

# Analysis of clinker and cement

## Thermo Scientific ARL OPTIM'X WDXRF Sequential Spectrometer

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### 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 oxygen ( $^{16}\text{O}$ ) to americium ( $^{253}\text{Am}$ ). 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 ( $^{23}\text{Na}$ ), magnesium ( $^{24}\text{Mg}$ ) and even for fluorine ( $^{19}\text{F}$ ). Ease of operation is obtained through the state-of-the-art OXSAS software running under Windows® 10 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 boric acid 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  $\text{Na}_2\text{O}$  determination.

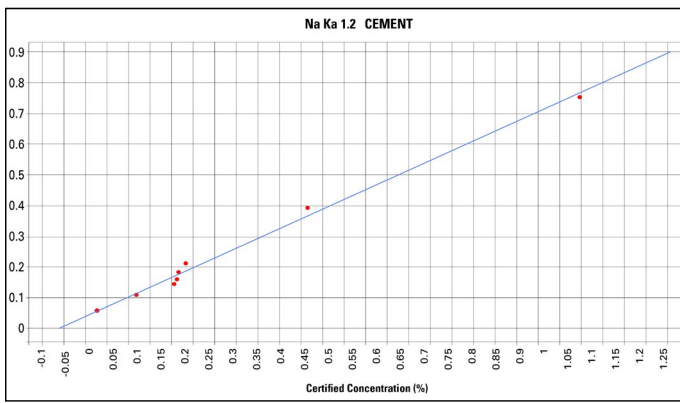


Figure 1: Calibration curve for Na<sub>2</sub>O in cement using NIST standard samples. Standard error of estimate is 0.02% in a range from 0.02% to 1.1%

### 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 and 20 seconds for MgO on the SmartGonio. Average concentrations and standard deviations are shown in Table 2 (below).

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 (below) shows the results obtained with a sequential configuration: a pressed pellet was analyzed during 16 hours (178 measurements). A counting time

Run #	CaO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MgO	SO <sub>3</sub>	Na <sub>2</sub> O	K <sub>2</sub> O	TiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	Mn <sub>2</sub> O <sub>3</sub>
# 1	62.27	20.79	4.43	2.66	4.62	2.78	0.254	1.02	0.191	0.139	0.085
# 2	62.21	20.81	4.44	2.63	4.59	2.77	0.264	1.01	0.187	0.136	0.086
# 3	62.28	20.79	4.42	2.65	4.60	2.77	0.248	1.01	0.191	0.134	0.084
# 4	62.25	20.83	4.44	2.65	4.59	2.76	0.234	1.01	0.189	0.131	0.085
# 5	62.28	20.80	4.44	2.64	4.60	2.77	0.242	1.01	0.190	0.129	0.084
# 6	62.25	20.80	4.43	2.65	4.61	2.76	0.247	1.02	0.185	0.140	0.086
# 7	62.23	20.81	4.42	2.63	4.60	2.78	0.246	1.02	0.185	0.134	0.082
# 8	62.25	20.81	4.42	2.63	4.57	2.76	0.252	1.01	0.186	0.136	0.086
# 9	62.27	20.83	4.43	2.64	4.60	2.76	0.251	1.02	0.188	0.139	0.083
# 10	62.29	20.83	4.43	2.64	4.58	2.77	0.236	1.02	0.187	0.141	0.086
<b>AVG</b>	62.26	20.81	4.43	2.64	4.60	2.77	0.248	1.01	0.188	0.136	0.085
<b>Std Dev</b>	0.025	0.015	0.009	0.01	0.014	0.008	0.009	0.003	0.002	0.004	0.001
<b>Time</b>	<b>10 s</b>	<b>10 s</b>	<b>10 s</b>	<b>10 s</b>	<b>20 s</b>	<b>10 s</b>	<b>10 s</b>	<b>10 s</b>	<b>10 s</b>	<b>10 s</b>	<b>10 s</b>
<b>Desired Std Dev</b>	0.03	0.02	0.02	0.015	0.015	0.012	0.02	0.02	0.015	0.012	0.015
<b>Pass or fail</b>	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK

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

of 10 seconds was chosen for each element and 20 seconds for MgO on the SmartGonio so that the total counting time was 120 seconds. The sample is unloaded from the instrument after each analysis. Average concentrations and standard deviations are shown in Table 3 for the first six runs and the last five runs.

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	Portland Cement Typical Range [%]	LoD [ppm] 100s	Typical SEE [%] Full range
CaO	57.5 – 67.4	n.r.	0.48
SiO <sub>2</sub>	20 – 22.3	n.r.	0.19
Al <sub>2</sub> O <sub>3</sub>	3.9 – 7.1	16	0.25
Fe <sub>2</sub> O <sub>3</sub>	0.3 – 3.1	9	0.05
MgO	0.81 – 4.5	24	0.12
SO <sub>3</sub>	2.04 – 4.6	6.4	0.18
Na <sub>2</sub> O	0.2 – 1.07	42	0.021
K <sub>2</sub> O	0.16 – 1.27	4.3	0.026
Cl	0.004 – 0.013	9	0.0013
P <sub>2</sub> O <sub>5</sub>	0.025 – 0.22	13	0.016
Mn <sub>2</sub> O <sub>3</sub>	0.013 – 0.26	7	0.0053

Table 1: Concentration ranges, SEE and LoDs 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

Run #	CaO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MgO	SO <sub>3</sub>	Na <sub>2</sub> O	K <sub>2</sub> O	TiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	Mn <sub>2</sub> O <sub>3</sub>
# 1	65.60	20.57	3.86	1.90	0.861	3.02	0.169	0.641	0.223	0.111	0.257
# 2	65.73	20.57	3.86	1.90	0.881	3.02	0.175	0.639	0.222	0.108	0.259
# 3	65.68	20.56	3.87	1.91	0.881	3.01	0.174	0.640	0.220	0.112	0.256
# 4	65.73	20.60	3.87	1.91	0.890	3.02	0.166	0.642	0.220	0.108	0.258
# 5	65.67	20.60	3.89	1.90	0.872	3.01	0.170	0.643	0.227	0.111	0.257
# 6	65.62	20.57	3.88	1.90	0.882	3.01	0.169	0.641	0.221	0.122	0.260
..	..	..	..	..	..	..	..	..	..	..	..
# 174	65.63	20.60	3.88	1.91	0.879	3.02	0.179	0.640	0.217	0.118	0.255
# 175	65.59	20.60	3.89	1.90	0.881	3.02	0.171	0.634	0.222	0.114	0.256
# 176	65.62	20.60	3.87	1.90	0.888	3.02	0.180	0.641	0.222	0.118	0.260
# 177	65.57	20.62	3.88	1.89	0.879	3.03	0.163	0.644	0.222	0.123	0.256
# 178	65.65	20.60	3.88	1.91	0.883	3.02	0.175	0.644	0.222	0.117	0.256
<b>AVG</b>	65.63	20.60	3.88	1.90	0.879	3.02	0.172	0.641	0.221	0.114	0.256
<b>Std Dev</b>	0.046	0.020	0.013	0.006	0.008	0.008	0.007	0.003	0.003	0.003	0.002
<b>Time</b>	<b>10 s</b>	<b>10 s</b>	<b>10 s</b>	<b>10 s</b>	<b>20 s</b>	<b>10 s</b>	<b>10 s</b>	<b>10 s</b>	<b>10 s</b>	<b>10 s</b>	<b>10 s</b>

Table 3: Results of a long term test on cement pressed pellet B (178 consecutive runs) for a sequential configuration at 200 W (only the first six and last five runs are shown, but average and standard deviation are those obtained on the 178 results).

### 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<sub>2</sub>O, P<sub>2</sub>O<sub>5</sub>, TiO<sub>2</sub> and Na<sub>2</sub>O thus reducing the total counting time to just 1 minutes and a half for 11 elements.

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