Lab Report XRF 119

S2 RANGER with XFlash

Determination of Fe, Ti, Al, K, and Ca in Quartz Sands by EDXRF

Introduction

Quartz sand is an essential raw material in a number of industrial processes. Large quantities of glass sand are used in the production of all kinds of glass including bottles, float glass and glassware used in analytical laboratories. Monitoring the elemental composition and purity of such sands is vital to the production process because different glass products require starting materials of different composition and purities. Elements such as Fe, Ti, Al, K and Ca are of particular importance to the glass manufacturing industry. Fe in low concentration can color glass, so this element must be carefully monitored. For the production of clear glass, Fe concentrations are required to stay in the lower ppm range below 50 ppm Fe_2O_3. Sands which fulfill these requirements, achieve higher selling prices in the market.

Analyzing the elements of interest can easily be performed by the energy dispersive X-ray fluorescence (EDXRF) spectrometer S2 RANGER. The instrument guarantees fast and simple monitoring of all elements required and does not need time-consuming sample preparation steps that might be necessary using other analytical techniques. These techniques, e.g. titration, atomic absorption spectrometry (AAS) or inductively coupled plasma spectrometry (ICP-OES, ICP-MS), require a digestion of the sample with acidic and hazardous chemicals such as hydrofluoric acid (HF). This reduces the sample throughput for these techniques and increases the costs per sample.

Figure 1: Extraction of sand by walking excavators

Instrument

The EDXRF system S2 RANGER was utilized for these measurements. The S2 RANGER is an all-in-one benchtop system with an easy-to-use TouchControl™ interface. The system was equipped with an XFlash® Silicon Drift Detector (SDD) and a Pd target X-ray tube.

The XFlash detector is able to handle high count rates, which minimizes the statistical errors and leads to very precise results. The superior energy resolution of the detector separates the element lines in an appropriate way and allows the determination of the required elements. Figure 2 shows typical spectra of various sand standards and indicates that Fe is appropriately resolved.

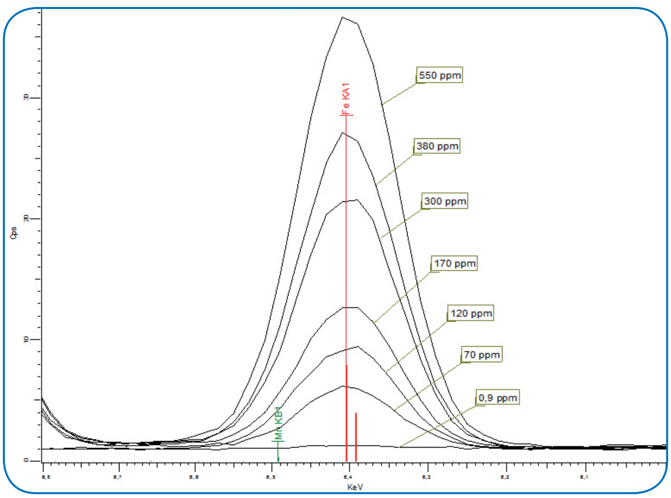

Figure 2: Overlayed spectra of selected sand standards in the concentration range from 0.9 to 550 ppm Fe_2O_3

Sample preparation

The quartz samples were prepared as pressed pellets. A representative quantity of sample (typically between 20 and 100 g) was ground carefully in a swing disk mill in containers made of tungsten carbide. Then 5 g of sample was mixed thoroughly with 1 g of wax (HOECHST Wax C micropowder). The mixture was pressed on a supporting layer of Boreox, an organic boric acid replacement, in a 40 mm diameter aluminum cup. In order to avoid any contamination from the steel piston of the press, a pre-cut pellet film from Fluxana (d = 40 mm) was used to protect the measuring surface during pressing.

Measurement parameters

Two excitation conditions were used, where the tube current was optimized in order to gain optimum counts for the different elements. All measurements were performed under vacuum. Table 1 shows the measurement parameters.

Table 1: Measurement parameters for the different elements

Elements	Tube voltage [kV]	Tube current [µA]	Filter	Measurement time [s]
Al	10	800	None	100
K, Ca, Ti, Fe	40	550	500 µm Al	100

Calibration

A set of international certified reference materials (CRMs) and in-house standards were used to setup a calibration for Al, K, Ca, Ti and Fe. Table 2 shows the concentration ranges of the different standards used for the calibration of the system.

Table 2: Concentration ranges of standards used for the calibration

Element	Minimum concentration [%]	Maximum concentration [%]	Standard deviation of calibration curve [%]
Al_2O_3	0.036	0.77	0.018
K_2O	0.002	0.50	0.0032
CaO	0.00006	2.21	0.0051
TiO_2	0.0002	0.59	0.0048
Fe_2O_3	0.00009	0.13	0.0014

Figure 3 and 4 show the calibration curves for K_2O and TiO_2 in Quartz sand, while figure 5 shows the calibration curve for Fe_2O_3 in the lower concentration range.

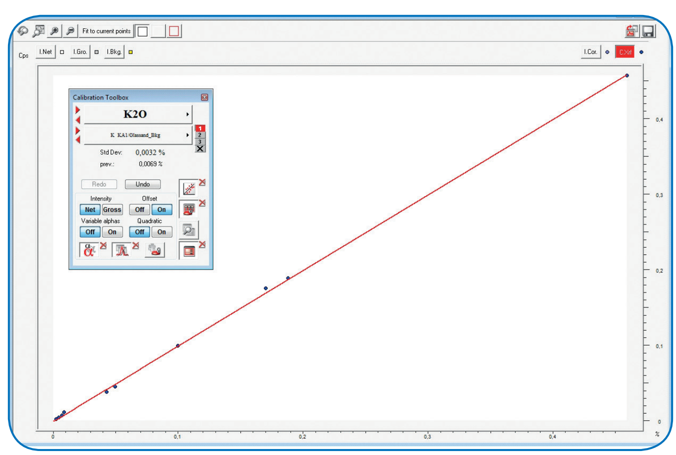

Figure 3: Calibration curve for K_2O (calibration range up to 0.50% K_2O)

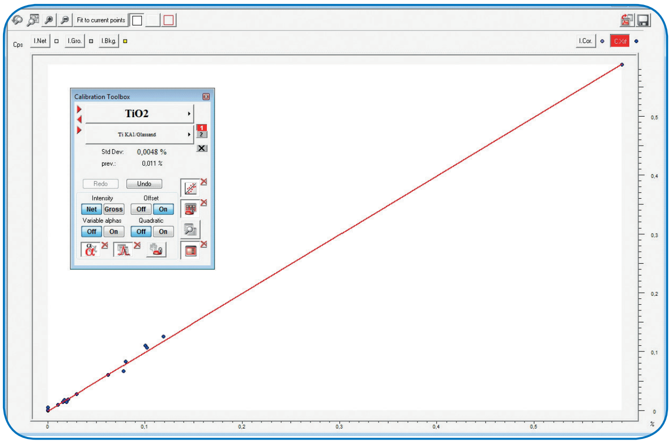

Figure 4: Calibration curve for TiO_2 (calibration range up to 0.59% Ti_2O)

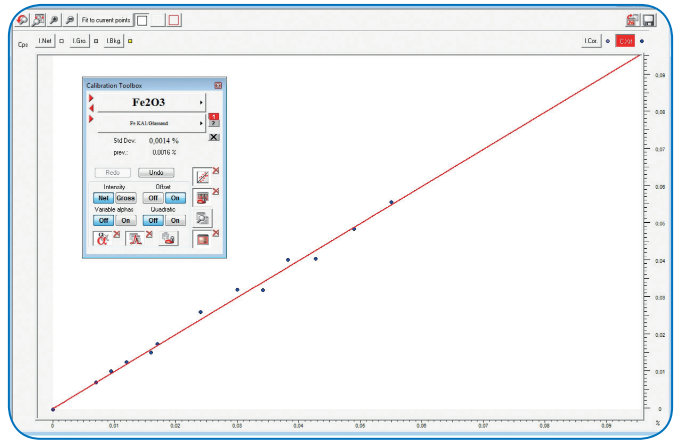

Figure 5: Extract of the low concentration range of the calibration curve for Fe_2O_3 (shown standards are between 0.9 to 550 ppm Fe_2O_3)

Results

In order to prove the quality of the calibration, different reference standards and sand samples were measured against the calibration. To demonstrate the accuracy and the precision of the instrument, ten repetitions of one standard with higher element concentrations and one with lower element concentrations are shown in Table 3 and 4.

Figure 6 and 7 show the repeatability of Fe_2O_3 in a glass sand and a certified standard over a period of 30 hours. The red lines show the 3-sigma confidence levels of the measurements. In the instrument software, threshold values can be defined for each element which leads to a warning in case of 'out-of-spec' samples.

The figures show the excellent long-term stability of the instrument and demonstrate the suitability to monitor and control of quartz sand.

Table 3: Accuracy and precision test of ten repetitions of certified reference material FF 12

Repetition	Al_2O_3 [%]	K_2O [%]	CaO [%]	TiO_2 [%]	Fe_2O_3 [%]
1	0.78	0.098	0.97	0.58	0.325
2	0.78	0.099	0.97	0.59	0.322
3	0.78	0.097	0.95	0.59	0.326
4	0.77	0.090	0.98	0.59	0.323
5	0.78	0.096	0.95	0.59	0.321
6	0.78	0.091	0.97	0.59	0.323
7	0.78	0.101	0.99	0.59	0.323
8	0.78	0.098	0.97	0.58	0.322
9	0.78	0.098	0.95	0.59	0.325
10	0.76	0.101	0.99	0.59	0.324
Mean value [%]	**0.78**	**0.097**	**0.97**	**0.59**	**0.323**
Abs. std. dev. [%]	**0.0055**	**0.0037**	**0.0141**	**0.0049**	**0.0015**
Certified value [%]	**0.77**	**0.1**	**0.97**	**0.59**	**0.34**

Table 4: Accuracy and precision test of ten repetitions of certified reference material BCS 313/1

Repetition	Al_2O_3 [%]	K_2O [%]	CaO [%]	TiO_2 [%]	Fe_2O_3 [%]
1	0.032	0.004	0.0037	0.019	0.0129
2	0.038	0.009	0.0072	0.018	0.0119
3	0.032	0.006	0.0019	0.016	0.0118
4	0.033	0.014	0.0098	0.018	0.0120
5	0.039	0.007	0.0057	0.017	0.0119
6	0.037	0.004	0.0083	0.019	0.0124
7	0.027	0.005	0.0111	0.017	0.0121
8	0.031	0.002	0.0053	0.019	0.0122
9	0.035	0.009	0.0060	0.018	0.0121
10	0.036	0.006	0.0022	0.015	0.0122
Mean value [%]	**0.034**	**0.0065**	**0.0061**	**0.0177**	**0.0122**
Abs. std. dev. [%]	**0.0035**	**0.0031**	**0.0029**	**0.0013**	**0.0003**
Certified value [%]	**0.036**	**0.005**	**0.006**	**0.017**	**0.012**

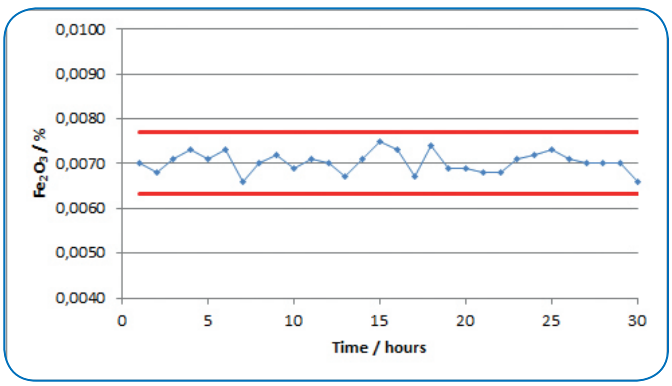

Figure 6: Process control chart for Fe_2O_3 from a glass sand sample over a period of 30 hours

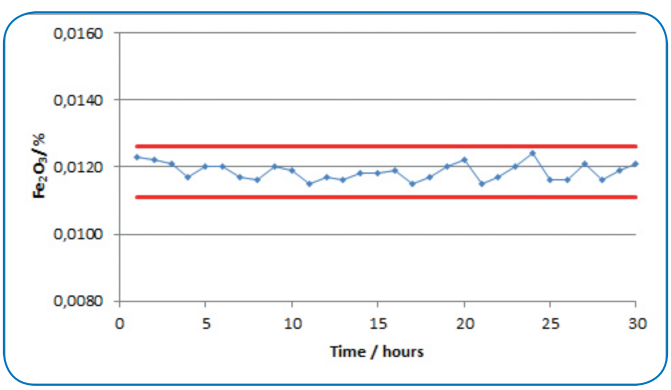

Figure 7: Process control chart for Fe_2O_3 from a certified standard over a period of 30 hours (BCS313/1)

Conclusions

With a set of international certified reference materials and calibration standards, the 5 most important elements in quartz sands can be determined in the required concentration ranges. The samples were prepared as pressed pellets which makes the sample preparation simple, fast and straight forward. The time consuming sample preparation steps required for wet chemical analysis are avoided, which leads to low cost of ownership and results in an immediate analytical feedback to the monitoring and control process. Based on the high excitation efficiency of 50 W and the direct beam path of the S2 RANGER the achievable counting statistical error is outstanding. The data show the optimal analytical performance of the EDXRF spectrometer S2 RANGER, matching the requirements for the analysis of low concentration Fe in quartz sands.

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