Analysis of cement according to ASTM C114 and JIS R5204 using Supermini benchtop WDX spectrometer

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1. Introduction

Owing to the recent developments in emerging nations, the consumptions and, therefore, the productions of cement are increasing rapidly. Worldwide demands for benchtop X-ray fluorescence spectrometers, as main analyzing systems in medium-size cement factories or as backup systems in large factories and laboratories, are rising very quickly.

Since Supermini is a benchtop wavelength dispersive X-ray fluorescence (WDX) spectrometer equipped with an air-cooled X-ray tube and without the need of using cooling water, it meets such demands. Supermini offers the XRF analysis with high precision and sensitivity even for light elements, which are the most well-known features of a WDX spectrometer over an Energy dispersive X-ray fluorescence (EDX) spectrometer.

Results on a cement analysis using Supermini according to the U.S. ASTM (American Society for Testing and Materials) C114 standard test(1) as well as the Japanese JIS R5204 "Chemical analysis method of cement by x-ray fluorescence" method,(2) are reported and discussed.

2. ASTM C114

The technical specifications of the ASTM C114 standard test methods for chemical analysis of hydraulic cement are outlined as follows;

(1) "Standard Reference Material" (SRM) supplied by National Institute of Standards and Technologies (NIST) shall be used.
(2) Two rounds of test including sample preparation and measurement of each SRM shall be carried out on nonconsecutive days.
(3) The differences between values and averages of the values from the two rounds of tests shall be calculated. When seven SRM's are used in the qualification procedure, at least six of the seven differences between duplicates obtained for any single component shall not exceed the given limits prescribed by ASTM C114, and at least six averages for each oxide component shall not differ from the certified concentrations. The remaining differences and averages shall not exceed or differ by no more than twice the prescribed limits. When more than seven SRM's are used, the values for at least 77% of the samples shall be within the prescribed limits, while the values for the remainder shall differ by no more than twice that value. When a lesser number of SRM's are required, all of the values shall be within the prescribed limits.

According to the "Performance Requirement for Rapid Test Methods" of ASTM C114, at least seven SRM's should be used. The results of the analysis according to the rapid test methods are reported in this article.

The results of the analysis using briquette samples, which meet ASTM C114, have already been introduced in reference (3). Those using fused bead samples meet the standard in wider range of components because of the elimination of heterogeneity effect, which have also been introduced in reference (4).

3. Experimental procedure

3.1. Sample

The NIST standard samples used in this study are listed in Table 1. The content range of each oxide component is shown in Table 2.

3.2. Sample preparation

The specifications on the ASTM C114 rapid test methods don't define the sample preparation and analysis methods. On the other hand, JIS R5204 describes XRF analysis using fused bead method. For a direct comparison of the results of these two standard test methods, the fused bead method was employed.

Each sample was mixed with flux (lithium tetraborate)

Table 1. Cement sample used for analysis.

Sample	Type
SRM1881a	Portland Cement (Blended with Slag and Fly Ash)
SRM1882a	Calcium Aluminate Cement
SRM1883a	Calcium Aluminate Cement
SRM1884a	Portland Cement
SRM1885a	Portland Cement
SRM1886a	Portland Cement (White Portland Cement with Low Iron)
SRM1887a	Portland Cement
SRM1888a	Portland Cement
SRM1889a	Portland Cement (Blended with Limestone)

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Table 2. Content range of each component.

Component	Content range (mass%)		
CaO	29.52	-	67.87
SiO_2	0.24	-	22.38
Al_2O_3	3.875	-	70.04
Fe_2O_3	0.078	-	14.67
SO_3	2.086	-	4.622
MgO	0.19	-	4.475
K_2O	0.014	-	1.228
TiO_2	0.020	-	1.786
Na_2O	0.021	-	1.068
P_2O_5	0.003	-	0.306
Mn_2O_3	0.003	-	0.2588
ZnO	0.001	-	0.107

at the ratio of sample 1.0 g to flux 4.0 g after ignition at 950°C. The mixture of the sample and flux was fused in a platinum crucible with a benchtop fluxer to make a fused bead.

3.3. Measuring conditions

Measuring conditions are shown in Tables 3 and 4.

4. Results

4.1. Creation of calibration curves

Matrix correction was applied to correct influence of coexisting components in creating calibration curves. The coefficients of the matrix correction were theoretically calculated using the fundamental parameter (FP) method, also called "theoretical alphas". In the FP calculation, all elements are assumed to be distributed homogeneously in a sample and theoretical intensities of all elements are calculated from fundamental parameters (chemical composition, physical parameters and sensitivity of the analyzing system). The software for Supermini has an automatic computation program, which calculates theoretical alphas when a correction model and representative components are given. The de Jongh model was used in the calculation with CaO set as the base component. The theoretical alphas were adopted in creating calibration curves as shown in Figs. 1 to 12. The open circles in the figures represent the plots before the matrix correction and the blue squares represent those after the correction.

Table 3. Measuring conditions of the Supermini system.

System	Benchtop WDX spectrometer "Supermini"
X-ray tube	Pd target, 200 W
Tube voltage	50 kV
Tube current	4 mA
Measuring diameter	30 mm
Path atmosphere	Vacuum

4.2. Evaluation according to ASTM C114

According to the specifications of ASTM C114, a quantitative analysis for each pair of NIST standard samples of cement was carried out using the calibration curves shown in Figs. 1 to 12. The results of the analysis were tabulated in Tables 5 and 6. In Table 5, "Maximum difference (experimental result)" stands the maximum value of the differences between two analysis values of the same standard sample. In Table 6, it represents the maximum value of the differences between the average of two analysis values and the certificate value of each SRM. All results are within the ASTM C114 specifications, which indicates that Supermini meets ASTM C114 qualification requirements.

4.3 Evaluation according to JIS R5204

The procedure for JIS R5204 is outlined as follows;

(1) More than 7 certified standard samples shall be used to create calibration curves and at least one pair of fused beads of a certified standard sample, which must not be contained in the calibration, shall be prepared as "glassbeads for validation".
(2) Quantitative analysis shall be carried out on the fused beads for validation.
(3) The differences between the duplicates and those of the averages of the duplicate from the certificate values, in the same manner as ASTM C114, shall be calculated and they shall be within standard values.

Unlike ASTM C114, the standard values are determined depending on the averaged value of duplicates.

In this article, SRM1881a to 1888a were used for calibration and SRM1889a was used for evaluation and

Table 4. Measuring conditions for each element.

Component	CaO	SiO_2	Al_2O_3	Fe_2O_3	SO_3	MgO	K_2O	TiO_2	Na_2O	P_2O_5	Mn_2O_3	ZnO
Element	Ca	Si	Al	Fe	S	Mg	K	Ti	Na	P	Mn	Zn
Measured line	Kα	Kα	Kα	Kα	Kα	Kα	Kα	Kα	Kα	Kα	Kα	Kα
Primary beam filter	out	out	out	out	out	out	Al	out	out	out	out	out
Analyzing crystal	PET	PET	PET	LiF(200)	PET	RX25	PET	LiF(200)	RX25	PET	LiF(200)	LiF(200)
Detector	F-PC	F-PC	F-PC	SC	F-PC	F-PC	F-PC	SC	F-PC	F-PC	SC	SC
Measuring time (sec)	60	40	40	20	20	60	40	20	60	40	20	20

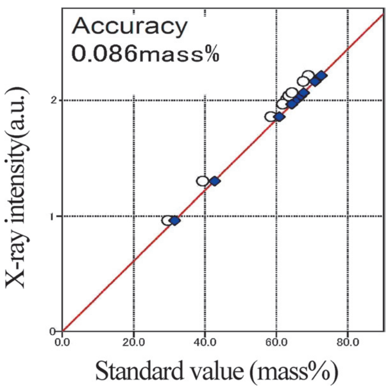

Fig. 1. Calibration curve (CaO).

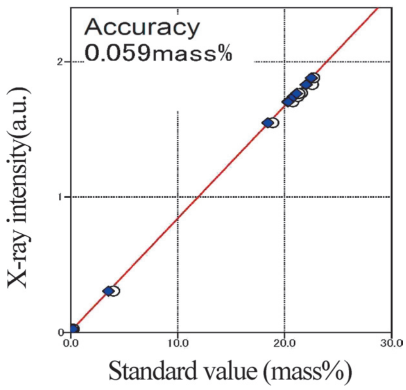

Fig. 2. Calibration curve (SiO_2).

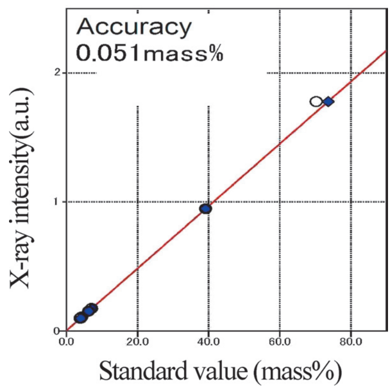

Fig. 3. Calibration curve (Al_2O_3).

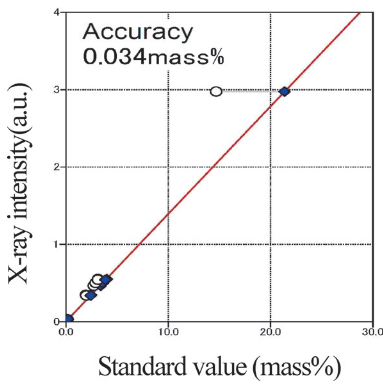

Fig. 4. Calibration curve (Fe_2O_3).

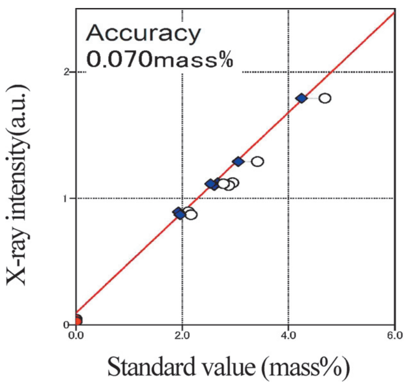

Fig. 5. Calibration curve (SO_3).

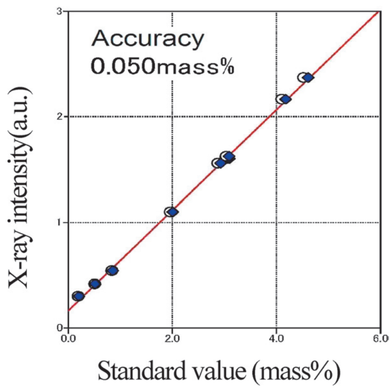

Fig. 6. Calibration curve (MgO).

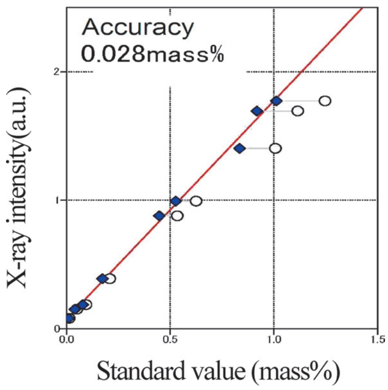

Fig. 7. Calibration curve (K_2O).

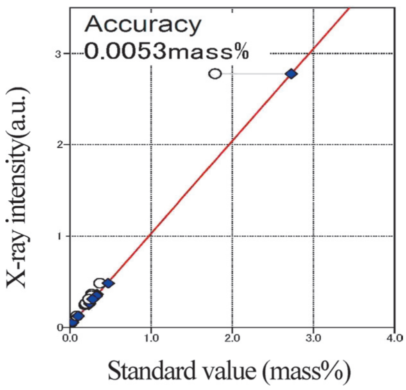

Fig. 8. Calibration curve (TiO_2).

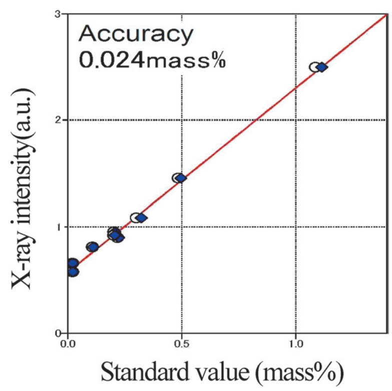

Fig. 9. Calibration curve (Na_2O).

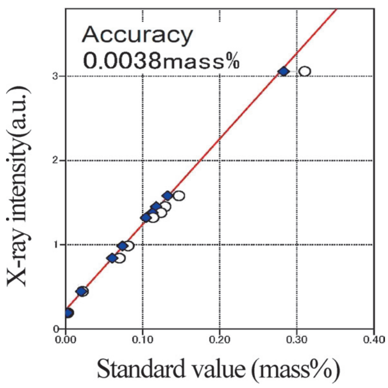

Fig. 10. Calibration curve (P_2O_5).

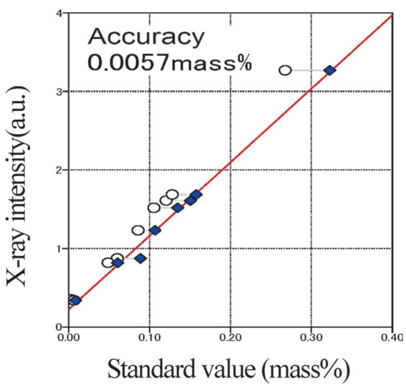

Fig. 11. Calibration curve (Mn_2O_3).

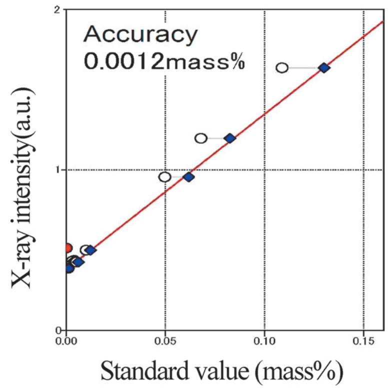

Fig. 12. Calibration curve (ZnO).

Table 5. Result of the evaluation for ASTM C114 (difference between duplicates, unit: mass%).

Component	ASTM C114 requirement	Maximum difference (experimental result)
CaO	0.20	0.13
SiO_2	0.16	0.09
Al_2O_3	0.20	0.09
Fe_2O_3	0.10	0.02
SO_3	0.10	0.08
MgO	0.16	0.05
K_2O	0.03	0.01
TiO_2	0.02	0.01
Na_2O	0.03	0.03
P_2O_5	0.03	0.00_3
Mn_2O_3	0.03	0.00_4
ZnO	0.03	0.00_1

Table 6. Result of the evaluation for ASTM C114 (difference between the average of duplicates and the certificate value, unit: mass%).

Component	ASTM C114 requirement	Maximum difference (experimental result)
CaO	0.3	0.1
SiO_2	0.2	0.1
Al_2O_3	0.2	0.2
Fe_2O_3	0.10	0.05
SO_3	0.1	0.1
MgO	0.2	0.1
K_2O	0.05	0.05
TiO_2	0.03	0.01
Na_2O	0.05	0.03
P_2O_5	0.03	0.01
Mn_2O_3	0.03	0.01
ZnO	0.03	0.00_2

Table 7. Result of the evaluation for JIS R5204 (difference between duplicates).
(Evaluation sample: SRM1889a, unit: mass%)

Component	JIS R5204 requirement	Experimental result
CaO	0.236	0.074
SiO_2	0.136	0.057
Al_2O_3	0.061	0.000
Fe_2O_3	0.044	0.011
SO_3	0.051	0.045
MgO	0.029	0.026
K_2O	0.025	0.011
TiO_2	0.016	0.011
Na_2O	0.014	0.014
P_2O_5	0.011	0.002
Mn_2O_3	0.017	*0.001*
ZnO	0.002	0.000

Table 8. Result of the evaluation for JIS R5204 (difference between the average of duplicates and the certificate value).
(Evaluation sample: SRM1889a, unit: mass%)

Component	JIS R5204 requirement	Experimental result
CaO	0.25	0.05
SiO_2	0.15	0.08
Al_2O_3	0.08	0.08
Fe_2O_3	0.08	0.00
SO_3	0.08	0.06
MgO	0.03	0.00
K_2O	0.03	0.01
TiO_2	0.02	0.01
Na_2O	0.02	0.01
P_2O_5	0.02	0.01
Mn_2O_3	0.02	0.01
ZnO	0.02	0.00

verification of the suitability of Supermini for JIS R5204. The results of the verification are shown in Tables 7 and 8. It should be noted that the analytical result for Mn_2O_3 (shown in italics in Table 7) is for information only, because its content is out of the calibration range. These results verify the suitability of using Supermini for the JIS R5204 test.

5. Summary

Our evaluation results clearly show that Supermini meets the qualification specifications of both ASTM C114 and JIS R5204. In addition, the low dilution fused bead method enables the cement analysis conforming with these standards in wide ranges of oxide concentrations in aluminum cement as well as Portland cement.

References

(1) ASTM C114: Standard Test Methods for Chemical Analysis of Hydraulic Cement.
(2) JIS R5204: Chemical analysis method of cement by x-ray fluorescence.
(3) Rigaku Application Report XRF196, Analysis of Portland Cement according to ASTM C114 in Powder Method Using Benchtop WDX Spectrometer Supermini.
(4) Rigaku Application Report XRF197, Analysis of Cement according to ASTM C114 in Fusion Bead Method Using Benchtop WDX Spectrometer Supermini.