APPLICATION NOTE # XE-2012-3189

Quantitative analysis of fused and pressed cement samples.

Objective

The quantitative determination of cement composition.

Background

Controlling even relatively small changes in the composition of cement during the production process has become a high priority interest of progressive manufacturers worldwide. Timely and accurate analytical results during every stage of production are the keys to quality control. Xenemetrix X-Calibur Energy Dispersive X-Ray Fluorescence (EDXRF) spectrometers can play an important role in assuring that consistent quality is documented at every manufacturing step. The highly sensitive and extremely count efficient silicon drift detector combined with a newest rapid digital pulse processor technology makes the X-Calibur SDD the world most competitive analyzer in the cement industry. Specifically EDXRF can play a critical role in resolving these challenges by providing the following benefits: 1) simple and rapid sample preparation, 2) automated analyzes, via a multi-position sample carousel, couples with rapid data collection for high throughput without operator intervention, 3) high precision for major constituents, 4) minimal maintenance and at-line operation for low-cost-per-analysis, and 5) non-technical operation.

In order to demonstrate the efficacy of EDXRF for this purpose, a set of customer supplied reference materials were used. The investigation examined the ability of EDXRF to quantify all the major components in a manner useful for quality assurance in routine manufacturer operations .

Table 1: Analytical Configuration of X-Calibur SDD

Instrument	X-Calibur SDD EDXRF Benchtop Spectrometer System
Excitation	Rh anode X-Ray tube, 50W, 50kV
Detector	High resolution and high count efficient Silicon Drift Detector (SDD)
Type of analysis	Quantitative analysis using regression method
Environment	Vacuum
Sample preparation	Fused cement samples for major elements. Pressed samples for SO3

I. Determination of MgO, Al_2O_3, SiO_2, P_2O_5 CaO and Fe_2O_3 concentrations in cement using fused reference samples.

1. Calibration Results

Measurements were done on ten fused cement reference samples provided by the cement manufacturer. A calibration curve for each element was established using regression analysis and a model taking into account the different matrix effects. In Table 2 are shown the analytical results of the calibration. Given and calculated concentrations for the different elements of each reference standard are tabulated in the table and are plotted in the calibration plots shown in Figures 1-7. Standard deviations and correlation data are also included for each element in Table 2.

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Table 2: Calibration data of the major oxides in cement using fused reference samples

	MgO		Al_2O_3		SiO_2		P_2O_5	
Fused Samples	**Std.Dev**. 0.011% **Correlation**: 0.993		**Std.Dev**. 0.058% **Correlation**: 0.999		**Std.Dev**. 0.077% **Correlation**: 1.000		**Std.Dev**. 0.012% **Correlation**: 0.998	
Ref ID	**Given Conc %**	**Calc'd Conc %**	**Given Conc %**	**Calc'd Conc %**	**Given Conc %**	**Calc'd Conc %**	**Given Conc %**	**Calc'd Conc %**
Ref 1	0.66	0.67	3.32	3.37	14.20	14.29	0.08	0.09
Ref 2	0.46	0.46	1.44	1.36	6.08	6.13	0.00	0.01
Ref 3	0.49	0.51	1.87	1.81	8.04	7.98	0.01	0.00
Ref 4	0.73	0.73	3.78	3.88	16.50	16.48	0.05	0.05
Ref 5	0.55	0.60	2.73	2.71	11.44	11.50	0.03	0.04
Ref 6	0.71	0.71	4.13	4.10	16.73	16.74	0.07	0.05
Ref 7*	0.68	0.65	3.28	3.25	14.11	13.93	0.41	0.42
Ref 8	0.61	0.60	2.67	2.70	11.37	11.41	0.41	0.39
Ref 9	0.57	0.56	2.35	2.26	9.81	9.76	0.41	0.40
Ref 10	0.72	0.72	3.74	3.76	16.05	16.09	0.39	0.40

* Reference sample Ref 7 was excluded from the calibration data due to the large deviation in CaO and in SiO2 concentrations from given values.

Table 2 cont'd: Calibration data of the major oxides in cement using fused reference samples Calibration data of SO_3 using pressed reference samples.

	CaO		Fe_2O_3	
Fused Samples	**Std.Dev**. 0.038% **Correlation**: 1.000		**Std.Dev**. 0.020% **Correlation**: 0.999	
Ref ID	**Given Conc %**	**Calc'd Conc %**	**Given Conc %**	**Calc'd Conc %**
Ref 1	43.10	43.11	1.93	1.91
Ref 2	50.18	50.21	0.78	0.81
Ref 3	48.61	48.55	1.04	1.04
Ref 4	41.25	41.21	2.21	2.21
Ref 5	46.63	45.53	1.46	1.43
Ref 6	41.22	41.23	2.02	2.05
Ref 7*	43.18	43.34	1.60	1.67
Ref 8	45.68	45.64	1.30	1.28
Ref 9	46.98	47.02	1.10	1.10
Ref 10	41.44	41.48	1.92	1.93

	SO_3	
Pressed Samples	**Std.Dev**. 0.02% **Correlation**: 1.000	
Ref ID	**Given Conc %**	**Calc'd Conc %**
S1	11.10	11.10
S2	4.55	4.54
S3	2.17	2.20
S4	1.97	1.96
S5	0.29	0.27

2. Calibration Plots

Figure 1: Calibration Plot of Al_2O_3

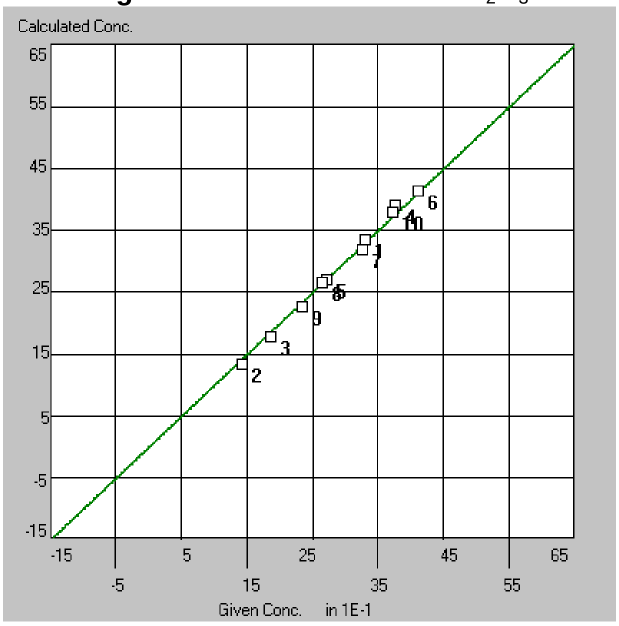

Figure 2: Calibration Plot of SiO_2

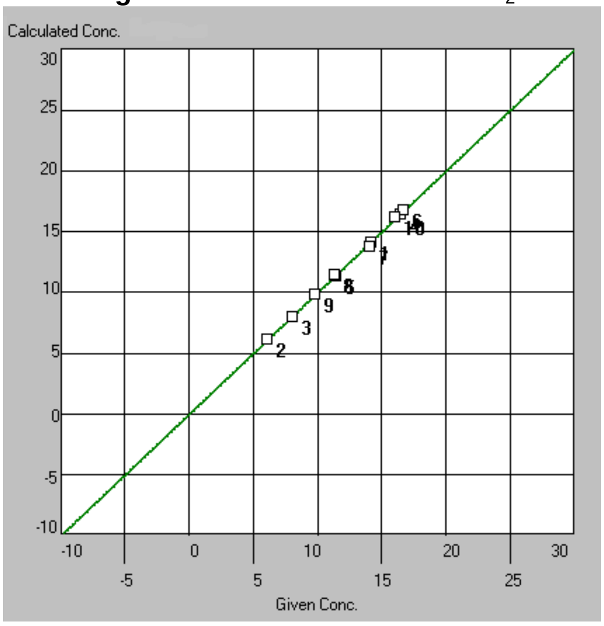

Figure 3: Calibration Plot of CaO

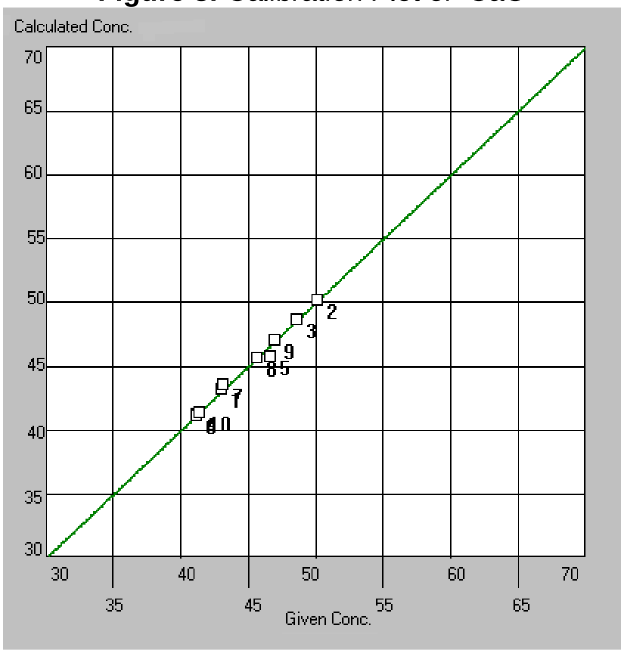

Figure 4: Calibration Plot of SiO_2

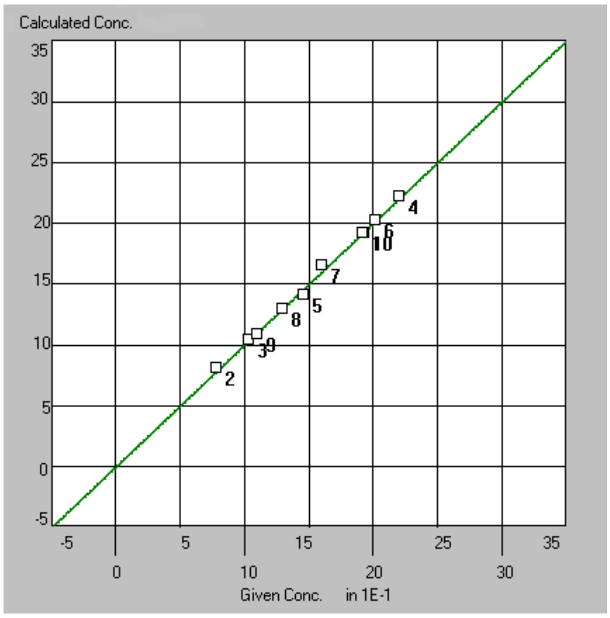

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Figure 5: Calibration Plot of MgO

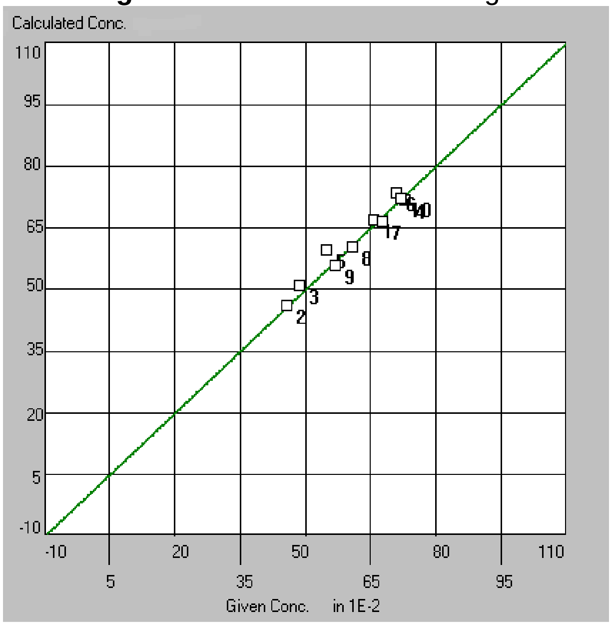


Figure 6: Calibration Plot of P_2O_5

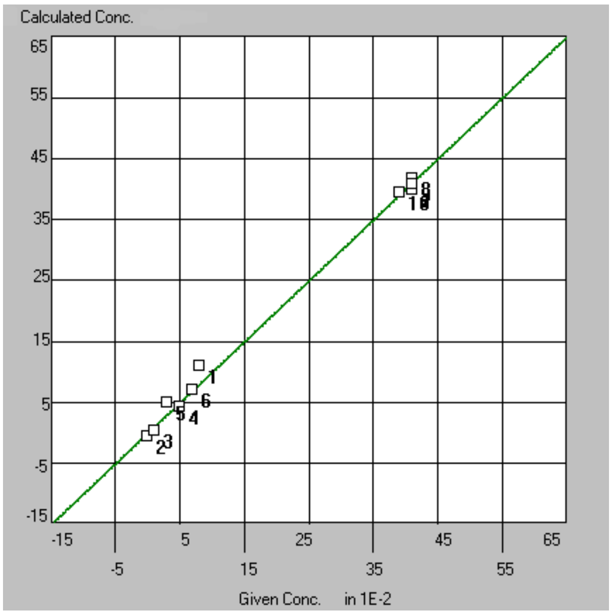
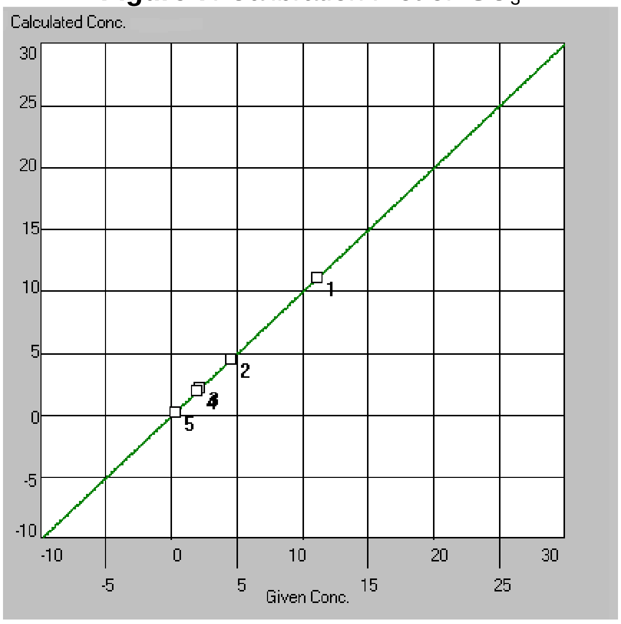


Figure 7: Calibration Plot of SO_3



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3. Precision Data

To show the excellent repeatability on Xenemetrix EDXRF analyzers a precision studies were performed both on fused and on pressed reference samples. Ten repeated acquisitions were done on a sample without moving it from the measurements position between the ten runs. The dispersion of results , i.e. the standard deviation were calculated per element and are presented in Table 3.

Table 4 provides a statistical summary of the results from ten repeat analyses on reference standard RR8.

Table 3: Precision results on Ref 8 sample

Element	MgO	Al_2O_3	SiO_2	P_2O_5	CaO	Fe_2O_3
Std. Dev. %	0.01	0.03	0.04	0.01	0.03	0.01

Table 4: Precision results on S5 sample.

Element	SO_3
Std. Dev. %	0.03

4. Spectra

Typical spectra of a few of the samples are shown in Figures 8-9

Figure 8: Spectrum of fused cement reference sample Ref 8.

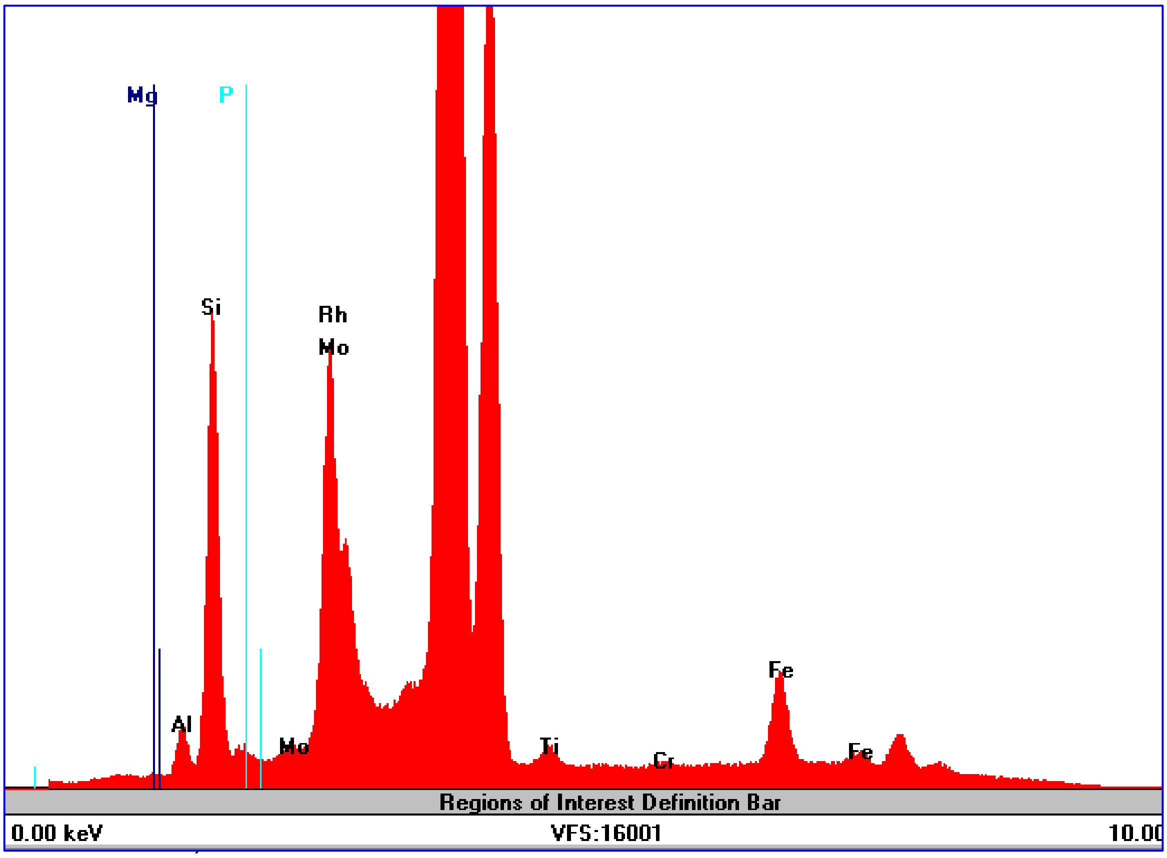
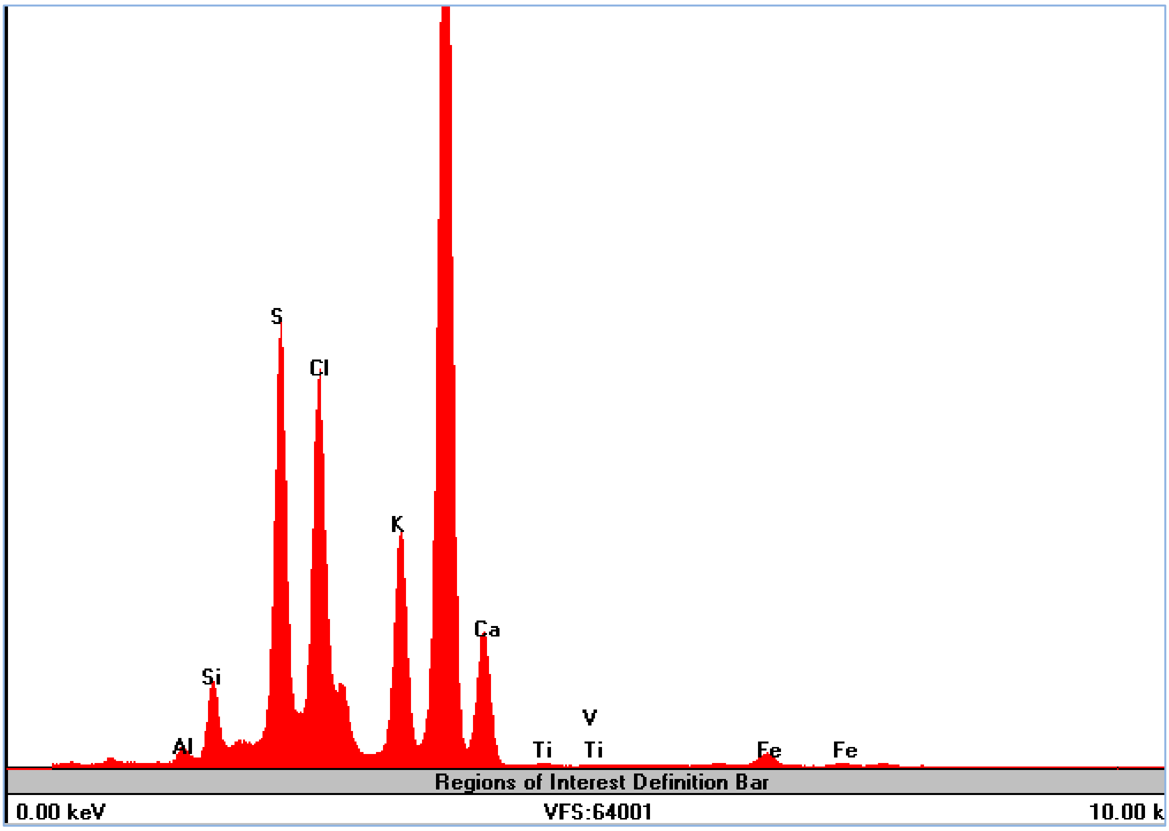


Figure 9: Spectrum of pressed reference cement standard S1.



Conclusion

Calibration and precision data demonstrate the capabilities of Energy Dipspersive X-Ray Fluorescence as an on-line analytical tool in the cement industry. The accuracy of the results can be improved by more and more accurate prepared reference standards.
In conclusion this study provides an excellent illustration of the capabilities of the Xenemetrix X-Calibur SDD Energy Dispersive XRF Benchtop Analyzer for elemental analysis of cement with a minimum of sample preparation ad a minimum of handling time which will greatly enhance the efficiency in the cement industry.

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