



Determination of trace constituents in thoria by laser induced breakdown spectrometry

Arnab Sarkar, Devanathan Alamelu, Suresh Kumar Aggarwal*

Fuel Chemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400 085, India

ARTICLE INFO

Article history:

Received 12 June 2008

Accepted 12 November 2008

ABSTRACT

Trace constituents were determined in thorium oxide powder using laser induced breakdown spectrometry (LIBS). Thoria powder was pressed into a pellet prior to LIBS analysis. The optimum laser energy and delay time were determined to be about 50 mJ energy and 6 μ s, respectively, for thoria analysis. Calibration curves were obtained for seven impurities (Mg, Al, Ca, Ni, Fe, Cu and Mo) with thoria certified reference materials (CRM) prepared and supplied by nuclear fuel complex, Hyderabad, India. The results obtained by LIBS were found to be in good agreement with the certified values for the trace impurities. The LIBS technique provides an independent approach for impurities determination in thoria without any dissolution or removal of bulk of thorium.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

Determination of impurities in nuclear materials is of great importance as their presence affects the mechanical property of the material during irradiation as well as the neutron economy inside a reactor. Specification limits have been laid down for various impurities in different nuclear fuels. Quantitative determination of impurities constitutes an important step for quality assurance at different stages of fuel fabrication. Since many of the nuclear materials pose radiation hazards, it is desirable to develop methods which involved minimum sample handling procedures with an objective to minimize the radiation exposure to the workers.

Spectrochemical methods based on atomic emission such as inductively coupled plasma atomic emission spectroscopy (ICP-AES), DC-arc optical emission spectroscopy (DC-arc OES) etc. have been extensively applied for the determination of different trace constituents in a variety of matrices. Laser induced breakdown spectrometry (LIBS) is another emission spectrometric technique which has gained popularity over the last decade for multi elemental determination. It is a versatile analytical technique with several advantages over the conventional emission spectrometric techniques, especially for nuclear applications. These include (a) reduction of sample size and analysis steps, (b) micro analysis of inhomogeneous sample [1], (c) reduced turnaround time, with a possible to implement for quality assurance during the fabrication stages, (d) possibility of analyzing both electrically conducting and non-conducting samples, (e) applicable in hostile industrial environments [2,3] and (f) in-situ remote analysis via optical fiber.

The basic theory of the technique has been described in several reviews [3–7].

India has limited resources of uranium and abundant resources of thorium (~300,000 tons) [8,9], which is a fertile material and can be used for obtaining the fissile material ^{233}U by thermal neutron irradiation in a nuclear reactor. India is planning to build advanced heavy water reactors (AHWR) based on use of mixed oxides of (Th + U) and (Th + Pu) for utilizing the thorium resources for electricity generation. Currently, thoria bundles are used for neutron flux flattening in pressurized heavy water reactors (PHWR) and also as blanket in the fast breeder test reactor (FBTR).

Thoria being a refractory material, the dissolution of sintered thoria pellets is time consuming and difficult. The conventional emission spectrometric techniques such as ICP-AES require quantitative dissolution of the samples. Also the complex emission spectrum of thorium necessitates chemical separation of impurities from bulk of thorium. These limitations can be circumvented by employing techniques having capability for direct solids analysis. Some of these include DC-arc-carrier distillation method, laser ablation inductively coupled mass spectrometry (LA-ICP-MS), glow discharge mass spectrometry (GD-MS), glow discharge optical emission spectrometry (GD-OES) and LIBS. There have been several reports of LIBS analysis of power samples of different form, e.g. organic compounds [10], geological materials [11], soils, sand, sewage sludge [12], phosphate ores [13] etc.

In the present work, we have optimized the LIBS analysis conditions for the determination of trace impurities in ThO_2 samples. Since impurity standards in thoria matrix are not available commercially, certified reference materials (CRM) prepared by M/s. Nuclear Fuel Complex, Hyderabad, India in association with radio chemistry division (RCD), BARC, Mumbai, were employed in this work. The emission spectrum of ThO_2 being very complex,

* Corresponding author. Tel.: +91 22 25593740; fax: +91 22 25505151.

E-mail addresses: skaggr@barc.gov.in, skaggr2002@rediffmail.com (S.K. Aggarwal).

impurities which were present in significant amounts (above tens of ppmw) were analyzed. Linear calibration curves were obtained for seven impurities using these standards. This paper presents details of the work carried out to optimize the experimental parameters like laser energy and acquisition delay time in LIBS and also present the calibration curves obtained for different impurities in thoria matrix.

2. Experimental

2.1. Instrumentation

The Spectrolaser 1000 M, from M/s. Laser analysis technologies (now known as XRF scientific), Victoria, Australia was used in this work. The instrument comprises of an excitation laser, optical spectrograph, gated charge couple device (CCD) detectors. A high power Q-switched Nd:YAG laser which yields up to 200 mJ of pulse energy at the fundamental IR wavelength (1064 nm), in a 7 ns pulse, with a repetition rate of 10 Hz is used. The laser is focused on the surface of the sample by a plano-convex lens having a focal length of 5 cm. The spot size was measured to be 500 μm which yields a laser fluence of 100 J/cm². The sample is mounted on a fast translational stage, which moves the sample with a velocity of 1.67 mm/sec between two laser pulses, thereby exposing new and fresh region of the sample to each successive laser pulse. The emission from the micro plasma formed on the surface of the sample is coupled to four optical fibers, which transmit the emission light into the entrance slit of spectrographs in Czerny–Turner (C–T) configuration with a resolution of about 0.6 nm at 300 nm. Gated CCDs are used as detectors. The system has a wide spectral coverage from 180 nm to 850 nm for observing the elemental fluorescence. The output from each of the four CCD's is digitized by a fast analog to digital (ADC) circuitry. Thus the emission output of the entire spectral range is recorded simultaneously for each laser pulse. The spectral acquisition can be delayed by a gating circuit to achieve the required delay between plasma ignition and recording of the emission spectrum. The whole system is integrated and is operated by a personal computer.

2.2. Samples

The material used in this work to establish calibration curves were produced during an Inter Laboratory Comparison Experiment (ILCE) conducted by the Department of Atomic Energy (DAE), India. During this ILCE, 13 laboratories of DAE had participated.

The impurities in these ThO₂ samples were determined using five different analytical techniques based on different physico-chemical principles. The techniques employed were (1) inductively coupled plasma–atomic emission spectrometry (ICP–AES), (2) inductively coupled plasma–mass spectrometry (ICP–MS), (3) atomic absorption spectrometry (AAS), (4) total reflection X-ray fluorescence (TXRF) and (5) DC–arc–carrier distillation technique. Four samples of homogeneous ThO₂ powder were prepared containing 20 impurities in varying amounts. The following samples were prepared in view of the application of ThO₂ as a fuel for AHWR reactors. (a) ThO₂–B containing impurities at base level, (b) ThO₂–S containing impurities at specified level, (c) ThO₂–D containing impurities at double the specified limit and (d) ThO₂–MOS mixed oxide of Th and U in the composition that has been proposed for the fuel of AHWR.

Table 1 gives the data on the different impurities present in the samples. For certification of impurities, F-test was conducted on the data from the different techniques employed. Thoria powder was prepared based on the method used by Allred et al. [14] through the oxalate precipitation route. Though the RSD values is

Table 1

Concentrations of impurities (ppmw) in different thoria samples used for calibration in LIBS. The mean values and % RSD are taken from ILCE evaluation report.

Element	ThO ₂ –B		ThO ₂ –S		ThO ₂ –D		ThO ₂ –MOS	
	Mean	% RSD	Mean	% RSD	Mean	% RSD	Mean	% RSD
Al	6.9	42.2	39	28.2	65	24.2	38	27.7
B	0.77	66.8	1.2	50	0.8	50	0.79	49.2
Be	<0.1	–	0.34	23.4	<0.1	–	<0.1	–
Ca	73	28.5	351	29.5	586	27.8	479	23.7
Cd	<0.1	–	1.1	46.1	2.0	37.3	1.3	43.6
Ce	1.3	62.5	5.6	41.1	11	22.4	7.6	43.7
Cr	8.5	17.6	7.3	28.2	13	30.2	19	20.4
Cu	3.1	27.4	63	29.5	110	29.1	71	18.7
Dy	<0.1	–	0.28	41.1	0.55	42.7	0.3	45.5
Er	<0.1	–	0.28	43.7	0.54	31.6	0.34	48
Eu	<0.1	–	0.12	41.1	0.22	38.3	0.12	37.1
Fe	56	29.7	78	29	134	29.1	137	30
Gd	–	–	0.42	49.8	0.7	42.9	0.48	47
Mg	4.8	37.2	168	29	74	29.7	36	24.1
Mn	3.0	34.8	4.3	37.5	7.3	36.4	5.5	28
Mo	1.2	52.2	22	27.5	45	25.7	22.4	33.2
Ni	11	20.9	32	25.7	57	29.1	38	21.9
Sb	<0.5	–	2.4	40.5	5.0	36.4	1.9	33.6
Sm	–	–	0.63	45.8	1.2	40.9	0.81	46.5
V	0.21	50.9	3.0	42.1	5.9	37.5	3.3	33.9

quite large for some of the elements in Table 1, they are within expectable limit for material to be used in nuclear industry and follow the statistical evaluation criteria of international atomic energy agency (IAEA) for inter-comparison experiments [15].

2.3. LIBS analysis

For LIBS analysis 4 gm of samples (particle size 10–40 μm) were taken in an aluminum cup having an inner diameter of 3 cm and 8 mm height. A pressure of 2×10^9 Pa was applied for 5 min to prepare a pellet. The LIBS spectral data were analyzed using the instrument software and applying non-linear least squares regression analysis. The spectra of 30 shots were averaged and used for analysis in the present work. During these analyses, the spectra with variation of intensity ratio more than $\pm 10\%$ of the average intensity ratio were neglected.

3. Results and discussion

3.1. Time resolution

The sensitivity of LIBS analysis increases when the plasma light detection is time resolved and the technique is then reframed to as time resolved laser induced breakdown spectroscopy (TRLIBS) [16,17]. The high temperature plasma formed immediately after the laser bombardment contains highly ionized species and emits a broad continuum due to 'Inverse Bremsstrahlung' along with the emission lines of different species. The emission lines are also broadened by Stark effect due to high electron density that exists in the initial life-time of the emission. The signal to noise ratio (SNR) can, therefore, be improved by electronically gating off the early part of signal. The choice of time parameter was assessed experimentally with zirconium as a model. Zr was chosen as its melting point (MP) (2125 K) is closer to that of Th (2115 K). MP has been found to be an important parameter in the variation of ablation threshold fluence [18]. This particular route was taken because studying the time resolution in ThO₂ spectrum is difficult due to the numerous emission lines. In this work, laser energy of 50 mJ and an acquisition delay of 6 μs was used; with fixed gate width of 10 μs available in the instrument.

3.2. ThO₂ spectra

Fig. 1(a) and (b) shows the typical spectrum obtained for one of the samples used for obtaining the calibration curves for different impurities. A relatively smaller number of shots (30) were chosen considering our ultimate aim to develop an on-line remote analysis technique, and to reduce the spreading of thorium dust in the sample chamber. As can be seen, the emission spectrum is quite complex and identification of suitable emission lines for calibration is a major challenge. For every element, the region of interest was selected on the basis of the well-known criteria:

- The emission lines used in ICP-AES experiment during ILCE work performed were selected for LIBS analysis. It must be noted that for analysis by ICP-AES, the matrix thorium was separated by solvent extraction initially using 40% solution of tri-*n*-butylphosphate (TBP) in CCl₄ and later with 0.2 M tri-*n*-octylphosphinic oxide (TOPO) in CCl₄. If ICP-AES experimental line was not detectable, then emission line reported by other researchers from LIBS experiments in literature was used.
- The emission line should be spectrally pure.
- The emission line with $E_{\text{lower}} = 0$ or as low as possible was preferred.
- The emission line having a high transition coefficient (A) is desirable.
- High SNR at the particular condition.

Table 2 gives the data on the spectral lines used for calibration of seven impurities present (Mg, Al, Ca, Ni, Fe, Cu and Mo) in the ThO₂ samples along with seven other elements (Mn, Na, V, Be,

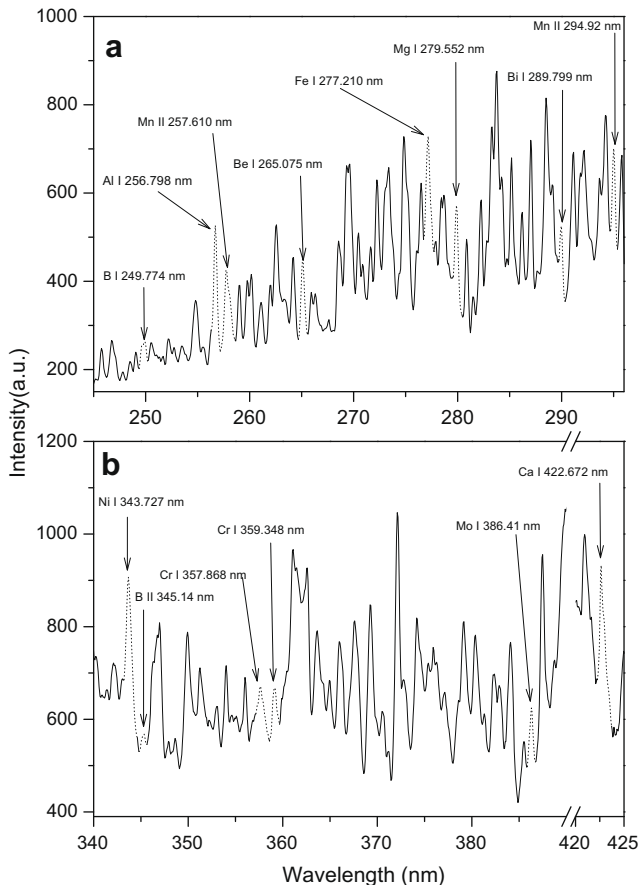


Fig. 1. Emission spectrum of ThO₂-S in the (a) 245 nm to 295 nm region and (b) 340 nm to 425 nm region with the emission lines of impurities (broken line).

Table 2

Chosen emission lines and their spectroscopic data [19] for various elements.

Element	Species	Wavelength (nm)	E_{lower} (cm ⁻¹)	Transition coefficient (A) (10 ⁸ s ⁻¹)	Remarks
Mg ^a	II	279.552	0	2.600	Quantification possible
Al ^a	I	256.798	0	0.230	
Ca ^a	I	422.672	0	2.200	
Ni ^a	I	301.914	0	0.06	
Fe ^a	I	277.210	704	0.4199	
Cu ^a	I	327.395	0	1.400	
Mo ^a	I	386.410	0	0.624	
Mn ^b	II	257.610	0	2.8	Only detection was possible
	II	294.920	9472.97	1.94	
Na ^b	I	588.994	0	0.616	
	I	589.592	0	0.614	
V ^b	I	478.353	2311.36	0.089	
Be ^b	I	265.075	21981.27	4.24	
Ce ^b	I	487.704	0	12	
B ^b	I	249.774	15.287	1.67	
	II	345.14	73396.51	0.54	
Cr ^b	I	357.868	0	1.48	
	I	359.348	0	1.50	

^a Calibration curves of these elements were constructed.

^b Elements were only detected.

Ce, B and Cr) which could only be detected. The Mg(II) 279.552 nm line was the same as that used for ICP-AES work. Ca(I) 422.672 nm, Cu(I) 327.395 nm, Fe(I) 277.210 nm lines were based on the reported LIBS work. Emission lines of other three elements (Al, Ni and Mo) were selected from the spectrum obtained under the present experimental conditions. These seven elements were chosen for quantitative analysis, since they were present in significant concentrations in the calibration standards as well as the range of the concentration variation in the standards was more than 10%.

3.3. Calibration curves

The calibration curves for different impurities in thorium matrix were obtained by using three ThO₂ calibration standards (Fig. 2). The calibration curves were constructed by plotting the intensity ratio of impurity with respect to Th(II) 318.019 nm versus the known element concentrations (weight percentage). Each point displayed in the calibration graphs is the mean value obtained from triplicate measurements and the error bars correspond to one standard deviation ($\pm 1\sigma$). The calibration curves were found to be linear for all the impurities in the concentration range present in the samples. The root mean square error in prediction (RMSEP) for the calibration curve is given by

$$\sqrt{\frac{\sum \{y_i - y_m(I_i)\}^2}{n}}$$

where n is the number of points in the calibration, y_i is the concentration of the i th calibration point and $y_m(I_i)$ is the concentration predicted by the calibration curve for the i th intensity. This measure indicates the likely difference between the actual concentration of an impurity in the sample and the value predicted by the calibration curve. The plots have RMSEP of 10⁻³ range, which is reasonable, considering the limited number of calibration points.

3.4. Precision and detection limit

To check the calibration curves obtained in the present work, a sample was prepared by mixing ThO₂-S with ThO₂-D in 3:1 by weight basis. Table 3 gives the results obtained from six replicate

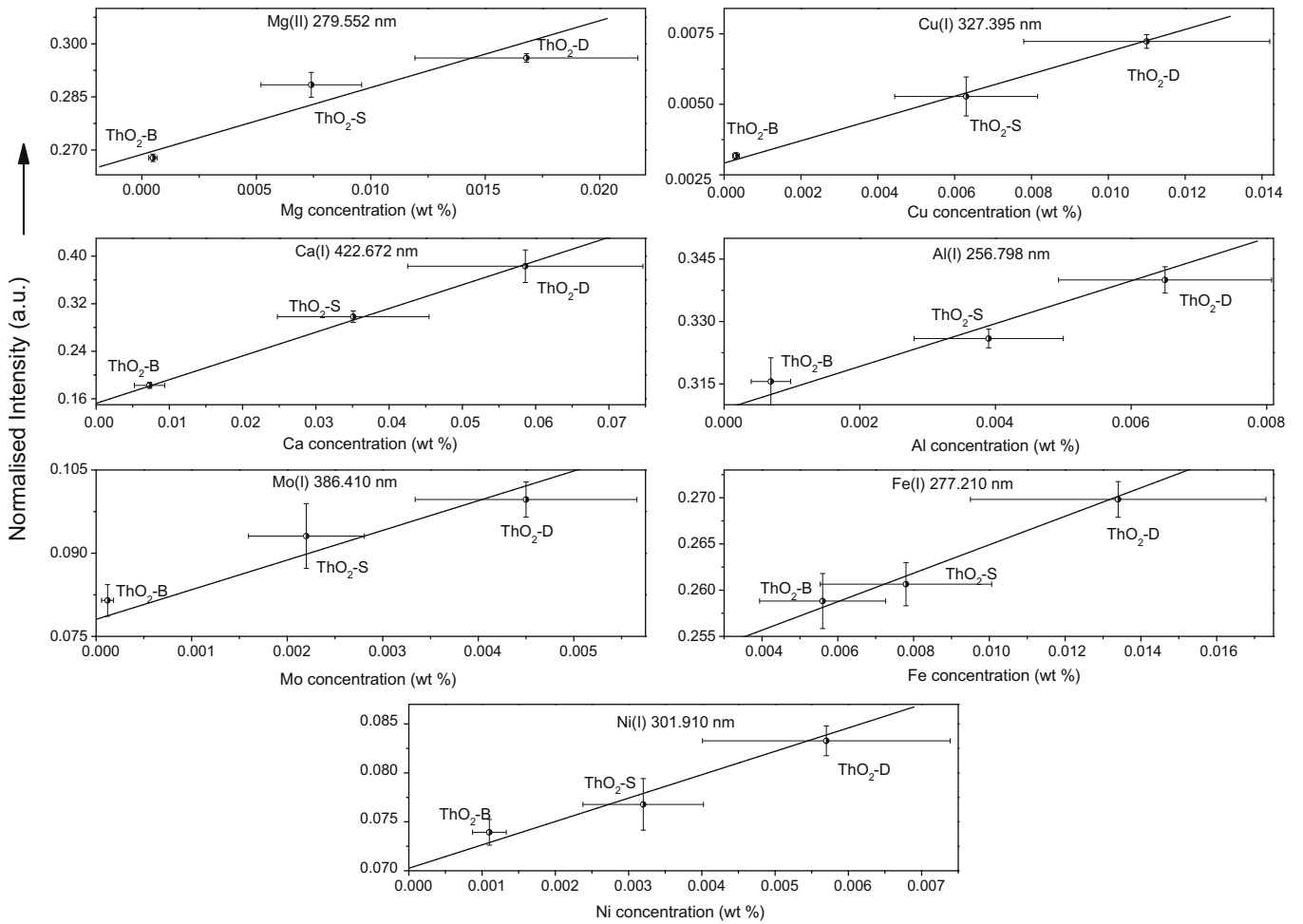


Fig. 2. Calibration curves obtained for different impurities in thoria by LIBS.

analysis of this mixture under the identical conditions of analyses as those used for calibration samples. It can be seen that the mean values of concentrations of different impurities are in good agreement with the expected values and the precisions lies in the range of 7–22%. Fig. 3 shows the distribution of the six replicate analysis values for the unknown. The distribution clearly indicates the random nature of the analytical value against the certified values.

Mixed oxide sample (ThO₂-MOS) containing around 2.5% weight of UO₂, prepared by NFC and characterized during ILCE was also analyzed by LIBS under the identical conditions of analysis. The LIBS spectrum obtained was quite different from those of ThO₂ samples. This was attributed to complex emission spectrum

Table 3
Elemental concentrations (in ppmw) in mixture of ThO₂-S and ThO₂-D mixed in a 3:1 amount ratio.

Element	Emission line used (nm)	Expected concentration		LIBS	
		Mean (ppmw)	% RSD	Mean (ppmw)	% RSD
Al(I)	256.798	50	27.3	53.7	21.8
Ca(I)	422.672	449	31.1	524	7.3
Cu(I)	327.395	82	33.6	90	10
Fe(I)	277.210	113	30.4	134	11.4
Mg(II)	279.552	56	33.8	68	21
Mo(I)	386.410	33	30	55	21
Ni(I)	301.914	45	31.8	55	18

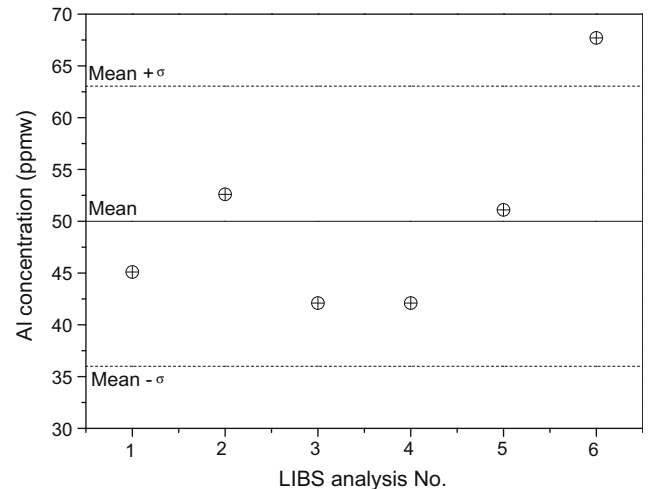


Fig. 3. A comparison of LIBS results of six replicate determinations of Al concentration in thoria with certified concentration of 50(±13) ppmw (Table 3).

of UO₂ which adds to the complexity in the ThO₂-MOS spectrum. Since UO₂ present in the MOS sample is hygroscopic in nature and can pick up moisture, the sample was dried in a furnace at 100 °C for more than two days and then cooled overnight in desiccator prior to LIBS analysis. Among the seven impurities,

Table 4
Comparison of LODs in ThO₂ matrix with those reported for UO₂ and PuO₂ matrix.

Element	Literature			Present work	
	Wavelength (nm)	Matrix	Detection limit (ppmw)	Wavelength (nm)	Detection limit (ppmw)
Al	396.153	UO ₂	200 [15]	256.798	18
Ca	–	–	–	422.672	26
Cu	324.754	UO ₂	150 [15]	327.395	46
	324.754	PuO ₂	90 [15]	–	–
Fe	–	–	–	277.210	32
Mg	285.213	UO ₂	70 [15]	279.552	38
Mo	–	–	–	386.410	19
Ni	–	–	–	301.914	24

Fe(I) 277.210 nm, Mg(II) 279.552 nm and Mo(I) 386.410 nm could not be identified due to high spectral background. The results for other impurities were found to be positively biased (out of calibration range) when compared to the expected concentration values. This observation is characteristic of matrix effect, implying the need to have calibration standards with similar composition.

Detection limits for seven impurity elements in ThO₂ were determined using the formula $LOD = 3\sigma/m$, where m is the slope of the calibration line and σ is the uncertainty in the intensity for the calibration point with the lowest concentration. The LOD's of the elements in ThO₂ matrix are given in Table 4. As is seen, these LODs are better than the LOD's for these elements in UO₂ and PuO₂ reported about a decade ago [20], which were based on two point extrapolation method.

4. Conclusions

It is known that analysis of ThO₂ for impurities determination by emission spectroscopy is a challenging task. But any analytical method which does not employ the sample dissolution is to be preferred for the analysis of ThO₂ samples. Owing to the increased thrust for the deployment of Th in nuclear fuel cycle, this work would be useful for quick characterization of the ThO₂ fuel materials. Moreover, due to the remote analysis capability of LIBS, it can be applied for the direct monitoring during fuel pellet

fabrication. In this paper, we have reported the studies for quantitative analysis of elements in Thoria by LIBS. Fourteen elements were detected and calibration curves were obtained for seven elements using indigenously developed calibration samples. The detection limits obtained by LIBS for these elements are lower than their specification limits in ThO₂ nuclear fuel. There is a need to develop calibration standards of mixed oxides to facilitate ThO₂–MOS quantification.

Acknowledgements

The authors express their sincere thanks to Dr V Venugopal, Director, Radiochemistry and Isotope Group, BARC for his continuous interest, support and encouragement.

References

- [1] C. Geertens, J.L. Lacour, P. Mauchien, L. Pierraard, Spectrochim. Acta Part B 51 (1996) 1403.
- [2] J.M. Vadillo, J.J. Laserna, Spectrochim. Acta Part B 59 (2004) 147.
- [3] D. Cremers, L. Radziemski, Hand Book of Laser Induced Breakdown Spectroscopy, first Ed., Wiley, West Sussex, 2006.
- [4] V. Majidi, M.R. Joseph, Crit. Rev. Anal. Chem. 23 (1992) 143.
- [5] A.V. Pakhomov, W. Nichols, J. Borysow, Appl. Spectrosc. 50 (1996) 880.
- [6] L.J. Radziemsky, T.R. Loree, D.A. Cremers, N.M. Hoffman, Anal. Chem. 55 (1983) 1246.
- [7] E.H. Evans, J.A. Day, W.J. Price, C.M.M. Smith, K. Sutton, J.F. Tyson, J. Anal. At. Spectrom. 18 (2003) 808.
- [8] J.B. Hedrick, US Geological Survey, Mineral Commodity Summaries, January 1998, p. 177.
- [9] <http://www.uic.com.au/nip67.htm>.
- [10] S. Rai, A.K. Rai, S.N. Thakur, Appl. Phys. B 91 (2008) 645.
- [11] J.M. Anzanos, M.A. Villoria, A. Ruiz-Medina, R.J. Lasheras, Anal. Chim. Acta 575 (2006) 230.
- [12] R. Wisbrun, I. Schechter, R. Niessner, H. Schroder, K.L. Kompa, Anal. Chem. 66 (1994) 2964.
- [13] S. Rosenwasser, G. Asimellis, B. Bromley, R. Hazlett, J. Martin, T. Pearce, A. Zigler, Spectrochim. Acta Part B 56 (2001) 707.
- [14] V.D. Allred, S.R. Buxton, J.P. McBride, J. Phys. Chem. 61 (1957) 117.
- [15] K.J. Grant, G.L. Paul, J.A. O'Neill, Appl. Spectrosc. 44 (1990) 1711.
- [16] M. Doubek, G. Baglino, S. Deron, IAEA/RL/116 (1985).
- [17] D.A. Cremers, Appl. Spectrosc. 41 (1987) 572.
- [18] L.M. Cabalin, J.J. Laserna, Spectrochim. Acta Part B 53 (1998) 723.
- [19] http://physics.nist.gov/PhysRefData/ASD/level_form.html.
- [20] P. Fichet, P. Mauchien, C. Moulin, Appl. Spectrosc. 53 (1999) 1111.