Application Note WDXRF1115

View on rigaku.com

XRF1115 - Cement analysis by the fusion method on benchtop WDXRF Supermini200 according to ASTM C114-18

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.

Since the fusion method can eliminate sample heterogeneity, such as grain size and mineralogical effects, it is possible to obtain high accuracy for cement samples and also to establish calibrations using a variety of materials. Therefore, X-ray fluorescence (XRF) spectrometry by the fusion method has been the method of choice in cement production processes.

ASTM C114-18(1) covers chemical analysis of hydraulic cements. In this standard, mainly wet chemical analysis procedures are described, and 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 and aluminate cements by the fusion method according to ASTM C114-18 on Rigaku Supermini200, a benchtop sequential wavelength dispersive XRF spectrometer.

ASTM C114-18 and calibration standard

This is how standard ASTM C114-18 describes “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 sample preparation steps . Calculate the differences between values and the averages of the values from the two rounds of tests. When more than seven CRMs are used in the qualification procedures, at least 77% of the differences between duplicates obtained for 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 more than seven CRMs are used in the qualification procedure, at least 77% of the averages for each analyte shall not differ from the certified concentrations by more than the value shown in Table 1, and the remaining average by no more than twice that value.

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

Analyte	Maximum difference between duplicates	Maximum difference of the average of duplicates from the certified 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
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

The maximum permissible variations in analysis results defined in ASTM C114-18 are listed in Table 1. ASTM C114-18 specifies NIST CRMs or other reference cements traceable to the NIST CRMs as acceptable reference cements.

In this application note, nine NIST CRMs (SRM1881a, 1882a, 1883a, 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 and P relative to EDXRF systems, and does not show any spectral overlap between typical analytes for cement, 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, using 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

The samples were ground using a tungsten carbide container with n-hexane (the wet grinding method). Then, the ground fine powder samples were ignited at 950°C for 1 hour. For fusion, 1.0 g of the ignited sample and 4.0 g of flux (lithium tetraborate, pre-dried at 675°C) were weighed out and mixed. The mixture was fused at 1200°C.

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. Measurement conditions are shown in Table 2.

Table 2: Measurement conditions

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**	**Na**
Line	Kα	Kα	Kα	Kα	Kα	Kα
Primary filter	Out	Out	Out	Out	Out	Out
Crystal	PET	PET	LiF	PET	RX26	RX26
Detector	PC	PC	SC	PC	PC	PC
Counting time (s)	40	40	20	60	60	60
Element	**K**	**Ti**	**P**	**Zn**	**Mn**	
Line	Kα	Kα	Kα	Kα	Kα	
Primary filter	Al	Out	Out	Out	Out	
Crystal	PET	LiF	PET	LiF	LiF	
Detector	PC	SC	PC	SC	SC	
Counting time (s)	40	20	40	20	20	

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

Calibration

The results obtained for the calibration curves are shown in Table 3 and Figure 1.
A matrix correction was 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.

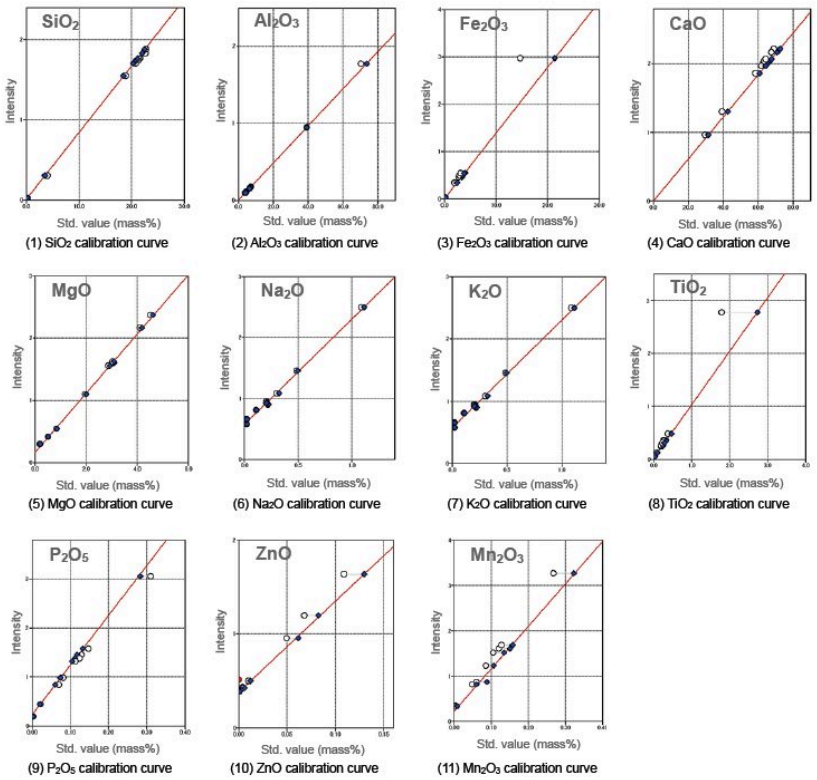

Figure 1: Calibration curves of Portland and alumina cement

The accuracy of the 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.

Table 3: Calibration results (unit: mass%)

Analyte	Calibration range	Accuracy
SiO_2	0.24 – 22.38	0.058
Al_2O_3	3.875 – 70.04	0.051
Fe_2O_3	0.078 – 14.67	0.034
CaO	29.52 – 67.87	0.086
MgO	0.19 – 4.475	0.050
Na_2O	0.021 – 1.068	0.024
K_2O	0.014 – 1.228	0.033
TiO_2	0.020 – 1.786	0.005

P_2O_5	0.003 – 0.306	0.004
ZnO	0.001 – 0.107	0.001
Mn_2O_3	0.003 – 0.259	0.006

Qualification test for ASTM C114-18

Quantitative analyses were carried out for the nine NIST SRMs of Portland and alumina cement using the calibration curves obtained above. The results are listed in Table 4 compared with the values of the ASTM C114-18 requirements.

The results prove that the analysis method demonstrated in this application note meets the requirements described in ASTM C114-18.

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

Analyte	Difference between duplicates		Difference of the average of duplicates from the certified values	
	Limit (ASTM)	Maximum difference	Limit (ASTM)	Maximum difference
SiO_2	0.16	0.09	0.2	0.1
Al_2O_3	0.20	0.09	0.2	0.2
Fe_2O_3	0.10	0.02	0.10	0.05
CaO	0.20	0.13	0.3	0.1
MgO	0.16	0.05	0.2	0.1
Na_2O	0.03	0.03	0.05	0.03
K_2O	0.03	0.01	0.05	0.05
TiO_2	0.02	0.01	0.03	0.01
P_2O_5	0.03	0.003	0.03	0.01
ZnO	0.03	0.001	0.03	0.002
Mn_2O_3	0.03	0.004	0.03	0.01

Repeatability test

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

In comparison with the values of the limits defined in ASTM C114-18 shown in Table 4, the standard deviations of the repeatability test are sufficiently low. The results demonstrate that the performance of the Supermini200 meets and exceed the precision requirements for analysis of hydraulic cement, including Portland and alumina cements, stated in ASTM C114-18.

Table 5: Repeatability test results (unit: mass%)

Analyte	Certified value (SRM1889a)	Results of 10-time consecutive measurements			
		1st fused bead		2nd fused bead	
		Average	Standard deviation	Average	Standard deviation
SiO_2	20.66	20.585	0.032	20.619	0.030
Al_2O_3	3.89	3.805	0.032	3.806	0.019
Fe_2O_3	1.937	1.941	0.009	1.944	0.005
CaO	65.34	65.410	0.047	65.404	0.030
MgO	0.814	0.747	0.012	0.751	0.012
Na_2O	0.195	0.200	0.017	0.193	0.019
K_2O	0.605	0.622	0.007	0.623	0.010
TiO_2	0.227	0.231	0.007	0.231	0.007
P_2O_5	0.110	0.114	0.002	0.114	0.002
ZnO	0.0048	0.0044	0.0008	0.0047	0.0007
Mn_2O_3	0.2588	0.2565	0.0033	0.2573	0.0027

Conclusion

The qualification test for ASTM C114-18 demonstrated that the test results on the Supermini200 by the fusion method meet and/or exceed the requirements for analysis of hydraulic cement defined in ASTM C114-18.

Application Note XRF1114(2) reported that the qualification test results for ASTM C114-18 on the Supermini200 by the pressed powder method meet the requirements, using only Portland cement. Since the fusion method is employed in the analysis demonstrated in this application note, it is possible to establish a single calibration for wide concentration ranges, including both Portland and alumina cements. The precision obtained by the repeatability test is much better than the defined values required in ASTM C114-18.

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 for heavy elements.

References

(1) ASTM C114-18, Standard Test Methods for Chemical Analysis of Hydraulic Cement, ASTM International, 2018, 33pp.
(2) Application Note XRF1114, Cement Analysis by the Pressed Powder Method on Benchtop WDXRF Supermini200 According to ASTM C114-18, Rigaku Corporation.

Related products

Supermini200

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