Study on the Spectral Interference of Thorium on Critical Elements and Rare Earths by CCD-based ICP-AES

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ABSTRACT

Thorium is one of the key elements in the three-stage nuclear energy program of India. Due to the line-rich emission spectra of thorium, it is likely to interfere in the determination of trace metallic impurities by ICP-AES in a Th matrix. In this work, a systematic study was carried out to understand the spectral interference of Th on rare earths and all the critical elements (Ag, B, Ce, Eu, Gd, Dy, Sm, La, Nd, Er, Y, Ce, Lu, Pr, Yb) which have very stringent specification limits for the chemical quality control of Th-based fuels and nuclear materials. Due to the advancement of the capacitatively coupled detector (CCD) system, additional analytical lines of the analytes are available, which enhances the possibility of choosing relatively interference-free alternative analytical lines.

The present study includes the development of an ICP-AES-based analytical method for the determination of Th, which is essential for calculating correction factors of interfered lines. The calibration curves established for four different analytical lines of Th (274.716 nm, 283.231 nm, 283.730 nm,

and 401.913 nm) revealed the best analytical performance for Th at the 401.913 nm line. It was also observed that all four analytical lines can be used for the determination of Th up to 1000 µg/mL within a RSD of 2%. The spectral interference of Th was studied along with the correction factors and the tolerance level of Th on several recommended analytical lines of all the rare earths and critical elements mentioned above. The analytical performance, including the detection limits and sensitivity of all these lines, were studied in the presence of a Th matrix. For the critical elements Ag at 338.289 nm, B at 208.959 nm, Cd at 214.438 nm, Sm at 442.434 nm, Gd at 335.047 nm, and Dy at 364.540 nm, the analytical lines of the corresponding elements were found to have the least spectral interference from Th. The analytical lines of Nd at 406.109 nm, Er at 326.478 nm, Y at 371.030 nm, Pr at 422.535 nm, La at 379.478 nm, Ce at 418.660 nm, Lu at 261.542 nm, Yb at 328.937 nm, and La at 379.478 nm are suitable for the determination of these analytes in the presence of a Th matrix.

nuclear materials by inductively coupled plasma atomic emission spectrometry (ICP-AES) is the spectral interference of matrix elements such as U, Pu, Zr, Th, etc., originating from their line-rich emission spectra. Chemical (7-12) or physical (13-18) separation of the major matrix followed by the determination of trace metallic impurities in the raffinate is a well accepted protocol in the nuclear industry. Separation involves handling of the materials, which increases the chances of contamination, loss of analytes, etc. The charge-coupled detector (CCD) has the flexibility of choosing additional analytical lines for the selected analyte, which can have less interference from the major matrix (19-22).

Concerns about the limits of worldwide uranium resources motivated the initial interest in the thorium fuel cycle (23). It was envisioned that as uranium reserves get depleted, thorium would supplement uranium as a fertile material. However, for most countries uranium was still relatively abundant and research in thorium fuel cycles waned. A notable exception was India's three-stage nuclear power program (24). In the twenty-first century, thorium's potential for improving proliferation resistance and waste characteristics led to renewed interest in the thorium fuel cycle (25-27). Thorium is estimated to be about three to four times more abundant than uranium in the Earth's crust (28), although present knowledge of reserves is limited. Current demand for thorium has been satisfied as a by-product of rare earth extraction from monazite sands. Thorium-based fuels exhibit several attractive prop-

INTRODUCTION

Trace metallic impurity analysis is one of the prime tasks of chemical quality control of nuclear fuels and associated materials (1-6). Due to the high neutron absorption cross-section of the rare earth elements of Ag, B, and Cd, they have

stringent specification limits. The presence of these elements beyond the specification limits can also change the metallurgical properties of the fuel materials. To achieve the desired burn-up, the successful life span of the fuel in the reactor, and the successful running of the reactor, it is required to have stringent physical and chemical quality control and quality assurance measures of the nuclear fuels and associated materials. The major problem in the determination of trace analytes in

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erties relative to uranium-based fuels. The thermal neutron absorption cross-section (σ_a) and resonance integral (average of neutron cross-sections over intermediate neutron energies) for ^{232}Th are about three times and one third of the respective values for ^{238}U ; consequently, fertile conversion of thorium is more efficient in a thermal reactor. Also, although the thermal neutron fission cross-section (σ_f) of the resulting ^{233}U is comparable to ^{235}U and ^{239}Pu , it has a much lower capture cross-section (σ_c) than the latter two fissile isotopes, providing fewer non-fissile neutron absorptions and improved neutron economy. Finally, the ratio of neutrons released per neutron absorbed (η) in ^{233}U is greater than two over a wide range of energies, including the thermal spectrum. As a result, thorium-based fuels can be the basis for a thermal breeder reactor. Thorium-based fuels also display favorable physical and chemical properties, which improve reactor and repository performance.

In view of the above, in the present work an attempt was made to understand the spectral interference of thorium on rare earths and critical elements. The study includes identification of relatively interference-free analytical lines, correction factors, and Th tolerance levels along with the analytical performance of these lines. An ICP-AES-based method was also developed to determine Th, which is important in order to evaluate the correction factors due to thorium contribution.

EXPERIMENTAL

Instrumentation

A computer-controlled, high resolution, simultaneous atomic emission spectrometer (Spectro Arcos, Germany) with ICP and DC arc as excitation sources and a charge coupled device (CCD) detector was utilized for carrying out all analyti-

cal experiments. The instrumental specifications and experimental parameters are summarized in Table I. The detector system, consisting of linear arrays of the CCD detector (3648 pixels/array), thermally stabilized together with an optical system, provides the ability to choose the alternate analytical lines.

Standard Solutions and Reagents

Standard solutions for rare earth and other critical elements were prepared from CertiPUR® ICP multi-standard solutions (E-Merck, Darmstadt, Germany) by proper dilution with 0.5 M HNO_3 . Suprapur® HNO_3 (E-Merck, Darmstadt, Germany) and quartz doubly distilled water were used to prepare 0.5 M HNO_3 . Multi-point standard-

ization was carried out using 0.5M HNO_3 as the lower standard and 0.05–1000 $\mu\text{g/mL}$ of the corresponding elemental standard as the higher standards for each line after proper peak search.

Methods

A series of Th solutions having a concentration range between 0.05 $\mu\text{g/mL}$ to 1000 $\mu\text{g/mL}$ were fed to the plasma. The contribution of Th in different analytical channels of the critical elements and the rare earths were monitored to understand the spectral interference of Th.

The analytical performance, i.e., detection limits, sensitivity, linear dynamic range, establishing the calibration curves of all the analytical lines of Th, critical elements and

TABLE I
Specifications and Operating Conditions of ICP-AES

Instrumental Specifications	
Optical design	Paschen-Runge mounting, Circular design
Focal length	750 mm
Grating	Holographic
Groove density	1800 grooves/mm (1), 3600 grooves/mm (2)
Wavelength range	130–800 nm
Entrance slit width	15 microns
Resolution (FWHM)	0.01 nm from 130–450 nm 0.02 nm from 450–800 nm
Thermal regulation	Controlled to $30 \pm 1^\circ\text{C}$
Frequency	27.12 MHz
Pump	Dual channel peristaltic pump
Detector	Linear arrays of CCD (3648 pixels/array)
Nebulizer	Concentric nebulizer with cyclonic spray chamber
ICP torch	Demountable, radial viewing
Operating Condition	
Coolant flow	6 L/min
Auxiliary flow	0.6 L/min
Total time of measurement	28 s
Pump speed	30 Rpm
RF power output	0.8 – 1.5 kW
Input power	230 V AC

rare earths, was studied. The sensitivity and detection limits of the above-mentioned analytical lines were evaluated using the slopes of the calibration curves and the concentration equivalent to the intensity equal to the average of the blank value + three times the standard deviation of the above measurements, i.e., $\bar{x} + 3\sigma$.

RESULTS AND DISCUSSION

Development of ICP-AES-based Methodology for the Determination of Th

Due to the line-rich emission characteristic of thorium, the study of the spectral interference of Th on rare earths and critical elements is necessary during trace metal characterization of the Th-based fuel and nuclear materials which is an integral part of chemical quality control. To study the spectral interference of thorium, it is required to determine Th simultaneously since the interference is highly dependent on the concentration of the interfering elements. Exploring the

superior analytical performance of the CCD-based detector system, an analytical method was developed for the determination of Th by ICP-AES. The study includes identification of the suitable analytical lines. The four analytical lines of Th identified for the present study are: 274.160 nm, 283.736 nm, 283.231 nm, and 401.913 nm. The calibration curves of those lines (Figure 1) and their analytical performance including sensitivity, detection limits, etc., were studied. The sensitivity and detection limits of the 283.231 nm and 283.736 nm analytical lines were found to be similar (sensitivity $\sim 35,000$ counts/ $\mu\text{g/mL}$ and detection limit ~ 0.001 $\mu\text{g/mL}$). The Th 401.913 nm line was found to have higher sensitivity and better detection limits ($\sim 64,000$ counts/ $\mu\text{g/mL}$ and 0.0009 $\mu\text{g/mL}$, respectively) among the four lines chosen in the present case. Synthetic samples having different Th concentrations (0.05 $\mu\text{g/mL}$ to 1000 $\mu\text{g/mL}$) were fed to the plasma, and these four analytical lines of Th were monitored, which revealed that

though all of these analytical lines can be used for the determination Th by ICP-AES, the Th 401.913 nm line is the best. The analytical results of the Th determination in synthetic samples are summarized in Table II. The MultiComponent Spectral Fitting (MSF) approach involving solutions of complicated mathematical equations were adopted by many researchers to address the solution of spectral interference problems in ICP-AES (29-32). But we believe our methodology in the simultaneous determination of Th along with the analytes is simple and not only useful in evaluating the correction factors due to the Th spectral interference, but also the fissile content in nuclear materials.

Spectral Interference of Th on Critical Elements

Since B, Cd, Ag, Eu, Gd, Dy, and Sm have stringent specification limits due to their large neutron absorption cross-section, a careful control of these constituents at each step of fuel fabrication is essential. Therefore it is required to study the spectral interference of Th on the analytical lines of those elements to avoid the overestimation of these elements, which is detrimental in qualifying the nuclear materials for the reactor. Table III summarizes the outcome of the spectral interference study of Th on the critical elements, while Table IV summarizes the analytical performance of those lines in the presence of the Th matrix.

Silver, Boron, and Cadmium

Silver (Ag)

Four different analytical lines of Ag (328.068 nm, 338.289 nm, 224.641 nm, and 243.779 nm) were chosen for the present purpose. The Ag 224.641 nm line was found to be highly interfered by Th, and the tolerance level of Th is below 0.05 $\mu\text{g/mL}$, whereas at the 50 $\mu\text{g/mL}$ tolerance level of Th, the

Fig. 1. Calibration curves for different analytical lines of thorium.

TABLE II
Determination of Th by ICP-AES Using Different Analytical Lines

Th (µg/mL)	Th 401.913 nm (µg/mL)	Th 283.730 nm (µg/mL)	Th 274.716 nm (µg/mL)	Th 283.231 nm
0.05	0.06	0.04	0.04	0.04
1	0.86	0.98	0.94	0.98
0.5	0.49	0.47	0.47	0.50
5	4.8	4.7	4.8	4.9
10	9.8	9.9	9.7	9.9
50	51.8	49.3	50.5	50.2
100	98.5	102.1	100.3	101.6
500	497.2	499.1	497.9	502.1
1000	1000.9	998.6	994.9	1001.3
D.L. (µg/mL)	0.0009	0.001	0.0028	0.0015
Sensitivity (counts/µg/mL)	64055	39423	16149	33832

TABLE III
Spectral Interference of Th on Critical Elements

Metal	Analytical Lines (nm)	Contribution From 1000 µg/mL of Th (µg/mL)	Correction Factor (µg/mL per µg/mL of Th)	Tolerance Level of Th (µg/mL)	Metal	Analytical Lines (nm)	Contribution From 1000 µg/mL of Th (µg/mL)	Correction Factor (µg/mL per µg/mL of Th)	Tolerance Level of Th (µg/mL)
Ag	328.068	3.37	3.37E-03	10	Dy	353.17	1.386	1.39E-03	50
	338.289	0.85	8.50E-04	50		394.468	0.739	7.39E-04	100
	224.641	7.93	7.93E-03	< 0.05		340.78	1.638	1.64E-03	50
	243.779	5.25	5.25E-03	0.1		353.602	1.153	1.15E-03	50
B	249.773	0.47	4.70E-04	100	Eu	364.54	0.572	5.72E-04	100
	249.677	0.51	5.10E-04	50		420.505	0.126	1.26E-04	500
	182.641	0.19	1.90E-04	100		381.967	BDL	-	1000
	208.959	0.16	1.60E-04	100		393.048	0.264	2.64E-04	500
	136.246	3.94	3.94E-03	2		390.71	0.228	2.28E-04	500
Cd	214.438	BDL	-	1000	Gd	342.247	1.159	1.16E-03	50
	226.502	0.09	9.00E-05	500		335.047	0.508	5.08E-04	100
	228.802	0.26	2.60E-04	100		336.223	5.226	5.23E-03	5
	361.051	196	1.96E-01	0.05		335.862	200	2.00E-01	0.5
Sm	359.26	1.99	1.99E-03	10					
	442.434	0.35	3.50E-04	100					
	428.079	10	1.00E-02	5					
	360.428	2.01	2.01E-03	10					

BDL : Below detection limit.

Ag 338.289 nm line is least interfered among the group. On the basis of the analytical performance, the Ag 328.068 nm and 338.289 nm lines were found to be better. Considering both facts, the 338.289 nm line of Ag is the best analytical line in the presence of Th.

Boron (B)

Five different analytical lines of B (249.773 nm, 249.667 nm, 182.641 nm, 208.959 nm, and 136.246 nm) were considered for the present purpose. The B 136.246 nm line showed maximum spectral interference and minimum tolerance level of Th (2 µg/mL), while the 249.773 nm, 182.641 nm, and 208.959 nm lines showed maximum tolerance

of Th (100 µg/mL). Considering both the spectral interference and the analytical performance, the 182.641 nm B line is the best analytical line in the presence of the Th matrix with a detection limit of 0.0025 µg/mL.

Cadmium (Cd)

Among the four chosen analytical lines of Cd of 214.438 nm, 226.502 nm, 228.802 nm, and 361.051 nm, practically no spectral interference of Th was observed on the 214.438 nm Cd line up to 1000 µg/mL of Th. Fortunately, for Cd, the best analytical line (214.438 nm) showed no spectral interference of Th; hence, it can be successfully used for the determination of Cd in the Th matrix, even without separation of Th.

Europium, Gadolinium, Samarium, and Dysprosium

Europium (Eu)

For Eu, four analytical lines (420.505 nm, 381.967 nm, 393.048 nm and 390.710 nm) were chosen for the investigation. No spectral interferences were seen for the 381.967 nm line of Eu up to 1000 µg/mL of Th with best analytical performance. Hence, the 381.967 nm Eu line can be used for its determination in 1000 µg/mL of Th matrix directly, even without any separation.

Gadolinium (Gd)

Though there is proximity in the position of the 335.047 nm and 335.862 nm lines of Gd, the former showed least spectral interference of Th with a tolerance level of 100 µg/mL of Th as well as the best analytical performance with a detection limit of 0.0011 µg/mL. However, the latter line is the most interfered line with the poorest analytical performance among the chosen analytical lines of Gd (342.247 nm, 335.047 nm, 335.862 nm, and 336.223 nm).

TABLE IV
Analytical Performance of
Specified Analytical Lines of Critical Elements

Elements	Analytical Lines (nm)	D.L. (µg/mL)	Sensitivity (counts/µg/mL)
Ag	224.641	0.18	624
	243.779	0.029	2286
	328.068	0.0006	145353
	338.289	0.0007	67516
B	136.246	0.109	333
	182.641	0.0025	12052
	208.959	0.0093	27298
	249.677	0.0098	10496
	249.773	0.0041	14490
Cd	214.438	0.0018	115513
	226.502	0.0014	127721
	228.802	0.0031	41729
	361.051	0.017	2579
Dy	340.78	0.004	38728
	353.17	0.0005	191940
	353.602	0.002	52369
	364.54	0.0017	65767
	394.468	0.001	51335
Eu	381.967	0.00003	444758
	390.71	0.0002	662917
	393.048	0.0014	226439
	420.505	0.0007	321797
Gd	335.047	0.0011	86618
	335.862	0.012	53425
	336.223	0.002	69432
	342.247	0.001	65218
Sm	359.26	0.001	39906
	360.428	0.001	15091
	428.079	0.0005	22564
	442.434	0.0049	36387

Samarium (Sm)

For Sm, the best line at 428.079 nm showed maximum spectral interference from Th, while the least interfered line of 442.434 nm showed poor analytical performance. Out of four chosen lines of Sm (359.260 nm, 442.434 nm, 428.079 nm, and 360.428 nm), the 359.260 nm line is the best option for Sm determination in the presence of the Th matrix. Appropriate correction factors as shown in Table III should be applied during estimation.

Dysprosium (Dy)

The tolerance level of Th for Dy at the 353.170 nm, 394.468 nm, 340.780 nm, 353.602 nm, and 364.540 nm analytical lines were found to be 50 µg/mL, 100 µg/mL, 50 µg/mL, 50 µg/mL, and 100 µg/mL, respectively. Higher sensitivity and better detection limits were observed for the 353.170 nm line of Dy (sensitivity = 191940 counts/µg/mL and D.L. = 0.0005 µg/mL). It can be concluded that the 394.468 nm Dy line is a better choice for Dy determination in a Th matrix after applying the suitable correction factors specified in Table III.

Spectral Interference of Th on Other Rare Earth Elements

All other rare earth elements not only dilute the fissile content of the fuel and associated nuclear materials, but are also important from the neutron economy point of view. Further, most of the rare earth elements have line-rich emission spectra; therefore, it was also of interest to study the spectral interference of Th on their determination. The spectral interference of Th on different analytical lines of rare earths is presented in Table V, whereas Table VI presents the analytical performance of these lines in the presence of Th matrix.

TABLE V
Spectral Interference of Th on Rare Earth Elements

Metal	Analytical Lines (nm)	Contribution From 1000 µg/mL of Th (µg/mL)	Correction Factor	Tolerance Level of Th (µg/mL)
Nd	401.225	0.65	6.50E-04	100
	430.358	0.26	2.60E-04	100
	406.109	0.19	1.90E-04	100
	417.731	2.96	2.96E-03	5
Er	337.271	1.88	1.88E-03	10
	349.91	2.23	2.23E-03	10
	326.478	0.49	4.90E-04	100
	323.058	0.42	4.20E-04	100
Ce	418.66	0.29	2.90E-04	50
	448.691	Large spectral interference	Rejected	< 0.05
	413.765	4.08	4.08E-03	5
	413.38	4.39	4.39E-03	5
Y	393.373	Large spectral interference	Rejected	< 0.05
	371.03	0.096	9.60E-05	100
	324.228	1.929	1.93E-03	10
	360.073	0.949	9.49E-04	10
	224.306	Large spectral interference	Rejected	< 0.05
	377.433	1.148	1.15E-03	10
	320.332	1.003	1.00E-03	10
	349.609	1.773	1.77E-03	10
Pr	362.871	0.345	3.45E-04	10
	442.259	1.424	1.42E-03	5
	411.846	4.746	4.75E-03	5
	417.939	Large spectral interference	Rejected	< 0.05
Lu	422.535	0.465	4.65E-04	50
	414.311	4.632	4.63E-03	5
	261.542	BDL	-	1000
	291.139	1.924	1.92E-03	10
Yb	307.76	0.434	4.34E-04	500
	219.554	0.169	1.69E-04	500
	328.937	BDL	-	1000
	369.419	0.353	3.53E-04	100
La	222.446	0.402	4.02E-04	100
	289.138	0.778	7.78E-04	50
	408.672	Large spectral interference	Rejected	< 0.05
	333.749	4.055	4.06E-03	10
	379.478	0.904	9.04E-04	50

BDL: Below detection limit; Correction factor = (µg/mL per µg/mL of Th).

TABLE VI
Analytical Performances of Different Analytical Lines
of Rare Earth Elements

Elements	Analytical Line (nm)	D.L. (µg/mL)	Sensitivity (counts/µg/mL)
Ce	393.373	0.17	97131
	413.38	0.006	11397
	413.765	0.009	13022
	418.66	0.01	12577
	448.691	0.06	10610
Er	323.058	0.001	2656
	326.478	0.0003	8980
	337.271	0.0007	17204
	349.91	0.0016	8987
La	333.749	0.0028	9852
	379.478	0.002	12197
	408.672	0.0003	9633
Lu	219.554	0.005	4034
	261.542	0.0003	3592
	291.139	0.0009	4234
	307.76	0.0005	7373
Nd	401.225	0.002	8206
	406.109	0.0036	8543
	417.731	0.018	14769
	430.358	0.009	10510
Pr	411.846	0.009	10912
	414.311	0.0055	11662
	417.939	0.009	12682
	422.535	0.003	12779
Y	224.306	0.033	4955
	320.332	0.0014	10494
	324.228	0.0003	6628
	349.609	0.002	9076
	360.073	0.0001	6949
	362.871	0.002	6337
	371.03	0.00008	9964
	377.433	0.0001	11297
Yb	442.259	0.027	11457
	222.446	0.0045	3743
	298.138	0.0006	3696
	328.937	0.00005	9328
	369.419	0.0001	8914

Neodymium, Erbium, Cerium and Yttrium

Neodymium (Nd)

Spectral interference of Th on the 401.225 nm, 430.358 nm, 406.109 nm and 417.731 nm Nd lines revealed that though the tolerance limit of Th is 100 µg/mL for the first three analytical lines, the 406.109 nm line showed the least contribution from Th (i.e., least spectral interference). The analytical performance of the 401.225 nm line is the best among the specified lines, followed by 406.109 nm. Therefore, the 406.109 nm line for Nd can be chosen for trace determination of Nd in a Th matrix, while the Nd 417.731 nm line is most interfered having the poorest analytical performance.

Erbium (Er) and Yttrium (Y)

Four analytical lines for Er (337.271 nm, 349.910 nm, 326.478 nm and 323.058 nm) and nine lines for Y (371.030 nm, 324.228 nm, 360.073 nm, 224.306 nm, 377.433 nm, 320.332 nm, 349.609 nm, 362.871 nm, and 442.259 nm) were chosen for the present study. For both analytes, the best performing analytical line of Er at 326.478 nm and Y at 371.030 nm was found to show least spectral interference. Both the above-mentioned lines of Er and Y showed 100 µg/mL of Th tolerance, while the detection limits were found to be 0.0003 µg/mL and 0.00008 µg/mL, respectively.

Cerium (Ce)

The 393.373 nm and 448.691 nm analytical lines of Ce showed high spectral interference from Th. Due to the numerous spectral interferences, these lines could not be used for trace determination of Ce in a Th matrix and hence, were rejected. The tolerance level of Th is 50 µg/mL for the 418.66 nm Ce line and 5 µg/mL for the 413.765 nm and 413.380 nm Ce lines; the latter two lines have slightly better detection limits (0.009 µg/mL) than the former line (0.01 µg/mL). We

believe that the 418.660 nm Ce line might be the best choice of analytical line in the presence of Th.

Praseodymium, Lutetium, Lanthanum, and Ytterbium

Praseodymium (Pr)

Out of the four chosen analytical lines of Pr (411.846 nm, 417.939 nm, 422.535 nm and 414.311 nm), the 417.939 nm line showed drastic spectral contribution from the Th spectra and can be rejected, while the best performing analytical line, i.e., Pr at 422.535 nm, showed the lowest Th interference with a tolerance limit of 50 µg/mL of Th.

Lutetium (Lu) and Ytterbium (Yb)

The 261.542 nm analytical line was found to be the best analytical line of Lu among the group of analytical lines studied in the present case (261.542 nm, 291.139 nm, 307.760 nm, and 219.554 nm) and is free of spectral interference from thorium. Similarly for Yb, the best performing analytical line of 328.937 nm was found to be free of spectral interference from Th among its four analytical lines of 328.937 nm, 369.419 nm, 222.446 nm, and 289.138 nm under present investigation.

Lanthanum (La)

For La, unfortunately the best analytical line of 408.672 nm is highly interfered by Th; hence, this line is not recommended for the determination of La in a Th matrix. Between the other two analytical lines of La (i.e., 333.749 nm and 379.478 nm) which were investigated, the 379.478 nm line showed a higher tolerance of Th (up to 50 µg/mL), while both of the lines have similar detection limits (~ 0.002 µg/mL). Therefore, the 379.478 nm La line should be the choice for trace determination of La in a Th matrix.

Determination of Cd, Eu, Lu, and Yb in Thorium Matrix Without Separation

Due to the emission-rich spectra of U, Pu, Am, Zr, etc., the methodology proposed for the determination of trace elements in nuclear materials involves the quantitative separation of the major matrix without loss of impurities even at the trace level, followed by feeding of the raffinate to the plasma for trace analysis. The above spectral interference study revealed that there was no spectral interference of Th on the Cd 214.438 nm, Eu 381.967 nm, Lu 261.542 nm, and Yb 328.937 nm lines. This suggests the possibility of direct determination of Cd, Eu, Lu, and Yb in a thorium matrix without separation. Three synthetic samples were prepared as follows:

1. S-1 = 0.1 µg/mL of Eu, Yb, Cd, and Lu in 1000 µg/mL of Th
2. S-2 = 1 µg/mL of Eu, Yb, Cd, and Lu in 1000 µg/mL of Th
3. S-3 = 10 µg/mL of Eu, Yb, Cd, and Lu in 1000 µg/mL of Th

These synthetic samples were analyzed directly by ICP-AES without chemical separation. It was observed that Eu, Cd, Lu, and Yb can be determined up to 0.1 µg/mL with a RSD of less than 2%. The analytical results were compared with the routinely employed method, i.e., quantitative extraction of thorium by CYANEX-923, followed by analysis of the raffinate for trace analytes (33). This proposed method for the direct determination of the analytes compared well with routinely employed methods (Table VII). Since chemical separation is not required for the newly adopted method, the chances of contamination or loss of analytes are minimized. The overall recovery and precision were also found to be better using the present method.

TABLE VII
Direct determination of Cd, Eu, Lu, and Yb in Thorium Matrix

Synthetic Sample	Element	Analytical Line (nm)	Actual Conc. (µg/mL)	Estimated Conc. Present Method	(%) Recovery	Estimated Conc. After Chemical Separation	(%) Recovery
S-1	Eu	381.967	0.1	0.096	96	0.089	89
	Cd	214.438	0.1	0.098	98	0.091	91
	Yb	328.937	0.1	0.11	110	0.09	90
	Lu	261.542	0.1	0.1	100	0.093	93
S-2	Eu	381.967	1	1.1	110	0.9	90
	Cd	214.438	1	1	100	0.87	87
	Yb	328.937	1	0.99	99	0.92	92
	Lu	261.542	1	1	100	0.93	93
S-3	Eu	381.967	10	9.9	99	9.1	91
	Cd	214.438	10	10	100	8.5	85
	Yb	328.937	10	11	110	9.2	92
	Lu	261.542	10	9.7	97	9.1	91

Determination of Other Analytes in a Th Matrix Without Separation After Incorporating Appropriate Correction Factors

In a similar fashion as above, synthetic samples were prepared and fed to the plasma for the determination of the analytes. The Ag 338.289 nm, B 182.641 nm, Gd 335.047 nm, Dy 394.468 nm, Sm 359.260 nm, Nd 406.109 nm, Er 326.478 nm, Y 371.030 nm, Pr 422.535 nm, Ce 418.660 nm, and La 379.478 nm lines were used for this purpose. It was observed that all of these analytes can be determined even at 1 µg/mL in the presence of a Th matrix (1000 µg/mL) without chemical separation, and after applying appropriate correction factors as calculated above. Table VIII summarizes the analytical results of the synthetic samples.

CONCLUSION

A systematic study on the spectral interference of thorium on rare earths and critical elements was carried out. Several analytical lines of the elements were identified for this purpose. The study included identification of the relatively interference-free analytical line, evaluation of the correction factors wherever necessary, and the tolerance level of thorium on the analytical lines. The analytical performance of these analytical lines were studied in detail. The analytical lines that are somewhat free from Th spectral interference can be chosen for the determination of analytes without error. Hence, the analytical methodology becomes simpler and much more reliable. Since the metallurgical properties of the Th-based fuel depends on the presence of impurities even at trace levels, using interference-free lines will give the correct estimates of these analytes which in turn decides whether the quality of Th is of nuclear grade or not. The

TABLE VIII
Direct Determination of Other Analytes in Thorium Matrix
After Incorporating Appropriate Correction Factors

Element	Analytical Line (nm)	S-4		S-5	
		Actual Conc. (µg/mL)	Amount Estimated (µg/mL)	Actual Conc. (µg/mL)	Amount Estimated (µg/mL)
Ag	338.289	1	1.1	10	9.6
B	182.641	1	0.97	10	10.5
Gd	335.047	1	1	10	10.3
Dy	394.468	1	1	10	10
Sm	359.26	1	1.2	10	9.9
Nd	406.109	1	0.99	10	9.8
Er	326.478	1	0.99	10	10
Y	371.03	1	0.97	10	10.1
Pr	422.535	1	0.98	10	10.1
Ce	418.66	1	1.1	10	9.8
La	379.478	1	1	10	9.9

study revealed that Ag at 338.289 nm, B at 182.641 nm, Gd at 335.047 nm, Dy at 394.468 nm, Sm at 359.260 nm, Nd at 406.109 nm, Er at 326.478 nm, Y at 371.030 nm, Pr at 422.535 nm, Ce at 418.660 nm, and La at 379.478 nm are suitable analytical lines for the determination of these analytes in the presence of a Th matrix. It was also noted that the analytical lines of Cd at 214.438 nm, Eu at 381.967 nm, Lu at 261.542 nm, and Yb at 328.937 nm were free from any spectral interference of thorium even at 1000 µg/mL of Th. Since the spectral interference largely depends on the amount of thorium concentration, an ICP-AES-based method was developed for the simultaneous determination Th. Of the four Th analytical lines identified, the 401.913 nm Th line showed the best analytical performance.

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