



Analytical note

Laser Induced Breakdown Spectroscopy analysis of europium and samarium in aluminum oxide[☆]Kristian G. Myhre^{a,b,*}, Mihir J. Mehta^c, Madhavi Z. Martin^d, Miting Du^b^a The Bredesen Center for Interdisciplinary Research and Graduate Education, University of Tennessee, Knoxville, TN 37996, United States of America^b Nuclear Security and Isotope Technology Division, Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, TN 37831, United States of America^c Chemical and Biomolecular Engineering Department, University of Tennessee, Knoxville, TN 37996, United States of America^d Biological Sciences Division, Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, TN 37831, United States of America

A B S T R A C T

The use of Laser Induced Breakdown Spectroscopy as a technique for analysis of europium and samarium concentrations in ceramic aluminum oxide samples was investigated for application to studying lanthanide separation processes. Metal oxide powders of europium and/or samarium were mixed with aluminum oxide at varying concentrations and pressed into pellets. A comparison of different approaches to building a univariate simple linear regression analysis curve is presented. A linear behavior was seen over the total lanthanide concentration range from 0.086 to 12.358 weight percent (wt%). The calculated limits of detection for the univariate calibration curves were determined to range from 0.001 to 0.108 wt% and 0.001 and 0.183 wt% for europium and samarium, respectively.

1. Introduction

The rare earth elements are used in many advanced science and technology applications. However, separating the rare earths from each other is extremely difficult. This is especially true for lanthanide pairs adjacent to each other on the periodic table, such as europium (Eu) and samarium (Sm) [1]. As such, a great deal of research and development effort is put forth toward improving current separation methods and developing new ones. Recently, work carried out at Oak Ridge National Laboratory (ORNL) has investigated the novel use of beta"-alumina (BDPA) as a separation material for separating lanthanides from each other [2]. Several approaches to using BDPA to accomplish separations have been investigated with a common parameter of interest being the concentration of the rare earths in the BDPA material at various points throughout the separation process.

Previously, Neutron Activation Analysis (NAA) has been used to quantitatively determine the elemental concentrations of the rare earths, such as Eu and Sm, in the BDPA matrix [2]. NAA is advantageous because it has a very high sensitivity, is not matrix dependent,

and requires little to no preparation of the samples [3]. The ability to analyze samples without sample preparation is particularly useful given the chemical and physical robustness of alumina ceramics such as BDPA [4]. Many other and more common analytical techniques, such as Inductively Coupled Plasma Mass Spectrometry (ICP-MS), require difficult sample digestion steps and dilutions by several orders of magnitude to be performed prior to analysis. However, a major drawback to NAA is that the samples become radioactive and remain so for a long period of time, given the long half-lives of many lanthanide activation products. This prevents the exact same samples from being analyzed multiple times throughout the separation process and therefore inhibits a more accurate picture of the separation process from being constructed. It also requires the use of a neutron source with a high flux, such as ORNL's High Flux Isotope Reactor, for high-sensitivity measurements, which is not a commonly available resource. It is therefore desirable to use a different technique capable of quantitatively determining the concentrations of the rare earths in BDPA that would be essentially nondestructive and applicable to the robust alumina matrix. For these reasons, Laser Induced Breakdown Spectroscopy (LIBS) was

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investigated for use in quantifying Eu and Sm concentrations in an alumina matrix.

LIBS is a technique capable of analyzing a wide variety of sample matrices, including physically and chemically robust ceramic matrices such as BDPA, without the need of lengthy and cumbersome sample preparation [5]. LIBS analysis involves the formation of a plasma on the surface of the material being analyzed which then emits light representative of the elemental composition of the plasma. The plasma is formed from a small amount (few hundred nanograms) of laser-ablated material and therefore is effectively nondestructive for larger samples. This technique is especially advantageous when analyzing samples that are difficult to digest, as is the case with ceramics such as high-density alumina. However, it can be difficult to obtain quantitative information from LIBS measurements for reasons including: inhomogeneity within samples; and differences in plasma formation from shot to shot due to variability in the laser pulse parameters, as well as the physicochemical nature of the samples of interest [6].

A variety of methodologies have nonetheless been successfully utilized to obtain quantitative information from LIBS measurements [5–7]. The most commonly used involve the building of some form of a linear regression model using a set of standards. It is often the case that the standards used must have essentially the same matrix as the unknown samples to overcome the common issue of matrix effects. For example, a regression model for quantification of Eu and Sm concentrations in samples with a carbon matrix, as was built by Martin et al., would likely not be useful for analyzing samples with an aluminum oxide matrix, despite all other parameters and instrumentation being the same [8]. Regression models measure the response values in the LIBS spectral data for standards and correlate them with known concentrations of the analytes of interest [6]. Regression models fall into two categories, namely univariate and multivariate. The former correlates one value of response in the LIBS spectral data to one value of analyte concentration. The latter correlates multiple response values in the LIBS spectral data to determine the concentration of one or more analytes. Other methodologies are under development which are calibration-free and have shown promise but require a significant amount of additional work prior to widespread implementation [7].

This paper focuses on the application of univariate linear regression analysis methodologies for the analysis of Eu and Sm in an alumina oxide matrix.

2. Experimental

2.1. Instrumentation

LIBS measurements were performed at ORNL's Radiochemical Engineering Development Center. The measurements were taken using a LIBSCAN-150 Laser Induced Breakdown Spectrometer system from Applied Photonics Ltd., based in the United Kingdom. The laser used in the system was a passively Q-switched Nd:YAG laser (manufactured by Applied Photonics Ltd.). The mean pulse energy of the laser is 161 mJ with a standard deviation of 2.25 mJ and the output wavelength is 1064 nm. The fluence was calculated to be nominally 82 J cm^{-2} . Measurements from six spectrometers were stitched together to give a wavelength measurement range of 182.27 nm to 909.37 nm. The characteristics of the LIBS system are listed in Table 1. The LIBS software package (version 16.1) from Applied Photonics Ltd. was used to perform the LIBS measurements.

2.2. Sample preparation

The samples used as calibration standards were prepared by mixing high-purity metal oxide powders of Sm and/or Eu (purity > 99.95%, Alfa Aesar) with high purity Al_2O_3 (purity > 99.99%, Alfa Aesar). The lanthanide concentrations in ten single element standards containing either Eu or Sm ranged from 0.086 to 12.358 wt%. The four multi-

Table 1
Characteristics of laser and spectrometers.

Laser characteristics	
Wavelength	1064 nm
Energy per pulse	$161 \pm 2.25 \text{ mJ}$
Pulse length	~5 ns
Spot size diameter	500 μm
Laser fluence	82 J cm^{-2}
Spectrometer characteristics	
Wavelength ranges (nm)	FWHM (nm)
182.27 to 314.30	0.06
314.31 to 909.37	0.18

element standards that contained both Sm and Eu had individual lanthanide concentrations ranging from 0.860 to 5.300 wt%. After each metal oxide powder mixture was prepared, the mixtures were pressed into pellets using a manual hydraulic press with a pressure of approximately 15 ton cm^{-2} . A blank pellet of pure Al_2O_3 was prepared in addition to those containing Eu and/or Sm. The pellets formed had a diameter of 1 cm and average thickness of 2 mm. The pellets were put under pressure for approximately 2 min. No binder was used to form the pellets. The pellets were stored in small plastic bags after being pressed prior to and after performing the LIBS measurements.

2.3. Acquisition of the spectral data

Spectral data were acquired at three locations on each side of the pellets for a total of six locations on each pellet. The data for each spot were acquired using ten shots of the laser. No conditioning shots were used. Inert argon gas was flowed at a constant rate prior to and throughout the LIBS measurements. The integration time used was 1.10 ms and the integration delay was 1.27 μs .

2.4. Selection of the emission lines for univariate analysis

Several useful emission lines were identified from a survey of the literature on LIBS measurements of Eu and Sm in conjunction with processing the spectral data produced in this study [8–11]. Many of the spectral lines noted in the literature were present in the measured spectra and found to be correctly assigned to each element. However, many of the emission lines noted in the literature had a significant amount of noise or interference, making them undesirable for use in building univariate regression models. Three emission lines each for Eu and Sm as well as two for Al were selected for use in building the univariate regression models. This was accomplished by comparing the spectral lines found in the spectra of pure Al_2O_3 , $\text{Eu}_2\text{O}_3\text{-Al}_2\text{O}_3$, and $\text{Sm}_2\text{O}_3\text{-Al}_2\text{O}_3$ pellets. The selected emission lines used to build the univariate regression models are given in Table 2. The spectral range that was integrated over to calculate the integrated intensity for each peak is given in Table 2 as well.

Table 2
Wavelengths of the emission lines used for univariate analysis.

Element	Wavelength (nm)	Spectral range (nm)	Reference(s)
Eu	390.69	390.40–390.94	[8]
Eu	412.94	412.58–413.34	[8,9]
Eu	663.36	663.62–665.00	This work
Sm	425.62	425.65–425.78	This work
Sm	431.87	431.72–432.07	This work
Sm	474.56	474.32–474.68	This work
Al	308.21	307.77–308.64	[12]
Al	309.28	308.80–309.74	[12]

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