliminate these heterogeneity effects in all powder samples, especially with materials such as soils, rocks, ores, etc., which are composed of different types of grains. Therefore, large differences can occur between analysis results and the actual chemical content.

Both the fusion method and the pressed powder method have advantages and disadvantages as described above. Generally, the optimal sample preparation method for each material is determined by considering requirements such as precision, cost, preparation time, etc. This report provides a comparison between analysis results using the fusion method and the pressed powder method applied to three materials: iron ores, silicate rocks and cements. In the industrial and research fields, the X-ray fluorescence technique is commonly used to control manufacturing processes, to monitor product quality and to determine geochemical characterization. In these three material fields, either the fusion method or the pressed powder method is selected in accordance with the purpose of analysis.

In this report, calibration curves for major components are prepared by both sample preparation methods, and analyses of identical samples with chemical values are performed by each method. The standard error of the estimate (formula (1)) as accuracy obtained by the differences between chemical values and analyzed values of calibration standards is calculated and compared between the two methods.

$$\sigma_{est} = \sqrt{\frac{\sum (X - X')^2}{N}} \qquad (1)$$

X: Chemical value
X': Analysis value by XRF
N: Number of samples

This report focuses on sample preparation methods in XRF analysis and regards the differences observed between the two methods as being mainly caused by differences in sample preparation. Analytical errors actually include many factors, such as statistical errors, measurement conditions, and the correction method for matrix effects, in addition to those arising from the sample preparation method. Even when the same sample preparation method is performed, some differences in conditions of preparation can cause differences in results. Therefore, it is generally difficult to evaluate the data in this report quantitatively. The results shown in this report should be regarded as qualitative observations.

2. Iron ores

Commercially available certified reference materials (CRM), supplied by numerous institutions around the world, were used as standard samples for iron ore analysis. These standard materials are composed of both natural ore and processed ore, including sinter and pellet.

Fused beads were prepared such that the well-dried samples were fused with lithium tetraborate, $Li_2B_4O_7$ as a flux, with sample to flux ratio 1 : 10(3). A fusion machine was used for fusing at 1150°C. 50 μL of a 50% solution of LiI was added as releasing agent, and 0.24 g of $NaNO_3$ was also added as an oxidizing agent.

Calibration curves by the fusion method were prepared using 26 CRMs. The spectrometer used for iron ore analysis was Rigaku's ZSX Primus IV wavelength dispersive sequential X-ray fluorescence (WDX) spectrometer equipped with 4 kW X-ray tube. Corrections for inter-element effects were applied to

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each calibration using theoretical alpha coefficients generated by the fundamental parameter program. These coefficients are calculated considering ignition loss. The dilution ratio correction was also applied to correct for weighing error.

Sample specimens for the pressed powder method were prepared as follows. Powder of iron ore sample was ground with a vessel of tungsten carbide by the wet method and pressed into an aluminum ring at 250 kN. No binding agent was used. Measurements were performed using the same ZSX Primus IV spectrometer as for the fusion method above. Calibration curves were obtained using 30 CRMs. The matrix correction for Fe used the Compton scattering internal standard correction with the theoretical alpha method(4),(5). Calibrations for all other components are corrected using the conventional theoretical alpha method.

Twenty-one standard samples, which were used for both calibrations by the fusion method and the pressed powder method, were analyzed as test samples. Table 1 shows the standard error of the estimate for each component using all analysis results. The calibration range and accuracy of calibration are shown in Table 2. In the fused bead, all components exist as oxides after fusing. Therefore, the results are output for the oxide

Table 1. Calculated standard error of the estimate (Iron ores: 21 samples).

Component	Pressed powder method (mass%)	Fusion method (mass%)
Total Fe	0.20	0.15*
MnO	0.0072	0.0067
TiO_2	0.011	0.0039
CaO	0.087	0.063
K_2O	0.016	0.0025
S	0.0082	0.0082*
P	0.0094	0.0034*
SiO_2	0.74	0.099
Al_2O_3	0.43	0.028
MgO	0.50	0.044

*: Recalculated to element form

Table 2. Calibration curves of iron ores.

Component	Pressed powder method (mass%)		Fusion method (mass%)	
	Calibration range	Accuracy of calibration	Calibration range	Accuracy of calibration
Total Fe	20–69	0.13	20*–71*	0.091*
MnO	(0)–1.0	0.0051	(0)–1.3	0.0066
TiO_2	(0)–6.3	0.0065	(0)–7.7	0.0057
CaO	(0)–19	0.11	(0)–22	0.077
K_2O	(0)–(0.67)	0.010	(0)–0.72	0.0047
S	(0)–0.84	0.0099	(0)–0.84*	0.0076*
P	(0)–0.59	0.0067	(0)–0.71*	0.0040*
SiO_2	(0)–53	0.65	(0)–53	0.12
Al_2O_3	(0)–6.4	0.42	(0)–7.2	0.032
MgO	(0)–3.4	0.13	(0)–3.2	0.035

*: Recalculated to element form

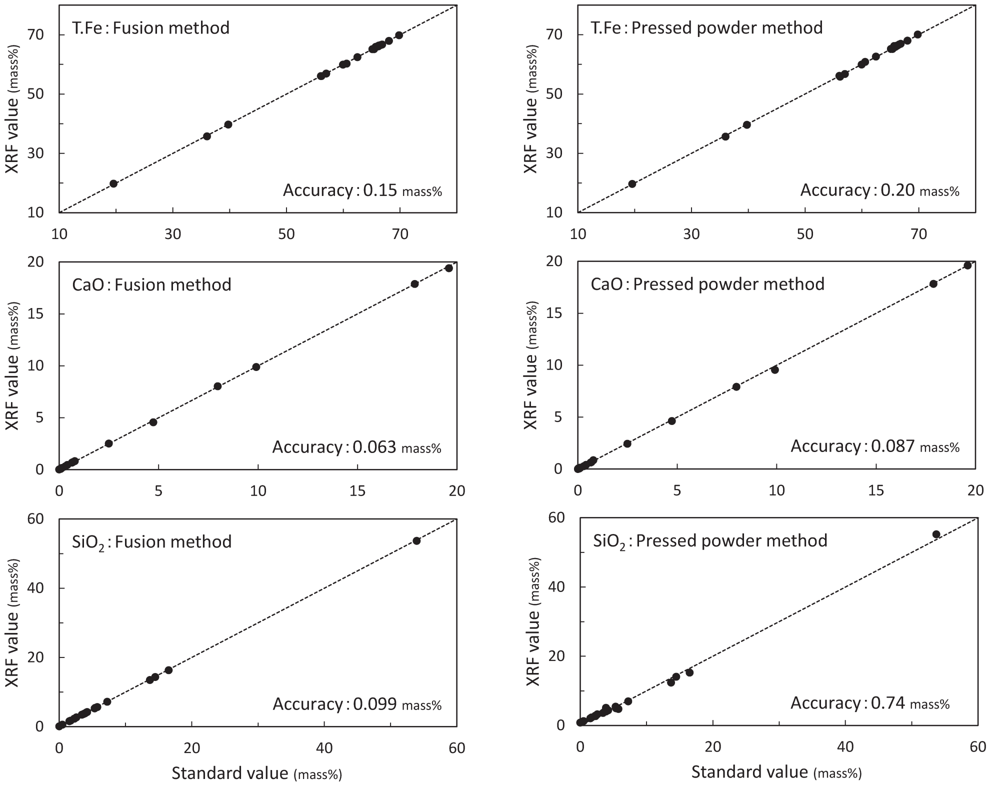

Fig. 1. Representative results of iron ore analysis.

form in the fusion bead analysis. Three components in the fusion method, Fe_2O_3, P_2O_5 and SO_3, are converted to total Fe, P and S in the element form for comparison (see Table 1 and 2). The relationships between the standard value and the XRF value for total Fe, CaO and SiO_2 are shown in Fig. 1.

The fusion method shows good accuracy for all components except for sulfur, which are almost the same results between the two methods. The difference has a tendency to be larger with lighter components.

3. Silicate rocks

For the silicate rock analysis, calibration curves were prepared using geochemical reference samples issued by the Geological Survey of Japan (GSJ). The reference samples used in this analysis range from ultramafic to felsic rocks. All test samples analyzed were selected from geochemical reference samples used for preparing calibration curves.

Low dilution fusion beads were prepared with mixed flux, Spectroflux100B, at a dilution ratio of 1 : 2, sample to flux.

Calibration curves were prepared from measurements of 14 standard samples, performed with the WDX spectrometer ZSX Primus IV. Matrix effects were corrected by the theoretical alpha method, the same as with the iron ore analysis reported above. Theoretical alpha coefficients were calculated considering ignition loss during fusion.

The pressed pellet samples were prepared by pressing sample material into a polyvinyl chloride (PVC) ring

Table 3. Calculated standard error of the estimate (Silicate rocks: 9 samples).

Component	Pressed powder method (mass%)	Fusion method (mass%)
Fe_2O_3	0.37	0.053
MnO	0.0031	0.0019
TiO_2	0.056	0.0080
CaO	0.088	0.073
K_2O	0.074	0.030
P_2O_5	0.010	0.0044
SiO_2	0.62	0.35
Al_2O_3	0.53	0.069
MgO	0.81	0.042
Na_2O	0.15	0.033

Table 4. Calibration curves of silicate rocks.

Component	Pressed powder method (mass%)		Fusion method (mass%)	
	Calibration range	Accuracy of calibration	Calibration range	Accuracy of calibration
Fe_2O_3	0.77–15	0.42	0.77–15	0.054
MnO	0.016–0.21	0.0039	0.016–0.21	0.0022
TiO_2	0.0060–1.6	0.055	0.044–1.6	0.0089
CaO	0.093–14	0.16	0.093–14	0.053
K_2O	0.0030–4.7	0.071	0.059–4.7	0.026
P_2O_5	0.0020–0.29	0.011	0.0020–0.29	0.0043
SiO_2	43–76	0.58	44–76	0.22
Al_2O_3	0.66–23	0.64	12–23	0.065
MgO	0.040–44	0.85	0.037–9.6	0.043
Na_2O	0.021–4.7	0.15	0.92–4.7	0.030

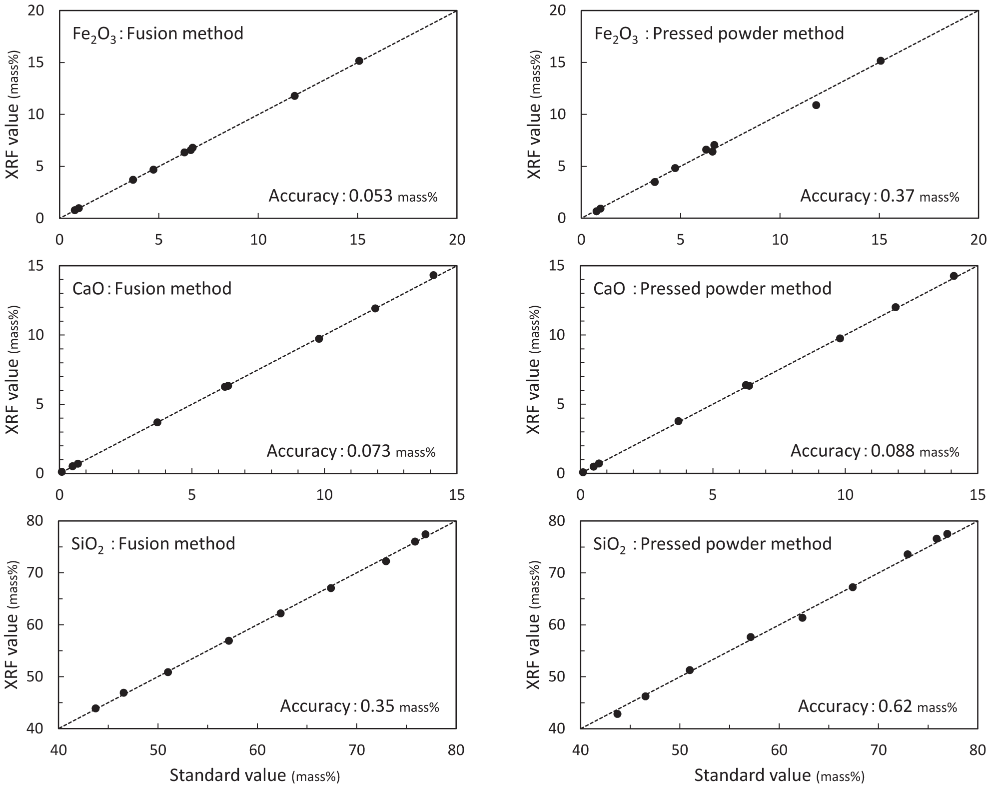

Fig. 2. Representative results of silicate rock analysis.

at 150 kN after drying. Additional grinding was not performed. Terashima *et al*. reported the geochemical reference samples of GSJ are less than 10 μm in average grain size except for some reference samples in the earliest issue(6). As the GSJ reference samples used in this analysis don't include these earliest issued samples, samples were used without any grinding. Calibration curves were prepared using 13 standards with the ZSX Primus IV.

Nine reference materials were analyzed for testing. The standard error of the estimate is shown in Table 3. Table 4 shows the accuracy of calibration. Figure 2 shows the plot of XRF results to standard values for Fe_2O_3, CaO and SiO_2.

The fusion method shows good results relative to the pressed powder method for all components. The differences between the two methods are more remarkable than the iron ore results.

4. Cement

In the cement analysis, certified reference materials of cement issued by the National Institute of Standards and Technology (NIST) were used.

Sample preparation for fusion method is as follows. Sample 1.0 g, which was ignited at 950°C in advance and lithium tetraborate flux 4.0 g were exactly weighed and then mixed together. The mixture was fused by a fusion machine at 1200°C(7). Nine fusion beads were used as calibration standards. Matrix effects were corrected by the theoretical alpha method. The values normalized without ignition loss were used for calibration standard values because all samples were ignited.

The pressed pellets were prepared by grinding with the tungsten carbide vessel. The grinding was performed under wet conditions with n-hexane as a grinding aid. After grinding, well-dried samples were pressed into an aluminum ring at 150 kN(8). Seven pressed pellets were prepared for calibration standards and the ZSX Primus IV was calibrated using them. The theoretical alpha correction was applied to correct matrix effects.

Seven Portland cement standards used as calibration standards were analyzed for testing. The standard error of the estimate calculated by analysis results is shown in Table 5. The accuracy of the calibration is summarized in Table 6. The results of the fusion method were recalculated to the values including ignition loss. Analytical results for Fe_2O_3, CaO and SiO_2 are plotted in Fig. 3.

In cement analysis, the fusion method shows good results for elements lighter than sulfur. No difference is found between the two sample preparation methods for elements heavier than phosphorus, unlike for iron ores and silicate rocks.

5. Discussion

In the experiments for the iron ores and silicate rocks, differences are found between the fusion method and the pressed powder method. In contrast, cement shows almost no difference except for some light elements.

When the differences between materials observed in this report were mainly caused by mineralogical effects, this observation can be explained as follows.

In the cement (Portland cement) manufacturing process, limestone, clay, silica and iron oxide are mixed together and heated at high temperature to make clinker and then the clinker is mixed with gypsum to make cement product. The main component phases comprising the clinker are four minerals, alite ($3CaO\cdot SiO_2$, tricalcium silicate), belite ($2CaO\cdot SiO_2$, dicalcium silicate), aluminate phase ($3CaO\cdot Al_2O_3$, tricalcium aluminate) and ferrite phase ($4CaO\cdot Al_2O_3\cdot Fe_2O_3$, tetracalcium aluminoferrite). The properties of cement depend on the proportion of these 4 phases. Most types of cement are composed of 70–80% alite + belite. All cement samples used for this analysis are Portland cement. They have the same mineral assemblage and have small variations in mineralogical proportion so mineralogical effects are suggested to be relatively less than for other materials. Silicate rocks are composed of a variety of rock forming minerals. Some

Table 5. Calculated standard error of the estimate. (Portland cement: 7 samples).

Component	Pressed powder method (mass%)	Fusion method (mass%)
Fe_2O_3	0.022	0.021
Mn_2O_3	0.0008	0.0010
TiO_2	0.0031	0.0023
CaO	0.12	0.13
K_2O	0.0042	0.025
SO_3	0.056	0.074
P_2O_5	0.0022	0.0014
SiO_2	0.092	0.034
Al_2O_3	0.099	0.035
MgO	0.049	0.030
Na_2O	0.0063	0.0087

Table 6. Calibration curves of cement.

Component	Pressed powder method (mass%)		Fusion method (mass%)	
	Calibration range	Accuracy of calibration	Calibration range	Accuracy of calibration
Fe_2O_3	0.16–3.0	0.024	0.078–14	0.023
Mn_2O_3	0.0070–0.25	0.0010	0.0030–0.26	0.0051
TiO_2	0.084–0.36	0.0038	0.020–1.7	0.0030
CaO	58–67	0.14	30–68	0.14
K_2O	0.093–1.2	0.0051	0.014–1.2	0.026
SO_3	2.1–4.6	0.068	0–4.6	0.089
P_2O_5	0.022–0.30	0.0026	0.0030–0.31	0.0015
SiO_2	19–22	0.18	0.24–22	0.037
Al_2O_3	3.9–7.0	0.12	3.9–70	0.039
MgO	0.82–4.4	0.058	0.19–4.5	0.040
Na_2O	0.021–1.0	0.0073	0.021–1.0	0.0091

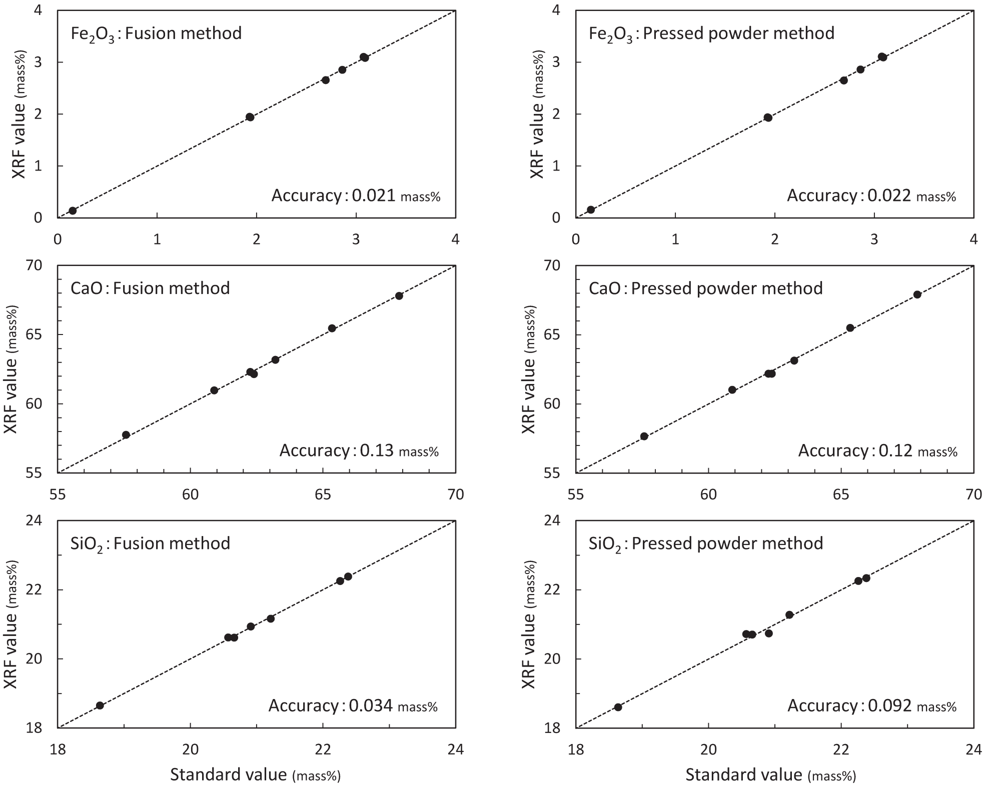

Fig. 3. Representative results of Portland cement analysis.

mineral species form solid solutions and show diverse chemical compositions. Mineral assemblage in silicate rocks varies widely with variations of rock facies and bulk chemical composition so that rock samples are significantly affected by mineralogical effects. Iron ore samples have smaller variations in mineral assemblage than silicate rocks. Iron minerals dominantly consisting of iron ores are markedly different from ore types. In the pressed powder method, generally, mineralogical effects appear largely in iron ore analysis except for the case where samples matched in mineral assemblage are used in the analysis.

6. Summary

Comparisons were made with accuracy between two sample preparation methods, the fusion method and the pressed powder method. The results demonstrate that the fusion method is better than the pressed powder method for silicate rocks and iron ores. On the contrary, results for cement show no significant difference between the two methods except for some light elements. Although it is true that the fusion method eliminates grain size and mineralogical effects in powder sample analysis, observations in this report indicate that analytical results for the fusion method are not always better than the pressed powder method in every situation.

For elements lighter than sulfur, it is observed that the fusion method is better than the pressed powder method. When the materials are limited to the three used in this study, the fusion method can be concluded superior than the pressed powder method in analytical accuracy for light element analysis.

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