Multivariate Limit of Detection Interval for PLS calibration models via Laser Induced Breakdown Spectroscopy on ^{235}U and ^{238}U enriched glasses

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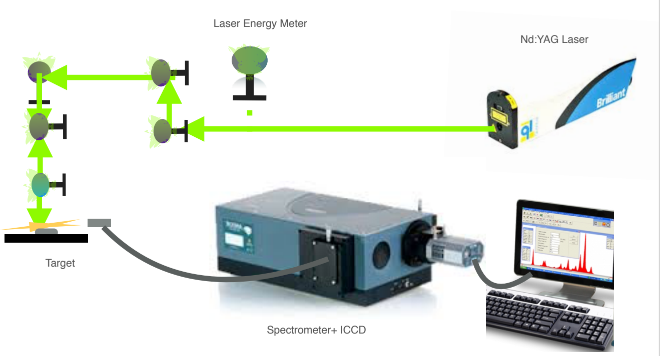
Abstract

A calibration model was created to illustrate the detection capabilities of laser induced breakdown spectroscopy (LIBS) discrimination in isotopic analysis. The sample set was manufactured by the uranium enrichment facilities at Y-12 National Security Complex. Triuranium (U_3O_8) Lithium Borate glasses with ^{235}U abundances ranging from 0.7% to 93% ^{235}U were loaded into sample cubes with quartz windows and sent to Lawrence Berkeley National Laboratory (LBNL) for U-isotopic measurements using LIBS. Each sample set was interrogated with a Q-switched Nd:YAG nanosecond ablation laser operating at 1064 nm. The measured isotopic abundances by high-resolution mass spectrometry was compared with the PLSR LIBS predictions. An IUPAC novel approach for determining a multivariate Limit of Detection (LOD) interval was used to predict the detection of the desired isotopic ratios. The predicted multivariate LOD is dependent on the variation of the instrumental signal and other composites in the calibration model space.

Introduction

Recent developments for the detection of nuclear materials have been fueled by the nation's need to respond promptly and scientifically to nuclear threats both post and pre detonation. While the detection of fissile materials is difficult due to weak light emission, new developments in applied spectroscopy have the capability to selectively excite desirable element emission lines in complex matrices. In an effort to improve the limit of detection analysis, remotely, special techniques such as Laser induced breakdown spectroscopy (LIBS) coupled with available signal enhancement methods are very useful. LOD is a common measurement used in spectroscopy community for calibration curves. Effectively quantifying the LOD via a partial least squares method will further illustrate the benefit of LIBS and classifies the detectors' capability in measuring and later predicting accurate isotopic ratios

Methodology



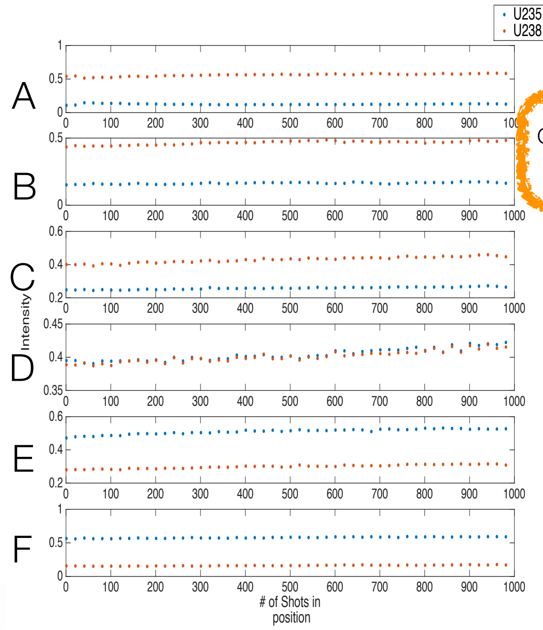
Laser Parameters	Q-Switched Nd:YAG 1064 nm	Laser pulse energy ~ 100 mJ	FL: 75 mm
Light Collection Paramters	oriented ~90 degrees relative to sample stage	collimator to fiber optic cable	19 fiber optical bundle
Spectrometer Specifications	Horiba Jobin Yvon Spectrometer (f = 1.25 m)	3600 gr/mm grating Δλ = 0.02 nm	PI Max iCCD 1340 X 1300
Acquisition Settings	**1000 shot accumulation (20 shots/image 50 images total) per position**	Gate Delay: 20μs	Gate Width: 2 μs

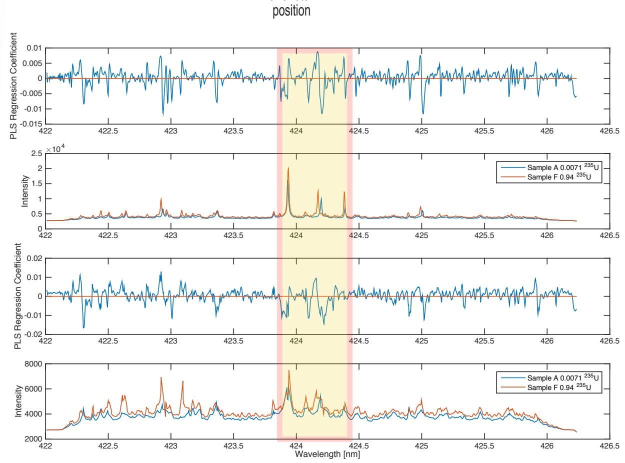
Common approaches towards Isotopic Analysis for LIBS signals

1) Calibration Modeling
- Requires enriched isotopic mixtures
- Biased for each individual detector
- Knowledge of different multivariate analyses

2) Calibration Free Modeling
- Requires known physical constants
- Fitted experimental spectra to simulated spectra

Shot to shot monitoring for optimal isotope emission intensities





- PLS regression coefficients vs. wavelength plots verify isotopic shifts observed in previous literature
- PLS plots can exploit these isotopic shifts with spectrometers with low spectral resolutions

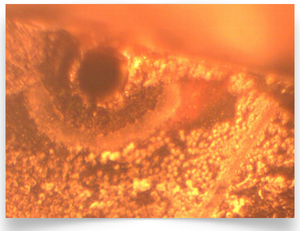
YCAL SET

Uranium glasses

Sample	$^{235}U/^{238}U$ Ratios (%)
A	0.72
B	9.96
C	29.98
D	50.10
E	70.80
F	94.49

Also known as the response or dependent variables to be predicted by PLSR

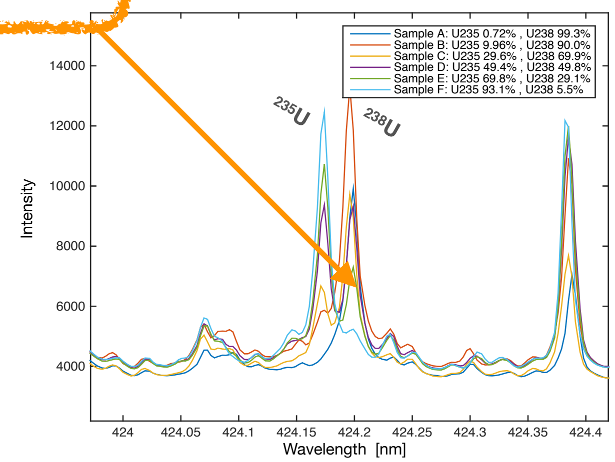
Crater formed in each sample from laser ablation Monitored homogenous plasma



Observed isotopic shift at 0.025 nm

XCAL SET

LIBS Plasma Emission



Also known as the independent variables or predictors

Preprocessing, Cross Validation and Test

- Individual calibration sets along with its respective test set was preprocessed using the mean-centered option to remove any mean offset from each variable
- A venetian blinds method was selected to cross-validate the calibration model to give
  - low RMSECVs
  - minimum number of principal components explaining the covariance in X_{CAL} and Y_{CAL}
  - low prediction bias
- Testing each model was done by leaving on sample concentration out and then using the PLS algorithm to predict the left out sample concentration

PLSR Predictions

Sample	Actual ^{235}U (%)	Determined ^{235}U (10 replicates) (%)	Bias (%)	#PCs	RMSEC
A	0.72	1.26 +/- 1.46	0.54	4	1.75
B	9.96	10.30 +/- 0.34	0.34	7	0.85
C	29.98	29.28 +/- 0.07	-0.70	6	1.03
D	50.10	50.15 +/- 0.02	0.05	3	1.87
E	70.80	71.58 +/- 0.02	0.78	4	1.73
F	94.49	95.25 +/- 0.02	0.76	6	0.91

Multivariate LOD interval

$$LOD_{min} = 3.3[SEN^{-2}var(x)+h_{0min}SEN^{-2}var(x) +h_{0min}var(y_{cal})]^{1/2}$$

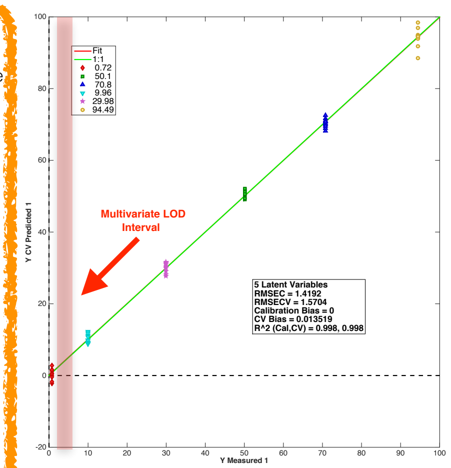
$$LOD_{max} = 3.3[SEN^{-2}var(x)+h_{0max}SEN^{-2}var(x) +h_{0max}var(y_{cal})]^{1/2}$$

$$LOD_{pu} = 3.3s_{pu}^{-1}[(1+h_{0min} + 1/I)var_{pu}]^{1/2}$$

where SEN is the inverse of the regression vector, var(x) is mean of the instrumental signal variance, var(y_{cal}) is calibration concentration variance, h_{0min} is minimum sample leverage h_{0max} is maximum sample leverage, s_{pu} is the slope of the pseudo univariate line, and var_{pu} is the regression residual variance.

- Instead of using a single LOD value, an interval of LODs is provided which depends on the variation of the background composition in the calibration space
- The LOD interval becomes a parameter characterizing the overall PLS calibration model and not each test sample in particular, as proposed in the past.

LOD_{psu}: 4.87%
LOD_{min}: 4.78%
LOD_{max} : 5.11%
No. PCs: 5
var(x_{cal}): 0.000008
var(y_{cal}): 0.001000



CONCLUSION

Classifying each detector by its LOD interval can be applied to real time predictions after laser ablation as a standard calibration source. In an effort to improve the limit of detection analysis, remotely, special techniques such as LIBS combined with PLSR calibration models are very useful. We can conclude that the amount of analyte cannot be detected in a given test sample since its predicted concentration is below the LOD_{min} or that is present if its predicted concentration is above the LOD_{max}. In addition to this, the the pseudovariate limit of detection was calculated and fell within the multivariate interval determination.

References:
1) Allegrini, F. and Olivieri, A. Anal. Chem. 2014, 86, 7858-7866.
2) Russo, R.E. et al. Spec. Chim Acta. B. 2011, 66, 99-104.