Report 3: Quantitative Analysis of Nepheline Samples, Using Laser Induced Breakdown Spectroscopy (LIBS) in On-Line, Real Time Mode.

01-06-2014

Current Report 3 is a continuation of previous reports:

1. **Quartz product on-line analysis report 14.01.2014**

2. **Clay on-line analysis report 06.03.2014**

1. **Technical task**

- Quantitative analysis of nepheline samples for content of: Al_2O_3, Fe_2O_3, K_2O, CaO, TiO_2, Na_2O and SiO_2.

- Evaluating possibility of on-line, real time LIBS analysis of nepheline content on a conveyer belt.

2. **The samples**

The received delivery contains 10 large bags each of white, homogeneous, sand like material.

Following table describes chemical content of nepheline samples:

| Sample	Fe2O3	Al2O3	TiO2	K2O	CaO	MgO	Na2O	SiO2
PR-015272-001	0.085	23.907	0.066	8.824	1.516	0.081	7.942	54.755
PR-015272-003	0.098	23.584	0.108	8.717	1.626	0.083	7.731	54.503
PR-015272-005	0.128	23.449	0.151	8.745	1.721	0.095	7.710	54.501
PR-015272-007	0.132	23.819	0.186	8.830	1.855	0.104	7.793	55.157
PR-015272-009	0.149	23.410	0.208	8.736	1.912	0.110	7.726	54.457
PR-015272-011	0.172	23.308	0.264	8.676	2.104	0.119	7.601	54.135
PR-015272-013	0.205	23.606	0.337	8.778	2.292	0.139	7.738	54.968
PR-015272-015	0.241	22.925	0.405	8.598	2.526	0.153	7.465	53.802
PR-015272-017	0.288	22.197	0.397	8.676	2.375	0.168	7.388	52.663
PR-015272-019	0.365	22.677	0.724	8.428	3.535	0.215	7.353	53.442

3. **Experimental section.**

The analytical method and equipment is described in previous reports.

Spectral collection done by UV (λ = 250-360 nm) and VIS (λ = 480-900 nm) spectrometers that were chosen as most suitable for current task.

4. Qualitative spectral analysis

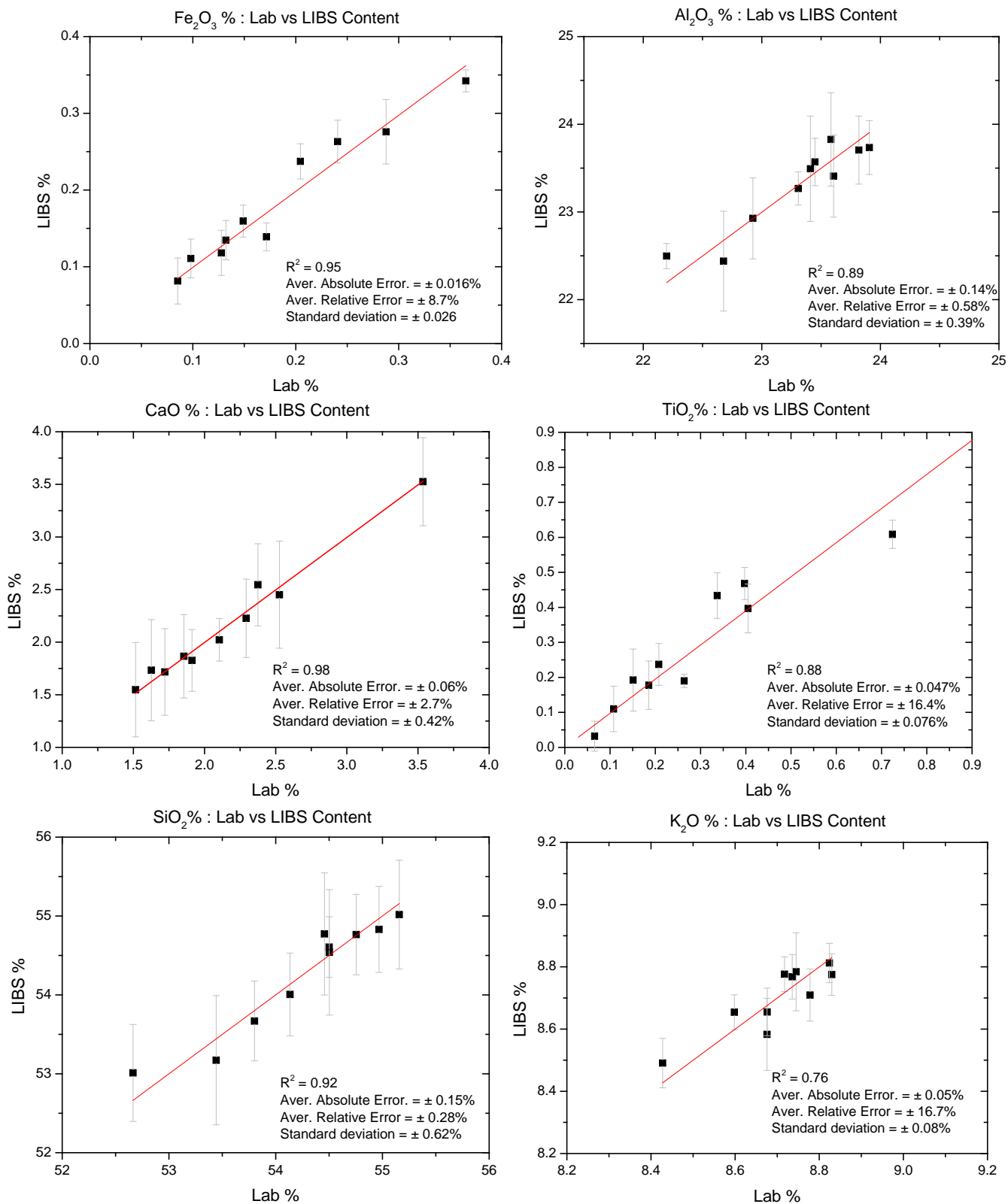Typical UV spectrum of nepheline material is demonstrated:
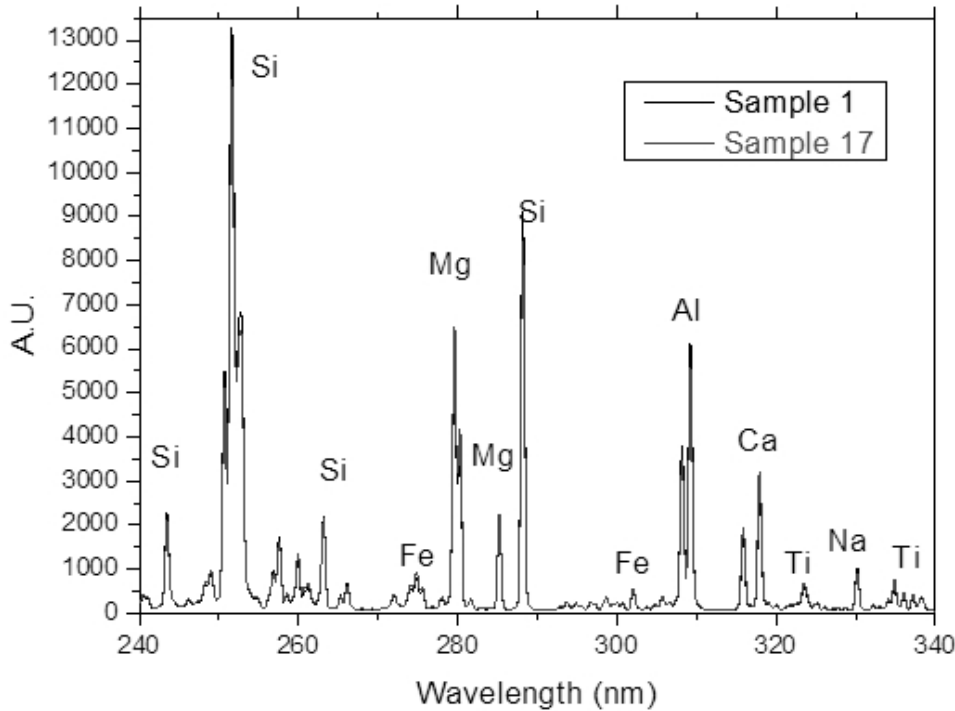
As can be seen from UV range spectra, well defined lines of: Si, Ti, Al, Ca, Fe, Mg and Na can be clearly detected. This chart shows quality comparison between sample 1(black) and sample 17 (red). As can be seen, while LIBS Si, Al and Na lines are higher in sample 1, Mg, Fe, Ti and Ca lines are higher in sample 17, as it should be, according to attached chemical data.
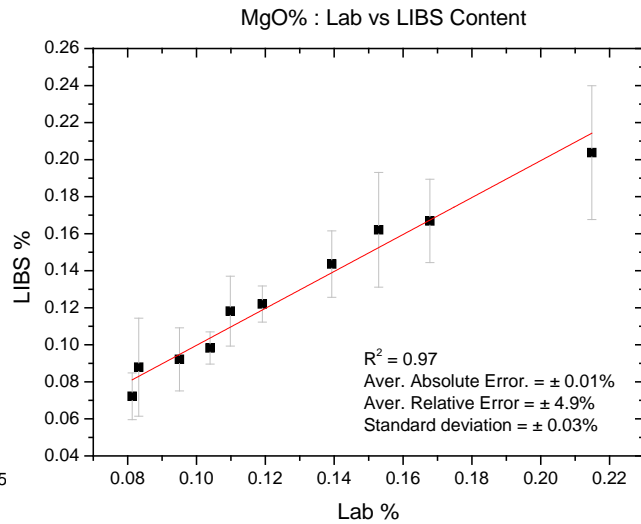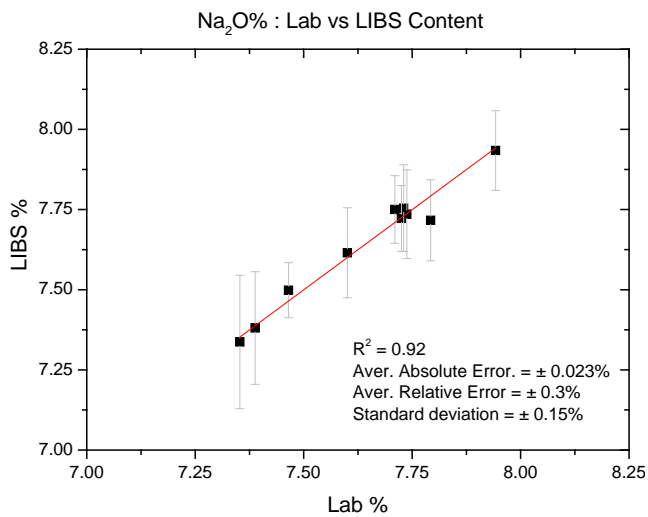
Other elements: Na, K as well as Mg and Ca can be detected in visible range of LIBS spectral data:
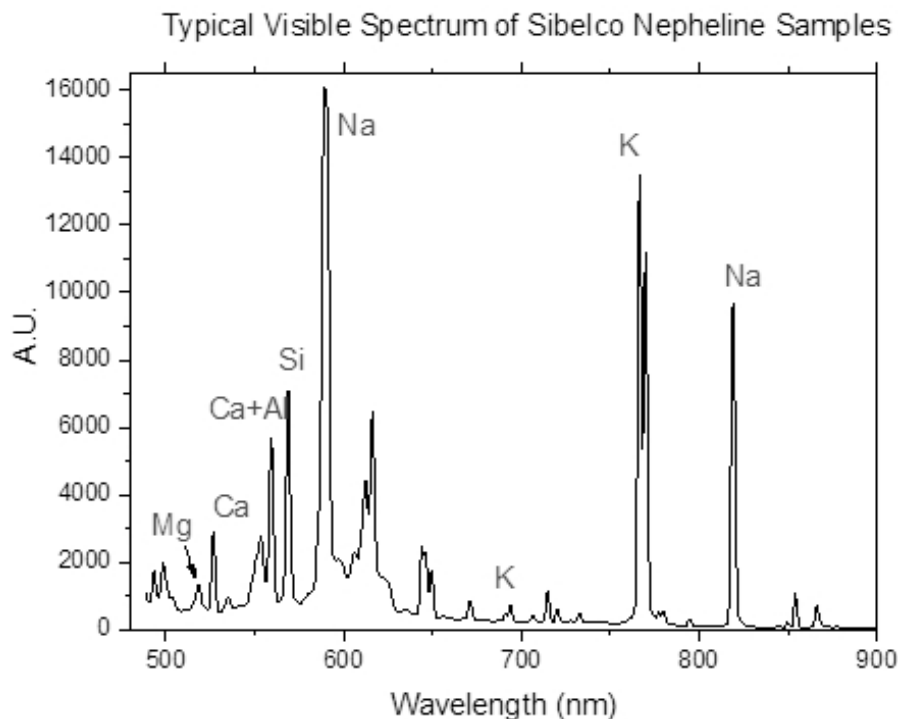
5. Quantitative analysis.

According to supplied laboratory data and LIBS analysis, calibration curves between LIBS and laboratory were developed. Vertical lines represent concentration deviation inside each sample.

Fe$_2$O$_3$ % : Lab vs LIBS Content

R^2 = 0.95
Aver. Absolute Error. = ± 0.016%
Aver. Relative Error = ± 8.7%
Standard deviation = ± 0.026

Al$_2$O$_3$ % : Lab vs LIBS Content

R^2 = 0.89
Aver. Absolute Error. = ± 0.14%
Aver. Relative Error = ± 0.58%
Standard deviation = ± 0.39%

CaO % : Lab vs LIBS Content

R^2 = 0.98
Aver. Absolute Error. = ± 0.06%
Aver. Relative Error = ± 2.7%
Standard deviation = ± 0.42%

TiO$_2$% : Lab vs LIBS Content

R^2 = 0.88
Aver. Absolute Error. = ± 0.047%
Aver. Relative Error = ± 16.4%
Standard deviation = ± 0.076%

SiO$_2$% : Lab vs LIBS Content

R^2 = 0.92
Aver. Absolute Error. = ± 0.15%
Aver. Relative Error = ± 0.28%
Standard deviation = ± 0.62%

K$_2$O % : Lab vs LIBS Content

R^2 = 0.76
Aver. Absolute Error. = ± 0.05%
Aver. Relative Error = ± 16.7%
Standard deviation = ± 0.08%

Na$_2$O% : Lab vs LIBS Content

R^2 = 0.92
Aver. Absolute Error. = ± 0.023%
Aver. Relative Error = ± 0.3%
Standard deviation = ± 0.15%

MgO% : Lab vs LIBS Content

R^2 = 0.97
Aver. Absolute Error. = ± 0.01%
Aver. Relative Error = ± 4.9%
Standard deviation = ± 0.03%

Calibration results between provided laboratory data and LIBS analysis, show proper correlation, thus possibility of on-line, real time LIBS analysis is definite.
Some analytes show lower linearity than others due to narrow concentration range.

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

Accuracy summary table				
Analyzed Element			Average Error	
	Linearity R^2	Absolute ± %	Relative ± %	Standard Deviation ± %
Al$_2$O$_3$	0.89	0.14	0.58	0.39
Fe$_2$O$_3$	0.95	0.016	8.7	0.026
TiO$_2$	0.88	0.047	16.4	0.076
CaO	0.98	0.06	2.7	0.42
SiO$_2$	0.92	0.15	0.28	0.62
Na$_2$O	0.92	0.023	0.3	0.15
K$_2$O	0.76	0.05	16.7	0.08
MgO	0.97	0.01	4.9	0.03

6. Conclusions:

- Good calibration curves between 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.

- K$_2$O, Al$_2$O$_3$ content range in the supplied samples is very narrow, thus linearity should increase if wider concentration range is provided.