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Quantitative Analysis of Cement Raw Meal Samples, Using Laser Induced Breakdown Spectroscopy (LIBS) in On-Line, Real Time Mode.

1. Technical task

- Quantitative analysis of elements of interest content: Al2O3, SiO2, Fe2O3, CaO, MgO, P_2O_5 and CO2 (LOI) content.
- Evaluating possibility of on-line, real time LIBS analysis, on a conveyer belt.

2. The samples

The received samples contain 13 bags white fine powder.

Following table describes chemical content of the samples:

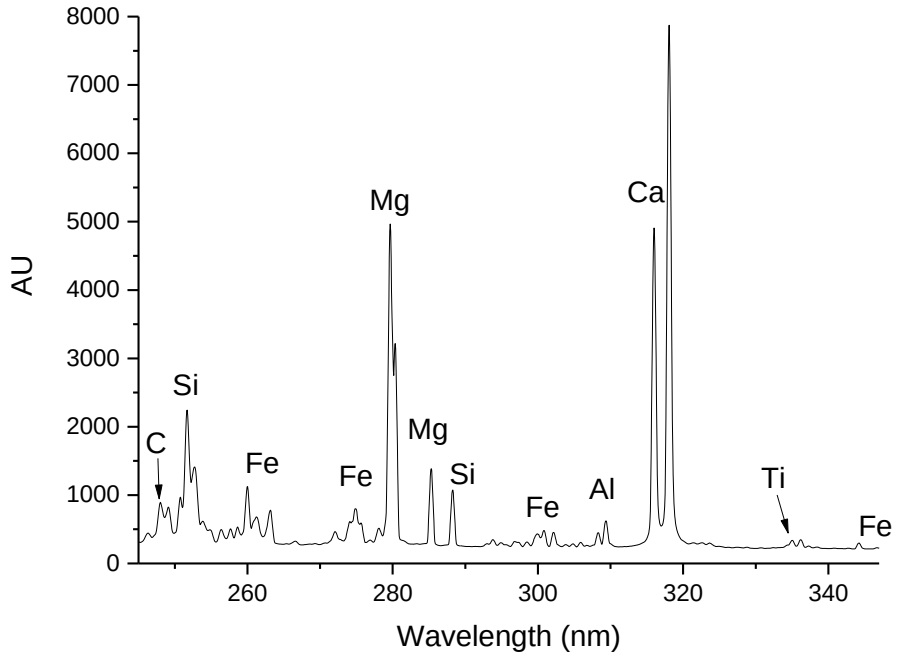
Sample No.	1	2	3	4	5	6	7	8	9	10	11	12	13
Name	Raw Mix No. 01	Raw Mix No. 02	Raw Mix No. 03	Raw Mix No. 04	Raw Mix No. 05	Raw Mix No. 06	Raw Mix No. 07	Raw Mix No. 08	Raw Mix No. 09	Raw Mix No. 10	Raw Mix No. 11	Raw Mix No. 12	Raw Mix No. 13
% LOI	35,23	35,54	35,79	36,01	36,24	36,39	36,58	36,79	36,99	37,12	37,25	37,37	37,50
% SiO_2	15,76	15,22	14,82	14,36	14,00	13,59	13,28	12,89	12,57	12,26	12,03	11,80	11,58
% Al_2O_3	3,89	3,77	3,66	3,54	3,45	3,36	3,27	3,17	3,11	3,03	2,96	2,91	2,85
% TiO_2	0,175	0,166	0,165	0,160	0,157	0,154	0,146	0,143	0,141	0,136	0,132	0,127	0,125
% Fe_2O_3	2,28	2,19	2,12	2,07	1,99	1,95	1,89	1,84	1,78	1,75	1,70	1,68	1,65
% Mn_2O_3	0,052	0,049	0,047	0,047	0,046	0,044	0,041	0,040	0,041	0,039	0,038	0,038	0,037
% CaO	41,30	41,68	42,17	42,49	42,88	43,16	43,55	43,80	44,23	44,39	44,80	44,81	45,13
% MgO	0,97	0,94	0,91	0,90	0,88	0,86	0,84	0,83	0,82	0,80	0,79	0,78	0,77
% SO_3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
% P_2O_5	0,146	0,142	0,140	0,138	0,134	0,129	0,126	0,123	0,123	0,118	0,118	0,115	0,111
% Na_2O	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
% K_2O	0,269	0,252	0,246	0,239	0,232	0,221	0,217	0,210	0,205	0,201	0,198	0,192	0,189

3. Experimental section.

The experiments were conducted using on-line analysis system equipped with laser of 50 mJ energy. Each sample was measured using 1000 laser pulses in each analysis in order to receive sufficient statistics. The samples were rotating under the laser beam, imitating conveyer belt movement so all the surface would be equally analyzed. Spectral data was received by using UV (λ = 250-360 nm) spectrometer. Spectral range was chosen as most suitable for elements of interest.

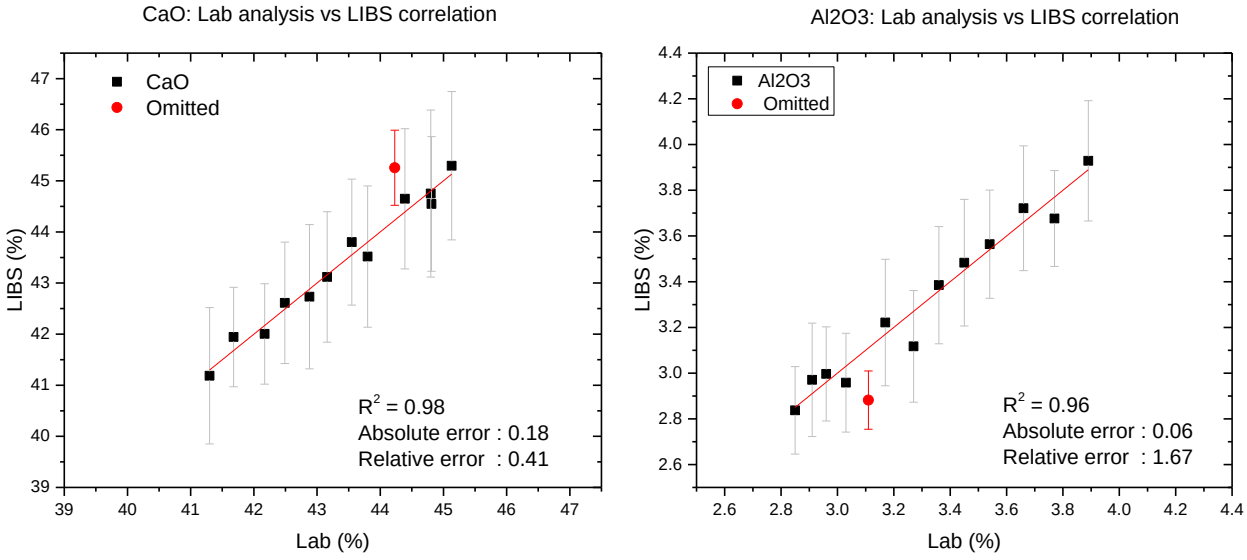
4. Qualitative spectral analysis

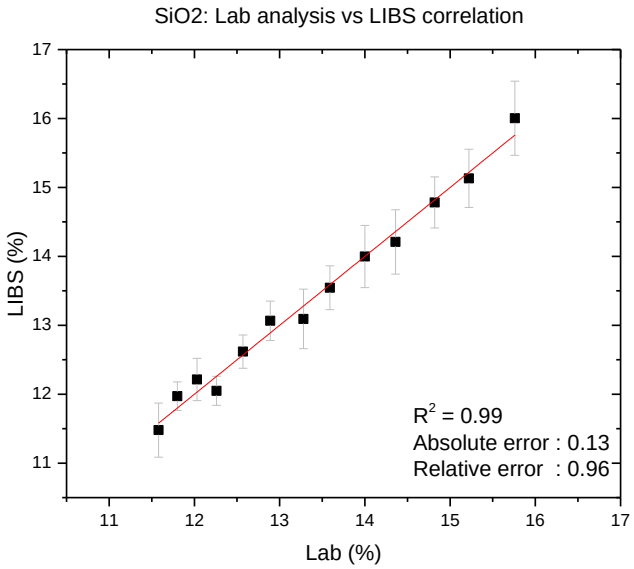
As can be seen from UV range spectrum, elements of interest – Si, Mg, Ca, Fe, C, Al, and Ti can be clearly detected and identified.

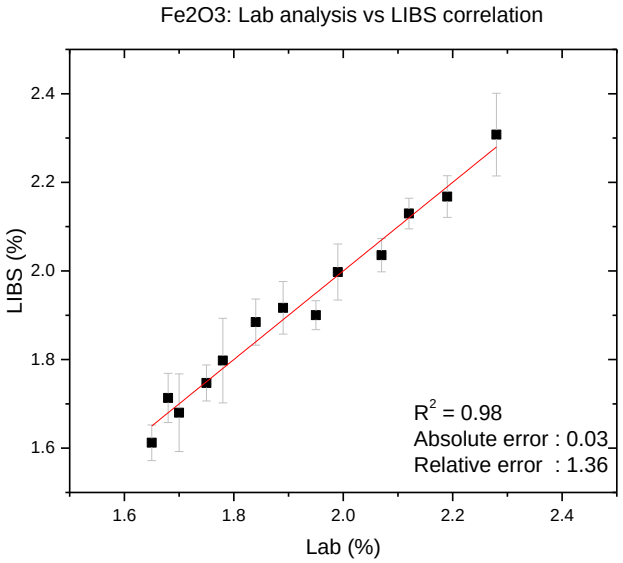


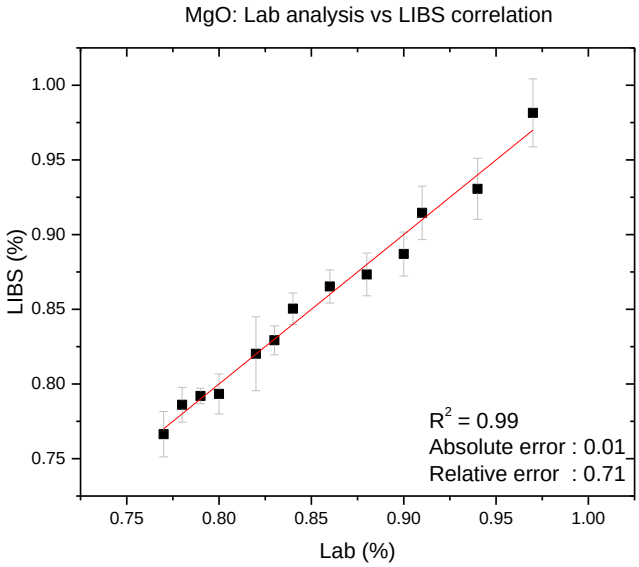
5. Quantitative analysis.

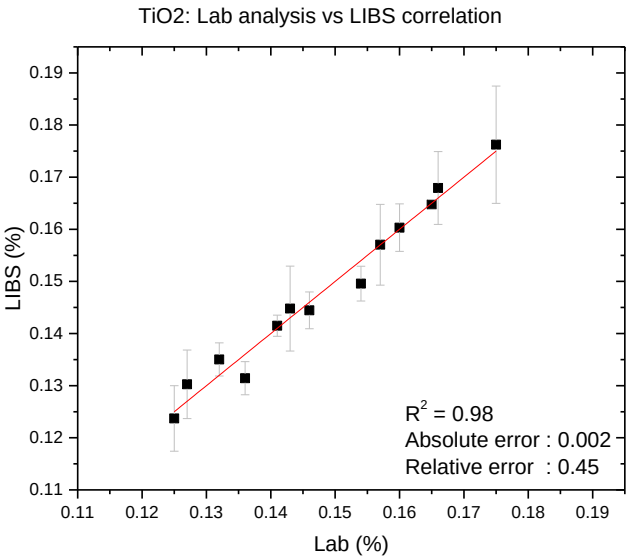
According to chemical data of 13 standard samples, "Lab vs LIBS" calibration curves were calculated. Lab refers to chemical data, while LIBS, to laser analysis.

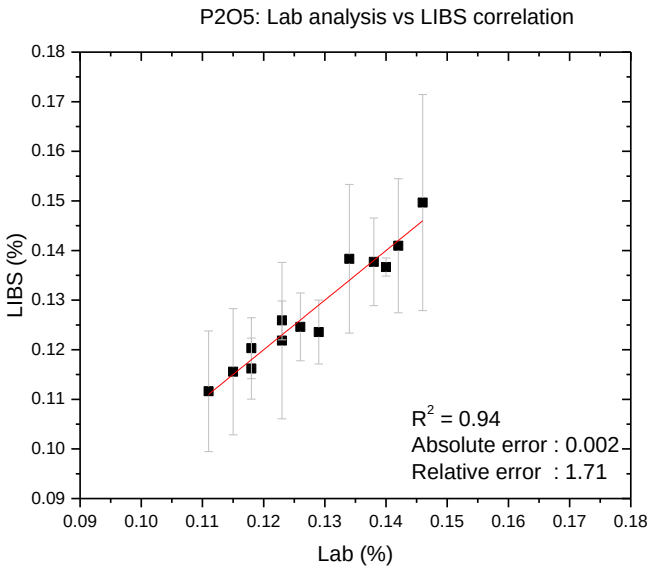


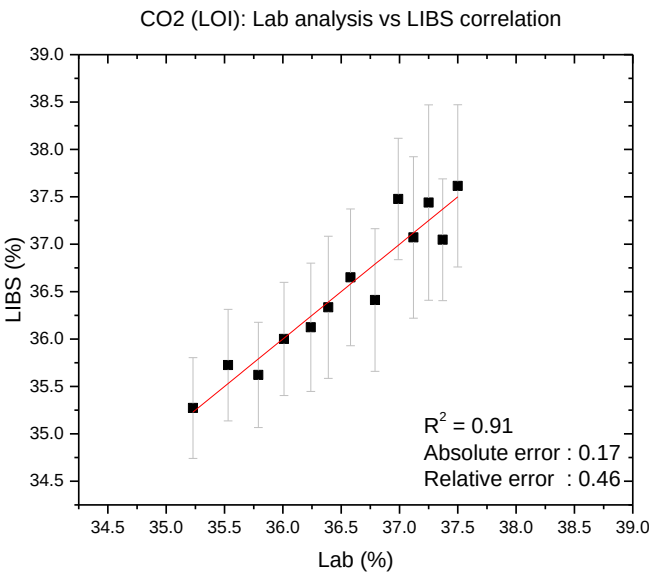












- Vertical lines represent concentration deviation inside each sample.
- Some samples (marked red) were omitted from the calculations due to reduced linearity.

All required elements of interest : Al_2O_3, CaO, Fe_2O_3 and SiO_2 as well as preferred : MgO, P_2O_5, CO_2 (LOI) and TiO_2 show good correlation between laboratory and LIBS measurements, allowing building calibration curves for "unknown" samples measurements and estimating of errors.

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

Accuracy summary table				
Analyzed Element		Average Error		
	Linearity R^2	Absolute ± %	Relative ± %	Standard Deviation ± %
Al_2O_3	0.96	0.06	1.67	0.25
Fe_2O_3	0.98	0.03	1.36	1.93
CaO	0.98	0.18	0.41	1.3
SiO_2	0.99	0.13	0.96	0.38
MgO	0.99	0.01	0.71	0.014
TiO_2	0.98	0.002	0.45	0.15
P_2O_5	0.94	0.002	1.71	0.01
CO_2 (LOI)	0.91	0.17	0.46	0.71

6. Blind samples results

Three blind samples were analyzed based on calibration of 13 standard cement raw meal samples.

The resulting comparison described in following table:

	Required Elements								Prefered Elements							
	SiO2		Al2O3		Fe2O3		CaO		MgO		CO2		P2O5		TiO2	
Sample	Lab	LIBS	Lab	LIBS	Lab	LIBS	Lab	LIBS	Lab	LIBS	Lab	LIBS	Lab	LIBS	Lab	LIBS
14	12.47	12.67	3.11	3.13	1.82	1.81	43.75	44.14	0.81	0.82	36.57	36.91	0.11	0.121	0.14	0.139
15	15.52	15.46	3.75	3.82	2.23	2.22	41.59	41.6	0.95	0.95	35.54	35.41	0.14	0.145	0.17	0.174
16	14.27	14.17	3.42	3.5	2.01	2.04	42.82	42.65	0.9	0.89	36.31	36.03	0.14	0.133	0.16	0.155

7. Conclusions:

- Good correlation between lab and LIBS data allows us to be sure in possibility of on-line, real-time LIBS measurement of raw meal and satisfying technical requirements.
- Calibration curve between laboratory data and LIBS spectral analysis for required elements: Al_2O_3, Fe_2O_3, SiO_2, CaO as well as for preferred: MgO, TiO_2, P_2O_5 and TiO_2 shows high linearity and low error.
- If on-line RAMAN, mineralogical analysis of calcite, clay and quartz of the raw meal is also required, then standard samples have to be supplied with mineral content.
- The comparison between supplied laboratory data and "blind" test results reveal good correlation and low error for all the required elements, indicating accurate on-line analysis possibility on a conveyer belt.