APPLICATION NOTE

Analysis of cement related materials

No. AN41705

ARL OPTIM'X WDXRF Spectrometer

Key words
ARL OPTIM'X, cement, raw meal, X-ray fluorescence

Introduction

X-ray fluorescence allows the analysis of major and minor oxides present in the raw materials and products found in the cement industry.

Instrumentation

The Thermo Scientific ARL OPTIM'X is an entry level WDXRF instrument designed for ease of use with minimal running and maintenance costs. An ARL OPTIM'X XRF spectrometer configured as a sequential-simultaneous unit was used to obtain the results presented in this application note. The instrument was fitted with a SmartGonio™ covering elements from Al (Z=13) to U (Z=92) and with fixed channels for elements Mg (Z=12) and Na (Z=11).

The ARL OPTIM'X XRF spectrometers are fitted with a low power Rh anode X-ray tube and the geometry of the instrument is optimized to provide the highest sensitivity. It does not require external or internal water cooling. The spectrometer superior precision, short and long term stability. It can analyse Na and Mg without problem. Ease of operation is obtained through OXSAS, our modern, powerful and user-friendly software supporting instrument operation and data handling.

Sample preparation

For the sake of comparison, two types of sample preparation have been used.

For preparing pressed pellets, 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.

When samples originate from various locations differences of mineralogy can produce adverse effects on the final accuracy of analysis. In such cases a preparation through fusion with a mixture of lithium tetraborate/lithium metaborate will eliminate these mineralogical effects as well as any grain size effects. The obtained samples are called fusion beads.

Superior accuracy can be obtained with this method but the preparation takes a longer time and is not as simple as the pressed pellet method. For this test a dilution ratio of 1:3 sample to flux was chosen.

Calibration and results

A series of NIST certified reference materials have been used for calibration of the ARL OPTIM'X. These standard samples allow the concentration ranges shown in Table 1 to be covered. Both preparation methods described above have been used.

A working curve is established for each element using the Multi-Variable-Regression incorporated in the OXSAS software package. 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 of a given oxide.

Table 1 shows the limits of detection for the various elements/oxides derived from the calibration curves for sample preparation either as pressed pellet or fused bead.

Light elements like Na and Mg can be successfully analyzed with the ARL OPTIM'X. Figure 1 shows a calibration curve for Na_2O determination for fused beads. Limits of detection for Mg and Na using fixed channels and SmartGonio and different counting times are listed in Table 2.

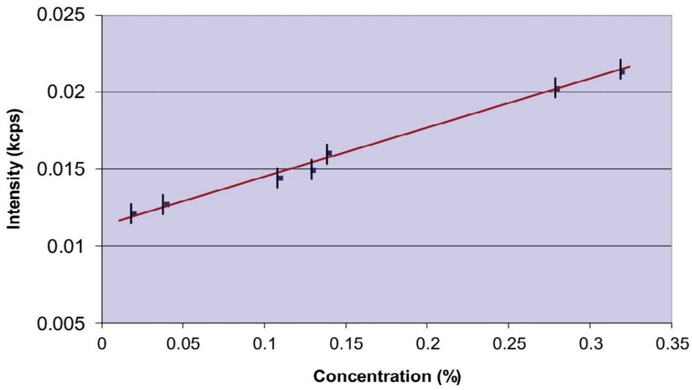

Figure 1: Calibration curve for Na_2O in cement using sample preparation as fusion beads. Standard error of estimate is 0.011 % in a range from 0.02 % to 0.32 %

Elements/ oxides	Analytical device	Calibration ranges (%)	Pressed pellets		Fusion beads (dilution 1:3)	
			SEE (%)	LOD (%)	SEE (%)	LOD (%)
CaO	SmartGonio	28 -67	0.19	n.r	0.13	n.r
SiO_2	SmartGonio	20 - 23.2	0.2	n.r.	0.18	n.r.
Al_2O_3	SmartGonio	3.3 -72	0.08	n.r.	0.08	n.r.
Fe_2O_3	SmartGonio	0.1 -16	0.041	20 in 60s	0.027	30 in 60s
MgO	Fixed	0.3 -2.7	0.23	47 in 540s	0.02	85 in 540s
Na_2O	Fixed	0.04 -0.32	0.027	25 in 540s	0.011	137 in 540s
K_2O	SmartGonio	0.02 -1.2	0.026	6 in 60s	0.002	18 in 60s
SO_3	SmartGonio	0.02 -3.7	0.12	15 in 60s	0.05	60 in 60s
P_2O_5	SmartGonio	0.02 -0.29	0.007	55 in 60s	0.011	130 in 60s
TiO_2	SmartGonio	0.1 -16	0.02	25 in 60s	0.009	50 in 60s
Mn_2O_3	SmartGonio	0.01 -0.26	0.01	16 in 60s	0.006	26 in 60s

Table 1: Summary of performance for pressed pellets and fusion beads (dilution 1:3) for a sequential-simultaneous configuration. Fixed channels are usuallyprogrammed to measure during the entire time used by the SmartGonio for analysis of the other elements.
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

Elements/oxides	Analytical device	Pressed pellets	Fusion beads (dilution 1:3)
		LOD (ppm)	LOD (ppm)
MgO	Fixed	47 in 540s	85 in 540s
MgO	Fixed	141 in 60s	255 in 60s
MgO	SmartGonio	115 in 60s	210 in 60s
Na_2O	Fixed	25 in 540s	137 in 540s
Na_2O	Fixed	75 in 60s	411 in 60s
Na_2O	SmartGonio	60 in 60s	305 in 60s

Table 2: Comparison of performance for SmartGonio and fixed channels for Mg and Na analysis.

Stability tests

In order to show the excellent repeatability of the ARL OPTIM'X both in short and long term, stability tests were performed using raw meal samples. For short term repeatability 11 consecutive measurements were performed on a pressed standard. Counting time of 60 seconds and 20 seconds were chosen for each element measured on the SmartGonio. Mg and Na on fixed channel were analyzed in parallel during 540 seconds and 180 seconds respectively. Average concentrations and standard deviations are shown in Table 3.

For long term repeatability tests over 3 days two instruments were used. Table 4 shows the results obtained with a sequential-simultaneous configuration: a pressed pellet and a fusion bead were analyzed during 60 hours (120 consecutive measurements at an interval of 25 minutes). A counting time of 20 seconds was chosen for each element measured on the SmartGonio (except for Si, 40s). Mg and Na on fixed channel were analyzed in parallel during 200 seconds. Average concentrations and standard deviations are shown in Table 4.

Table 5 shows the reproducibility results obtained on a pressed pellet sample with a sequential configuration. Two different total counting times have been used for the repeat runs over the 3 day test. Typical standard deviations expected in cement industry are also shown.

Elements/ oxides	Analytical device	Average concentration (%)	Pressed powder			
			Counting Time A	Typical std. Dev. (%)	Counting Time B	Typical std. Dev. (%)
CaO	SmartGonio	42.35	60s	0.03	20s	0.05
SiO_2	SmartGonio	13.88	60s	0.02	20s	0.035
Al_2O_3	SmartGonio	3.34	60s	0.018	20s	0.03
Fe_2O_3	SmartGonio	1.18	60s	0.006	20s	0.01
MgO	Fixed channel	1.06	Fixed	0.003	Fixed	0.005
Na_2O	Fixed channel	0.198	Fixed	0.003	Fixed	0.005
K_2O	SmartGonio	0.54	60s	0.002	20s	0.003
SO_3	SmartGonio	0.056	60s	0.0002	20s	0.0003
P_2O_5	SmartGonio	0.038	60s	0.002	20s	0.003
TiO_2	SmartGonio	0.151	60s	0.002	20s	0.003
Mn_2O_3	SmartGonio	0.028	60s	0.001	20s	0.002
Total counting time			540s		180s	

Table 3: Results of a repeatability test on a pressed pellet of raw meal (11 consecutive runs) for a sequential-simultaneous configuration.

Elements/ oxides	Analytical device	Counting time	Pressed powder		Fusion beads (dilution 1:3)	
			Average concentration (%)	Typical std. Dev. (%)	Average concentration (%)	Typical std. Dev. (%)
CaO	SmartGonio	20s	42.35	0.07	42.28	0.05
SiO_2	SmartGonio	40s	13.88	0.08	13.32	0.045
Al_2O_3	SmartGonio	20s	3.34	0.028	3.39	0.033
Fe_2O_3	SmartGonio	20s	1.18	0.007	1.86	0.011
MgO	Fixed channel	Fixed	1.06	0.006	1.1	0.008
Na_2O	Fixed channel	Fixed	0.198	0.005	0.146	0.011
K_2O	SmartGonio	20s	0.54	0.004	0.65	0.007
SO_3	SmartGonio	20s	0.056	0.0014	0.061	0.006
P_2O_5	SmartGonio	20s	0.038	0.0024	0.034	0.006
TiO_2	SmartGonio	20s	0.151	0.003	0.21	0.005
Mn_2O_3	SmartGonio	20s	0.028	0.001	0.057	0.002
Total counting time		200s				

Table 4: Results of a 60 hours reproducibility test (120 runs) for a sequential-simultaneous configuration.

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Element/oxide	Concentration level	Required std. Dev.	Analysis time	Std. Dev.	Analysis time	Std. Dev.
CaO	63.8	0.03 - 0.035	30s	0.033	60s	0.026
SiO_2	20.3	0.02	40s	0.02	60s	0.017
Al_2O_3	5.2	0.02	20s	0.016	60s	0.01
Fe_2O_3	2.8	0.01-0.02	10s	0.014	60s	0.006
MgO	1.7	0.02	30s	0.024	60s	0.01
Na_2O	0.2	0.015	10s	0.007	60s	0.003
K_2O	0.9	0.02	6s	0.01	60s	0.003
SO_3	3.2	0.01-0.015	20s	0.013	60s	0.008
P_2O_5	0.2	0.01-0.015	10s	0.013	60s	0.007
TiO_2	0.1	0.015	10s	0.012	60s	0.005
Mn_2O_3		0.015	10s	0.008	60s	0.003
Total			196s		660s	

Table 5: Results of a 3 day reproducibility test on a cement pressed pellet for a sequential configuration: two different total counting times per run have been used (196s and 660s). The standard deviations that are typically required in the cement industry are shown in the third column.

Conclusion

The ARL OPTIM'X low power WDXRF instrument performs well for the analysis of the various elements in materials related to cement manufacture. Pressed pellet sample preparation is fast and simple and allows lower limits of detection and good precision. To get the best accuracy with materials of different origins it is necessary to prepare the samples as fused beads in order to avoid grain size effects and mineralogical effects.

Good repeatability and reproducibility is obtained with the ARL OPTIM'X using total counting time of about 200s. Up to two fixed channels can be fitted alongside the SmartGonio and programmed to analyze in parallel with the SmartGonio such as to improve the repeatability and decrease the total counting time.

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