Direct compositional quantification of (U-Th)O₂ - MOX nuclear fuel using ns-UV-LIBS and chemometric regression models

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Abstract

The determination of uranium with composition varying from 0% to 35 wt.% in (Th-U)O₂ mixed oxide fuel using laser induced breakdown spectroscopy (LIBS) utilizing partial least square regression (PLSR) has been demonstrated. Good agreement between expected and experiment results using 266 nm, 532 nm and 1064 nm was shown. The analytical results at 266 nm of 2-3% precision and ~1% accuracy (bias) satisfy the acceptance criteria range for chemical analysis in the nuclear industry.

Key words: *LIBS; Chemometrics; PLSR; Nuclear fuel; AHWR;*

1. Introduction

Majority of world's nuclear reactors use uranium (U) based fuels (Natural to ~10% ^{235}U). However, in India, due to scarcity of high quality U ore, there has been a long interest in using thorium (Th) as a fertile element to produce ^{233}U fissile isotope, which has the best neutronic property in the thermal neutron energy region and is a probable replacement of natural U in the Indian nuclear reactors. One-third of world's Th reserves is in India [1, 2]. Based on that, the Indian nuclear program is planned in three stages. The third stage is planned upon the ^{233}U -Th fuel after generating ^{233}U from Th placed around the nuclear reactor core as a blanket to capture escaped fission neutrons in Fast Breeder Reactors which use (U-Pu) O_2 fuel in the 2nd stage. The 1st stage is the production of nuclear power from natural uranium and generation of ^{239}Pu , which is used in the 2nd stage as fuel [3]. While the initiation of the third stage will take place in the future, for the timely development of thorium-based technologies for the entire thorium fuel cycle, an Advanced Heavy Water Reactor (AHWR) is being developed which will use (Th- ^{233}U) O_2 fuel of different composition varying from 3-3.75% for AHWR and 18-22.5% in AHWR300-LEU (low enriched uranium). In a AHWR reactor the composition of fuel (U wt.%) varied depending on the position of fuel rod in reactor, i.e., whether it is a centre circle fuel or peripheral fuel rod.

Accurate elemental composition analysis in nuclear materials is an important step for quality assurance at different stages of fuel fabrication from the point of view of the neutron economy inside a reactor. Presently, chemical and electrochemical methods are used for elemental composition analysis of (U-Th) O_2 fuel samples. Both these mentioned method have two common drawbacks – dissolution of sample and generation of nuclear waste. Thoria being a refractory material, the dissolution of sintered (U-Th) O_2 pellets is difficult and time consuming. In this respect, LIBS have huge potential for U determination in (U-Th) O_2 fuel pellets, especially in view of hazardous environment and remote application required in the nuclear industry. LIBS has many advantages over other conventional direct sample analysis techniques such as on-site analysis, pseudo non-destructive, noncontact, minimal to no sample preparation, minimum sample requirements, and capability to measure all elements of the periodic table. ICP-OES/MS methods may be used for this study, but required huge dilution after sample dissolution and hence instead of major matrix elements ICP-OES/MS method is used for trace elemental study after bulk separation. Sarkar *et al.* demonstrated the applicability of laser induced breakdown

spectroscopy (LIBS) for U-Th MOX samples using uni-variative calibration with ~10% accuracy and precision [4]. One drawback of the proposed method was among the emission lines used in the study, only U(II) 263.553 nm can be used for analyzing a maximum of approximately 32% U composition, for the remaining lines the limit is 18-20% U. These limits make the reported method borderline for analyzing AHWR300-LEU reactor samples. Moreover, for a technique to be utilized by the nuclear industry for quality assurance, 0.5-1% is required for acceptance as a routine technique and <5% when “go/no go” type answers are required. Among the different methods reported in the literature for improving analytical performance of LIBS, the use of UV-wavelengths for ablation [5-7] and multivariate regression calibration like partial least square regression (PLSR) or principle component regression (PCR) has shown significant potential [8-13].

In the present work, we measured LIBS spectra at UV (266 nm), Vis (532 nm) and IR (1064 nm) laser along with two different multivariate regression models (PLSR and ASD-PLSR) to obtain U quantification in MOX sample with $\leq 3\%$ precision which will fulfill the “go/no go” type answer in quality assurance laboratory.

2. Experimental

2.1. System, samples and analysis

A common LIBS configuration described elsewhere was used for present study [14]. Briefly, a Nd:YAG laser with 1064 nm, 532 nm and 266 nm wavelength was focused using a 1 inch diameter plano-convex lens ($f=10$ cm) to produce a laser induced plasma. The spot size of laser ablation was 150 μm . The emission light was collected through a collimator, (CC52, Andor, UK), placed at 6 cm from the plasma and fed to an echelle spectrometer (Mechelle, ME5000, Andor, UK) through an optical fiber of 200 μm core diameter. The echelle spectrometer has a spectral resolution of ~5000 CSR ($\lambda/\Delta\lambda$) at 10 μm entrance slit width and simultaneously covers 200–975 nm wavelength region. An ICCD, (iStar, Andor, UK), which is synchronized with the Q-switch of laser pulse to control acquisition time delay (t_d) and detector gate width (t_w) is attached with the echelle spectrometer. The samples were placed in an aluminium box with quartz window facility on an XYZ -translator stage and analyzed in ambient atmosphere. Keeping in the mind the nature of samples the complete work was carried out in a radiological laboratory.

A series of U-Th MOX standards were prepared due to unavailability of certified reference materials (CRMs) as per the described procedure in a radiological laboratory using a pressure of 2×10^9 Pa for 5 min in a press machine [15]. Pure ThO_2 and U_3O_8 powders of known weight were mixed to prepare 11 standards pellets sample of 3 cm diameter of different compositions. These standards were divided in two groups, a calibration set (CS) for construction of PLSR based calibration models and a validation set (VS) used for validation of PLSR based calibration models. VS consist of 4.9 wt.%, 10.8 wt.%, 18.6 wt.% and 20.5 wt.% of U in MOX samples, rest are part of CS (1.03 wt.%, 2.54 wt.%, 7.71 wt.%, 13.8 wt.%, 25.49 wt.%, and 34.7 wt.% U).

LIBS spectra were recorded in the wavelength region of 200-975 nm. Due to the absence of significant measurable emission lines in the spectra after 600 nm (probably caused by the low quantum efficiency of the detector above 600 nm ($<25\%$) [8]), the wavelength region above 600 nm was truncated and only 200-600 nm was used. Each MOX sample was analyzed 10 times at different locations at optimized laser energy and acquisition time delay (discussed latter) with fixed gate width of 25 μs and 2 Hz laser frequency. Predictive residual sum of squares (PRESS) and standard error of prediction (SEP) values were used as the figures of merit for comparison of analytical models [11]. A reduction in PRESS / SEP value represents a good analytical result for a model. An in-house PLSR-1 algorithm (details described elsewhere) program based on NIPLS model in LabVIEW (M/s National Instruments) was written for constructing calibration curves [8]. Since the ultimate goal is to achieve an “as low as possible” precision and high accuracy, the recently developed analytical spectral dependent partial least squares regression (ASD-PLSR) was used instead of simple PLSR [11]. In this modified process, spectral truncation to only utilize relevant pixel intensities based on the initial PLSR coefficient guidelines was applied.

3. Results and discussion

3.1. Experimental conditions optimization

The maximum signal to noise (SNR) ratio was used as the figure of merit to optimize the laser energy (E_L) and acquisition time delay (t_d). SNR was calculated by varying the t_d at particular E_L values using the CS sample with 35 wt.% U composition. U-Th MOX sample's emission spectra being very complex; the large number of lines makes the spectra appear like a band of emission lines. It is difficult to select pure emission lines (no spectral interferences) for U. To identify and confirm the presence of uranium emission lines, spectra of pure U as UO_2 ,

pure Th as ThO₂, and a MOX (35 wt.% U) samples were measured under identical conditions. Among several identified emission lines, the U(II) 447.233 nm was selected based on its spectral purity and used to calculate SNR. Fig. 1(a) shows the comparison of UO₂, ThO₂, and MOX spectrum in the 446 - 448.5 nm wavelength region using 1064 nm laser. Fig. 1(b) shows the contour diagram for U(II) 447.233 nm emission line of SNR for E_L vs. t_d . A similar result was found for U (II) 367.007 nm emission line, which led us to choose an E_L of 80 mJ and t_d of 1.4 μ s as optimum conditions for U analysis in the MOX samples. For analytical result comparison purpose, the same experimental condition was used for the 532 nm and 266 nm LIBS analysis.

Keeping in mind the out-of-phase property of noise, the gross noise contribution to a spectrum can be reduced by increasing signal accumulation [16]. To optimize number of accumulation per spectral analysis, 5 replicate analyses of the MOX (35 wt.% U) sample were carried out and background subtracted intensity of U(II) 447.233 nm emission line was plotted against the number of laser pulses (repetitive single-location) for 1064 nm, 532 nm and 266 nm as shown in Fig. 2. Replication was carried out randomly all over the sample in five places to minimize the effect of heterogeneity in the sample. A long-term drift due to crater formation was observed. The LIBS signal intensity becomes insignificant after ~85 shots at a same location due to defocusing of the laser, thereby, decreasing the mass ablation efficiency for 1064 nm. For the 532 nm and 266 nm laser wavelengths, an optimum accumulation of 60 and 45 pulses were obtained, respectively. With the reduction of laser wavelength, the mass removal increase, which is due to the better energy coupling provided, combined with reduced plasma shielding. Due to higher mass removal at 266 nm than 532 nm and 1064 nm, the crater effect occurs with fewer number of laser pulses [5, 17, 18] .

3.2. Spectral normalization & Factor optimization

Analytical results can be significantly affected by pulse-to-pulse spectral variations. These variations can be minimized by spectral normalization procedures. The effect of normalization procedures on spectral analysis before using PLSR was previously demonstrated by the authors [9]. In this study, four spectral normalization procedures were applied before PLSR analysis, details of which are described elsewhere [9]. The procedures were: (i) maximum intensity normalization, (ii) norm intensity normalization, (iii) mean intensity normalization and (iv) standard deviation of the intensity normalization. Factors number (equivalent to principal

components in PCR) was optimized for individual normalization procedures before comparing their analytical merit. The optimization of Factor number was determined by calculating PRESS values using the CS samples for U based on a 'leave-one-out' cross-validation method. Fig. 3(a) shows the change in PRESS(cv) against the number of Factors used in the different normalization models using the 1064 nm data. The Factor number corresponding to the minimum PRESS(cv) value in Fig. 3(a) indicates the optimum Factor number for U determination. The Factor(min) values were 6, 5, 4, 5 and 5 for raw, (i), (ii), (iii) and (iv) normalized data respectively.

Fig. 4 shows comparison of SEP, accuracy (or bias) and precision (in %RSD) obtained for different normalization procedures at optimum Factor using the PLSR for the VS samples. The methods (i), (ii), and (iv) generate nearly identical precision but for accuracy, procedure (i) (normalization with maximum intensity) was the best. Hence, SEP was also best for procedure (i) at 1064 nm. This is contrary to the previous reported method where Norm intensity was found to be best, although the samples were different in that work [16]. Principle component analysis (PCA) was carried out with the intensity data to understand the better normalization capacity of procedure (i). PC2 vs. PC3 for 10 replicate analyses of the MOX (18.6 wt.% U) sample under different normalization conditions shows that the smallest cluster is created by maximum intensity normalized spectra, indicating conversion of raw spectral data pattern to very similar spectral data pattern for the replicate samples, which results in better analytical figures of merit as obtained in Fig. 4. For 532 nm and 266 nm laser, normalization procedure (i) was also used but with optimization of Factor in respective wavelengths. The optimum Factor was found to be 5 for normalization procedure (i) irrespective of the laser wavelength as shown in Fig. 3(b). This indicates an identical noise pattern in spectra for all the wavelengths of laser ablation.

3.3. Quantitative results.

Spectra measured with optimized conditions for each laser were used to compare the analytical figures of merit, i.e., accuracy in terms of absolute bias and precision in term of %RSD of the methods. Details of the ASD-PLSR were discussed in our previous study [9]. Comparison of analytical results using uni-variate LIBS [4], PLSR-LIBS and ASD-PLSR-LIBS for U determination using 1064 nm laser provided %RSD of 8.5%, 4.8% and 3%, respectively. Since, only those pixels in the spectra whose PLSR coefficient values were greater than PLSR

coefficient threshold (T^c) (indicating strong covariance with the concentration) were used in ASD-PLSR, the error level was reduced in ASD-PLSR. All further chemometric regression analyses were carried out using ASD-PLSR.

Fig. 5 shows the comparison of average %RSD and accuracy obtained for the different laser. For all samples, the %RSD for U analysis improved with decreasing wavelength; the %RSD was 4-5% for 1064 nm, 3-4.5% for 532 nm and 2-3% for 266 nm. The intensity variation for the U(II) 447.233 nm emission line was calculated for all three wavelengths (up to 45 laser pulses). The %RSD for area under the peak was 6% for 1064 nm, 4.3% for 532 nm and 2.9% for 266 nm; which is essentially the same improvement as with the precision. This may be explained from the point of higher mass removal in 266 nm laser. Higher mass removal results higher emission intensity, and thereby lower percentage fluctuation in emission intensity. Accuracy also showed an improving trend similar to precision; the accuracy was ~2% for 1064 nm, to ~1.5% for 532 nm and ~1.1% at 266 nm. The analytical results at 266 nm of 2-3% precision and ~1% accuracy (bias) satisfy the acceptance criteria for “go/no go” type answer in quality assurance laboratory for chemical analysis in the nuclear industry. These results are significantly improved compared to the previously reported uni-variate work using 1064 nm accuracy and precision [4]. Fig. 6 shows the 10 replicate analyses at 266 nm laser wavelength for the four VS samples with the acceptance criteria region of the nuclear industry. The gray shaded area indicates 1% from the standard value, and the pattern shaded area is the experimental one-standard deviation area from the PLSR analysis. The strong overlap of the two areas clearly demonstrates the viability of use of LIBS for routine analysis in the nuclear industry, especially for fuel quality assurance programs, but need a little further improvement.

4. Conclusion

We demonstrated the capability of LIBS for rapid determination of U in MOX fuel samples with analytical performance acceptable to a nuclear quality control lab. The effect of different pre-treatment procedures was studied on raw data before PLSR. Maximum intensity normalization was found to give better analytical results for U determination using PLSR. Under optimum analytical condition, PLSR was utilized to study the effect of laser wavelength for U determination in MOX sample. Although good quantitative analytical performance was achieved for analysis of U in MOX using all three wavelengths; 266 nm provided the best accuracy and precision compared to 532 nm or 1064 nm. The accuracy and %RSD were found to be 1% and 2-

3%, respectively for U determination at 266 nm, levels that are acceptable by nuclear fuel quality control and assurance laboratories for the “go/no go” type answer for U determination. Further studies are going on to reduce the precision of LIBS by using double pulse LIBS, and make LIBS qualify next hurdle of 1% precision.

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Figure 1	(a) Comparison of pure U as UO_2 , pure Th as ThO_2 , and a MOX (35 wt.% U) spectra in the vicinity of the U(II) 447.233 nm emission lines under identical conditions of analysis of 80 mJ and 1.4 μs acquisition delay using 1064 nm laser. (b) Contour diagrams of U(II) 447.233 nm emission line showing the effects of acquisition time delay and laser energy on the signal to noise ratio.
Figure 2	Variation of the emission intensity of U(II) 447.233nm from the single-shot LIBS (repetitive single-location) of a MOX (35 wt.% U) sample against the number of laser pulses at 1064 nm (solid line), 532 nm (dash line) and 266 nm (dot line).
Figure 3	The variation of PRESS(cv) values for uranium against the number of Factor numbers included in PLSR algorithm using (a) different normalization procedure. (b) at different wavelengths at maximum intensity normalization. The circle indicates the minimum achieved PRESS(cv) value corresponding to the procedure.
Figure 4	Comparison of SEP, accuracy and %RSD obtained using different normalization procedure at optimum Factor using the PLSR approach for the VS samples.
Figure 5	Comparison of %RSD and accuracy results obtained using different laser wavelengths for four VS samples used for U composition determination. The downward bar from top axis indicted accuracy and the bar from bottom axis is for %RSD.
Figure 6	Replicate analyses at 266 nm laser wavelength for the VS samples (a) 4.9 wt.%, (b) 10.8 wt.%, (c) 18.6 wt.% and (d) 20.5 wt.% of U along with the acceptance criteria region (1%) for nuclear industry (gray shaded). The blue diagonal pattern shaded area is the experimental result region with one standard deviation obtained by PLSR analysis.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6