Cement Calibration - WDXRF vs. EDXRF results and implications on reproducibility

Abstract

The calibration set of JCA601B including a reproducibility test series was provided to Bruker in order to run WDXRF measurements. The results were compared those obtained by EDXRF which were discussed in Application Note 12/2017. For elements of lower atomic numbers like Na, Mg or Al, the quantitative analysis, including calibration and reproducibility, shows higher precision and accuracy according to ISO 29581-2 using a WDXRF spectrometer. Elements with higher atomic numbers only show insignificant analytical differences between both methods.

Key words

• **Borate Fusion** • **XRF** • **Quantitative Cement Analysis** • **Accuracy** • **Precision**

Introduction

Quick, precise and accurate results are one of the most important factors in industrial and scientific research.

In Application Note 12/2017 a general cement application was defined. Calibration as well as reproducibility including accuracy and precision of ISO 29581-2 was tested. Results were obtained by a PANalytical Epsilon 3XL energy dispersive XRF spectrometer. However, Na, an element of a low atomic number, did not lie within the ISO expert limits. Therefore, we provided the calibration as well as the reproducibility samples to Bruker for more precise wavelength dispersive XRF spectrometer measurements.

Method

The fused beads used for the cement calibration in Application Note 12/2017 were measured with a Bruker S8 Tiger.

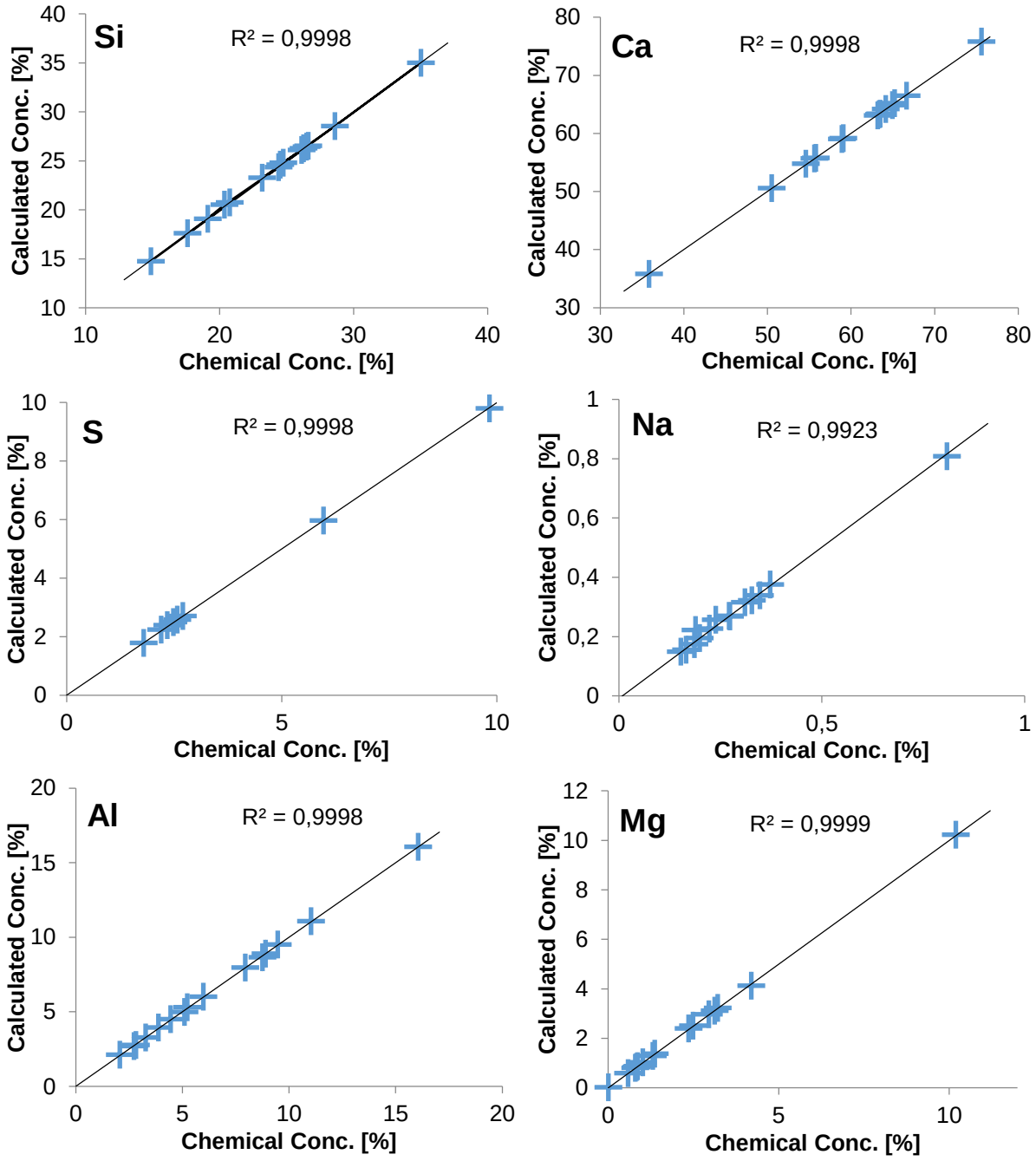
The LOI was determined according to ISO 26845. For the analysis, 0.6 g of JCA601B reference material was fused with 6 g Lithiumtetraborate in order to produce homogeneous beads of 40 mm diameter. The beads were fused using the semi-automatic HERZOG Bead One R benchtop resistance furnace. The material was fused for a period of 15 minutes at a temperature of 1075 °C. Subsequently, the melt was casted within the furnace.

Results- Calibration

The calibration sample set was provided to Bruker for WDXRF measurements. Figure 1 shows the calculated concentrations vs. chemical concentrations as well as the squared correlation coefficients.

Figure 1 shows 6 out of 12 calibration lines from the WDXRF. Sodium shows the lowest R^2 of 0.9923 of all calibration curves. Highest R^2 of 0.9999 was obtained for Mg. Most of the other elements show squared correlation coefficients of 0.9998.

Figure 1: Calculated concentration vs. chemical concentration of the cement application



Results- Correlation

Table 1 shows the squared correlation coefficients of the EDXRF and WDXRF results. The correlation is based on calculated concentration vs. chemical concentration as shown in Figure 1. WDXRF results show higher squared correlation coefficients for lighter elements like Na, Mg, Al, Si and P while elements with greater atomic number like Ca, Fe or Sr show slightly higher squared correlation coefficients using EDXRF measurements.

Table 1: Squared correlation coefficients obtained by EDXRF and WDXRF of calculated (calibration) concentrations and the chemical compositions of all measured elements

Element	EDXRF R^2	WDXRF R^2
Al	0.9995	0.9998
Ca	0.9999	0.9998
Fe	1.0000	0.9997
K	0.9979	0.9967
Mg	0.9996	0.9999
Mn	0.9997	0.9999
Na	0.9640	0.9923
P	0.9993	0.9999
S	0.9998	0.9998
Si	0.9995	0.9998
Sr	0.9988	0.9979
Ti	0.9970	0.9992

Reproducibility

The reproducibility test by means of accuracy and precision was performed according to ISO 29581-2. For assessment of accuracy and precision, reference material JCA-601B RM was used.
10 beads of JCA-601B no. 14 were fused and measured. Table 2 shows the precision and accuracy results for the WDXRF results in comparison with the EDXRF results from Application note 12/2017.
For industrial purposes, the ISO standard limit is sufficient, for scientific use, expert limits are recommended. WDXRF results show better reproducibility for elements with lower atomic number. Even sodium, which is difficult to detect by EDXRF, lies within the expert limits.

Quick, precise and accurate results can already be obtained using an EDXRF spectrometer. The differences of accuracy and precision of elements with higher atomic numbers is not significant.

Table 2: Results of accuracy obtained by EDXRF and WDXRF using JCA 601B 14

	Accuracy										
Analyte	Na2O	MgO	Al2O3	SiO2	P2O5	K2O	CaO	Ti2O	MnO	Fe2O3	SrO
EDXRF	0.05	0.09	0.15	0.17	0.02	0.01	0.13	0.01	0.00	0.02	0.00
WDXRF	0.02	0.10	0.09	0.17	0.00	0.01	0.12	0.00	0.00	0.02	0.01
Expert Limit	0.02	0.12	0.15	0.20	0.02	0.02	0.20	0.02	0.02	0.02	0.02
Standard Limit	0.05	0.30	0.35	0.50	0.05	0.05	0.50	0.05	0.05	0.05	0.05

Table 3: Precision results of JCA 601B 14 obtained by EDXRF and WDXRF

	Precision										
Analyte	**Na2O**	**MgO**	**Al2O3**	**SiO2**	**P2O5**	**K2O**	**CaO**	**Ti2O**	**MnO**	**Fe2O3**	**SrO**
EDXRF	0.023	0.047	0.045	0.112	0.017	0.004	0.095	0.006	0.004	0.023	0.002
WDXRF	0.023	0.041	0.067	0.140	0.002	0.006	0.114	0.006	0.001	0.006	0.002
Expert Limit	0.023	0.096	0.116	0.175	0.023	0.023	0.175	0.023	0.023	0.023	0.023
Standard Limit	0.057	0.240	0.290	0.437	0.057	0.057	0.437	0.057	0.057	0.057	0.057

Discussion

This study on the differences of EDXRF and WDXRF measurements validates the higher precision acquired by WDXRF measurements. High precision and accuracy for elements with higher atomic numbers can already be achieved using an energy dispersive XRF spectrometer. However, for elements with very low atomic numbers like Na, Mg or Al, WDXRF calibration shows better correlation.

The Bead One R is the optimal fusion device for a wide range of applications requiring the highest degree of precision and accuracy. The high concentration range of e.g. silicon and calcium of the calibration allows its application on many different materials.

References

[1] ISO 29581-2 Cement Test methods Part 2: Chemical analysis by X-ray fluorescence

[2] ISO 26845 Chemical analysis of refractories - General requirements for wet chemical analysis, atomic absorption spectrometry (AAS) and inductively coupled plasma atomic emission spectrometry (ICP-AES) methods

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