Novel reference materials for laser-induced breakdown spectroscopy [LIBS] microanalysis

SOMERS A.M.[1*]., NORDSTAD S[2].

[1] SciAps Inc., 7 Constitution Way, Woburn, MA01801, USA (asomers@sciaps.com)

[2] myStandards GmbH, Schauenburgerstr. 116, 24118 Kiel, Germany (nordstad@my-standards.com)

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Overview

- Conduct study to assess the performance of nano-particulate sample preparation of reference materials [RM's] on signal, calibrations and resultant data quality for LISB analysis.
- The LIBS analytical technique: Laser Induced Breakdown Spectroscopy -What is it and what can it do?
- Collaboration between LIBS manufacturer SciAps and novel nano-particulate reference material provider myStandards
- Observations, Comments and Conclusions

Experiment design brief

- To investigate the effects of nano-particulate sample preparation on LIBS analysis 4 commercially available certified reference materials [CRMs] and blended mixes of these CRMs were prepared to produce 2 sets of 10 samples with same chemistry but different particle size i.e. 20 samples in total=10 nano and 10 as per normal CRM particle size specifications
- To assess signal quality and heterogeneity differences between the 2 corresponding sample sets
- To assess calibration performance based upon use of the 2 corresponding samples sets on real world samples
- The focus of this study looks at lithium bearing pegmatite material

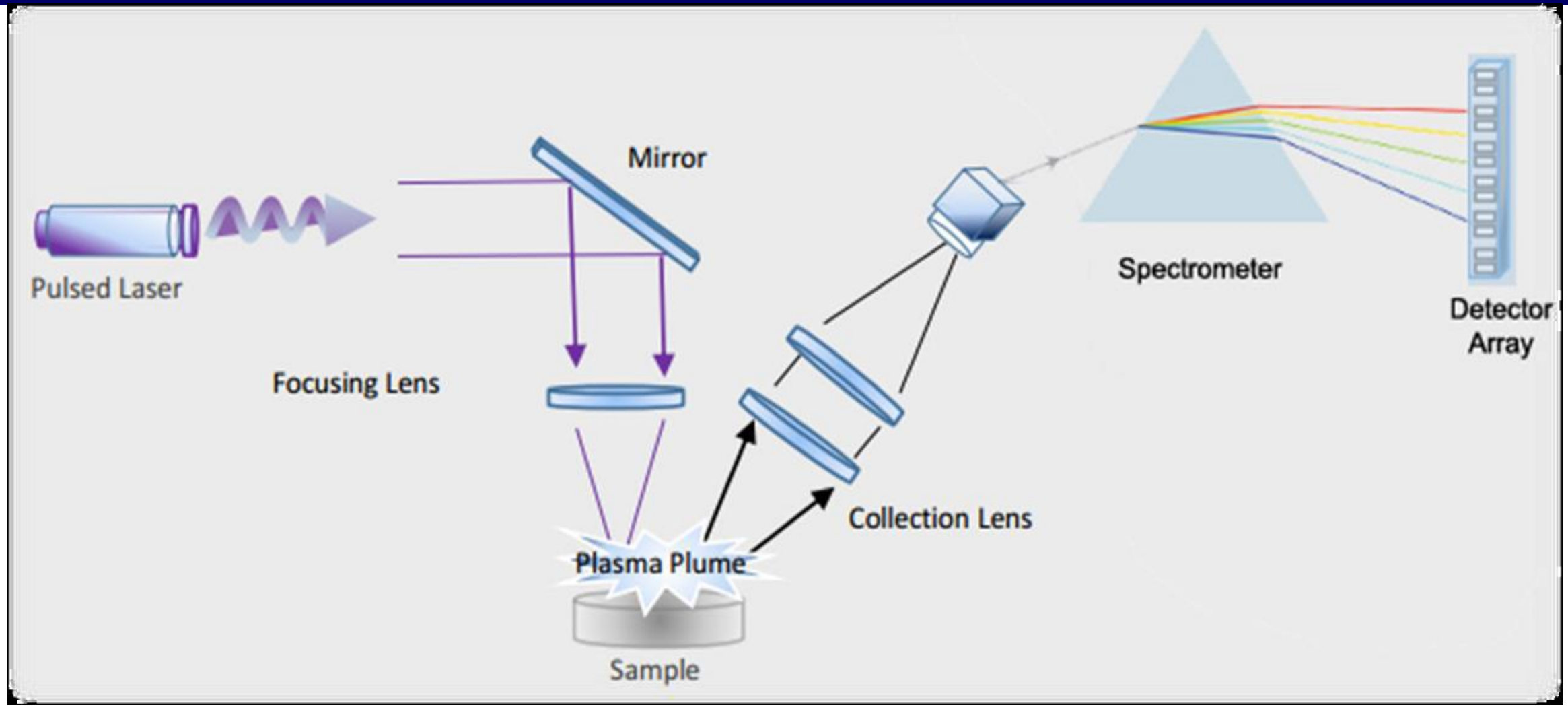
LIBS methodology

- 2 variants of a calibration model was developed each using 1 of the 2 corresponding sample sets as calibration standards but with identical parameters for testing and data modelling.
- Signal strength of LIBS data was assessed between the nano and original sample types
- Variance within the raster patterns of individual tests and within the averages of multiple aquisitions across sampes was studied to assess whether improved representivty was acheived using the nano particulate samples as compared to the orginal samples.
- The performance of the resultant calibrations was assessed on a real world samples set from a lithium bearing pegmatite.

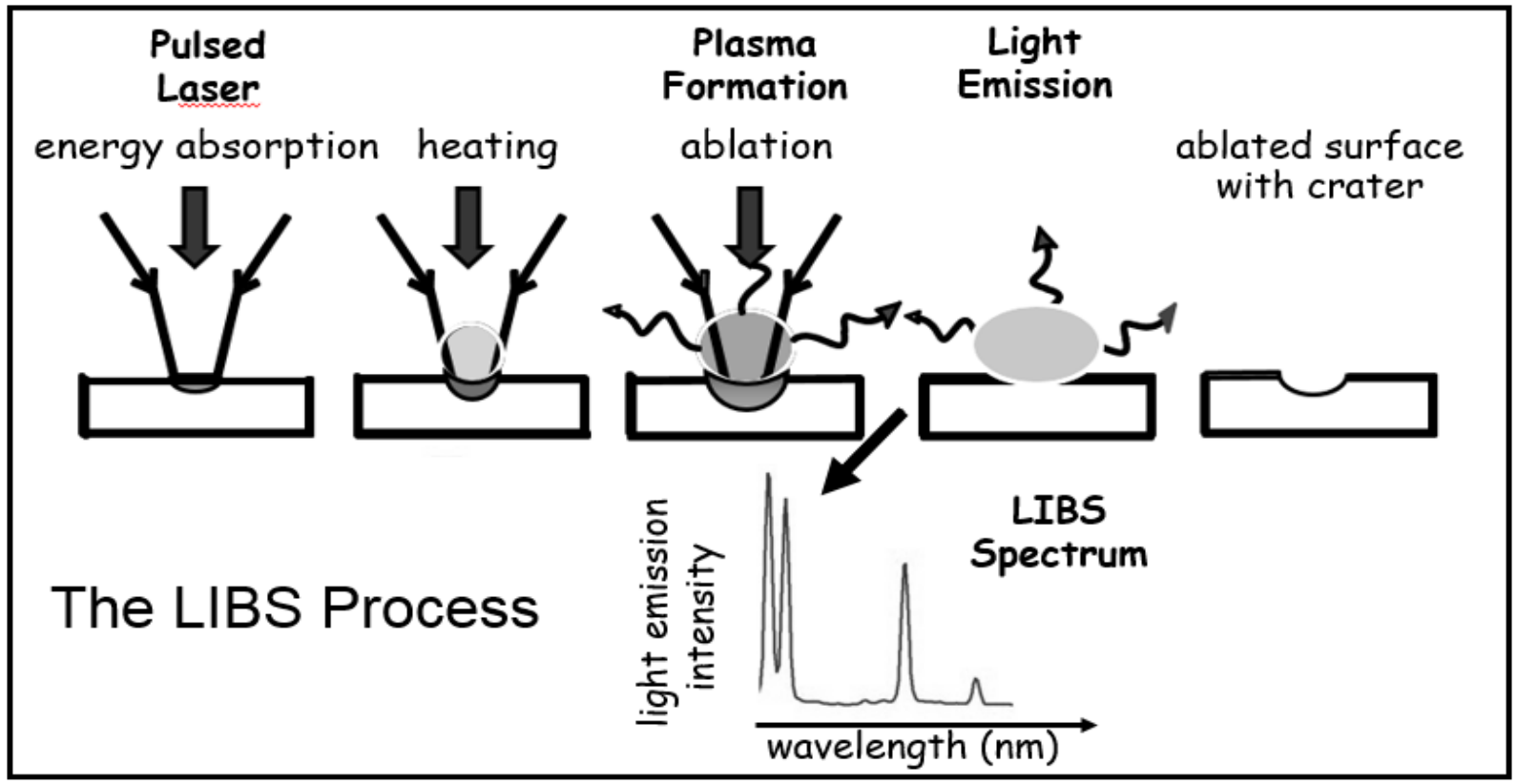
LIBS-What is it and what can it do?

- LIBS (Laser Induced Breakdown Spectroscopy)
  - Bench top technology for the past 50 years or so
  - Optical Technique: type of Atomic Emission [AES] Spectroscopy
- Advantages include:
  - Capable of Light Elements e.g. Li, Be, B, C, Na: wide element range possible but dependent on spectral range of system used
  - Fast! Individual tests conducted in less than 1 second
  - Spatially Precise: microanalytical technique
- Challenges include
  - Access to “fit for purpose” calibration standards that provide adequate homogeneity relative to laser spot size

Laser Induced Breakdown Spectroscopy (LIBS)



The LIBS Process



- occurs when laser energy couples to the surface of a solid sample
- a sub-mg amount of material is vaporised via both thermal and non-thermal mechanisms
- dissociating it into molecular, atomic and ionic species in a high-temperature plasma.
- Light emission occurs as the plasma cools and electrons return to lower-energy levels, with energy released as photons.
- The measured LIBS spectrum, termed ‘geochemical fingerprint’ in this study, is unique for every specimen of different composition.

Harmon, R. S., Hark, R. R., Throckmorton, C. S., Rankey, E. C., Wise, M. A., Somers, A. M. and Collins, L. M. (2017), Geochemical Fingerprinting by Handheld Laser-Induced Breakdown Spectroscopy. Geostand Geoanal Res, 41: 563-584. doi:10.1111/ggr.12175

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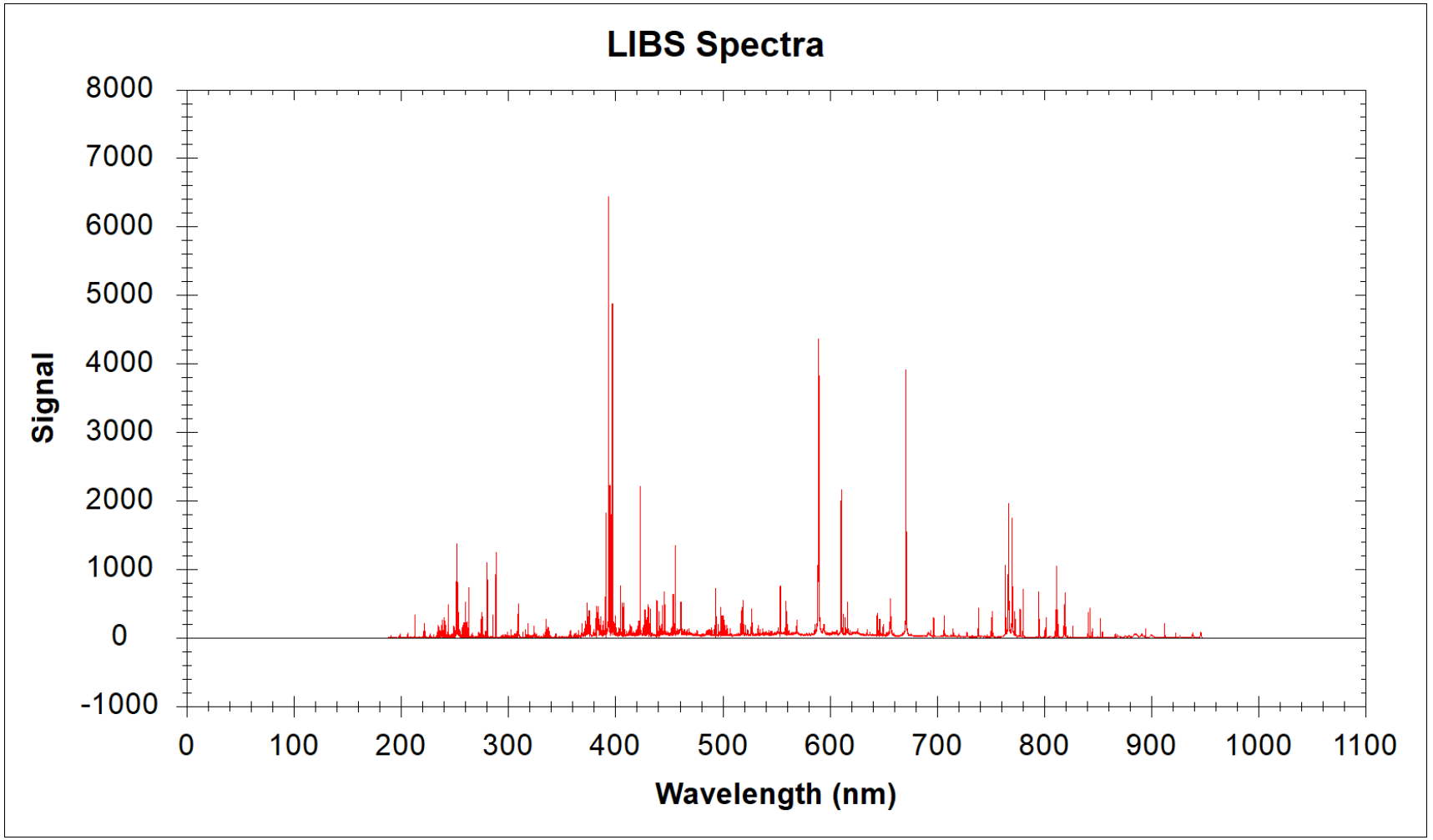
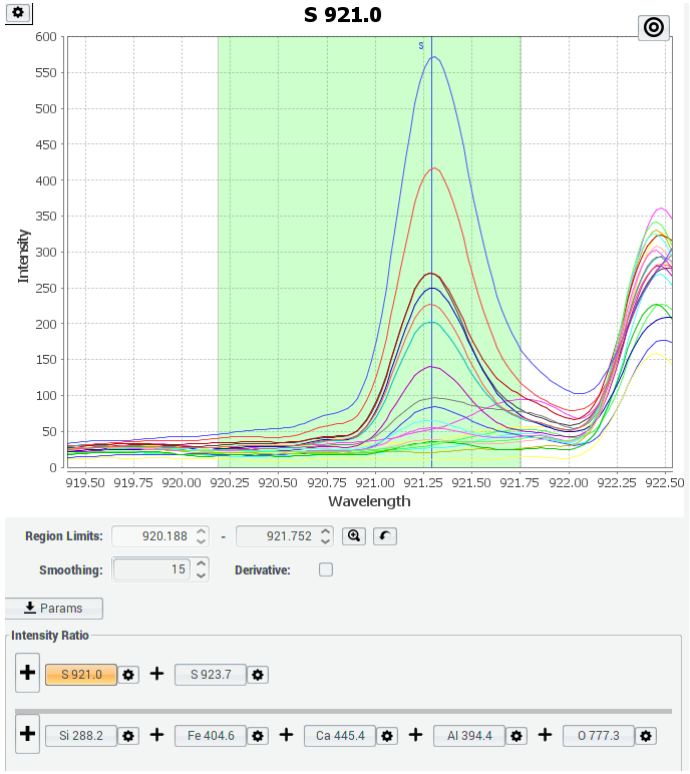
LIBS Spectra SciAps Z300 190-950nm

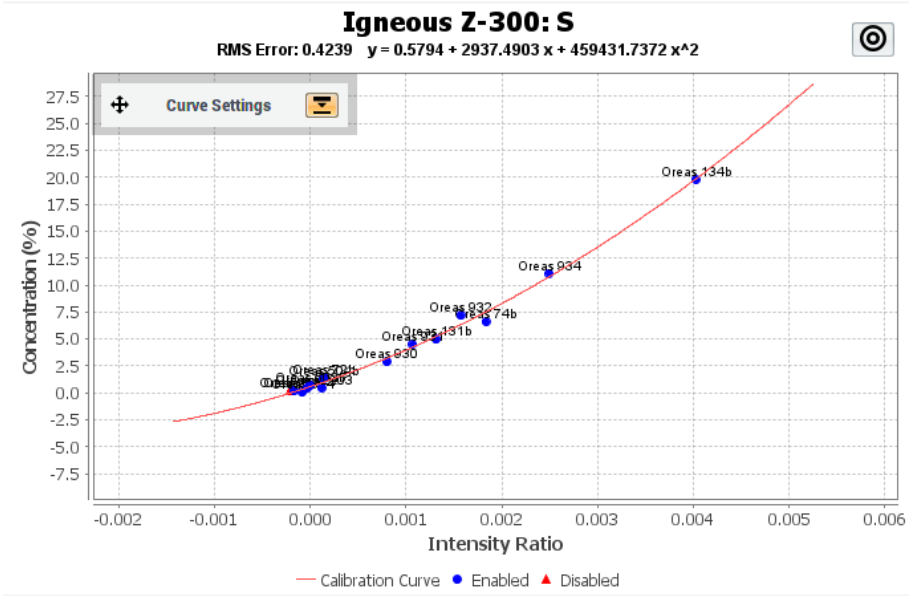


Quantitative Analysis: Empirical Calibrations

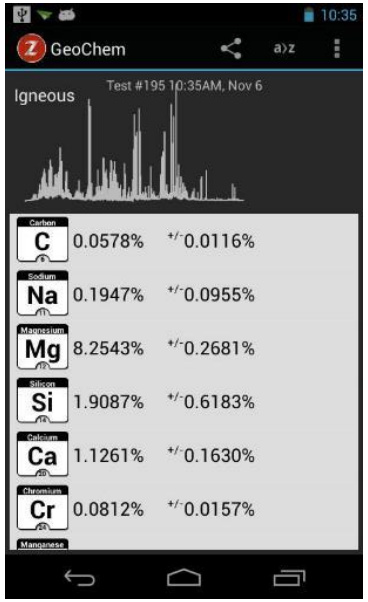
Peaks are integrated and normalized by the intensity of the base element. We call these: Intensity Ratios (IR)



IR's are plotted against known concentrations to find Calibration Curves



Calibration curves can be applied to achieve results in weight %



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Application of LIBS to characterising geological samples

- LIBS has been used extensively to test geological materials: GEOLIBS- Application of LIBS to the analysis of geological and environmental materials. Harmon, Russo and Hark (2013)
- All elements respond between 190-900nm but have variable sensitivities: spectral range is very important for testing geological materials
- Laser spot size on different LIBS systems can vary from microns to hundreds of microns: Heterogeneity of samples tested is a challenge for microanalytical methods
- Laser wavelength and power relate to data quality
- Use of purge gases such as Argon and Helium can improve data

Sample preparation: Considerations

- Particle Size/grain size vs spot size-can nano-particulate samples improve data quality when testing with a microanaltical technique such as LIBS?
- Coherence of samples is important for LIBS analysis as the laser ablation can destroy a loosely packed sample
- Binders used for particulate samples are able to be measured by LIBS as part of the sample and also can cause additional heterogeneity effects when mixing
- Coupling variation between reference materials and actual samples- compressed pulverised RMs vs fused glass RM's vs mineral standards?
- For samples with chemistry from other microanalytical techniques how representative are the data?

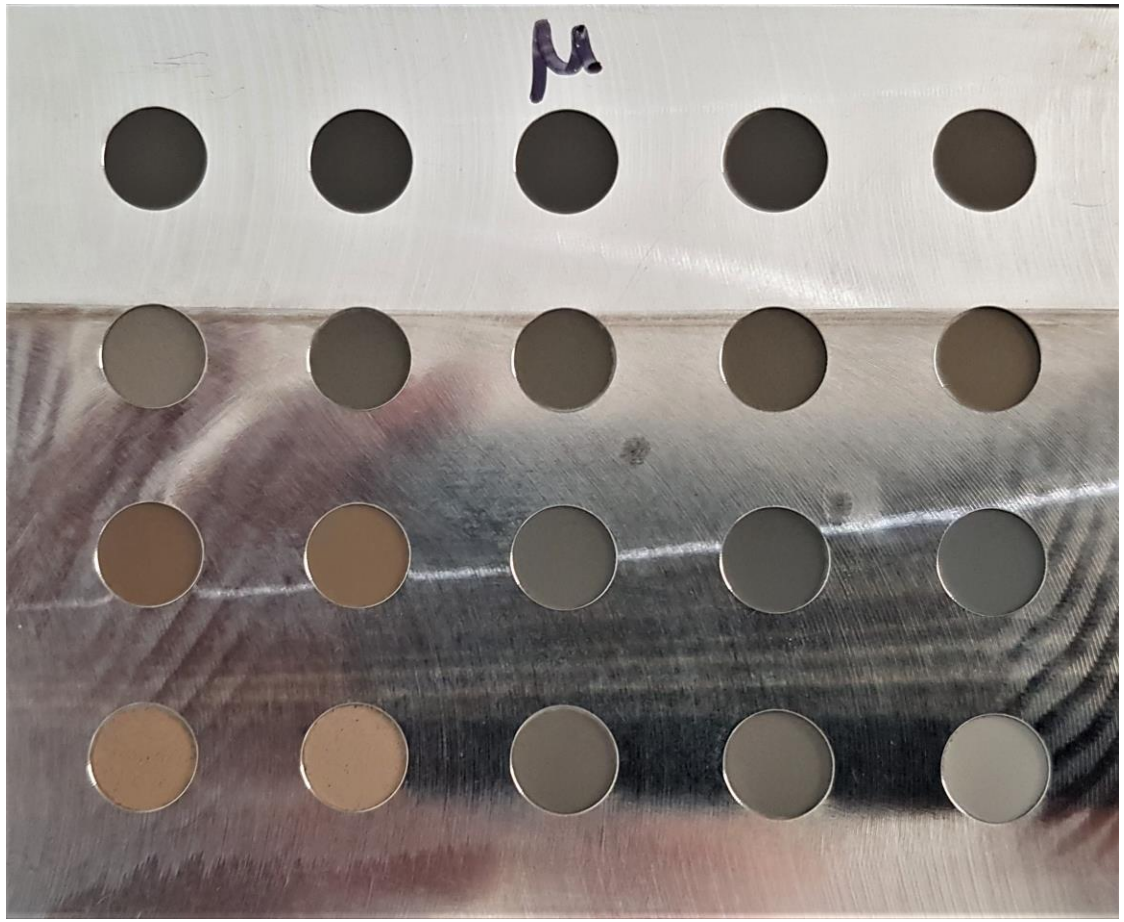
Milling Procedure

- Nano-particulate samples were prepared by suspension-milling
  - high-power planetary ball-mill
  - agate milling gear
  - deionised water (18,2 MΩ)
- Suspension was frozen and then freeze-dried
- Resulting powder re-homogenised in mill with agate ball to avoid heterogeneities caused by gravimetric settling while stationary in freezer

Pressing procedure

- 13 mm diameter pellets were pressed in an automatic and programmable hydraulic press to maximum allowed pressure of the pressing die (10 tonnes, metric)
- Pellets are surrounded by XRF-binder for mechanical stability: Sample is NOT mixed with binder only fortified
- Powders weighed-out according to desired concentrations and mixed in mill with agate balls
- Original powders, which were not mixed, were pressed directly from the original container
- Pressed into pellets using same procedure as was used for Nano-Pellets
- Mounted in prototype CNC-milled aluminium mount for LIBS analysis.

Resultant samples



Mounting plate with all samples on left

nano prepped sample of OREAS 147 and on right is for original sample of OREAS 147: Nano samples show lower better coherence after ablation

Samples used

- OREAS commercially available CRM's were selected:
  - OREAS 999 Spodumene concentrate
  - OREAS 147 Pegmatitic Li-Nb-Sn Ore
  - OREAS 148 Pegmatitic Li-Nb-Sn Ore
  - OREAS 24b Granodiorite lithogeochem/blank reference material

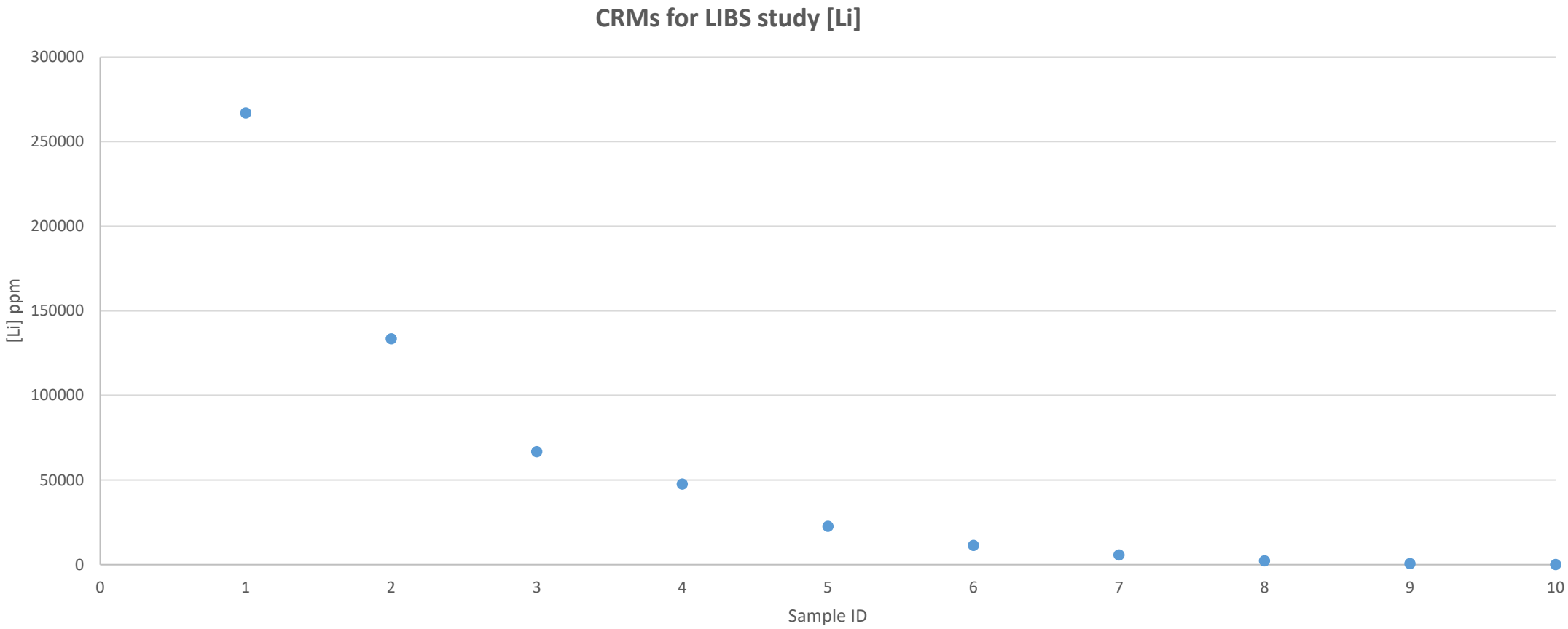
- Several blends of the aforementioned were also included to allow adequate calibrations points along the concentration continuum for lithium

- https://www.ore.com.au/

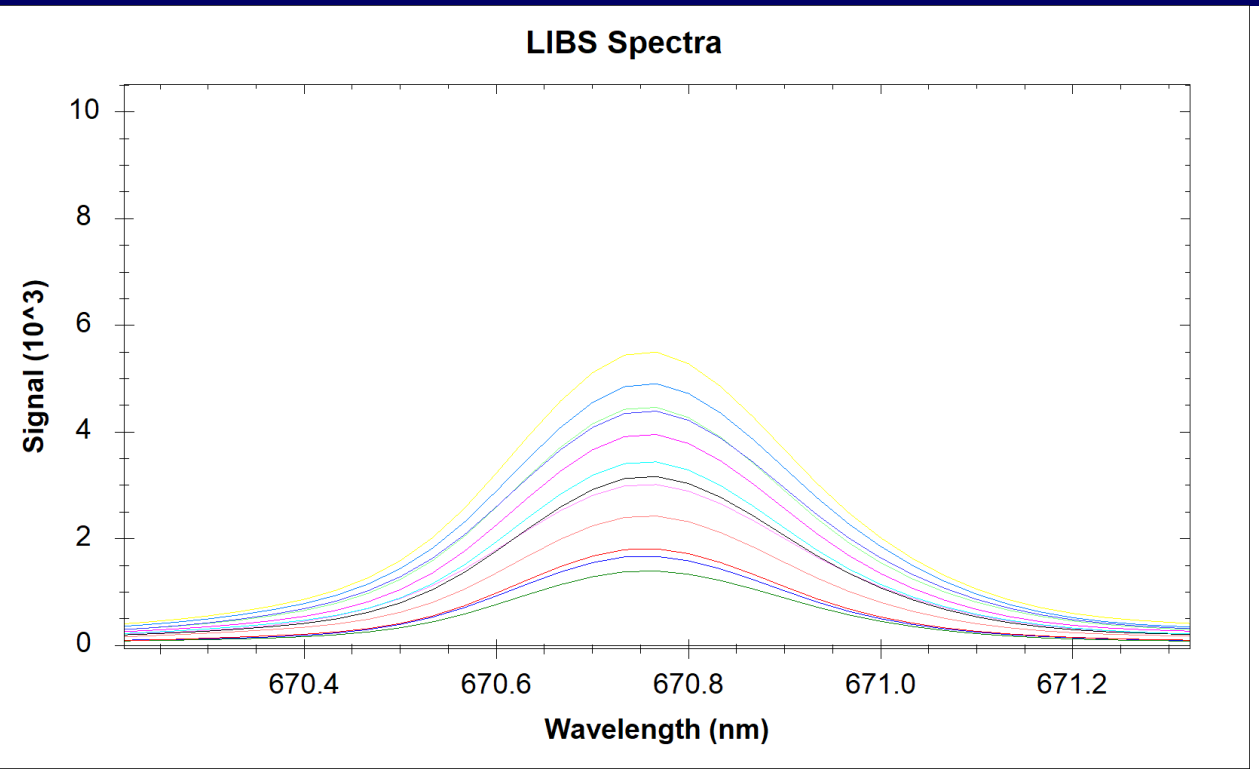
Samples used: Both Nano and Original

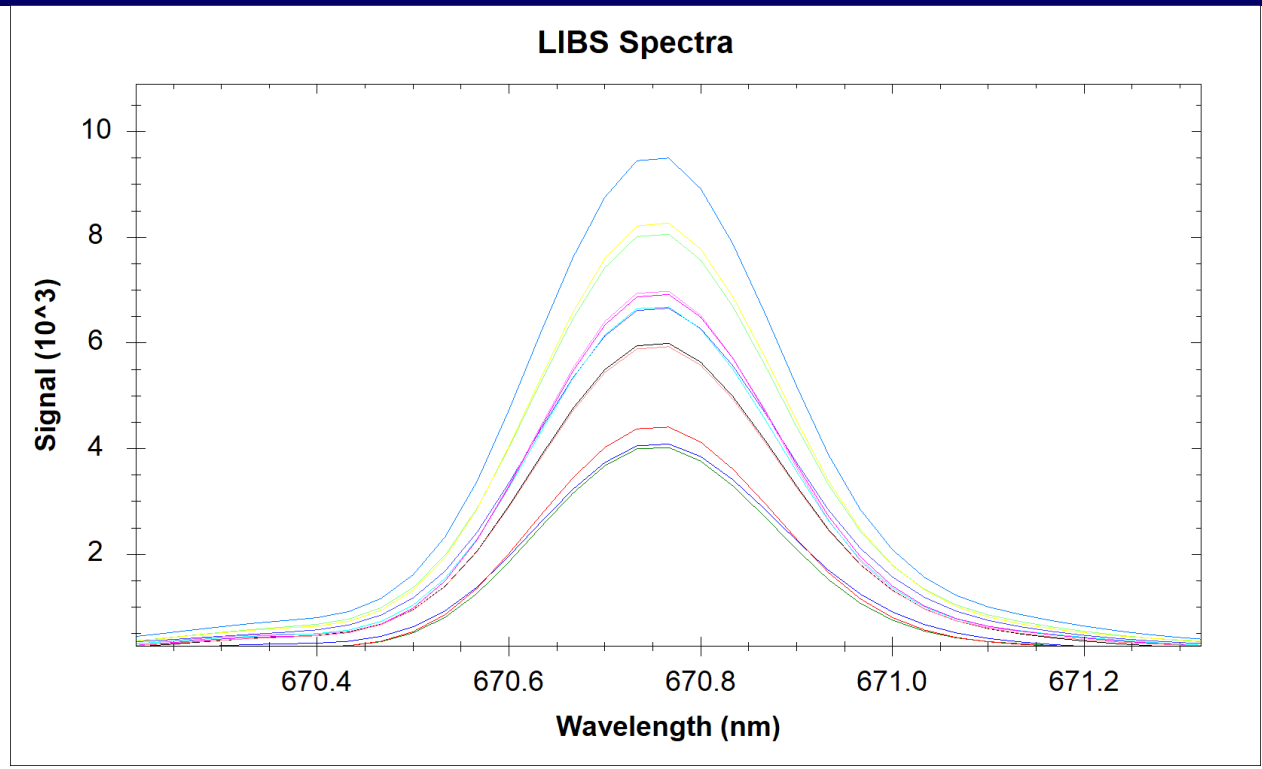
	Material	mass fraction Li [µg/g]	[wt-%]	Comment	Mixing [g]
1	OREAS 999	267000	2.67	Li-Concentrate as is	
2	µMix 1	133500	1.335	50:50 [999] : [24b]	5 & 5
3	µMix 2	66750	0.6675	25:75 [999] : [24b]	2,5 & 7,5
4	OREAS 148	47600	0.476	as is	
5	OREAS 147	22700	0.227	as is	
6	µMix 3	11350	0.114	50:50 [147] : [24b]	5 & 5
7	µMix 4	5675	0.057	25:75 [147] : [24b]	2,5 & 7,5
8	µMix 5	2270	0.023	10:90 [147] : [24b]	1 & 9
9	µMix 6	568	0.006	2,5:97,5 [147] : [24b]	0,25 & 9,75
10	OREAS 24 b	50	0.0005	as is	

Samples used: Li concentration range



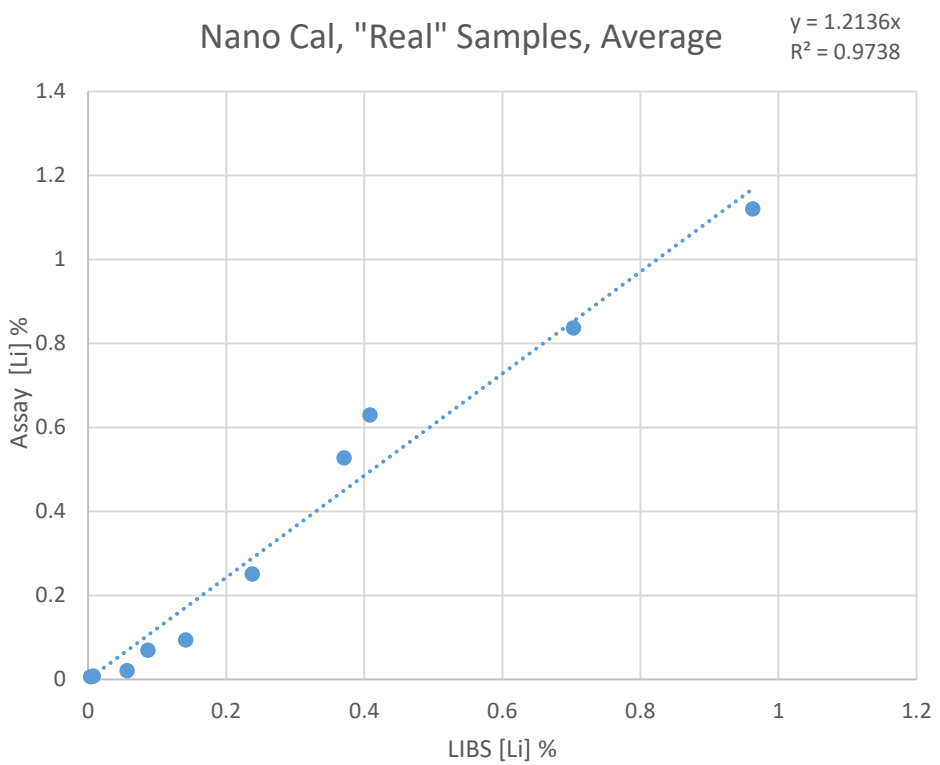
Data:repeatability

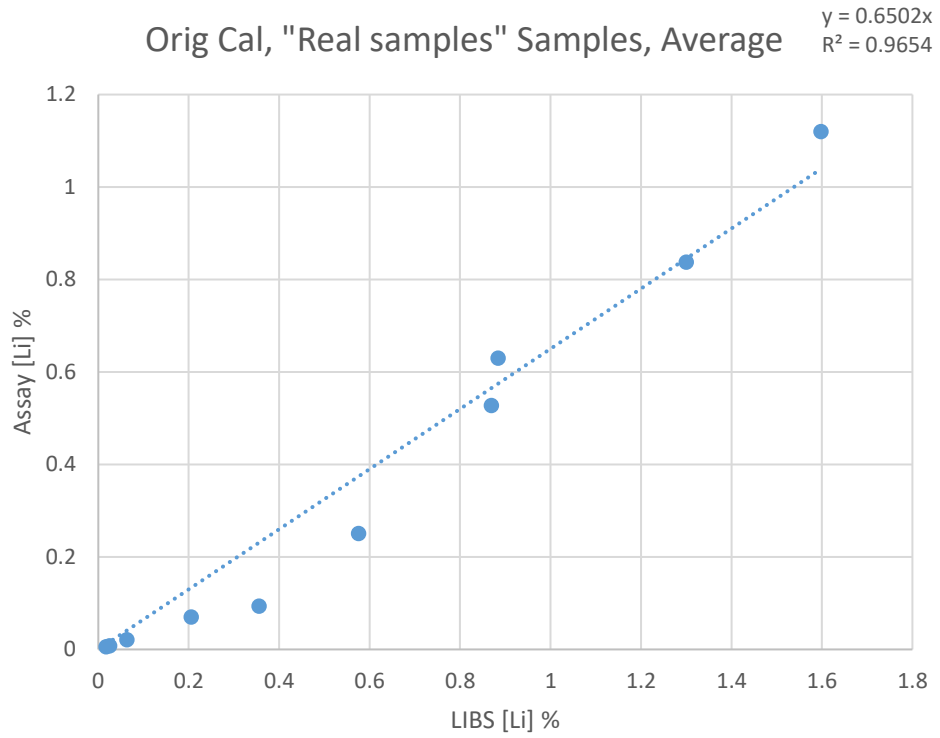




Data on left is for nano prepped sample of OREAS 147 and on right is for original sample of OREAS 147: Nano samples show lower intensities but better repeatability.

Data:performance on real samples





Data on left is for calibration developed using nano prepped samples and on right is for original samples: Nano samples result in better accuracy and precision

Conclusions

- Nano-particulate standards showed good coherence after ablation with LIBS analyser
- The potentyial durability bodes well for the application of this sample to ongoing QA/QC programs and calibrati
- Further research is required to better understand lower intensities observed when using nano-samples vs conventionally prepped standards.
- The collaboration between SciAps and uStandards will continue to improve the understanding of the utilisation of nano-particulate standards and samples to LIBS analysis.

Andrew Somers
SciAps Inc., 7 Constitution Way, Woburn, MA01801, USA
(asomers@sciaps.com)

Simon Nordstad
myStandards GmbH, Schauenburgerstr. 116, 24118 Kiel, Germany (nordstad@my-standards.com)

Thank You!