

XRF Analysis of Cement - ASTM C-114 Qualification

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Fig. 1: S4 EXPLORER XRF

Introduction

X-ray Fluorescence (XRF) has long been acknowledged as the accepted technique for analyzing cement, clinker, and all of the associated raw materials in the cement making process. The defining method for the analysis of these materials is the ASTM C-114 Standard Method for Chemical Analysis of Hydraulic Cement, which, for the most part, is a series of "wet" analysis procedures. However, by conforming to the "Performance Requirements for Rapid Test Methods", alternative methods may meet "Qualification". Among the many analytical techniques available, XRF has the unique capability of producing the most accurate and precise results in the shortest amount of time. Moreover, not all techniques can meet the "Qualification" for all of the elements. In particular, most cement producers consider the analysis of the standard eight oxides: CaO, SiO₂, Fe₂O₃, Al₂O₃, SO₃, MgO, Na₂O and K₂O, to be extremely important for the efficiency of their process. This article describes the ASTM C-114 Qualification method using the Bruker AXS SRS 3400 and S4 EXPLORER, the

sample preparation method, the results, and the calculations made to demonstrate "Qualification". Both the S4 EXPLORER and the SRS 3400 meet or exceed ASTM C-114 Qualification specifications while allowing users to meet more demanding budget requirements.

ASTM C-114 Qualification

The procedure for ASTM C-114 Qualification is as follows: Calibrate the instrument using valid curve-fitting procedures (point-to-point saw tooth fitting is not allowed). Prepare NIST Portland-Cement SRM's and analyze on Day 1. On a non-consecutive day, prepare a new set of SRM's and analyze again. Calculate the differences between the values on Days 1 and 2 for each element (oxide) and the averages of the values from days one and two. Compare the values obtained from the instrument to the values in Table 1. Be aware of significant digits for each value in the table. The differences between the measurements on Days 1 and 2 is a measure of the overall precision of the method. The difference of the average of the values from Days 1 and 2 to the certificate value of the element (oxide) is a measure of the overall accuracy of the method.

Table 1. Qualification ASTM C-114 - 97a. Maximum Permissible Variations in Results (abs. wt. %)

Oxide	Accuracy (Max. Diff. Mean vs. Cert. Value)	Precision (Max. Diff. Days 1 & 2)
SiO ₂	0.20	0.16
Al ₂ O ₃	0.20	0.20
Fe ₂ O ₃	0.10	0.10
CaO	0.30	0.20
MgO	0.20	0.16
SO ₃	0.10	0.10
Na ₂ O	0.05	0.03
K ₂ O	0.05	0.03
TiO ₂	0.03	0.02
P ₂ O ₅	0.03	0.03
ZnO	0.03	0.03
Mn ₂ O ₃	0.03	0.03

For Col. 2 and 3 in Table 1, the following variations are permissible: All values shall be within the prescribed limits when less than seven SRM's are used. If seven SRM's are used, six values must be within prescribed limits, and the seventh value no more than two times the prescribed limits. If more than seven SRM's are used, 77% of the values must be within prescribed limits, and the remainder within two times the prescribed limits. Interelement corrections are allowed for any oxide when the correction is applied to all standards used for that calibration. Qualification data shall be made available pursuant to the Manufacturers Certification Section of C 150, or the Certification Section of Specification C 595. Requalification is required at least every two years.



Fig. 2: SRS 3400 XRF

Table 2. ASTM C-114 Accuracy Data

Oxide	Conc. Range (wt. %)	Accuracy: Max. Diff. Mean vs. Cert. Value		
		ASTM (allowed)	SRS 3400	S4
Na ₂ O	0.02 - 0.38	0.05	0.02	0.02
MgO	0.7 - 4.0	0.20	0.1	0.1
Al ₂ O ₃	3.3 - 5.6	0.20	0.2	0.2
SiO ₂	19.8 - 23.2	0.20	0.2	0.2
P ₂ O ₅	0.02 - 0.30	0.03	0.02	0.02
SO ₃	2.0 - 4.6	0.10	0.1	0.1
K ₂ O	0.1 - 1.3	0.05	0.02	0.01
CaO	62 - 67	0.30	0.1	0.2
TiO ₂	0.15 - 0.30	0.03	0.00	0.01
Fe ₂ O ₃	0.3 - 4.4	0.10	0.02	0.04

Instrumentation

The data for these tests were collected on the S4 EXPLORER (Fig. 1) and the SRS 3400 (Fig. 2) X-ray Fluorescence Spectrometers. The SRS 3400 XRF with 4-kW X-ray tube represents the conventional high-performance sequential spectrometer used for ASTM C-114 Qualification. The S4 EXPLORER represents the latest technology (see accompanying article), eliminating conventional utilities such as water, compressed air and P-10 detector gas. These utilities are no longer required due to the development of a 1-kW air-cooled X-ray tube, electromechanical sample handling, and the Pro4 Sealed Detector for light elements. The 1-kW X-ray tube is a Rh target, 75-µm end-window design, giving excellent performance throughout the periodic table. The Pro4 detector incorporates a proprietary material that eliminates the need for P-10 gas to flow through the detector, yet gives performance equal to or better than the conventional flow detector for the light and ultra-light elements. These new developments, combined with optimized coupling of X-ray tube target-to-sample and crystals with collimators, give the S4 EXPLORER extremely high performance from beryllium through uranium. The components are packaged in an extremely compact metal cabinet with an integrated automatic sample changer.



Fig. 3: Sample grinding without Vertrel XF results in considerable contamination of the container after cleaning.



Fig. 4: Sample grinding with Vertrel XF results in a clean container with no contamination.

Both spectrometers have the capacity for eight crystals, four collimators, 10 primary beam filters, collimator masks for small sample analysis, and 32-bit applications software running under Windows NT, including full qualitative, standardless, and quantitative analysis capabilities. An integrated database and the TCP/IP networking protocol are standard.

Sample Preparation

The samples were prepared by adding 5.0X g cement, 0.5X g of cellulose, and 5 ml Dupont Vertrel XF™ to a ring and puck mill followed by grinding for 90 s. The powder was then pressed at 40,000 pounds in a 40-mm die mold on top of a boric acid backing. The use of

Table 3. ASTM C-114 - Precision Data

Oxide	Conc. Range (wt. %)	Precision: Max. Diff. of Duplicates		
		ASTM (allowed)	SRS 3400	S4
Na ₂ O	0.02 - 0.38	0.03	0.00	0.01
MgO	0.7 - 4.0	0.16	0.06	0.06
Al ₂ O ₃	3.3 - 5.6	0.20	0.08	0.08
SiO ₂	19.8 - 23.2	0.16	0.11	0.09
P ₂ O ₅	0.02 - 0.30	0.03	0.00	0.00
SO ₃	2.0 - 4.6	0.10	0.05	0.06
K ₂ O	0.1 - 1.3	0.03	0.01	0.01
CaO	62 - 67	0.20	0.19	0.20
TiO ₂	0.15 - 0.30	0.02	0.00	0.02
Fe ₂ O ₃	0.3 - 4.4	0.10	0.03	0.02

Vertrel XF as a grinding aid enables one to use a standard hardened steel container instead of a W/C container. Vertrel XF also eliminates contamination that otherwise remains after cleaning (Figs. 3 and 4).

Table 4. XRF Technology comparison over two decades.

	1980's	1990's	2000
Instrument Size	6 m ³	4 m ³	1 m ³
Power	3 kW	4 kW	1 kW
Utilities	water, compr. air, P-10 gas	water, compr. air, P-10 gas	NONE
Price	\$225 000	\$180 000	\$130 000
Flexibility	10 oxides	B - U Semi-Quant.	B - U Standardless
Interelement Corrections	Empirical Lachance-Trail	Fixed Theoretical Alphas	Variable Theoretical Alphas
Analysis Time (8 elements)	180 s	210 s	300 s

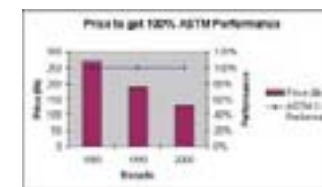


Fig. 5: Investment required to obtain 100% ASTM C-114 Performance.

Results

The results in Tables 2 and 3 show that both the S4 EXPLORER and the SRS 3400 meet or exceed ASTM C-114 Qualification specifications for both precision and accuracy. The performance of the two spectrometers is virtually identical. Sample preparation errors represent the largest form of systematic error since both spectrometers give more than enough count rate to eliminate statistical counting errors. In addition, interelement effects are corrected for with the Variable Alpha form of Fundamental Parameters, which corrects for all elements on each other, and eliminates operator decision during the calibration process.

Conclusions

Table 4 shows how the XRF technology has changed over the last two decades. The size, power, and cost of instrumentation have dropped significantly, while the time of analysis has increased slightly. Flexibility which is required by changing fuels and additives, has been extended to the full capability of XRF (B - U), including standardless analysis. Operator decisions concerning interelement corrections have been eliminated through the use of Variable Theoretical Alphas. Requirements for cooling water, compressed air and P-10 gas have also been eliminated. The investment required for 100% ASTM C-114 performance has decreased by over 50% (Fig. 5). Both the S4 EXPLORER and the SRS 3400 meet or exceed ASTM C-114 Qualification specifications, while also allowing users to meet more demanding budget requirements.