

Cement analysis according to ASTM C114 with the ARL QUANT'X EDXRF Spectrometer

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Keywords

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Introduction

One of the most important applications of X-ray fluorescence (XRF) spectrometry is the analysis of cement in a production environment. Usually wavelength dispersive instruments are preferred because of their precision, accuracy, speed and long-term stability. In recent years, more and more Energy-Dispersive XRF (EDXRF) instruments are installed as well. In large cement plants EDXRF is often set up as a backup of Wavelength-Dispersive XRF (WDXRF) while smaller plants might employ EDXRF as their sole XRF for production control.

ASTM C-114 requirements

Without doubt the most widely used standard test method used to evaluate the performance of XRF instruments (and other analysis techniques) for the analysis of cements is ASTM C-114. This standard describes a very strict protocol to evaluate both accuracy and precision of the technique while setting strict performance requirements.

The protocol consists of properly calibrating an XRF instrument after which it is used to analyze a set of at least seven reference cements, preferably NIST certified reference materials (CRMs).

Two rounds of analyses are to be completed on different days repeating all steps of sample preparation. Differences between values and averages of the values from the two rounds are to be calculated.



When seven CRMs are used – as is the case in this application note – at least six of the seven differences obtained for any single analyte shall not exceed the limits shown in column 3 of Table 1 and the remaining differences by no more than twice that value.

Similarly, at least six of the seven averages for each analyte shall not differ from the certified concentrations by more than the value shown in column 4 of Table 1, and the remaining average by more than twice that value.

Table 1: Max. permissible variations in results according ASTM C-114.

Analyte	Unit	Max. difference between duplicates	Max. difference of avg. of duplicates from CRM certificate values
Na ₂ O	%	0.03	0.05
MgO	%	0.16	0.2
Al ₂ O ₃	%	0.20	0.2
SiO ₂	%	0.16	0.2
P ₂ O ₅	%	0.03	0.03
SO ₃	%	0.10	0.1
K ₂ O	%	0.03	0.05
CaO	%	0.20	0.3
TiO ₂	%	0.02	0.03
Mn ₂ O ₃	%	0.03	0.03
Fe ₂ O ₃	%	0.10	0.1
ZnO	%	0.03	0.03

Instrumentation

The Thermo Scientific™ ARL QUANT'X™ XRF Spectrometer is an EDXRF system which provides a fast and cost-effective analytical capability. It is fitted with an air-cooled Rh end-window tube with thin Be window (0.05 mm) and has a maximum power of 50 Watts. The ARL QUANT'X Spectrometer is equipped with an electrically cooled silicon drift detector (SDD) with an area of 30 mm². The instrument features a total of nine primary beam filters ensuring that an optimal excitation condition is always found. An optional 10-position sample changer allows for unattended analysis.

Excitation conditions

Two excitation conditions were used to cover all the analytes listed in Table 1. One condition at 4 kV without filter to excite all light elements from sodium up to sulfur and a second condition at 16 kV with a thin Pd filter for all remaining analytes. We used a total live time of 300 s to complete one sample analysis. All measurements are executed in vacuum. Table 2 gives an overview of the conditions.

Table 2: Excitation conditions.

Condition	Voltage (kV)	Filter	Time (s)	Atmosphere	Analytes
Low Za	4.00	None	200	Vacuum	Na ₂ O, MgO, Al ₂ O ₃ , SiO ₂ , P ₂ O ₅ , SO ₃
Mid Za	16.00	Thin Pd	100	Vacuum	K ₂ O, CaO, TiO ₂ , Mn ₂ O ₃ , Fe ₂ O ₃ , ZnO



Sample preparation

Seven cement CRMs of the 18xx series (NIST SRMs 1880a, 1881a, 1884a, 1885a, 1887a, 1888a and 1889a) were prepared as pressed powders. Cement CRMs were ground with a puck and ring mill for 90 s and pressed onto a boric acid backing at 20 tons to produce a pellet of 32 mm Ø.

Results

Table 3a and 3b give an overview of the results obtained for the different cement CRMs. Table 3a compares the difference between duplicates with the maximum permissible value while Table 3b does the same for the average of duplicates. Results for the majority of analytes meet the requirements of ASTM C-114. Table 3b shows one value for SiO₂ which differs more than the maximum difference listed in Table 1. This value was obtained for NIST SRM 1887a but is still within the rounding error and less than twice the permissible value. As such, requirements according ASTM C-114 are still met for this analyte.

Table 3a: Difference between values obtained on day 1 & 2.

Analyte	Unit	Max. possible difference between duplicates	Max. observed difference between duplicates
Na ₂ O	%	0.03	0.02
MgO	%	0.16	0.03
Al ₂ O ₃	%	0.20	0.03
SiO ₂	%	0.16	0.13
P ₂ O ₅	%	0.03	0.01
SO ₃	%	0.10	0.02
K ₂ O	%	0.03	0.01
CaO	%	0.20	0.04
TiO ₂	%	0.02	0.01
Mn ₂ O ₃	%	0.03	0.01
Fe ₂ O ₃	%	0.10	0.01
ZnO	%	0.03	0.00

Table 3b: Difference between averages of values and certified values.

Analyte	Unit	Max. permissible difference of the average of duplicates from CRM certificate values	Max. observed difference of the average of duplicates from CRM certificate values
Na ₂ O	%	0.05	0.03
MgO	%	0.2	0.05
Al ₂ O ₃	%	0.2	0.07
SiO ₂	%	0.2	0.23
P ₂ O ₅	%	0.03	0.03
SO ₃	%	0.1	0.06
K ₂ O	%	0.05	0.02
CaO	%	0.3	0.20
TiO ₂	%	0.03	0.01
Mn ₂ O ₃	%	0.03	0.00
Fe ₂ O ₃	%	0.1	0.04
ZnO	%	0.03	0.00

Table 4: Minimum detection limits.

Analyte	Unit	Minimum detection limits
Na ₂ O	%	0.018
MgO	%	0.011
Al ₂ O ₃	%	0.006
SiO ₂	%	0.003
P ₂ O ₅	%	0.002
SO ₃	%	0.001
K ₂ O	%	0.005
CaO	%	0.003
TiO ₂	%	0.003
Mn ₂ O ₃	%	0.001
Fe ₂ O ₃	%	0.001
ZnO	%	0.001

Detection limits

Table 4 shows the detection limits obtainable with the ARL QUANT'X Spectrometer for the different analytes in a cement matrix. The limits are reported for measurement times and excitation conditions as used in this application note (Table 2) to meet ASTM C-114.

Conclusions

The results shown in this document demonstrate that a compact EDXRF instrument such as the ARL QUANT'X Spectrometer meets the requirements of ASTM C-114 for the analysis of cement. It also shows that analysis times can remain short without sacrificing performance.

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