

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

06-03-2014

1. Technical task

- Quantitative analysis of clay samples for content of: Al₂O₃, Fe₂O₃, K₂O, CaO, TiO₂, Na₂O and SiO₂.
- Evaluating possibility of on-line, real time LIBS analysis of clay content on a conveyer belt.

2. The samples

The received delivery contains 10 buckets of 5 liters each. Samples are of different color and texture:

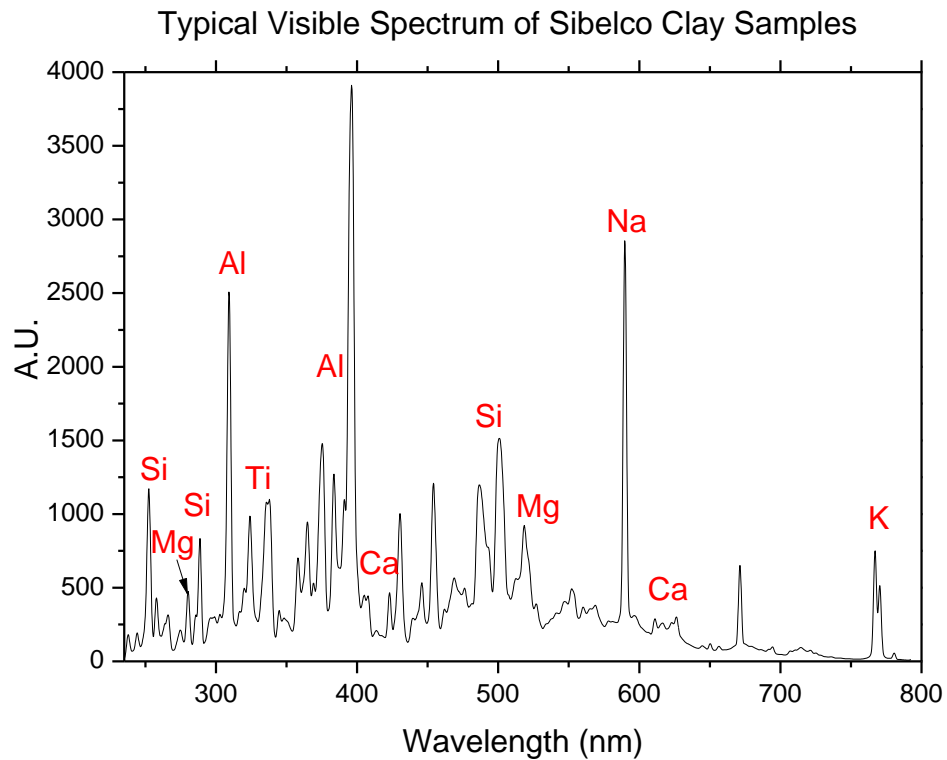
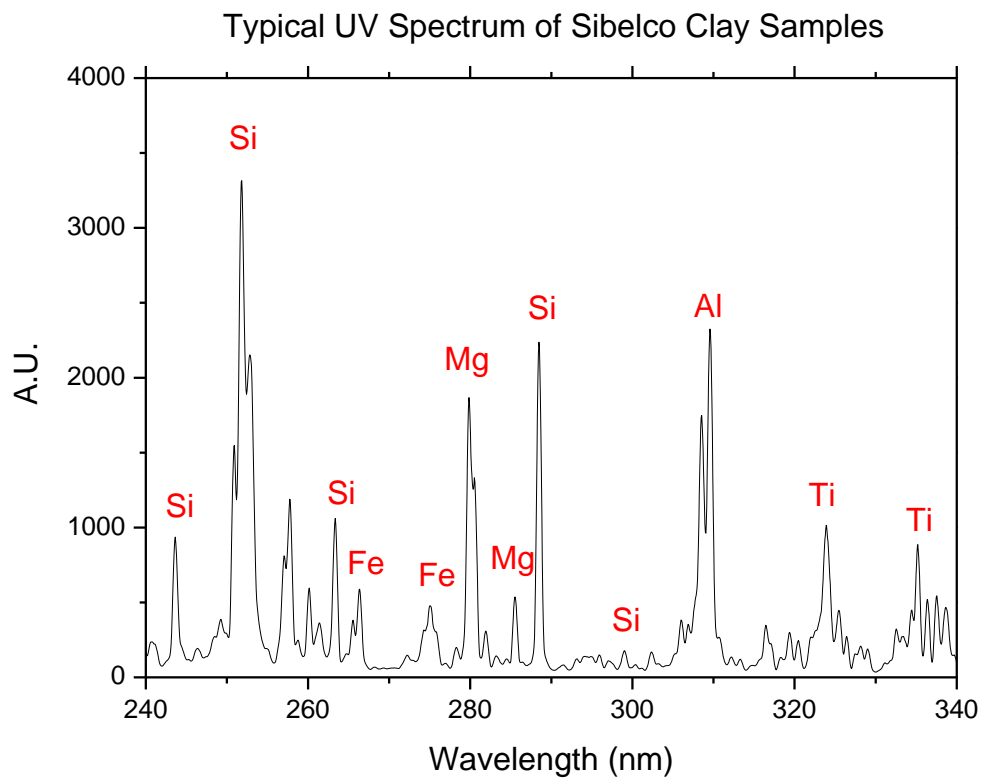
Following table describes chemical content of clay samples provided by Sibelco:

Sample	Chemical XRF							
	Fe2O3	Al2O3	TiO2	K2O	CaO	MgO	Na2O	SiO2
PR-015178-001	1.09	30.91	0.61	1.4	0.21	0.25	0.17	41.6
PR-015178-002	1.00	32.74	1.05	2.5	0.18	0.34	0.39	49.2
PR-015178-003	0.99	32.43	1.01	3.0	0.16	0.39	0.45	52.7
PR-015178-004	0.86	25.26	1.58	2.6	0.14	0.32	0.40	62.1
PR-015178-005	0.74	17.58	1.59	1.8	0.05	0.31	0.31	72.9
PR-015178-006	1.73	16.41	0.13	2.8	0.05	0.33	0.29	74.5
PR-015178-007	1.45	16.65	0.11	5.7	0.05	0.24	0.46	72.6
PR-015178-008	0.87	36.78	0.03	2.3	0.04	0.37	0.11	47.8
PR-015178-009	1.02	27.04	1.33	2.1	0.13	0.34	0.34	57.6
PR-015178-010	0.90	23.53	1.56	2.0	0.10	0.32	0.34	64.3

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 2000 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 ($\lambda = 250-360$ nm) and UV-VIS ($\lambda = 235-800$ nm) spectrometers that were chosen as most suitable for current task.

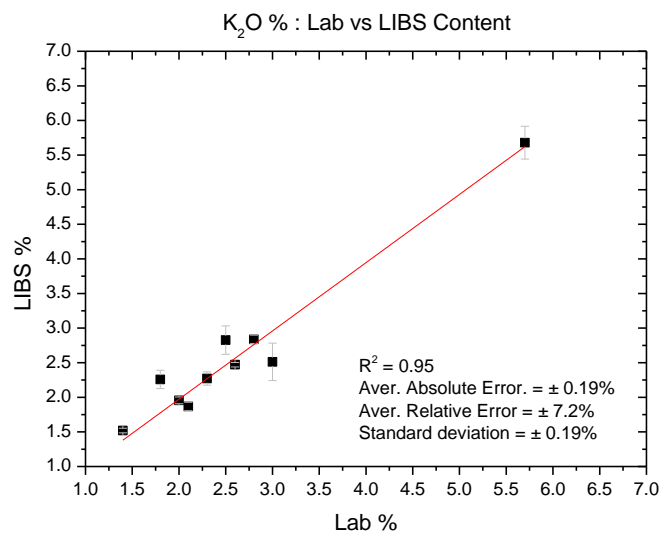
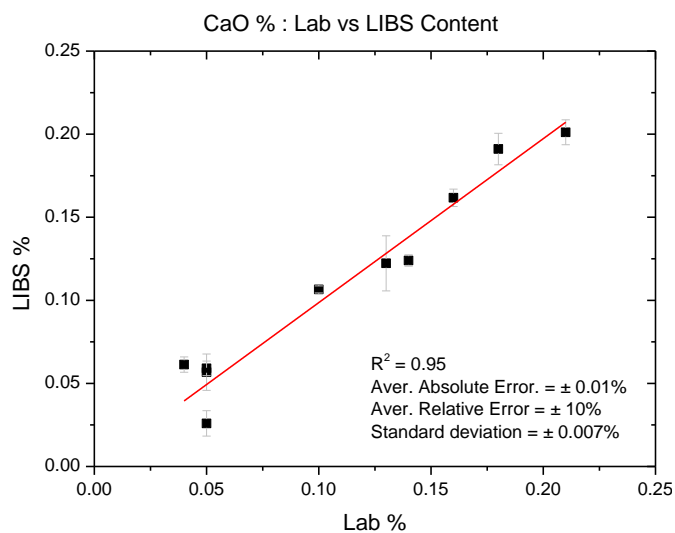
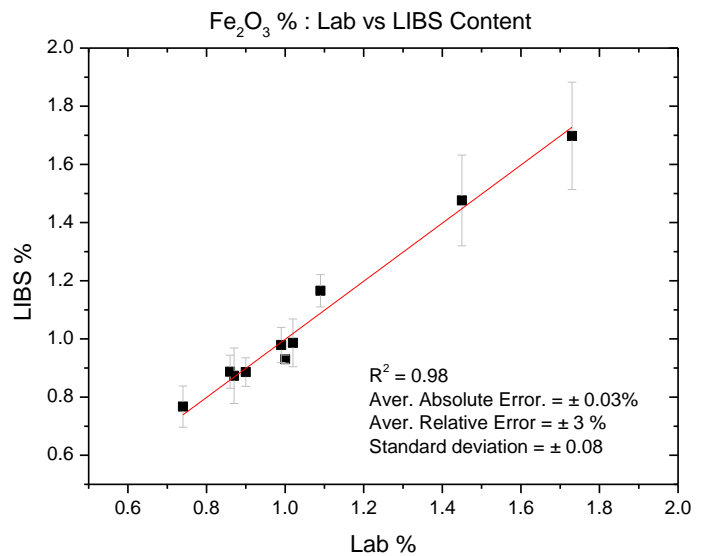
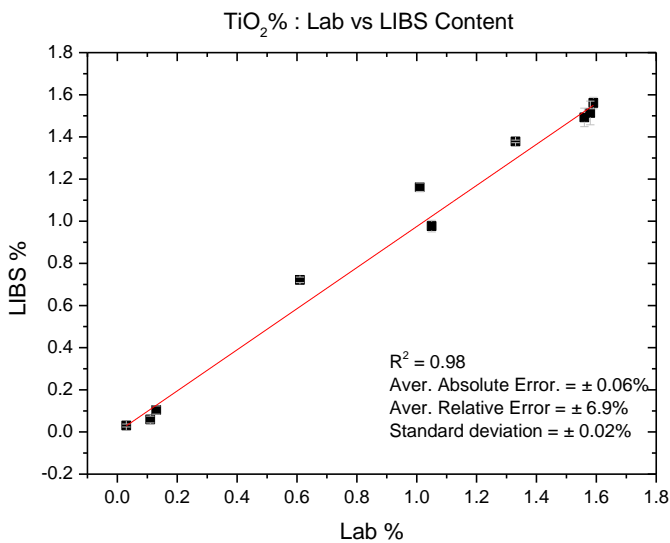
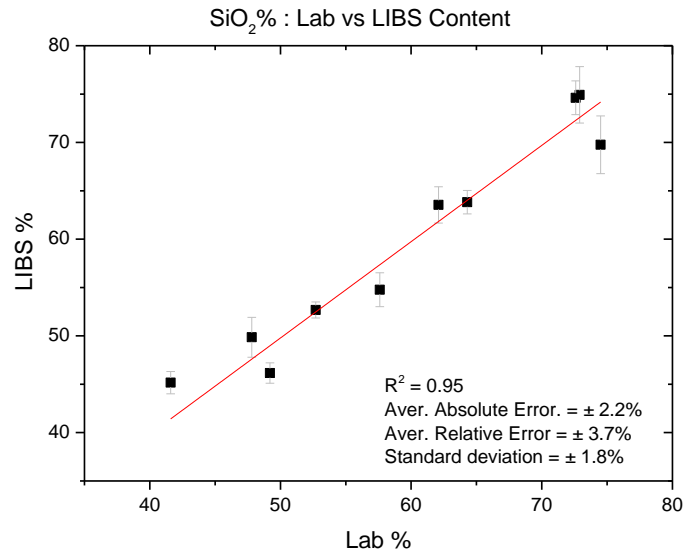
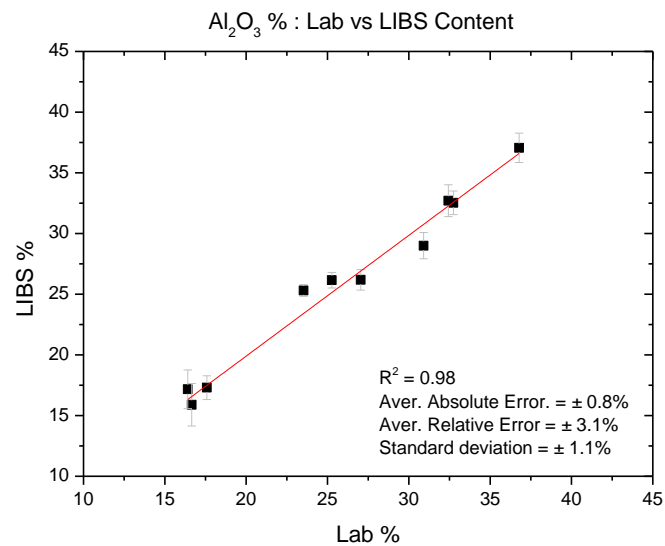
4. Qualitative spectral analysis

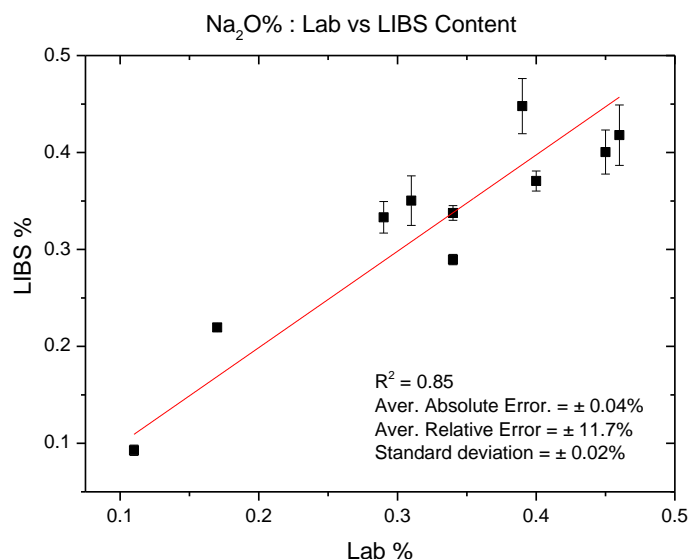


As can be seen from UV and UV-Visible range spectra, well defined lines of: Si, Ti, Al, Ca, Na and K can be clearly detected.

5. Quantitative analysis.

Using XRF data of clay samples calibration curves of LIBS measurement were developed. Vertical lines represent concentration deviation inside each sample.





Calibration results show good linearity between XRF and LIBS analysis, thus enabling possibility of on-line, real time LIBS analysis.

Calibration charts table:

Fe ₂ O ₃		Al ₂ O ₃		TiO ₂		K ₂ O		CaO		Na ₂ O		SiO ₂	
Lab	LIBS	Lab	LIBS	Lab	LIBS	Lab	LIBS	Lab	LIBS	Lab	LIBS	Lab	LIBS
1.09	1.17	30.91	29.00	0.61	0.72	1.40	1.52	0.21	0.20	0.17	0.22	41.60	45.16
1.00	0.93	32.74	32.53	1.05	0.98	2.50	2.83	0.18	0.19	0.39	0.45	49.20	46.16
0.99	0.98	32.43	32.70	1.01	1.16	3.00	2.51	0.16	0.16	0.45	0.40	52.70	52.68
0.86	0.89	25.26	26.15	1.58	1.51	2.60	2.47	0.14	0.12	0.40	0.37	62.10	63.54
0.74	0.77	17.58	17.30	1.59	1.56	1.80	2.26	0.05	0.03	0.31	0.35	72.90	74.92
1.73	1.70	16.41	17.17	0.13	0.10	2.80	2.84	0.05	0.06	0.29	0.33	74.50	69.76
1.45	1.48	16.65	15.89	0.11	0.06	5.70	5.68	0.05	0.06	0.46	0.42	72.60	74.62
0.87	0.87	36.78	37.06	0.03	0.03	2.30	2.27	0.04	0.06	0.11	0.09	47.80	49.85
1.02	0.99	27.04	26.18	1.33	1.38	2.10	1.87	0.13	0.12	0.34	0.29	57.60	54.77
0.90	0.89	23.53	25.31	1.56	1.49	2.00	1.96	0.10	0.11	0.34	0.34	64.30	63.82

Estimated accuracy calculation according to 10 clay samples is described in following table:

Accuracy summary table				
Analyzed Element	Average Error			
	Linearity R ²	Absolute \pm %	Relative \pm %	Standard Deviation \pm %
Al ₂ O ₃	0.98	0.8	3.1	1.1
Fe ₂ O ₃	0.98	0.03	3	0.08
TiO ₂	0.98	0.06	6.9	0.02
CaO	0.95	0.01	10	0.007
SiO ₂	0.95	2.2	3.7	1.8
Na ₂ O	0.85	0.04	11.7	0.02
K ₂ O	0.95	0.19	7.2	0.19

6. Conclusions:

- Good calibration curves between XRF laboratory data and LIBS spectral analysis for all required elements shows high linearity and low error, thus on-line, real time LIBS measurement is applicable.
- Relative errors are around XRF levels and will decrease even further with additional samples.
- The samples have high content variation and differ both in texture and color, thus, more samples of each kind have to be used for proper calibration curve. Current calibration should be considered as rough estimation of on-line LIBS abilities.