Quantification of Rare-Earths in the Parts-per-Million Range- a Novel Approach in the Application of Laser-Induced Breakdown Spectroscopy

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Abstract

This work extends a previous percentage level concentration study of the optical emission spectra for six rare earth elements, europium (Eu), gadolinium (Gd), lanthanum (La), praseodymium (Pr), neodymium (Nd), and samarium (Sm), along with the transition metal, yttrium (Y) using laser induced breakdown spectroscopy (LIBS). The concentration of these six rare earth elements and yttrium have been attempted for the first time systematically down to parts-per-million concentration levels ranging from 30 – 300 ppm. The authors have developed multivariate models for each element capable of predicting concentration with acceptable to excellent levels of accuracy. Additionally, partial least squares regression coefficients were used to identify key spectral features able to be used in this lower concentration regime. This study has demonstrated that it is conceivable to quantify the six rare earth elements along with yttrium at low concentrations in the parts-per-million levels.

Introduction

This important work is related to the national need for rare earth elements (REEs) as strategic minerals, as well as related to the recycling of the growing amount of electronics containing them. Furthermore, REEs are typical byproducts of nuclear fission, the reaction used for nuclear power production involving the splitting of uranium or plutonium atoms into two lighter elements and generating heat. After nuclear fuel, typically UO_2, has undergone several cycles in a nuclear powerplant the fuel pellets have accumulated a sizable amount of radioactive fission products (FPs) and minor actinides e.g., Eu-152, Gd-157, La-139, Nd-144, Pr-147 and Sm-150, etc. The capability to assess the composition of these used fuel elements is crucial for nuclear safeguards. The compositional measurements are especially relevant to nuclear fuel reprocessing, where irradiated fuel is treated through aqueous or molten salt methods to remove FPs from still fissile material.[1] This necessitates the tracking of mixed actinides, REEs, and other FPs throughout the various separation process steps.

Standard analytical techniques such as ICP-MS or ICP-OES/AES are largely used for measuring the quantities of rare earth and the actinide that are produced in irradiated fuel.[2-13] It is impossible to analyze as-produced solutions which have very high radiological doses. Instead, these solutions must be diluted as high as a million-fold to be handled safely and this dissolution contributes to analytical uncertainties. These procedures are very time-consuming and hence, expensive to accomplish. Laser induced breakdown spectroscopy (LIBS) is a strong candidate for in-situ compositional analysis. LIBS involves pulsing a focused high-energy laser onto a sample surface, where through thermal breakdown a plasma plume is formed from a minor amount of ablated material. This plasma emits characteristic elemental signatures as it cools which can be measured with a spectrometer. LIBS can be fiber-based or implemented at stand-off distances and is sensitive to nearly all elements making it well suited for extreme environment/sample measurement.

It has been well established that the spectral features for the REEs have very complex and extremely dense spectral signatures with roughly a thousand peaks each. This can make a positive identification of the actinides along with the other FPs and REEs from a concentrated mixture that is produced in a nuclear facility very difficult. To identify strong characteristic peaks a detailed and comprehensive study of several major REEs (Eu, Gd, La, Pr, Nd, Sm, and Y) using LIBS was performed previously[14]. Martin, et.al. demonstrated the capability to quantify these REEs in the 1 – 50% concentration range using multivariate analysis. Detailed accounts of LIBS measurements of actinides and their surrogates have been demonstrated.[15-21] A number of articles have also shown LIBS for the measurement of REEs [22-46]. Most of these studies were performed with majority of the concentrations in the percent levels, whereas the goal of this study is to demonstrate the use of LIBS analysis for lower ppm concentration levels for individual REES. Furthermore, this will provide a down selected list of REE peaks that are still relevant to quantification in this lower concentration range. In certain applications, such as nuclear forensics, the detection of the REEs in low levels is an essential need as it can act as an indicator of a previous nuclear events.

Quantification using LIBS does have some has inherent limitations that are similar to other analytical techniques. One of the major limitations is that the laser that is exciting the sample will interact with different matrices differently and making the measured spectrum matrix dependent. In other words, for a robust calibration it is important to have calibration standards that are representative of the samples that are planned to be analyzed. Many authors have discussed the difficulties that are associated with getting direct quantitation for the LIBS technique.[47-49] The effect of sampling geometries and a few other sampling parameters, e.g., laser energy and laser wavelength on the on elemental emissions have been addressed in detail.[49,50] Windom and Hahn discuss several strategies to overcome these matrix-specific calibration in their review article.[51]

The main goal of this study is to determine the limits of detection for the six rare earth elements Eu, Gd, La, Pr, Nd and Sm, and one transition metal Y, by using LIBS. Samples with concentrations ranging from 10 – 300 ppm, for every element in oxide form homogeneously mixed in a graphite matrix was tested to develop separate calibration models for each element and enable the authors to identify the main spectral features still viable at these low concentration ranges. Furthermore, the multivariate calibration models were tested against validation samples for each individual element to demonstrate the ability of the loading parameters to classify each element without ambiguity. Lower ppm level detection for these important rare earth elements has not previously been demonstrated.

Experimental

In these experiments, a 532 nm Q-switched Big Sky laser (model CFR-Ultra) was used. In order get consistent spectra across the samples, the laser energy was held constant at 45 mJ and 5 replicates were collected for each sample composition. These replicates help account for any slight deviations in the pellet composition and/or laser energy. The laser was focused onto the sample using a 10 cm focal lens. The sample was located on an XYZ stage to provide high resolution three-dimensional adjustments and a 650 nm alignment laser was employed to ensure that the excitation laser was constantly focused on the sample surface. A set of fused silica lenses were used to collect the light emitted from the plasma that is generated onto to a low OH silica fiber. The light from the plasma was received by a Catalina Scientific SE 200 Echelle spectrometer allowing a measurement across the wavelength range from 190 – 800 nm with a nominal resolution of 0.06 nm. This spectrometer was coupled to an Andor iStar intensified charge coupled detector (ICCD). The spectra were acquired with a 1 microsecond delay and 10 microseconds for exposure time. The laser was operated at a 10 Hz repitition rate. A schematic of the experimental setup employed is shown in Fig 1.

<Figure 1>

The samples used in this study were pressed graphite pellets containing concentrations of 10, 30, 70, 100, and 300 ppm of REEs. These concentrations were selected to focus on the lower ppm levels such that any identified peaks would be ensured to be useful for this detection range. Eu_2O_3, Gd_2O_3, La_2O_3, Pr_6O_{11}, Nd_2O_3, Sm_2O_3 and Y_2O_3 were obtained from Alfa Aesar, Ward Hill, Massachusetts (USA). The oxide powders used in this research all had a purity of 99.99%. Graphite powder of microcrystalline grade and of 99.9995% purity was also obtained from Alfa Aesar. The particle sizes of the graphite and oxides ranged from 2 – 20 microns. The oxide powders were mixed and weighed with a balancing amount of graphite powder to prepare the desired concentrations. The total weight of the rare earth oxide and graphite powder was measured to be 75 mg. These concentrations were then mixed with 99-100% hydrolyzed polyvinyl acetate (PVA) to serve as a binder. The consistuents were added to a bottle and vortexed. Afterwards a heating plate was used to dry the mixture. Then the contents of the bottle were placed in a 0.635 cm die and then the contents were pelletized using 6672.33 N sustained for 1 minute.

Results and Discussion

Figure 2 shows a subregion (390 – 430 nm) of the collected spectra of Eu, Gd, La, Pr, Nd, Sm, and Y in a graphite matrix in each 30-ppm sample. Several spectral peaks have been labelled accordingly. These REE samples show that most of the prominent peaks that identify the individual elements are generally in a narrow region of the full spectrum e.g., the wavelength region of 350 – 450 nm. The number of peaks identified for the 30-ppm concentration are far fewer than those that were identified in our previous study of the same species at percent level concentrations.[1]

<Figure 2>

The measured LIBS spectra were split into two sets: calibration and validation. Using the calibration sets, partial least squares (PLS) models were built for the spectral region from 200 – 700 nm. The full broadband region of the spectra was used to identify a specific subregion in which the most peaks are identified for all the REEs. A very good PLS model was demonstrated for switch grass using infrared spectroscopy by Edmunds et al.[52] In the current study the main spectral features were identified by building PLS models to relate the measured spectra to the sample concentrations. The PLS models were evaluated by how well they predicted the validation set concentrations and the PLS regression coefficients reveal spectral features highly correlated to concentration.

The metrics that were used to evaluate the performance of LIBS-PLS models revolved around prediction. These parameters are the coefficient of determination (R^2), root mean squared error of calibration (RMSEC), and root mean squared error of prediction (RMSEP). The RMSEC and RMSEP are representative of the average prediction error for the calibration data set and the validation sample set, respectively. Both RMSEC and RMSEP have the same units as concentration because they are representative of the difference between the known and predicted values. The value of RMSEP is typically higher than that of RMSEC value because the validation sample set is not used to build the PLS model, whereas the calibration sample set used to build the model is used to calculate the RMSEC. The result of the PLS model is an array of regression coefficients that when multiplied by a measured spectrum would provide a concentration prediction. The regression coefficient is of the same dimension as the measured spectra. Here, a positive value indicates a positive correlation to concentration and conversely a negative value indicates a feature negatively correlated to an increase in concentration. These regression coefficients are very useful for identifying key spectral features, as they will reveal themselves as peaks in the regression coefficient versus wavelength plots.

For the calibration model it is important to use a low number of PLS factors. In the case of all the species that were studied in this article the number of PLS factors remained between 2 – 5. If an extraneous number of factors are used to build the PLS model, then the model will become overfit as it begins to model noise rather than real variance. The PLS models in this study were developed with the Unscrambler software. This software aids the user choose an optimal number of factors for each element to avoid overfitting. Another important note is that sample preparation methods, such as grinding, humidifying, and pelletization of different rare earth compounds could have adverse effects on model implementation. These preparation methods should be kept constant and consistent across the sample set to avoid matrix changes causing degradation the model performance.

PLS models were built for each REE and then tested using a validation dataset. Table 1 summarizes the model metrics for all the individual REE LIBS-PLS models' calibration and validation datasets. Along with these metrics, the linear fit information for the measured versus predicted concentration plots is provided. Figure 3 shows the parity plots for each REE model's calibration and validation dataset.

Table 1. Evaluation Metrics of LIBS−PLS Models Developed.

Element	**Slope**	**Offset**	**RMSE(C/P)**	**R^2**	**Factors**
Eu (Calibration)	0.967	3.287	17.936	0.967	4
Eu (Validation)	0.940	7.661	23.898	0.941	4
Gd (Calibration)	0.997	0.252	4.947	0.997	3
Gd (Validation)	0.953	5.517	12.194	0.984	3
La (Calibration)	0.918	6.280	23.404	0.918	4
La (Validation)	0.803	13.011	34.475	0.823	4
Pr (Calibration)	0.966	2.789	18.019	0.966	4
Pr (Validation)	0.987	10.734	25.498	0.943	4
Nd (Calibration)	0.996	0.284	5.519	0.996	5
Nd (Validation)	0.858	15.500	22.051	0.955	5
Sm (Calibration)	0.985	1.222	11.225	0.968	4
Sm (Validation)	0.841	12.734	31.394	0.846	4
Y (Calibration)	0.952	4.949	23.448	0.952	3
Y (Validation)	0.852	13.358	33.471	0.904	3

Looking at the first model, Eu, the RMSEC and RMSEP were calculated to be 17.94 and 30.64, respectively. As mentioned previously the RMSEP is anticipated to be greater than the RMSEC, but on the similar scale. This is the trend across the species investigated in this paper, although some species (e.g., Gd, Nd) see a greater difference between the values. This may indicate species which are more difficult to measure in this range. The Eu R^2 values were calculated to be 0.967 for calibration and 0.914 for validation, indicating strong fits. The slopes of the linear fits for both calibration and validation datasets being nearly unity on the parity plots signify a strong model. A similar trend is seen amongst the elements investigated.

<Figure 3>

Figure 4 shows subregions of the PLS regression coefficients where several elemental features were identified for each species. The regression coefficient versus wavelength plots were meticulously checked against the NIST Atomic Spectra Database for each element that was investigated to ensure that the model accurately identified and modeled relevant spectral features for each species and to determine the ion state of the transitions.[53] Looking at Eu again, the negative region between 380 – 390 nm signifies that this spectral region decreases as the Eu concentration increases, so it may be correlated to a matrix signal that it not a Eu feature. By identifying peaks in these regression coefficient plots, key spectral features relevant to these low concentrations were identified. The main peaks identified for each species are listed in Table 2.

<Figure 4>

The parity plots in Fig. 3 show a larger variance for La and Sm, compared to Eu and Gd implying that La and Sm have a weaker signal at these low concentrations. The La and Sm PLS models also identified fewer distinct lines indicating the limit of detection for La may be near 10 – 30 ppm, the lower limits in this study.

These results show that LIBS spectra and along with PLS regression models for the detection and prediction of the concentration of the REEs can be used for high-throughput detection measurements with little sample preparation. The rapid collection of the LIBS spectrum of a REE sample is much preferred to time required for standard ICP-MS data acquisition, which requires very tedious sample preparation and dilutions that could smear out the real concentration. On the other hand, rapid methods such as LIBS have an inherent issue of low accuracy when compared to the standard laboratory-based techniques. Truly, these techniques complement one another; LIBS can be used for rapid results, while ICP-MS can then validate these measurements. This allows LIBS to be used for detecting off-normal events and detecting issues during processing. When online and at-line detection is needed in case of large sample sets LIBS is the desired technique.

Table 2. LIBS-PLS Identified Spectral Peaks for Parts-per-Million Detection.

Wavelength in nm and ion state						
Eu	Gd	La	Pr	Nd	Sm	Y
368.842 (II)	354.580 (II)	398.852 (II)	391.885 (II)	395.745 (II)	411.019 (II)	393.066 (II)
372.494 (II)	358.496 (II)	399.575 (II)	396.426 (II)	397.327 (II)	411.855 (II)	395.035 (II)
381.967 (II)	364.619 (II)	403.169 (II)	399.583 (II)	397.948 (II)	415.221 (II)	398.260 (II)
390.710 (II)	374.347 (II)	407.735 (II)	405.880 (II)	399.010 (II)	419.945 (II)	407.736 (II)
393.048 (II)	404.684 (II)	412.323 (II)	410.072 (II)	401.225 (II)	428.079 (II)	410.236 (I)
397.196 (II)	405.364 (I)	415.197 (II)	411.389 (II)	402.478 (II)		412.830 (I)
412.970 (II)	407.870 (I)	419.655 (II)	416.804 (II)	404.080 (II)		414.284 (I)
413.707 (I)*	409.372 (I)	423.838 (II)	417.939 (II)	410.946 (II)		417.754 (II)
420.505 (II)	418.425 (II)		422.293 (II)	415.626 (II)		419.927 (II)
	419.078 (I)			417.732 (II)		
	422.585 (I)					

*The measured signal is the convolution of the two transitions occurring at the same wavelength.

Conclusions

Multivariate models for 42 samples were built using PLS to determine the concentration of each REE (Eu, Gd, La, Pr, Nd, Sm, and Y). This concentration range was in the lower parts-per-million scale in a graphite matrix. Since conventional laboratory-based techniques can be expensive and time-consuming to measure REE concentrations, LIBS-PLS models offer a rapid, inexpensive, and reliable alternative for this application.

The coefficients of determination (R^2) for the validation of the models of Eu, Gd, Pr, Nd, and Y were determined accurately in an excellent range (0.890 – 0.933). In case of the elements such as, La and Sm the R^2 for validation of the models were in an acceptable range (0.730-0.839). Hence, it can be extrapolated from this study that if it is important to precisely quantify La and Sm within a mixture of all the REEs then there may be difficulties in identifying those elements especially at low parts-per-million concentrations.

The methodology used in this research can be applied to online screening of REE in mining environments or nuclear fuel reprocessing facilities, providing real-time feedback on processing needs, although the differences in sample matrices would need to be considered. This would be a very useful tool for process optimization and monitoring.

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Declaration of Conflicting Interests

The author(s) declare no potential conflicts of interest in the case of research, authorship, and/or publication of this article.

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Figure Captions

Figure 1. A schematic of the experimental setup and equipment used in this study.

Figure 2. The LIBS Spectra for the 30 ppm concentrations of the REEs Eu, Gd, La, Pr, Nd, Sm and the transition metal Y mixed with graphite powder and pelletized shown in a narrow spectral region (390-430 nm). There is a vertical offset intensity of 8000 between spectra.

Figure 3. PLS predicted concentrations of the various REEs calibration and validation datasets concentrations from collected LIBS spectra. Further fit details are listed in Table 1.

Figure 4. PLS model regression coefficients plotted against wavelength for all species examined in this study. Markers indicate the species peaks which were matched in the NIST database and their ion state.[53] Further peak information is listed in Table 2.