Application Note 41732

Analysis of Clinker and Cement with Thermo Scientific ARL OPTIM'X WDXRF Sequential Spectrometer

Didier Bonvin, Thermo Fisher Scientific, Ecublens, Switzerland

Key Words
ARL OPTIM'X 200 W, clinker, cement, X-ray fluorescence, XRF

Goal

To show that the Thermo Scientific™ ARL™ OPTIM'X WDXRF instrument permits successful analysis of various elements in cement and clinker in less than two minutes at 200 W.

Introduction

Wavelength dispersive X-ray fluorescence (WDXRF) allows measurement of up to 84 elements of the periodic table in samples of various forms and nature: solids or liquids, conductive or non-conductive. Advantages of XRF over other techniques are speed of analysis, generally easy sample preparation, very good stability, precision and wide dynamic range (from ppm levels to 100%). X-ray fluorescence is the technique of choice for elemental analysis in cement industry as it allows the analysis of major and minor oxides in the raw materials, clinker and cement.

Instrumentation

The ARL OPTIM'X is a WDXRF instrument designed for ease of use with minimal operation and maintenance costs. The instrument was fitted with a Thermo Scientific SmartGonio covering elements from fluorine (^{9}F) to uranium (^{92}U). A rhodium anode X-ray tube is used and the geometry of the instrument is optimized to provide the highest sensitivity. Two power versions exist, either a 50 W or the new 200 W version which has been used for the tests shown in this report.

The instrument does not require external or internal water cooling, and has 10 times better spectral resolution than a conventional EDXRF instrument as well as superior precision and stability. It has a good performance for sodium (^{11}Na), magnesium (^{12}Mg) and even for fluorine (^{9}F). Ease of operation is obtained through the state-of-the-art OXSAS software running under Windows® 7 environment.

Sample preparation

Samples were crushed and ground in a mill to less than 50 microns to reduce particle size effects. The fine powder is then pressed at 20 tons in a steel ring or on a borax support for mechanical stability. In general the pressed powder method is used for routine elemental determinations in cement and related materials, especially when simpler and faster preparation is required.

Calibration and results

A series of NIST certified reference materials have been used for calibration of the ARL OPTIM'X. These standard samples cover the concentration ranges shown in Table 1.

A working curve is established for each element using the Multi-Variable-Regression incorporated in the OXSAS analytical software. The Standard Error of Estimate (SEE) is a measure of the accuracy of analysis. It is the average error between the certified concentration of the standard samples and the calibration curve for a given oxide.

Figure 1 (on next page) shows the calibration curve for Na_2O determination.

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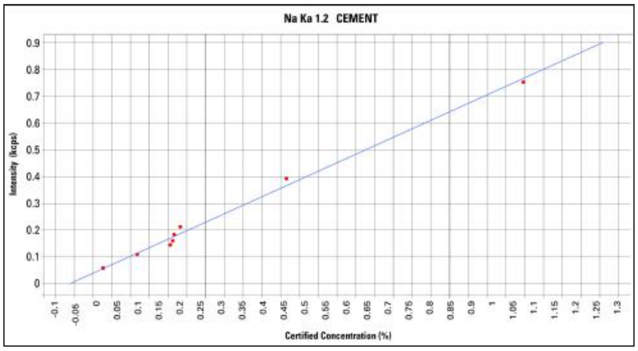

Figure 1: Calibration curve for Na_2O in cement using NIST standard samples. Standard error of estimate is 0.02% in a range from 0.02% to 1.1%

Table 1 shows the limits of detection for the various elements/oxides derived from the calibration curves. Light elements like Na and Mg can be successfully analyzed with the ARL OPTIM'X.

Elements	Typical Range [%]	Limits of detection [ppm] Collimator 100s	Typical SEE [%] Full range
CaO	57.5 - 67.4	n.r.	0.48
SiO_2	20 - 22.5	n.r.	0.19
Fe_2O_3	0.3 – 3.1	9	0.05
MgO	0.81 - 4.5	24	0.12
Al_2O_3	3.9 - 7.1	16	0.25
K_2O	0.16 - 1.27	4.3	0.026
Cl	0.004 - 0.013	9	0.0013
Na_2O	0.2 – 1.07	42	0.021
S	2.04 - 4.6	6.4	0.18
MnO	0.025-0.26	7	
P_2O_5	0.025-0.29	13	

Table 1: Concentration ranges and Standard Error of Estimate and limits of detection using the SmartGonio™ (0.29° collimator)
SEE = Standard error of estimate: it is a measure of the accuracy
LOD = limit of detection (3 sigma)
n.r. = not relevant in view of the high concentration ranges

Stability tests

In order to show the excellent repeatability of the ARL OPTIM'X at 200 W some stability tests were done.

For short term repeatability 10 consecutive measurements were performed on a cement pressed pellet with a counting time of 10 seconds per element on the SmartGonio. Average concentrations and standard deviations are shown in Table 2 (opposite).

Typical standard deviations expected in cement industry are also shown. The ARL OPTIM'X does comply with these values for all elements/oxides.

The long term repeatability test was done overnight. Table 3 (opposite) shows the results obtained with a sequential configuration: a pressed pellet was analyzed during 16 hours (178 measurements). A counting time of 10 seconds was chosen for each element measured on the SmartGonio. Average concentrations and standard deviations are shown in Table 3.

Run #	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	K_2O	Na_2O	MnO	K_2O	P_2O_5	Na_2O
# 1	62.27	20.79	4.43	2.66	4.60	1.02	0.254	2.78	0.139	0.191	0.085
# 2	62.21	20.81	4.44	2.63	4.59	1.01	0.264	2.77	0.136	0.187	0.086
# 3	62.28	20.79	4.42	2.65	4.62	1.01	0.248	2.77	0.134	0.191	0.084
# 4	62.25	20.83	4.44	2.65	4.57	1.01	0.234	2.76	0.131	0.189	0.085
# 5	62.28	20.80	4.44	2.64	4.60	1.01	0.242	2.77	0.129	0.190	0.084
# 6	62.25	20.80	4.43	2.65	4.62	1.02	0.247	2.76	0.140	0.185	0.086
# 7	62.23	20.81	4.42	2.63	4.60	1.02	0.246	2.78	0.134	0.185	0.082
# 8	62.25	20.81	4.42	2.63	4.59	1.01	0.252	2.76	0.136	0.186	0.086
# 9	62.27	20.83	4.43	2.64	4.60	1.02	0.251	2.76	0.139	0.188	0.083
# 10	62.29	20.83	4.43	2.64	4.56	1.02	0.236	2.77	0.141	0.187	0.086
AVG	62.26	20.81	4.43	2.64	4.60	1.01	0.248	2.77	0.136	0.188	0.085
Std Dev	0.025	0.015	0.009	0.01	0.020	0.003	0.009	0.008	0.004	0.002	0.001
Time	**10 s**	**10 s**	**10 s**	**10 s**	**10 s**	**10 s**	**10 s**	**10 s**	**10 s**	**10 s**	**10 s**
Desired Std Dev	0.03	0.02	0.02	0.015	0.015	0.02	0.02	0.012	0.012	0.015	0.015

Table 2: Results of a repeatability test on a cement pressed pellet (10 consecutive runs) for a sequential configuration at 200 W

Run #	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	K_2O	Na_2O	MnO	K_2O	P_2O_5	Na_2O
# 1	65.60	20.57	3.86	1.90	0.861	0.641	0.149	3.02	0.111	0.223	0.257
# 2	65.73	20.57	3.86	1.90	0.881	0.639	0.175	3.02	0.108	0.222	0.259
# 3	65.68	20.56	3.87	1.91	0.881	0.640	0.174	3.01	0.112	0.220	0.256
# 4	65.73	20.60	3.87	1.91	0.890	0.642	0.166	3.02	0.108	0.220	0.258
# 5	65.67	20.60	3.89	1.90	0.872	0.643	0.170	3.01	0.111	0.227	0.257
# 6	65.62	20.57	3.88	1.90	0.882	0.641	0.169	3.01	0.122	0.221	0.260
..	..	..	..	..	..	..	..	..	..	..	..
# 174	65.63	20.60	3.88	1.91	0.879	0.640	0.179	3.02	0.118	0.217	0.255
# 175	65.59	20.60	3.89	1.90	0.881	0.634	0.171	3.02	0.114	0.222	0.256
# 176	65.62	20.60	3.87	1.90	0.888	0.641	0.180	3.02	0.118	0.222	0.260
# 177	65.57	20.62	3.88	1.89	0.879	0.644	0.163	3.03	0.123	0.222	0.256
# 178	65.65	20.60	3.88	1.91	0.883	0.644	0.175	3.02	0.117	0.222	0.256
# 177	65.57	20.62	3.88	1.89	0.879	0.644	0.163	3.03	0.123	0.222	0.256
# 178	65.65	20.60	3.88	1.91	0.883	0.644	0.175	3.02	0.117	0.222	0.256
AVG	65.63	20.60	3.88	1.90	0.879	0.641	0.172	3.02	0.114	0.221	0.256
Std Dev	0.046	0.020	0.013	0.006	0.008	0.003	0.007	0.008	0.003	0.003	0.002
Time	**10 s**	**10 s**	**10 s**	**10 s**	**10 s**	**10 s**	**10 s**	**10 s**	**10 s**	**10 s**	**10 s**

Table 3: Results of a repeatability test on a cement pressed pellet (10 consecutive runs) for a sequential configuration at 200W.

Conclusion

The ARL OPTIM'X WDXRF instrument permits successful analysis of various elements in cement and clinker in less than two minutes. Pressed pellet sample preparation is fast and simple and allows lower limits of detection and good precision.

Good repeatability and reproducibility is obtained with the SmartGonio for all elements. If better results are required for any element, the counting time for that particular element can be increased, but in view of the excellent standard deviations obtained the counting time for some elements could even be decreased, e.g. to 4s for K_2O, P_2O_5, TiO_2 and MnO thus reducing the total counting time to just 1 minutes and a half for 11 elements.

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