Cement analysis according to ASTM C114 using Thermo Scientific ARL QUANT'X EDXRF spectrometer

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Key Words
ARL QUANT'X, EDXRF, Cement, ASTM C114

Goal
Quality control of cement in a production environment

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

Analyte	Unit	Max. difference between duplicates	Max. difference of avg. of duplicates from CRM certificate values
Na_2O	%	0.03	0.05
MgO	%	0.16	0.2
Al_2O_3	%	0.20	0.2
SiO_2	%	0.16	0.2
P_2O_5	%	0.03	0.03
SO_3	%	0.10	0.1
K_2O	%	0.03	0.05
CaO	%	0.20	0.3
TiO_2	%	0.02	0.03
Mn_2O_3	%	0.03	0.03
Fe_2O_3	%	0.10	0.1
ZnO	%	0.03	0.03

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

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.

Instrument
The ARL QUANT'X EDXRF is a compact benchtop instrument with a direct excitation geometry using eight primary beam filters. It is equipped with a 50 Watt air-cooled X-ray tube and a thermoelectrically cooled silicon drift detector (SDD) with active crystal thickness of 1 mm and active crystal area of 30 mm^2. This SDD combines high count rate capability with excellent resolution and good detection efficiency for higher X-ray energies. For this application it ensures high precision at short measurement times.

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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 300s at 30% dead time to complete one sample analysis. All measurements are executed in vacuum. Table 2 gives an overview of the conditions.

Condition	Voltage [kV]	Filter	Time [s]	Atmos-phere	Analytes
Low Za	4.00	None	200	Vacuum	Na_2O, MgO, Al_2O_3, SiO_2, P_2O_5, SO_3
Mid Za	16.00	Thin Pd	100	Vacuum	K_2O, CaO, TiO_2, Mn_2O_3, Fe_2O_3, ZnO

Table 2: Excitation conditions

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 90s and pressed onto a boric acid backing at 20 tons to produce a pellet of 32 mm Ø.

Analyte	Unit	Max. permissible difference between duplicates	Max. observed difference between duplicates
Na_2O	%	0.03	0.02
MgO	%	0.16	0.03
Al_2O_3	%	0.20	0.03
SiO_2	%	0.16	0.13
P_2O_5	%	0.03	0.01
SO_3	%	0.10	0.02
K_2O	%	0.03	0.01
CaO	%	0.20	0.04
TiO_2	%	0.02	0.01
Mn_2O_3	%	0.03	0.01
Fe_2O_3	%	0.10	0.01
ZnO	%	0.03	0.00

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

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 value for SiO_2 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.

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_2O	%	0.05	0.03
MgO	%	0.2	0.05
Al_2O_3	%	0.2	0.07
SiO_2	%	0.2	0.23
P_2O_5	%	0.03	0.03
SO_3	%	0.1	0.06
K_2O	%	0.05	0.02
CaO	%	0.3	0.20
TiO_2	%	0.03	0.01
Mn_2O_3	%	0.03	0.00
Fe_2O_3	%	0.1	0.04
ZnO	%	0.03	0.00

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

Detection limits

Table 4 shows the detection limits obtainable with the ARL QUANT'X EDXRF 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.

Analyte	Unit	MDL
Na_2O	%	0.018
MgO	%	0.011
Al_2O_3	%	0.006
SiO_2	%	0.003
P_2O_5	%	0.002
SO_3	%	0.001
K_2O	%	0.005
CaO	%	0.003
TiO_2	%	0.003
Mn_2O_3	%	0.001
Fe_2O_3	%	0.001
ZnO	%	0.001

Table 4: Minimum detecion limits

Conclusions

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

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