

Quantitative Analysis of Quartz Material, Using Laser Induced Breakdown Spectroscopy (LIBS) in On-Line, Real Time Mode.

1. Technical task

- Quantitative analysis of elements of interest content: Al₂O₃, Fe₂O₃, K₂O, CaO, TiO₂ and SiO₂ content .
- Analysis of material in different moisture levels : 10, 15 and 20 % H₂O.
- Evaluating possibility of on-line, real time LIBS analysis, on a conveyer belt.

2. The samples

The received samples contain 8 bags of white sand like powder.

Following table, describes chemical content of the samples:

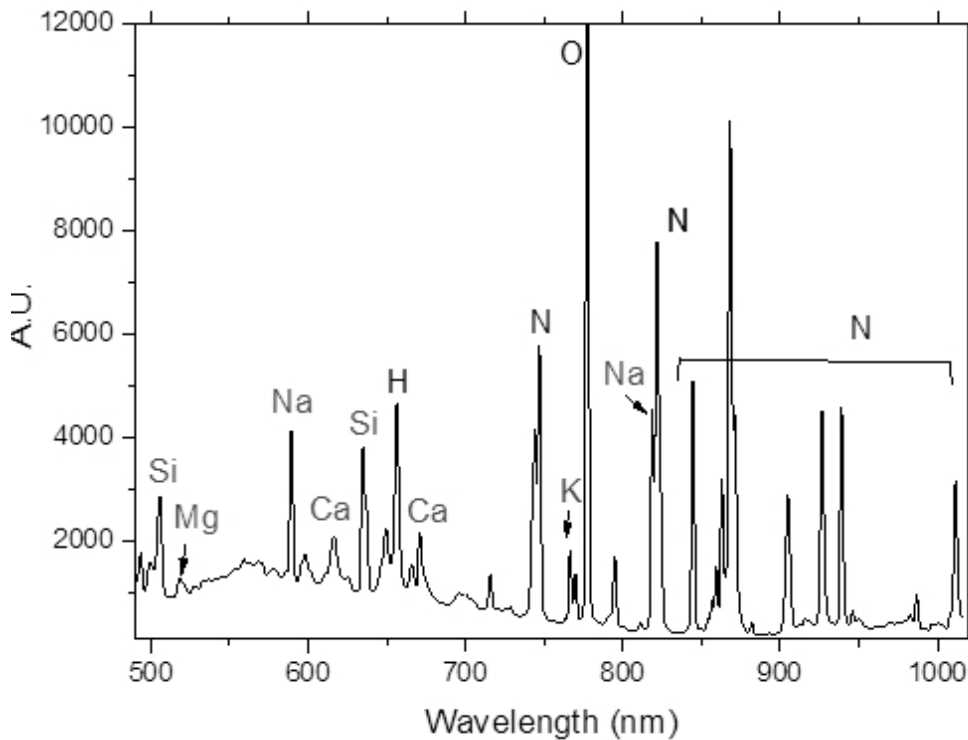
	Fe2O3	Al2O3	TiO2	K2O	CaO	MgO	Na2O	SiO2
	%	%	%	%	%	%	%	%
Ref 1	0.0063	0.016	0.017	0.001	0.006	0.000	0.000	99.80
Ref 2	0.0079	0.018	0.019	0.002	0.007	0.000	0.001	99.79
Ref 3	0.0087	0.024	0.019	0.004	0.007	0.000	0.001	99.78
Ref 4	0.0101	0.031	0.019	0.005	0.008	0.000	0.002	99.77
Ref 5	0.0133	0.050	0.019	0.010	0.008	0.000	0.001	99.74
Ref 6	0.0155	0.059	0.020	0.012	0.008	0.000	0.002	99.72
Ref 7	0.0229	0.122	0.037	0.033	0.009	0.002	0.003	99.61
Ref 8	0.0363	0.217	0.054	0.062	0.010	0.003	0.004	99.44

According to chemical data, main content is SiO₂ while content of other elements is found at trace o impurity levels.

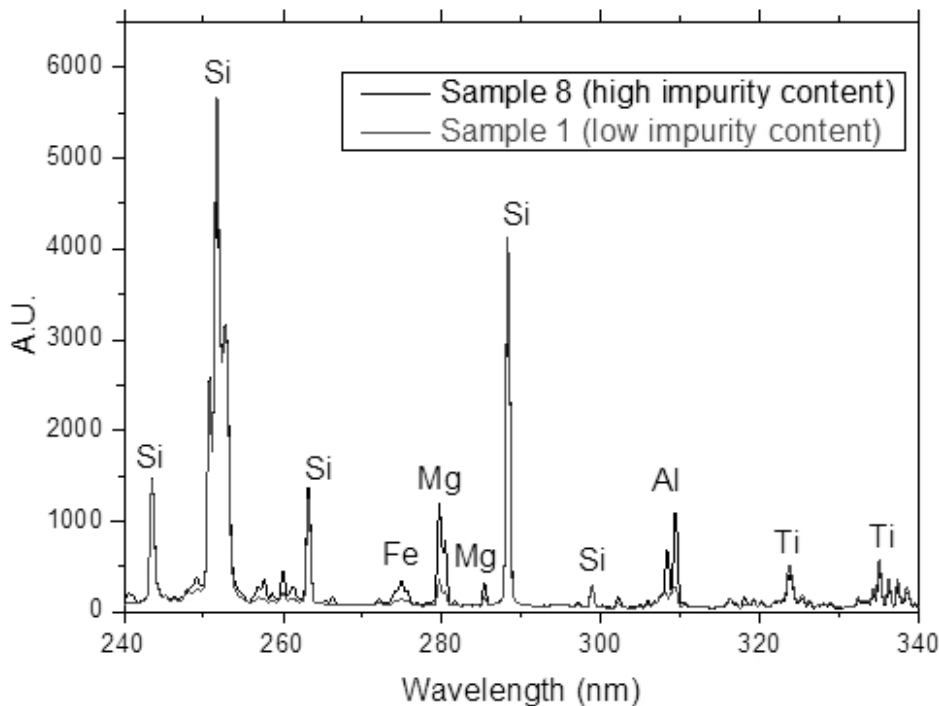
3. Experimental section.

The experiments were conducted using on-line analysis system equipped with double pulsed laser energy of 80 mJ Each sample was measured using 1500 laser pulses in each analysis in order to receive sufficient statistics. The samples were rotating under the laser beam, rotation imitating conveyer belt movement so all the surface would be equally analyzed. Spectral data was received by using UV ($\lambda = 250-360$ nm) and UV-VIS ($\lambda = 500-1000$ nm) spectrometer Spectral range was chosen as most suitable for elements of interest.

4. Qualitative spectral analysis



As can be seen from visible range spectrum, elements of interest – Si, Mg, Ca Na and K can be clearly detected.

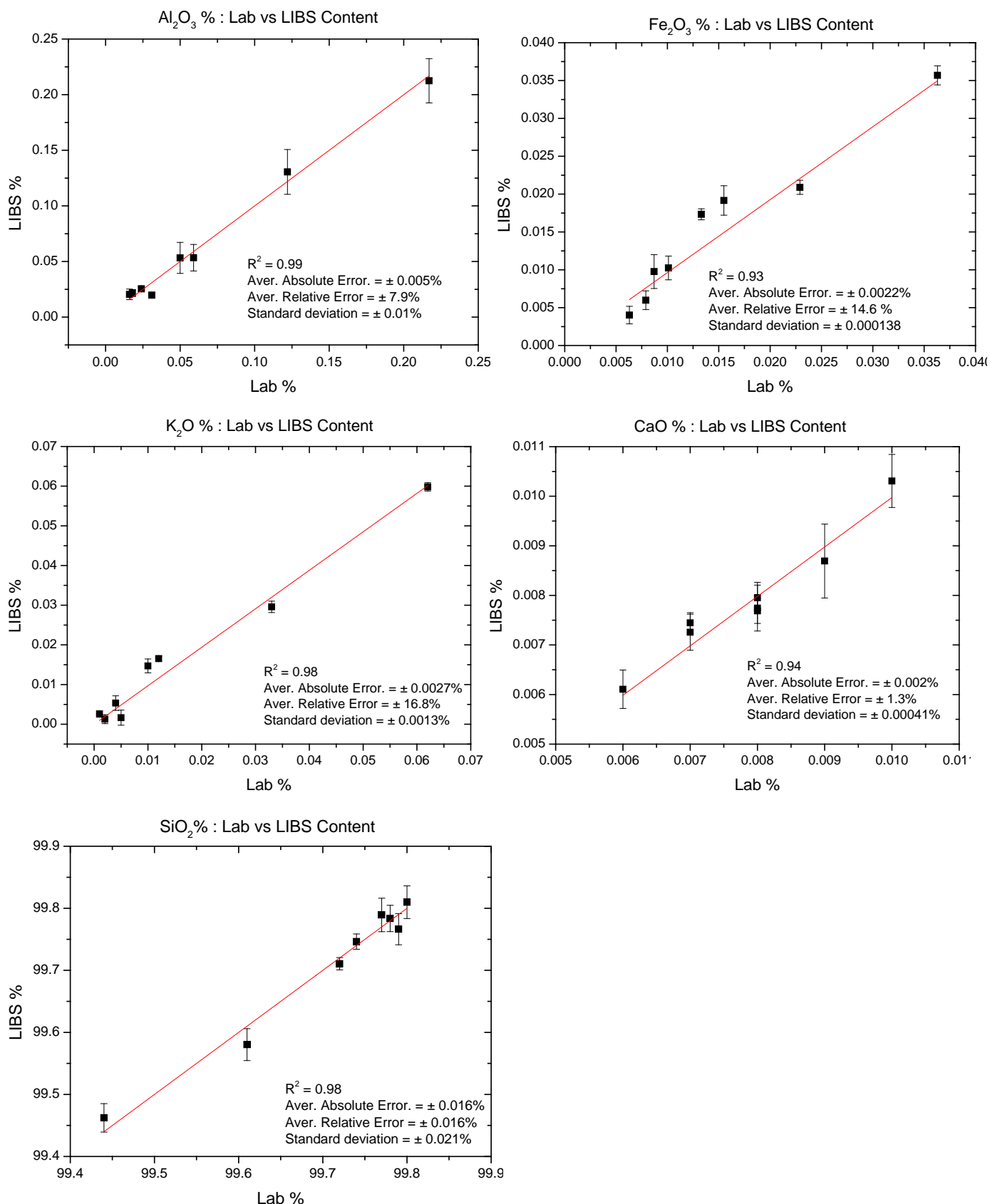


This chart shows quality comparison between **sample 1**(red), with low impurity content and sample 8 (black) with high impurity content. With same Si lines level, sample 8 has much higher Fe, Mg and Al peaks. UV range spectrum contains well defined lines of Si, Mg, Fe, Al and Ti.

5. Quantitative analysis on dry samples.

According to chemical data of 8 samples premeasured samples, "Lab vs LIBS" calibration curves were calculated. Lab refers to chemical data, while LIBS, to laser analysis.

- Vertical lines represent concentration deviation inside each sample.



Al_2O_3 , Fe_2O_3 , K_2O , CaO and SiO_2 show good correlation between laboratory and LIBS measurements allowing building calibration curves and estimating errors.

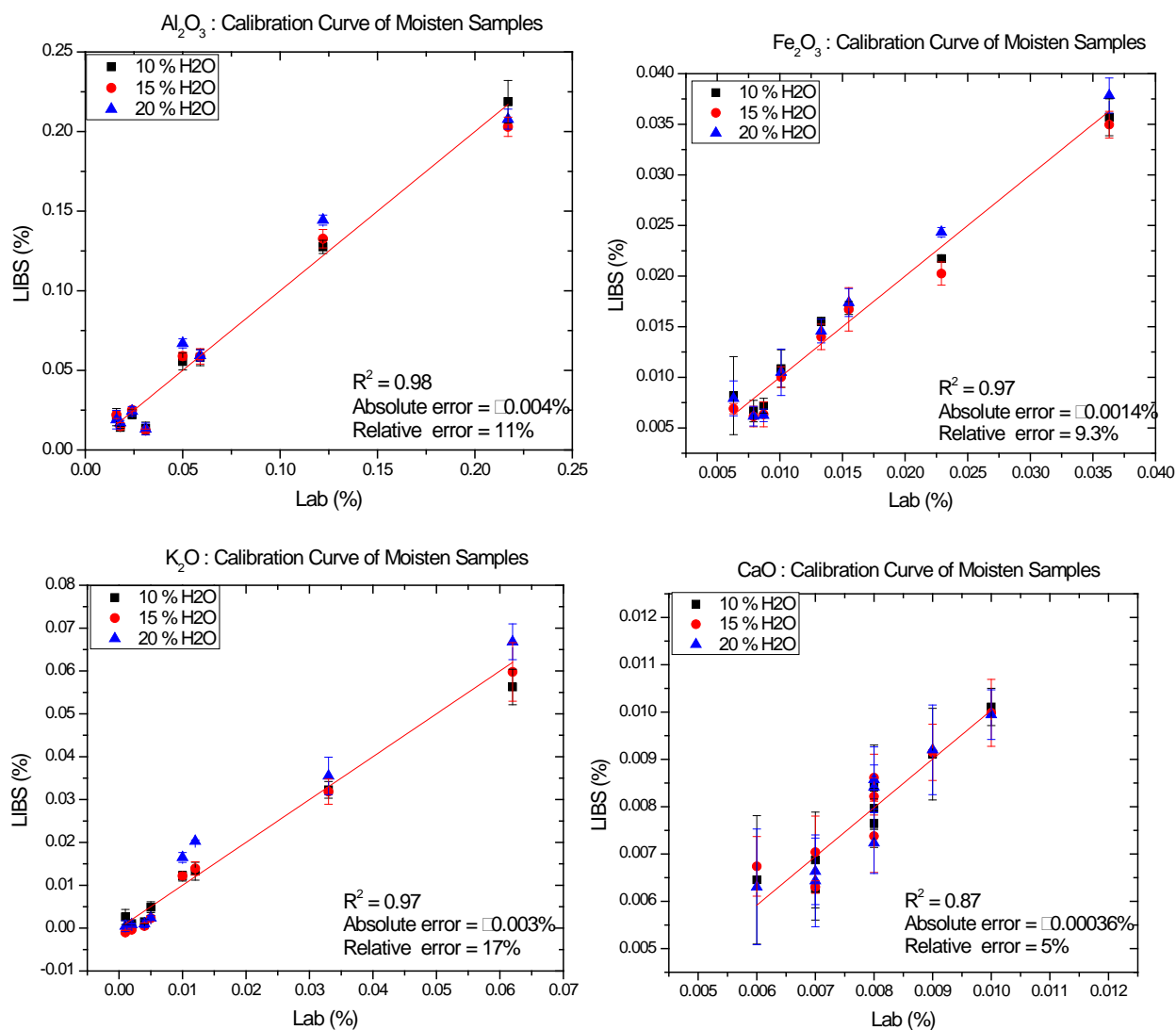
TiO₂ calibration wasn't done due to lack of correlation between laboratory data and LIBS spectra.

Following table summarizes potential errors that were calculated according to calibration curves:

Accuracy summary table				
Analyzed Element	Average Error			Standard Deviation ± %
	Linearity R ²	Absolute ± %	Relative ± %	
Al ₂ O ₃	0.99	0.005	7.9	0.01
Fe ₂ O ₃	0.93	0.0022	14.6	0.00014
K ₂ O	0.98	0.0027	16.8	0.0013
CaO	0.94	0.002	1.3	0.00041
SiO ₂	0.98	0.016	0.016	0.021

6. Quantitative analysis on moist samples.

Same analytical method was applied while samples were moistened using 10, 15 and 20 % (weight) of water. Following charts show calibration curves of moisten samples:



- Each moisture level show in different color. Vertical lines describe concentration deviation in each sample.

Moist samples show sufficient correlation for on-line analysis, while all moisture levels can be measured using same analytical algorithm on single calibration curve.

7. Conclusions:

- Good correlation between lab and LIBS data allows us to be sure in possibility of on-line LIBS measurement and satisfying technical requirements.
- Calibration curve for Al_2O_3 , Fe_2O_3 , K_2O , CaO and SiO_2 between laboratory data and LIBS spectral analysis shows high linearity and low error on both dry and moist samples.
- All moisture levels can be analyzed using single calibration curve allowing same analytical algorithm.
- Relative errors are around laboratory levels.
- Calibration curve calculation of TiO_2 wasn't done due to lack of linearity between LIBS and chemical data. Additional research in TiO_2 correlation will be conducted.