



Quantitative Analysis of Oxides in
Cement

OBJECTIVES

- (1) Calibrate the instrument for the six oxides: MgO, Al₂O₃, SiO₂, SO₃, CaO, and Fe₂O₃ in cement. Run the unknowns against the calibration.
- (2) Demonstrate the instrument repeatability

BACKGROUND

Cement is generally defined as any of a variety of substances used for bonding or settling to a hard material. Portland cement, currently the foundation of modern industrial construction techniques, is a mixture of calcium silicates and aluminates made by heating limestone with clay in a kiln. The resulting material is then ground to fine powder (cement). Controlling even relatively small changes in the composition of cements during the production process has become a high priority of interest in manufacturers worldwide. X-ray fluorescence is an accepted technique in the analysis of cement and the raw materials in the cement production process. EDXRF can play a vital role in this industry by giving accurate analytical results in a short amount of time.

EDXRF is an ideal method for a quick and simple elemental analysis for industrial control purposes offering the following advantages: 1) Fast and minimal sample preparation, 2) An automated analysis process, 3) Limited or no exposure to corrosive reagents used by other analytical techniques, 4) Ease of use for operation by non-technical or non-specialized personnel.

ANALYTICAL CONFIGURATION

Table 1: Analytical Configuration

Instruments	EX-Calibur bench top EDXRF Spectrometer
Excitation	50-keV Rh-Anode X-ray Tube
Detector	Peltier-cooled Si PIN-Diode High Resolution Detector
Analysis Time	480 seconds for Mg, Al, Si, S, Ca, 120 seconds for Fe
Calibration Method	Quantitative
Modifications	None
Environment	Vacuum for analysis for light elements, Air for Fe
Sample Preparation & Details	Samples were prepared by hydraulically pressing 5 grams of cement at 23,000 pounds in a die mold

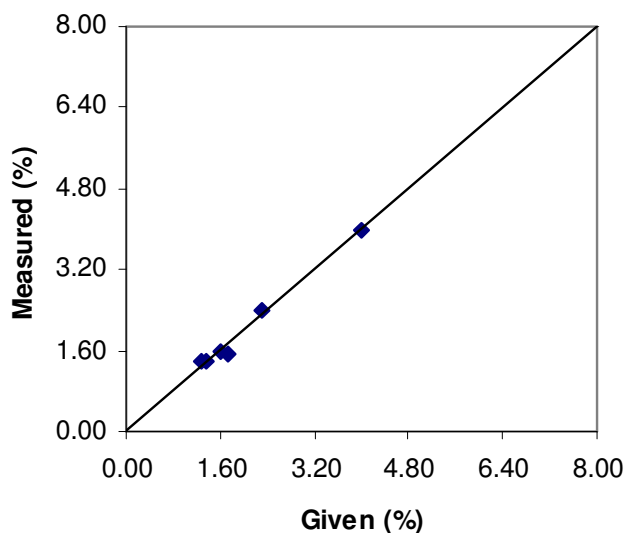
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RESULTS CALIBRATION

Table 2: Calibration data for Mg as MgO (units in %)

RMS Deviation: 0.10%		
R2 Correlation: 0.995		
Sample	Given	Measured
D1880a	1.72	1.52
D1884	2.32	2.38
D1885	4.02	4.00
D1886	1.60	1.59
D1887	1.26	1.38
D1889	1.38	1.41

Figure 1: Calibration plot for Mg as MgO

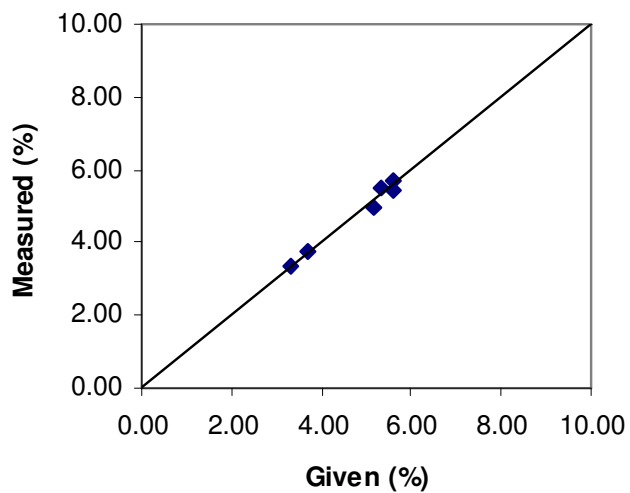


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Table 3: Calibration data for Al as Al₂O₃ (units in %)

RMS Deviation: 0.13%		
R2 Correlation: 0.996		
Sample	Given	Measured
D1880a	5.18	4.99
D1884	3.31	3.33
D1885	3.68	3.73
D1887	5.59	5.71
D1888	5.35	5.50
D1889	5.61	5.46

Figure 2: Calibration plot for Al as Al₂O₃

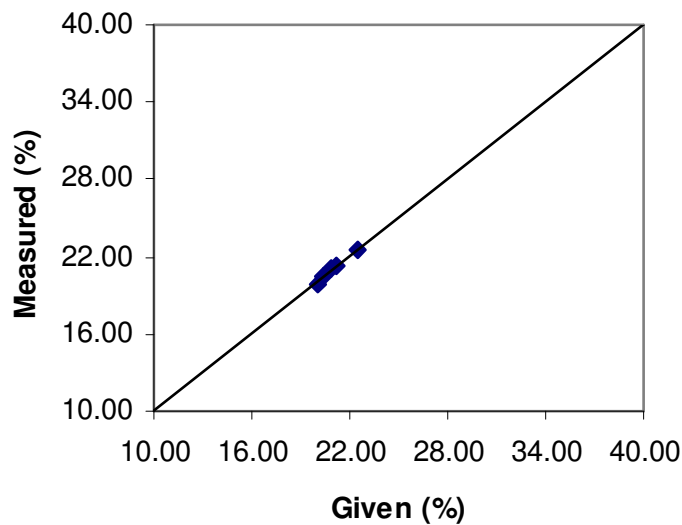


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Table 4: Calibration data for Si as SiO₂ (units in %)

RMS Deviation: 0.07%		
R2 Correlation: 0.997		
Sample	Given	Measured
D1885	21.20	21.23
D1886	22.50	22.44
D1887	20.00	19.96
D1888	20.90	21.01
D1889	20.40	20.39

Figure 3: Calibration plot for Si as SiO₂

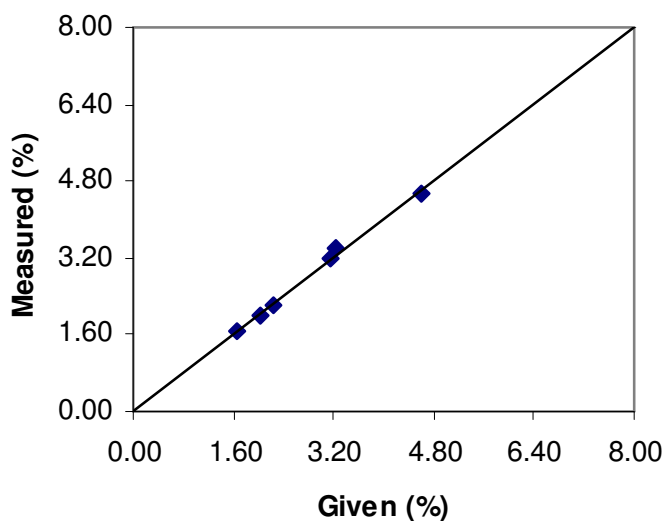


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Table 5: Calibration data for S as SO₃ (units in %)

RMS Deviation: 0.07%		
R2 Correlation: 0.997		
Sample	Given	Measured
D1880a	3.25	3.40
D1884	1.67	1.66
D1885	2.22	2.22
D1886	2.04	1.98
D1887	4.61	4.52
D1888	3.16	3.17

Figure 4: Calibration plot for S as SO₃

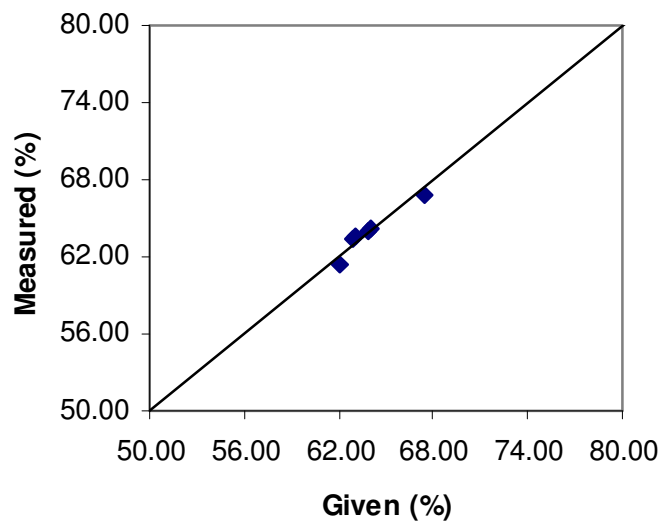


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Table 6: Calibration data for Ca as CaO (units in %)

RMS Deviation: 0.51%		
R2 Correlation: 0.953		
Sample	Given	Measured
D1880a	63.10	63.69
D1884	64.01	64.15
D1885	62.14	61.35
D1886	67.43	66.86
D1887	62.88	63.32
D1888	63.78	63.95

Figure 5: Calibration plot for Ca as CaO

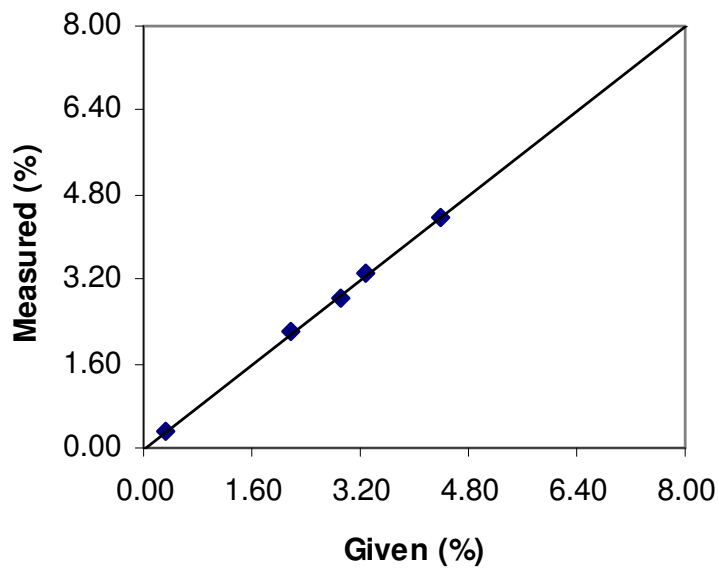


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Table 7: Calibration data for Fe as Fe₂O₃ (units in %)

RMS Deviation: 0.04%		
R2 Correlation: 0.999		
Sample	Given	Measured
H1880a	2.91	2.86
H1884	3.30	3.34
H1885	4.40	4.38
H1886	0.31	0.29
H1887	2.16	2.21

Figure 6: Calibration plot for Fe as Fe₂O₃



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OBSERVED STATIC PRECISION

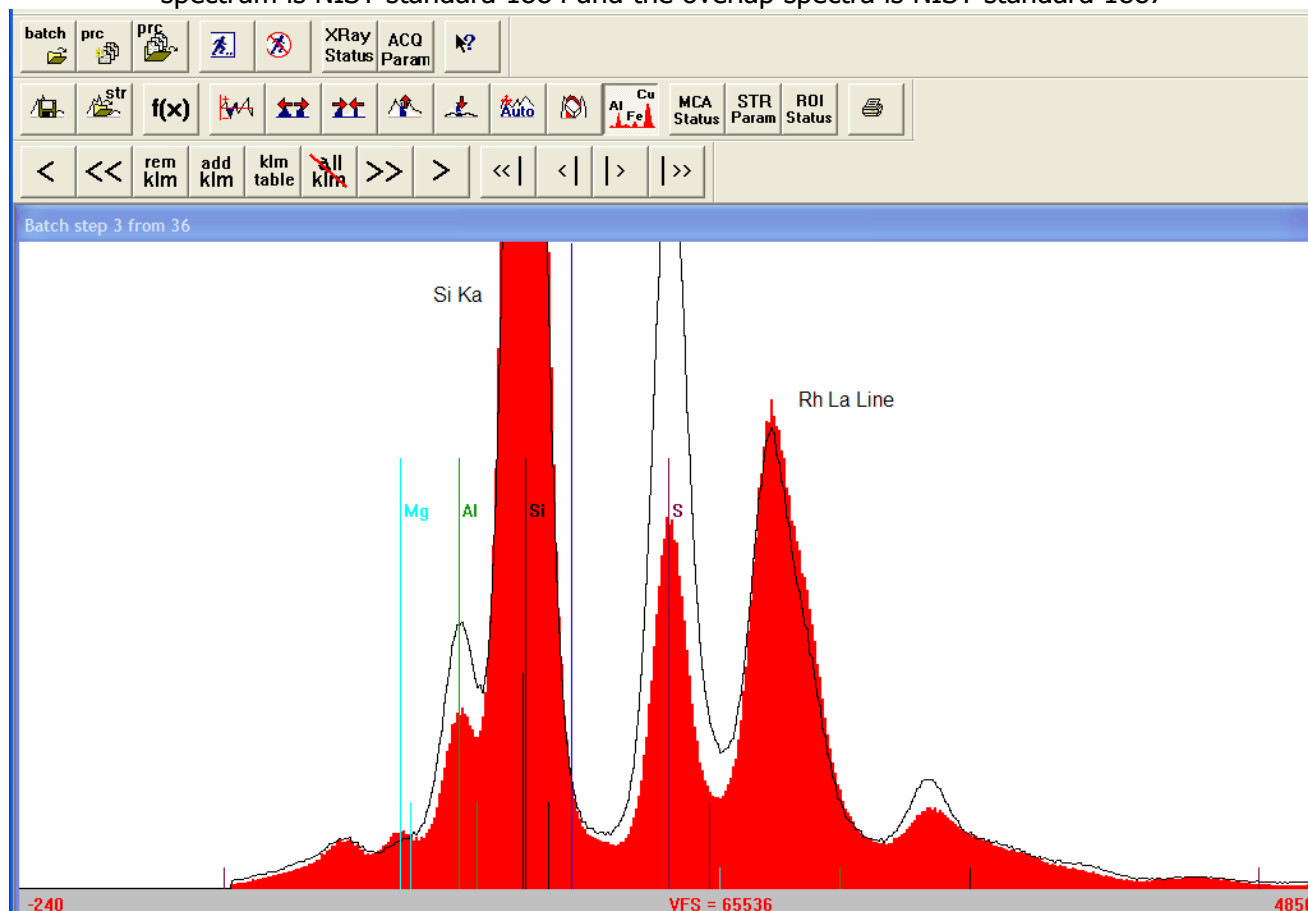
(10 repeat analysis at 480 seconds per analysis for the light elements, 120 seconds for Fe₂O₃.)

Table 8: Precision results on sample: NIST 1887 Portland Cement

Element	Given (%)	Mean (%)	Std. Dev. (%)	% Relative
MgO	1.26	1.39	0.01	0.68
Al ₂ O ₃	5.59	5.67	0.03	0.59
SiO ₂	20.00	19.90	0.11	0.55
SO ₃	4.61	4.53	0.01	0.30
CaO	63.78	63.40	0.24	0.38
Fe ₂ O ₃	2.16	2.26	0.03	1.42

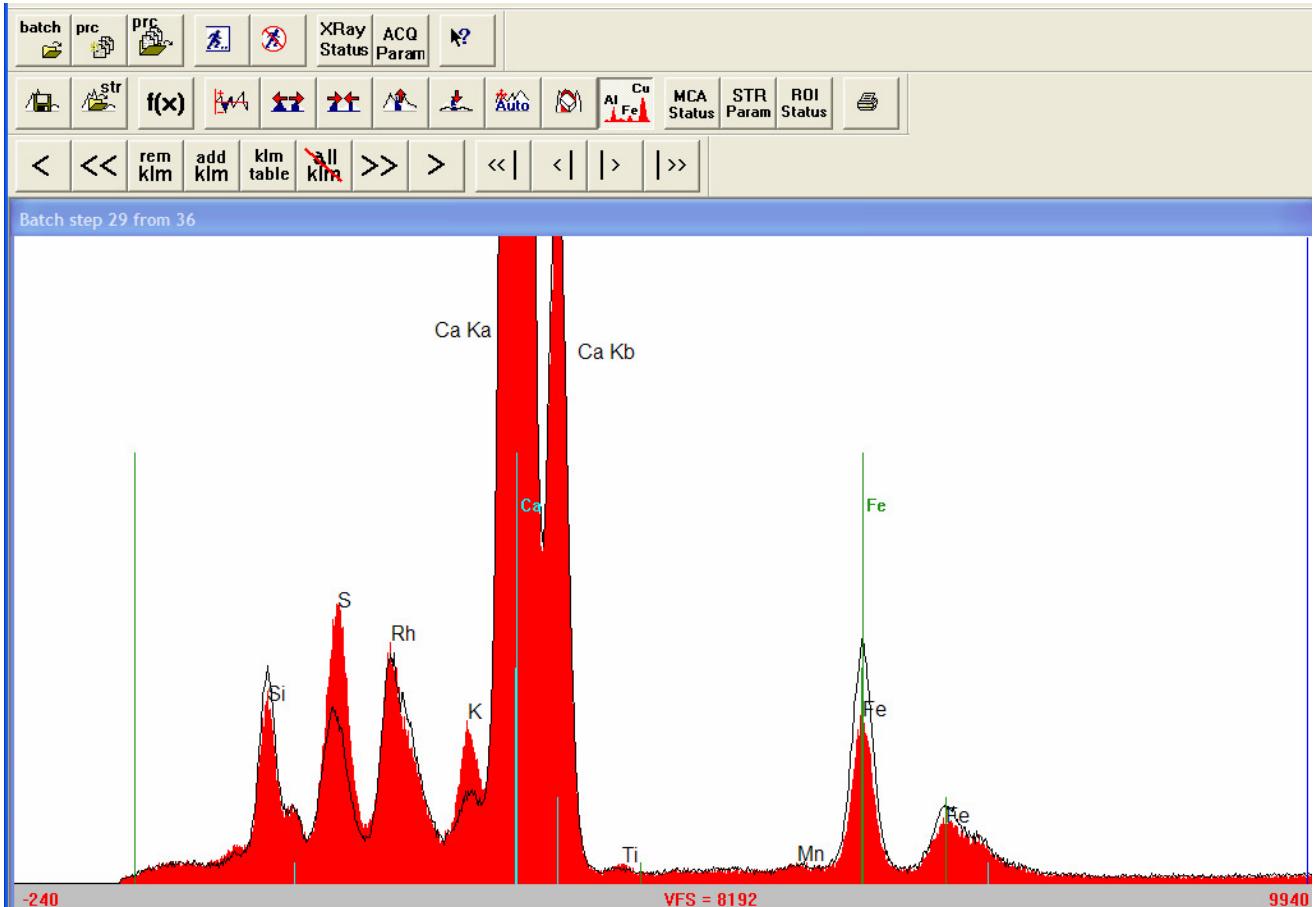
SPECTRA

Figure 7: Segment of the spectra of the Ca and Fe acquisition under air environment. The main spectrum is NIST standard 1884 and the overlap spectra is NIST standard 1887



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Figure 1: Segment of the spectra of the Ca and Fe acquisition under air environment. The overlap spectrum is NIST standard 1884 and the main spectra is NIST standard 1887.



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DISCUSSION

Calibration and precision data for this application demonstrate the capabilities of the Energy Dispersive X-ray Fluorescence (EDXRF) EX-Calibur spectrometer, as an analytical technique for the assay of the major oxides in cement. The EX-Calibur is a state-of-the-art benchtop EDXRF instrument, offering the analytical performance of an expensive EDXRF instrument in small footprint with the lowest price to performance ratio available. The High Resolution Si PIN Diode detector's enhanced peak to background ratio, ability to handle high count rates, and a resolution of $160\text{eV} \pm 10\text{ eV}$ at 5.9keV makes this possible.

EDXRF, like most analytical methods, is reference standard dependent. In a fast, non-destructive manner, XRF compares the elemental spectral intensities obtained from an unknown sample, to those previously obtained from a series of known standards. If the reference standards have not been accurately characterized, they will yield unacceptable answers. All of the concentrations of the elements-of-interest in the reference standards should be determined as accurately as possible. Furthermore, the sample matrix (all other constituents in the sample) should be well represented in the reference standards, as a different matrix will give a false representation of the actual sample. Choosing standards that closely match the unknowns will help produce reliable results. The NIST Portland Cement standards were chosen for this reason.

Two acquisitions (per sample) were performed to provide optimal performance for the element-of-interest. MgO, Al₂O₃, SiO₂, SO₃, and CaO analysis were performed under a vacuum environment in one acquisition and Fe₂O₃ was performed in a separate acquisition in an air environment. The EX-Calibur instrument employs a vacuum purge system for the analysis of light elements (low Z). Light elements (Na through Si) emit relatively weak signals and are easily absorbed by air. Using a vacuum purge effectively displaces the air in the analysis chamber and thereby increases the amount of fluorescence reaching the detector. Thus through purging and the use of the optimized detectors, overall precision and sensitivity of the measurement is improved.

The analysis of MgO, Al₂O₃, SiO₂, SO₃, CaO, and Fe₂O₃ demonstrate that superb results can be obtained by the EX-Calibur. The analysis on MgO, Al₂O₃, SiO₂, SO₃, CaO, and Fe₂O₃ can be found in tables 3, 4, 5, 6, and 7. A statistical summary of precision for NIST standard 1887 can be found in table 8.

All analyses were performed using the powerful nEXt software, which calculates all sensitivity monitoring, calibration routines and results automatically. nEXt is simple to use for non-technical personnel, yet powerful enough for research and development work.

CONCLUSION

The results of this study indicate that excellent performance is achieved using the EX-Calibur spectrometer. Optimum analysis of MgO, Al₂O₃, SiO₂, SO₃, CaO and Fe₂O₃ is due in part to the sensitivity of the High Resolution Si PIN Diode detector in the EX-Calibur. The 50 kV Rh X-ray tube allows for versatility in other types of applications should the need for high Z elements arise. Ease of use and powerful software of the EX-Calibur make this an ideal instrument for cement applications.