Determination of impurities in thoria (ThO$_2$) using Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS)

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ABSTRACT

Elemental impurities in nuclear grade thoria were determined using Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) employing ArF laser (20 ns, 193 nm, 20 Hz). Three certified standards of thoria, prepared in the Department of Atomic Energy (DAE), India were used for this work. Magnesium was used as an internal standard for quantification in view of its addition during fuel fabrication. The concentrations determined for 16 different elements (Al, B, Cd, Ce, Cu, Dy, Er, Eu, Fe, Gd, Mg, Mn, Mo, Ni, Sb, Sm and V), spanning four orders of magnitude, were within 20% of the certified values in the standards. The methodology is of interest to reduce the analytical effort with regard to dissolution of thoria samples, avoid the production of radioactive liquid waste streams and relatively simple mass spectrum as compared to complex emission spectra in atomic emission spectroscopy (AES) and laser induced breakdown spectroscopy (LIBS). The development and validation of analytical methodologies based on independent physico-chemical principles is of great relevance to characterize the in-house prepared working standards for routine applications.

1. Introduction

Determination of trace impurities in different nuclear materials is of great importance in nuclear technology and this constitutes an important part of chemical quality assurance of fuels and fuel materials. The presence or excess of certain elements can affect the mechanical performance of the material and can also influence the neutronics to a great extent in the reactor conditions. Due to these reasons, a strict chemical quality assurance is implemented for all the nuclear grade materials.

A wide variety of analytical methodologies are employed for the study of major, trace and ultra-trace constituents in nuclear materials. The normally employed analytical methods, such as ICP-AES and ICP-MS, for trace impurities determination necessitate the dissolution of the fuel samples followed by the separation of matrix elements such as U or Th [1]. This is necessary to overcome the possible matrix interferences as well as due to the radio-toxicity associated with the fission products present in the irradiated samples. It is also necessary to optimize the separation procedure to obtain 100% recovery of the analytes of interest, in cases where the isotope dilution methodology is not employed.

India has a large reserve of thorium which is poised to play a major role in the Indian nuclear energy program. Though ^{232}Th is not a fissile material for direct use as a nuclear fuel, it is utilized in the breeder reactors for the production of ^{233}U which is a fissile material, as well as for flux flattening in the Pressurized Heavy Water Reactors (PHWRs). It is highly promising nuclear material and is proposed for utilization in the advanced heavy water reactors (AHWRs) [2] where mixed oxide fuels of Th with U and Pu are proposed.

Though thoria can be dissolved using the Thorex reagent [3] consisting of 13 M HNO$_3$, 0.1 M Al(NO$_3$)$_3$·9H$_2$O and 0.05 M NaF, but it involves considerable effort to obtain a quantitative dissolution which is one of the pre-requisites for elemental analysis. Moreover, due to the radioactive nature of these materials, it is necessary to employ a suitable recovery procedure for the analytical waste generated and for unused sample solutions. Hence it is highly desirable to develop a direct solids analysis technique for the determination of the impurities in thorium based nuclear fuels.

Several direct solids analyses techniques have been employed for the analysis of nuclear materials. These include LIBS [4], Glow Discharge Optical Emission as well as Mass Spectrometry, LA-ICP-MS [5,6], X-ray based techniques such as Energy Dispersive X-ray Fluorescence (EDXRF) [7], and Secondary Ion Mass Spectrometry (SIMS) [8]. LIBS is promising for the direct determination of elemental impurities since it requires minimum sample preparation. But the method is of limited application in case of thoria samples due to the complex emission spectrum of thorium. Due to the interferences from emission lines of Th, only those impurities which are in significantly high amounts can be determined

by LIBS. EDXRF has the limitation due to the large matrix effects, which result in poor detection limits. Mass Spectrometry based techniques are highly useful, since the resultant mass spectra are simple in comparison to the emission spectra.

In order to utilize the unique advantage of direct solid analysis as well as the simultaneous multi-elemental analysis capability of LA-ICP-MS, in-house prepared thoria standards were employed. About 16 elements could be analyzed with concentration range over four orders of magnitude. Magnesium was used as an internal standard for analysis, since it is added in solution form to thorium nitrate solution in the first stage of fabrication of thoria based fuels and is uniformly distributed in the sample.

2. Experimental

The thoria samples employed in this work were produced by the oxalate precipitation route [9]. The certification was done in frame of a national inter-laboratory comparison experiment (ILCE) conducted by the Department of Atomic Energy (DAE), India, where 13 laboratories of DAE participated [10]. The samples were prepared with a view of standardizing the analytical methods for the trace determination in thoria to be used in AHWRs. Different analytical methodologies based on different physico-chemical principles such as (i) ICP-AES (ii) ICP-MS (iii) Atomic Absorption Spectrometry (AAS) (iv) Total Reflection X-ray Fluorescence (TXRF) and (v) DC-Arc Carrier Distillation were used. For the certification of the impurities in the three standards, F-test was conducted on the results of the different techniques.

For analysis of these samples by LA-ICP-MS, about 2 g of each of the samples (particle size 10–40 μm checked by dynamic light scattering) was pressed into pellet in an aluminium cup by applying a pressure of 2×10^9 Pa for 5 min. The operating conditions for the laser ablation and ICP-MS system are given in Table 1. Each of the three samples was analyzed three times for obtaining the intensity data.

Table 2 gives the data on the concentrations of different elements in the three certified samples of thorium. ThO₂-B, S and D stand for blank, specification limits values (based on reactor design) and double of specification limits, respectively. The different

Table 1
Operating parameters for the LA-ICP-MS system.

Parameter/system	Parameters used
Laser ablation system	UP-193, M/s. New wave research, USA
Laser	ArF
Wavelength	193 nm
Output energy	150 mJ (max.)
Pulse width	20 ns
Energy and energy density for experiments	1.31 mJ, 16.69 J/cm²
Crater sizes	100 μm (about 100 ng material ablated per shot)
Analysis mode	Raster scan; spacing between lines 200 μm, 1 pass, scan speed 100 μm/s
Warm up time for instrument	1 h
Repetition rate used	20 Hz
Carrier gas	Argon
ICP-MS type	ELAN DRC-e ICP-MS, M/s. Perkin Elmer, USA
Gas flow rates	
(a) Nebuliser gas	1.05 L/min
(b) Auxiliary gas	1.1 L/min
(c) Plasma gas	15 L/min
(d) Purge gas	1.2 L/min; 30 s
RF power	1200 W
Resolution mode	Low
Integration time	4500 ms
Detector operation	Dual mode

Table 2
Data on the concentrations of impurities in different thoria samples determined during inter-laboratory inter-comparison experiment.

Element	Sample details with concentrations of impurities in ppmw					
	ThO₂-B		ThO₂-S		ThO₂-D	
	Mean	%RSD	Mean	%RSD	Mean	%RSD
Al	6.9	42.2	39	28.2	65	24.2
B	0.77	66.8	1.2	50	0.8	50
Cd	<0.1	–	1.1	46.1	2.0	37.3
Ce	1.3	62.5	5.6	41.1	11	22.4
Cu	3.1	27.4	63	29.5	110	29.1
Dy	<0.1	–	0.28	41.1	0.55	42.7
Er	<0.1	–	0.28	43.7	0.54	31.6
Eu	<0.1	–	0.12	41.1	0.22	38.3
Fe	56	29.7	78	29	134	29.1
Gd	–	–	0.42	49.8	0.7	42.9
Mg	4.8	37.2	168	29	74	29.7
Mn	3	34.8	4.3	37.5	7.3	36.4
Mo	1.2	52.2	22	27.5	45	25.7
Ni	11	20.9	32	25.7	57	29.1
Sb	<0.5	–	2.4	40.5	5.0	36.4
Sm	–	–	0.63	45.8	1.2	40.9
V	0.21	50.9	3.0	42.1	5.9	37.5

standards were prepared with an aim for method development for thoria analysis, where the impurities in ThO₂-B are at base level, ThO₂-S are at specified level and in ThO₂-D at double the specified limit. Though the RSD values are quite large (>20%) for some of the elements, they are within the expected limits of the methodologies employed for certification of the standards.

Table 3 presents the published results of analysis of these standards by different methods viz. LIBS [11] and TXRF [12]. It can be seen that due to the complexity of the emission spectra as well as matrix effects, only the data on a few of the elements were obtained directly, i.e. without dissolution as well as without separation of the thorium matrix in LIBS. The complex emission spectrum of thorium also explains the large uncertainty in the reported values for the different elements in the standards, as the concentration data were obtained by the conventional method such as ICP-AES. The concentrations of different impurities in the present work were calculated using Mg as an internal standard, employing ThO₂-D for calibration. The relative sensitivity factors (RSFs) for different elements were obtained by taking the ratio of the intensity during each experiment and the concentration data of the impurity with respect to that of Mg in ThO₂-D.

3. Results and discussion

Table 4 gives the average intensities (cps) of the different elements obtained from LA-ICP-MS. It can be seen that the standard deviation of the mean intensities from replicate analyses is less than 20% for most of the elements determined in this work. This deviation could be due to differences in the ablated amounts during three independent analyses as well as inhomogeneity in the samples analyzed. The intensities given under the column "blank" refer to the system blank, where the data acquisition was done, with all parameters same (like purge gas, RF power, etc.) as those used for thoria samples but without applied laser energy. This was done to experimentally determine the system blank at different m/z values of interest.

Relative sensitivity factors (RSFs) of different elements with respect to Mg in thoria matrix are shown in Table 5. As is seen, RSFs for most of the elements with respect to Mg in thoria matrix lie within a narrow range (1–2) using the ns-laser available in our laboratory. The intensities obtained for the different elements were normalized with respect to that obtained for Mg and single point

Table 3
Concentrations of impurities in different standards of thoria by LIBS [10] and TXRF [11].

Technique	Elements quantified	Elements detected	Methodology
LIBS	Al (53.7 ± 11.7); Exp: 50 ± 13.7	Na	Direct solid analysis (data obtained for a synthetic mixture of ThO_2-S and ThO_2-D in the ratio 3:1)
	Ca (524 ± 38); Exp: 449 ± 140		
	Cu (90 ± 9); Exp: 82 ± 28		
	Fe (134 ± 15); Exp: 113 ± 34.4		
	Mg (68 ± 14); Exp: 56 ± 18.9		
	Mo (55 ± 11); Exp: 33 ± 10		
	Ni (55 ± 10); Exp: 45 ± 14.3		
TXRF	Ca (67 ± 7, 454 ± 8; 874 ± 116)	Ba, Co, K, Pb, Sr, Y, Zn	Dissolution of ThO_2 + separation of Th by TBP and TOPO in CCl_4; (data obtained for ThO_2-B, ThO_2-S and ThO_2-D, respectively)
	Cr (4.5 ± 0.6; 6 ± 1; 14.6 ± 0.3)		
	Cu (1.9 ± 0.4; 50 ± 3; 93 ± 4)		
	Fe (46 ± 8; 65 ± 6; 122 ± 2)		
	Mn (2.4 ± 0.2; 4.0 ± 0.5; 7 ± 1)		
	Ni (7.7 ± 0.6; 29 ± 2; 47 ± 2)		
	V (ND; 3.1 ± 1.2; 7 ± 2)		

Table 4
Measured intensities (cps) for different elements in thoria standards by LA-ICP-MS.

Element	Intensity (cps)							
	Blank		ThO_2-B		ThO_2-S		ThO_2-D	
	Mean[a]	1σ[b]	Mean[a]	1σ[b]	Mean[a]	1σ[b]	Mean[a]	1σ[b]
Al	381.3	33.1	4042	1238	22,360	1192	33,172	6672
B	11.7	3.9	693.9	29.3	5197	65	3556	855
Cd	4.9	1.6	19.2	8.2	646	297	1390	283
Ce	12.4	15.0	1609	232	10,854	1613	21,566	4465
Cu	118.5	97.0	1714	205	69,246	9602	108,816	22,803
Dy	1.5	0.3	13.1	2.2	297.1	4.3	490	135
Er	1.4	0.7	3.4	3.3	293.5	29.2	488	122
Eu	1.2	1.4	3.5	0.9	207.1	10.7	388	82
Fe	107.5	8.4	987	54	2171	89	2664	992
Gd	1.4	0.2	32.1	3.2	295.9	19.6	472	54
Mg	16.6	16.6	1589	788	87,341	15,868	37,365	9663
Mn	142.6	5.4	2880	339	6005	922	9863	2015
Mo	17.8	20.4	440.4	23.2	13,595	1407	26,432	7097
Ni	140.7	39.6	4846	1245	18,584	2434	35,995	7242
Sb	19.9	4.6	101.3	50.9	2370	307	5278	913
Sm	2.4	1.1	80.4	33.5	675.1	68.2	1068	216
V	806	81	965	154	3216	457	5197	797

[a] Gives the mean of three independent analyses of the pellets by LA-ICP-MS.
[b] Gives the standard deviation of the resultant intensity of the three experiments.

Table 5
Concentrations of different elements in thoria standards as determined by LA-ICP-MS.

Element	Relative sensitivity factor w.r.t. Mg in ThO_2	Concentration obtained ($\mu g\ g^{-1}$)			
		ThO_2-B	%Deviation from expected value	ThO_2-S	%Deviation from expected value
Al	0.89 (1%)	11.4 (0.9%)	65	42.2 (7.3%)	8.2
B	8.8 (2.8%)	0.29 (31%)	−63	1.24 (1.8%)	3.3
Cd	1.46 (2.2%)	0.03 (7%)	–	0.96 (17%)	−12.7
Ce	3.92 (4.6%)	0.72 (15%)	−45	5.24 (3.5%)	−6.4
Cu	2.05 (4.4%)	2.12 (6.4%)	32	63.4 (1.9%)	0.7
Dy	1.64 (4.0%)	0.02 (8%)	–	0.32 (0.2%)	13.7
Er	1.69 (0.1%)	0.016 (1.7%)	–	0.32 (7.8%)	13.7
Eu	3.6 (2.5%)	0.003 (25%)	–	0.12 (4.2%)	−0.2
Fe	0.045 (6.1%)	52.9 (6.4%)	−5.5	79.0 (6.5%)	1.3
Gd	1.11 (1.8%)	0.06 (23%)	–	0.45 (7.6%)	7.1
Mn	2.66 (0.7%)	2.8 (8.7%)	−6.7	3.84 (0.4%)	−10.8
Mo	1.16 (3.3%)	1.23 (13.3%)	2.7	21.6 (1%)	−1.8
Ni	1.26 (2.2%)	11.3 (8%)	2.8	28.6 (6.1%)	−10.6
Sb	1.99 (7%)	0.13 (1.2%)	–	2.1 (12.6%)	−13.7
Sm	1.83 (1%)	0.12 (14.5%)	–	0.68 (1%)	7.3
V	1.49 (9.8%)	0.3 (51%)	43	3.1 (1.9%)	3.2

Values in parentheses give the relative standard deviation calculated from $n = 3$ independent replicates.

calibration was employed. Using this normalized intensity relation with respect to the concentration ratio obtained for different ele-

ments in ThO_2-D sample, the concentrations of different elements in the other two standards viz. ThO_2-B and ThO_2-S were calculated.

The Table also includes the relative standard deviation (1s) calculated on RSFs determined from three independent experiments. The relative standard deviation (1s) calculated from three independent LA-ICP-MS analyses on the concentration values of different impurities are also included in the Table. The precision of the measurements for the different elements is within 10% for the replicate analyses. Combining this with 30% uncertainty on the calibrant (i.e. Mg) concentration data given in Table 2, an overall uncertainty of about 33% is calculated. As expected, the results are more precise when we employed the internal normalization using Mg. The concentration data for most of the elements in ThO_2-S deviates form the expected values within 20%. Due to the highly refractory nature of Be, it was not possible to obtain good signal strength and hence the measurement could not be performed for this element. There was significantly higher background in the present instrument for Cr and Ca and hence data for these elements are not reported.

4. Conclusions

LA-ICP-MS has been shown to be a promising technique for the determination of trace impurities in thoria samples since it does not involve any dissolution and separation of thorium matrix as well as provides data on many other elements without significant experimental effort. Since there is no significant waste generated for the analytical methodology, it is highly attractive for analyzing radioactive samples such as irradiated nuclear fuels. It is shown that multi-elemental determination is possible using an internal standard with reasonable precision and accuracy which is acceptable for chemical quality assurance of fuel materials. It is also promising for analyzing Pu bearing nuclear fuel samples after suitable adaptation in a glove box. Moreover, there is also a possibility of local analyses on fuel samples instead of the determination of the bulk composition after dissolution. Especially for irradiated material, it is highly beneficial to make a local characterization of the fission products and actinides since it is known that these elements are not homogeneously distributed across the fuel pellet cross section. Also in non-irradiated fresh fuel, inhomogeneities of impurities or the matrix elements can be detected with LA-ICP-MS but not after dissolution.

It will be interesting to analyse similar thoria samples using fs- and ps-lasers by those laboratories having access to these systems and obtain a comparison of the results of ns- versus ps- and fs-lasers in view of the studies reported for determination of thorium at trace to ultra-trace levels by LA-ICP-MS [13–16].

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