Application Note XRF 5045

# Cement Analysis by the Pressed Powder Method on Benchtop WDXRF Supermini200 According to ASTM C114-11

**Application**

Portland cement


**Instrument**

Benchtop wavelength dispersive X-ray fluorescence spectrometer
**Supermini200**

**Keywords**

cement
Portland cement
hydraulic cement
pressed powder method
pressed pellets
benchtop
ASTM C114

## 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 CRM’s (SRM1881a, 1884a, 1885a, 1886a, 1887a, 1888a and 1889a) were used for calibration and a qualification test.

**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 |

## 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 the 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 have and, therefore, the software is user-friendly and flexible.

## Sample preparation

The 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 Fig. 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.

## Measurement

*Without n-hexane (dry grinding)* *With n-hexane (wet grinding)*

**Figure 1 Comparison of the condition in the container after pulverizing**

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 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.

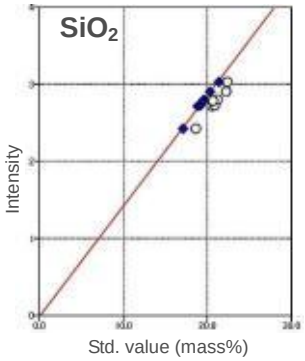
The accuracy of calibration is calculated by the following formula,

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

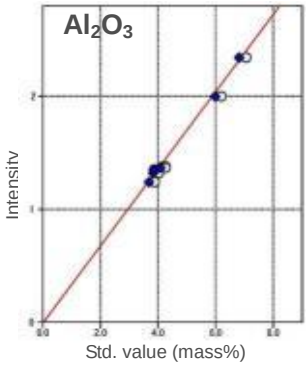
$C_i$ : calculated value of standard sample

$\hat{C}_i$ : reference value of standard sample

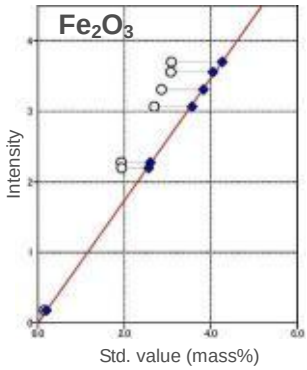
$n$ : number of standard samples.



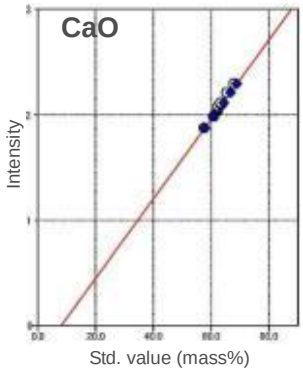

(1) $SiO_2$ calibration curve



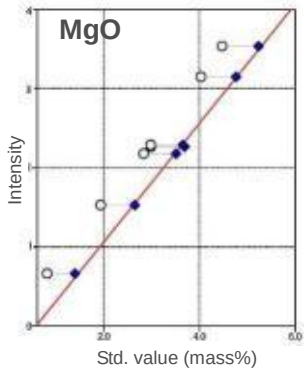

(2) $Al_2O_3$ calibration curve



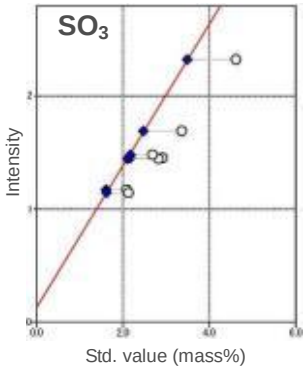

(3) $Fe_2O_3$ calibration curve



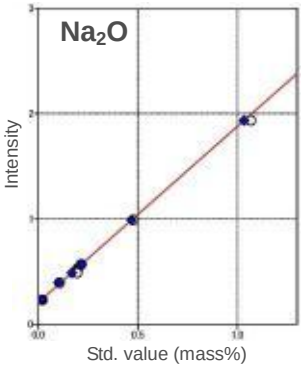

(4) CaO calibration curve



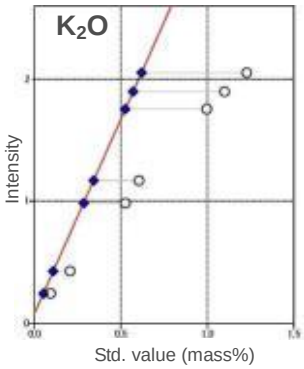

(5) MgO calibration curve



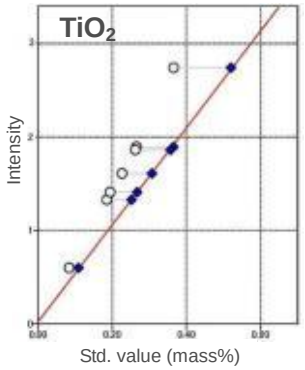

(6) $SO_3$ calibration curve



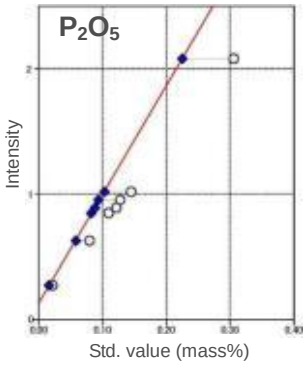

(7) $Na_2O$ calibration curve



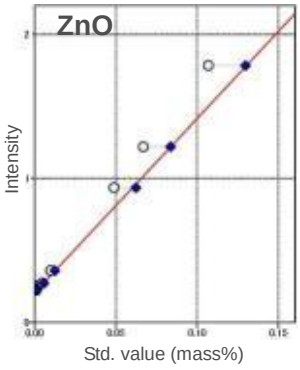

(8) $K_2O$ calibration curve



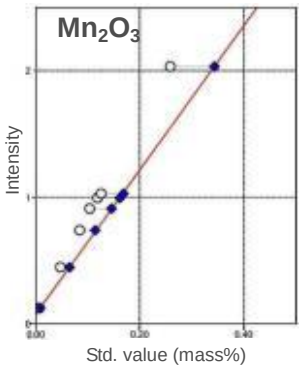

(9) $TiO_2$ calibration curve



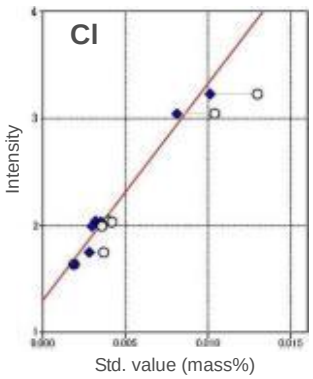

(10) $P_2O_5$ calibration curve




(11) ZnO calibration curve




(12) $Mn_2O_3$ calibration curve




(13) Cl calibration curve

**Figure 2 Calibration curves of Portland cement**

**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 |

## Qualification test for ASTM C114-11

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

**Table 4 Qualification rest 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** (unit: mass%)

| 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

Rigaku

Rigaku Corporation Tokyo Branch
4-14-4, Sendagaya, Shibuya-ku, Tokyo 151-0051, Japan
Phone +81-3-3479-0618 Fax +81-3-3479-6112 rinttyo@rigaku.co.jp

www.Rigaku.com

Rigaku Corporation
Head Office
3-9-12, Matsubara-cho, Akishima-shi, Tokyo 196-8666, Japan
Phone +81-42-545-8189 Fax +81-42-544-9223
rinttyo@rigaku.co.jp

Rigaku Americas Corporation
9009 New Trails Drive, The Woodlands, Texas 77381-5209, USA
Phone +1-281-362-2300 Fax +1-281-364-3628
info@rigaku.com

Rigaku Europe SE
Am Hardwald 11, 76275 Ettlingen, Germany
Phone +49-7243-94936-0 Fax +49-7243-93936-10
rese@rigaku.co.jp

Rigaku Corporation
Osaka Factory
14-8, Akaoji-cho, Takatsuki-shi, Osaka 569-1146, Japan
Phone +81-72-693-7991 Fax +81-72-693-6746
rinttyo@rigaku.co.jp

Rigaku Beijing Corporation
2601A, Tengda Plaza, No.168, Xizhimenwai Avenue,
Haidian District, Beijing 100044, P.R.China
Phone +86-010-8857-5768 Fax +86-010-8857-5748
info@rigaku.com.cn

(J0911)