Application Note WDXRF1045

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XRF1045 - Cement analysis by the pressed powder method according to ASTM C114-11

Introduction

Cement is one of the most important materials for construction. Many kinds of hydraulic cements, including Portland cement, with various physical properties, are produced by changing the composition of clinker minerals; therefore, it is important to control the chemical composition of cement products and interim products.
ASTM C114-11 covers chemical analysis of hydraulic cement. In this standard, procedures of wet chemical analysis are mainly described and X-ray fluorescence (XRF) spectrometry is mentioned as an example of "Rapid Test Methods." In practice, XRF spectrometry has been used for chemical composition analysis of cement owing to its simple sample preparation and high precision.

This application note demonstrates quantitative analysis for Portland cement by the pressed powder method according to ASTM C114-11 on Rigaku Supermini200, a benchtop sequential wavelength dispersive XRF spectrometer.

ASTM C114-11 and calibration standards

The standard ASTM C114-11 has the following descriptions about "Rapid Test Method":

- Using the test method chosen, make single determinations for each analyte under consideration on at least seven CRM (Certified Reference Material) samples. Complete two rounds of tests on different days, repeating all steps of sample preparation. Calculate the differences between values and averages of the values from the two rounds of tests.

- When seven CRMs are used in the qualification procedures, at least six of the seven differences between duplicates obtained of any single analytes shall not exceed the limits shown in Table 1 and the remaining differences by no more than twice that value.

- For each analyte and each CRM, the average obtained shall be compared to the certified concentrations. When seven CRMs are used in the qualification procedure, at least six of the seven averages for each analytes shall not differ from the certified concentrations by more than the value shown in Table 1, and the remaining average by more than twice that value.

The maximum permissible variations in analysis results defined in ASTM C114-11 are listed in Table 1.

ASTM C114-11 directs that acceptable reference cements are NIST CRMs, or other reference cements traceable to the NIST CRMs.

In this application note, seven NIST CRMs (SRM1881a, 1884a, 1885a, 1886a, 1887a, 1888a and 1889a) were used for calibration and a qualification test.

Instrument

The Supermini200, a benchtop sequential wavelength dispersive X-ray fluorescence (WDXRF) spectrometer, is designed to minimize the peripherals in installation such as cooling water, power supply, installation area, etc. The Supermini200 has good sensitivity for light elements such as Na, Mg, P and Cl relative to EDXRF systems, and does not show any spectral overlap between typical analytes for cement raw meal, owing to high spectral resolution of the WD optics.

The Supermini200 is equipped with an air-cooled 200 W X-ray tube and up to three analyzing crystals, in which elements from fluorine to uranium can be analyzed. The Supermini200 has the same base software as the ZSX Primus series and, therefore, the software is user-friendly and flexible.

Sample preparation

Sample preparation for X-ray fluorescence analysis is easier than other analytical methods in general. It is important to obtain fine grain size for samples when grinding in order to reduce the influence of grain size on analyzed results. In view of processing many samples continuously, the cleaning of grinding containers to avoid contamination from prior samples should be able to be performed in a simple manner. When grinding cement samples, the samples can stick to the inner wall of the container, which causes a problem in cleaning. In order to avoid the problem, n-hexane was added as a grinding agent to prevent the samples from sticking to the wall of the tungsten carbide container (the wet grinding method; see Figure 1).

A binder was mixed with the ground cement powder samples (the ratio of sample to binder was 10 to 1). Four grams of the mixture was pressed into an aluminum ring (inner diameter, 32 mm) at 150 kN.

Figure 1: Comparison of the condition in the container after pulverizing.

Measurement

Measurements were performed in vacuum on the Supermini200 with a 200 W Pd target X-ray tube for the components listed in Table 1.

Table 1: Maximum permissible variation (unit: mass%)

Analyte	Maximum difference between duplicates	Maximum difference of the average of duplicates from the certificate values
SiO_2	0.16	±0.2
Al_2O_3	0.20	±0.2
Fe_2O_3	0.10	±0.10
CaO	0.20	±0.3
MgO	0.16	±0.2
SO_3	0.10	±0.1
Na_2O	0.03	±0.05
K_2O	0.03	±0.05
TiO_2	0.02	±0.03
P_2O_5	0.03	±0.03
ZnO	0.03	±0.03
Mn_2O_3	0.03	±0.03
Cl	0.003	N/A

Measurement

Measurement condition is shown in Table 2.

Table 2: Measurement condition

X-ray tube	Pd target, 200 W end-window type
Tube condition	50 kV and 4.0 mA
Analysis area	30 mm in diameter
Path atmosphere	Vacuum

Element	Si	Al	Fe Ca	Mg	S	Na	
Line	Kα	Kα	Kα	Kα	Kα	Kα	Kα
Primary filter	Out	Out	Out	Out	Out	Out	Out

Crystal	PET	PET	LiF	PET	RX25	PET	RX25
Detector	PC	PC	SC	PC	PC	PC	PC
Counting time (s)	40	40	20	40	60	40	60
Element	K	Ti	P Zn	Mn	Cl		
Line	Kα	Kα	Kα	Kα	Kα	Kα	
Primary filter	Al	Out	Out	Out	Out	Out	
Crystal	PET	LiF	PET	LiF	LiF	PET	
Detector	PC	SC	PC	SC	SC	PC	
Counting time (s)	40	20	40	60	60	60	

Note) LiF: LiF(200), PC: F-PC

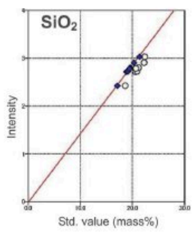
Calibration

The results obtained in the calibration curves are shown in Table 1 and Fig. 2. A matrix correction method is applied to the calibrations. The symbol ∘ shows the data point before the correction and the symbol ◆ shows the data after correction in the calibration charts.

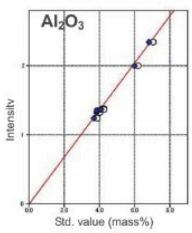
The accuracy of calibration is calculated by the following formula:

$$Accuracy = \sqrt{\frac{\sum_i (C_i - \hat{C}_i)^2}{n-2}}$$

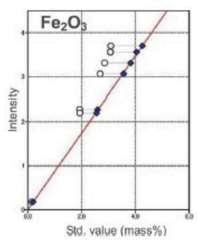
C_i: calculated value of standard sample
$\hat{C}_i$: reference value of standard sample
n : number of standard samples.



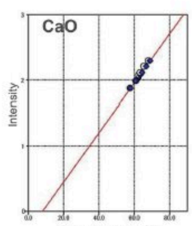
(1) SiO_2 calibration curve



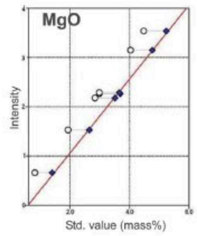
(2) Al_2O_3 calibration curve



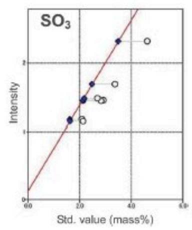
(3) Fe_2O_3 calibration curve



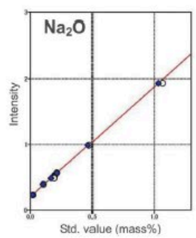
(4) CaO calibration curve



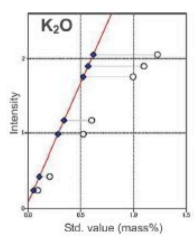
(5) MgO calibration curve



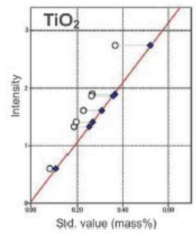
(6) SO_3 calibration curve



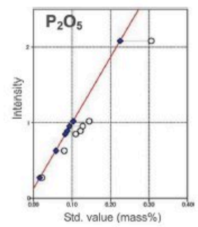
(7) Na_2O calibration curve



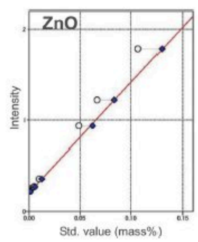
(8) K_2O calibration curve



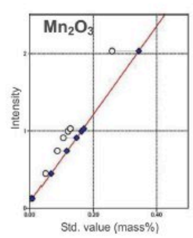
(9) TiO_2 calibration curve



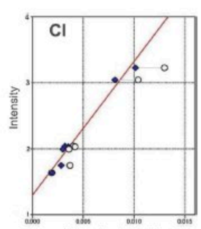
(10) P_2O_5 calibration curve



(11) ZnO calibration curve



(12) Mn_2O_3 calibration curve



(13) Cl calibration curve

Figure 2: Calibration curves of Portland cement.

Qualification test for ASTM C114-11

The results are listed in the Table 4, comparing with the values of ASTM C114 requirement.

The results prove that the analysis method demonstrated in this application note meets the requirements described in ASTM C114-11. (below)

Qualification test for ASTM C114-11

Quantitative analyses have been carried out for the seven NIST SRMs of Portland cement using the calibration curves obtained above.

Table 3: Calibration results (unit: mass%)

Analyte	Calibration range	Accuracy
SiO_2	18.637 - 22.38	0.15
Al_2O_3	3.875 - 7.06	0.096
Fe_2O_3	0.152 - 3.09	0.024
CaO	57.58 - 67.87	0.11
MgO	0.814 - 4.475	0.057
SO_3	2.086 - 4.622	0.049
Na_2O	0.021 - 1.068	0.0055
K_2O	0.093 - 1.228	0.0027
TiO_2	0.084 - 0.366	0.0022
P_2O_5	0.022 - 0.306	0.0014
ZnO	0.001 - 0.107	0.0009
Mn_2O_3	0.007 - 0.259	0.0029
Cl	0.0019 - 0.013	0.0007

Table 4: Qualification test results (unit: mass%)

Analyte	Difference between duplicates		Difference of the average of duplicate from the certificate values	
	Limit (ASTM)	Maximum difference	Limit (ASTM)	Maximum difference
SiO_2	0.16	0.08	0.2	0.2
Al_2O_3	0.20	0.03	0.2	0.1
Fe_2O_3	0.10	0.01	0.10	0.04

CaO	0.20	0.12	0.3	0.2
MgO	0.16	0.03	0.2	0.1
SO_3	0.10	0.06	0.1	0.1
Na_2O	0.03	0.00_5	0.05	0.01
K_2O	0.03	0.01	0.05	0.01
TiO_2	0.02	0.00_3	0.03	0.00_4
P_2O_5	0.03	0.00_3	0.03	0.00_3
ZnO	0.03	0.00_1	0.03	0.00_2
Mn_2O_3	0.03	0.00_2	0.03	0.00_2
Cl	0.003	0.00_1	N/A	0.00_1

Table 5: Repeatability test results

Analyte	Certified value (SRM1889a)	Results of 10-time consecutive measurements			
		1st pressed pellet		2nd pressed pellet	
		Average	Standard deviation	Average	Standard deviation
SiO_2	20.66	20.714	0.032	20.700	0.017
Al_2O_3	3.89	3.857	0.007	3.851	0.010
Fe_2O_3	1.937	1.915	0.005	1.917	0.008
CaO	65.34	65.349	0.031	65.388	0.026
MgO	0.814	0.882	0.005	0.879	0.004
SO_3	2.69	2.671	0.004	2.695	0.005
Na_2O	0.195	0.194	0.006	0.193	0.005
K_2O	0.605	0.607	0.004	0.606	0.004
TiO_2	0.227	0.227	0.005	0.226	0.007
P_2O_5	0.11	0.111	0.001	0.112	0.001
ZnO	0.0048	0.0050	0.0000	0.0047	0.0005
Mn_2O_3	0.2588	0.2590	0.0018	0.2607	0.0018
Cl	0.0019	0.0018	0.0004	0.0015	0.0005

Repeatability test

To demonstrate the stability of the instrument, the duplicated pressed pellets of NIST SRM 1889a were measured 10 times consecutively. The test results are listed in Table 5. The results show the good measuring precisions.

In comparison with the values of the limits defined in ASTM C114-11 shown in Table 4, the standard deviations of the repeatability test obtained meet or exceed the ASTM C114 limits. The results demonstrate that the performance of the Supermini200 meets or exceeds the precision requirements for hydraulic cement analysis as stated in ASTM C114-11.

Conclusion

The qualification test for ASTM C114-11 demonstrated that the test results on the Supermini200 using pressed powder briquettes of wet-ground samples meet the requirements for analysis of hydraulic cement defined in ASTM C114-11.

The precision obtained by the repeatability test is much better than the defined values required in ASTM C114-11.

The Supermini200 is a wavelength-dispersive benchtop X-ray fluorescence spectrometer equipped with a newly developed high-power air-cooled X-ray tube that does not require cooling water. The spectrometer configuration results in high sensitivity, relative to benchtop energy-dispersive XRF spectrometers, for light elements such as Na or Mg, as well as heavy elements.

Reference

ASTM C114-11 Standard Test Methods for Chemical Analysis of Hydraulic Cement.

Related products

Supermini200

Benchtop tube below sequential WDXRF spectrometer anal
yzes O through U in solids, liquids and powders