Application Note WDXRF1113

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XRF1113 - Cement analysis by the pressed powder method on the ZSX Primus III+ 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.

ASTM C114-18[(1)] covers chemical analysis of hydraulic cement. In this standard, mainly wet chemical analysis procedures are 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 of Portland cement by the pressed pellet method according to ASTM C114-18 on Rigaku ZSX Primus III+, a 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 steps of sample preparation. Calculate the differences between values and the averages of the values from the two rounds of tests.

· When seven CRMs are used in the qualification procedure, at least six of the seven differences between duplicates obtained from any single analyte 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 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.

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.

Table 1: Maximum permissible variation (in 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
SO3	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	±0.005

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

Instrument

The ZSX Primus III+, a tube-above sequential wavelength dispersive X-ray fluorescence (WDXRF) spectrometer, is optimized for routine analysis of powder samples.

The tube-above optics, the programmable, changeable vacuum speed and the powder trap of the ZSX Primus III+ enable secure analysis of powder samples and low frequency of maintenance by preventing pressed pellet specimens from breaking and falling and by protecting the vacuum pump and magnetic valves from fine particles scattered from specimens.

The ZSX Primus III+ has a pre-evacuation chamber. A specimen is evacuated in this chamber and then transported to the measurement position. During measurement, the next specimen to be analyzed can be loaded into the pre-evacuation chamber and waiting, which reduces the loading time. In addition, if a pressed pellet specimen should be broken because of vacuum, it happens inside the pre-evacuation chamber and the optical main chamber is not contaminated.

The system software is designed for ease of use in routine analysis. The Flowbar in quantitative analysis guides users in establishing calibration. Easy Analysis and the Program Operation help operators carry out daily analyses easily and smoothly.

Sample preparation

Cement powder samples were pulverized in a tungsten carbide container with n-hexane (the wet grinding method) for three minutes. Then, 4.5 grams of the resultant powders, pre-dried, were pressed at 150 kN. The wet grinding method prevents samples from sticking to the wall of the container and avoids inter-sample contamination, even after cleaning the container only briefly (Figure 1).

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

Measurement and Calibration

Measurements were performed on the ZSX Primus III+ with a 3 kW Rh-target X-ray tube for the components listed in Table 1. Measurement conditions are shown in Table 2. The total counting time is less than 5 minutes. The RX26 multilayer analyzing crystal, included in the standard configuration, has high sensitivity for Mg and Na and is capable of reducing interference from higher-order lines, such as Ca-Kα-3rd, which would interfere with Mg-Kα.

Table 2: Measurement conditions

Path atmosphere	Vacuum
Tube condition	50 kV and 50 mA
Analysis area	30 mm in diameter

Element	**Si**	**Al**	**Fe**	**Ca**	**Mg**	**S**	**Na**
Line	Kα	Kα	Kα	Kα	Kα	Kα	Kα
Attenuator	1/1	1/1	1/1	1/10	1/1	1/1	1/1
Slit	S4	S4	S2	S4	S4	S4	S4
Crystal	PET	PET	LiF	LiF	RX26	PET	RX26
Detector	PC	PC	SC	PC	PC	PC	PC

Element	K	Ti	P	Zn	Mn	Cl	
Line	Kα	Kα	Kα	Kα	Kα	Kα	
Attenuator	1/1	1/1	1/1	1/1	1/1	1/1	
Slit	S4	S2	S4	S2	S2	S2	
Crystal	LiF	LiF	PET	LiF	LiF	PET	
Detector	PC	SC	PC	SC	SC	PC	

Note) LiF: LiF(200), PC: F-PC
The calibration curves were generated with theoretical alphas (matrix correction coefficients calculated theoretically by the fundamental parameter method) for all the analytes.

The calibration curves for the representative analytes are shown in Figure 2.

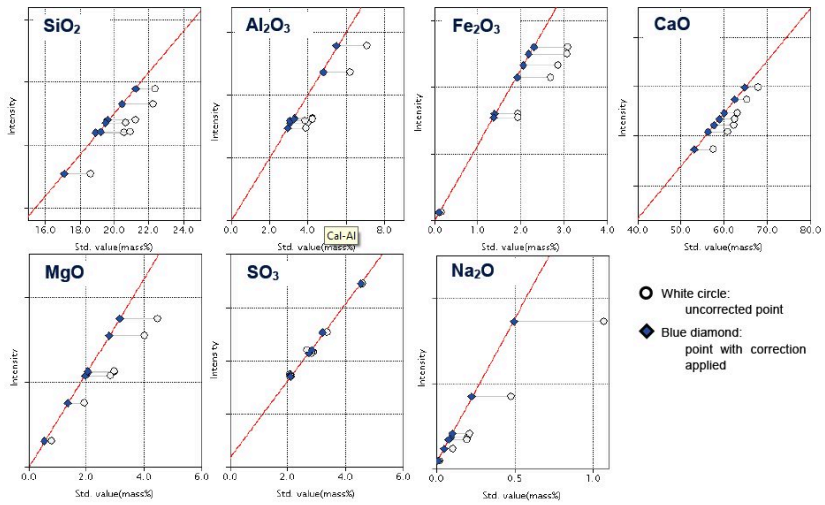

Figure 2: Representative calibration curves for the analytes of cement

Qualification test for ASTM C114-18

A qualification test for “Rapid Test Method” in ASTM C114-18 was carried out.

Pressed pellet specimens of the seven NIST CRMs were prepared and quantified with the calibration previously established. On a different day, the same procedure was repeated.

The test results are summarized in Table 3, which shows only the maximum values for both the differences between the duplicates and the differences of the averages of the duplicates from the certified values.

The qualification test results shown in Table 3 prove that the analysis method demonstrated in this application note meets the requirements described in ASTM C114-18.

Table 3: Qualification test result (unit: mass%)

Analyte	Calibration range	Difference between duplicates		Difference of the average of duplicates from the certificate values	
		Limit	Result*	Limit	Result*
SiO_2	18.637 – 22.38	0.16	0.10	0.2	0.2
Al_2O_3	3.85 – 7.06	0.20	0.04	0.2	0.1
Fe_2O_3	0.152 – 3.09	0.10	0.003	0.10	0.04
CaO	57.58 – 67.87	0.20	0.12	0.3	0.1
MgO	0.814 – 4.475	0.16	0.04	0.2	0.1
SO_3	2.086 – 4.622	0.10	0.05	0.1	0.1
Na_2O	0.021 – 1.068	0.03	0.02	0.05	0.01
K_2O	0.093 – 1.228	0.03	0.003	0.05	0.01
TiO_2	0.084 – 0.366	0.02	0.01	0.03	0.01
P_2O_5	0.022 – 0.306	0.03	0.01	0.03	0.004
ZnO	0.001 – 0.107	0.03	0.001	0.03	0.002
Mn_2O_3	0.007 – 0.259	0.03	0.001	0.03	0.002
Cl	0.0019 – 0.013	0.003	0.005**	0.005	0.006**

* In the "Results" columns, only the maximum values among the analysis results of the seven NIST CRMs are listed.
** The maximum differences for Cl exceed the limits while the differences of all the other CRMs are lower than the limits. The maximum differences are less than double the limit. This means that the test results meet the requirements.

Repeatability test

Specimens of NIST SRM1889a prepared for the qualification test were measured consecutively ten times. The repeatability test results are summarized in Table 4, which shows the averages and the standard deviations of the ten-fold measurement results for each specimen, together with the limits of the qualification test for ASTM C114-18 for reference.

Table 4: Repeatability test result using SRM1889a (unit: mass%)

Analyte	Certified value	Ten-time measurement result				Maximum difference of averages between duplicates	Maximum difference of the average of duplicate from the certificate values
		1st specimen		2nd specimen			
		Average	Std. dev.	Average	Std. dev.		
SiO_2	20.66	20.74	0.040	20.78	0.024	0.16	0.2
Al_2O_3	3.89	3.85	0.008	3.86	0.005	0.20	0.2
Fe_2O_3	1.937	1.912	0.0026	1.910	0.0019	0.10	0.10
CaO	65.34	65.41	0.048	65.42	0.031	0.20	0.3
MgO	0.814	0.864	0.0031	0.864	0.0027	0.16	0.2
SO_3	2.69	2.68	0.006	2.69	0.002	0.10	0.1
Na_2O	0.195	0.201	0.0022	0.199	0.0025	0.03	0.05
K_2O	0.605	0.610	0.0010	0.612	0.0008	0.03	0.05
TiO_2	0.227	0.225	0.0012	0.223	0.0013	0.02	0.03
P_2O_5	0.11	0.11	0.002	0.11	0.002	0.03	0.03
ZnO	0.0048	0.0042	0.0001	0.0040	0.0001	0.03	0.03
Mn_2O_3	0.2588	0.259	0.0005	0.259	0.0009	0.03	0.03
Cl	0.0019	0.0030	0.0001	0.0020	0.0001	0.003	0.005

As shown in the Table 4, the standard deviations obtained are much smaller than those required in ASTM C114-18; therefore, much shorter counting times could be used to qualify the ASTM C144-18 standard when higher throughput is required.

Conclusions

Hydraulic cement samples can be routinely analyzed with high accuracy and precision on the ZSX Primus III+ by the pressed pellet method, a simple sample preparation.

The ZSX Primus III+ is suitable for powder sample analysis owing to its tube-above optics and functions for measuring pressed pellet specimens securely.

The qualification test for “Rapid Test Methods” described in ASTM C114-18 demonstrated in this application note proves that the combination of the performance of the ZSX Primus III+ and wet grinding followed by pressing pulverized powder samples meets the requirements defined in ASTM C114-18.

Reference

(1) ASTM C114-18, Standard Test Methods for Chemical Analysis of Hydraulic Cement, ASTM International, 2018, 33pp.

Related products

ZSX Primus III NEXT

Affordable, high-end, tube-above Industrial WDXRF for the a
nalysis of solid samples