Application of High-Resolution ICP Atomic Emission Spectrometer for Characterization of Radioactive Samples

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INTRODUCTION

Uranium gained importance with the development of power programs based on nuclear energy. It is an important element in the atomic energy program and used as fuel in nuclear reactors for electricity generation. Uranium is the heaviest naturally occurring element on earth with an atomic number of 92 and well known for its chemical and radiotoxicity. It is a naturally radioactive element; atoms of uranium are unstable and decay by emitting particles and energy. However, uranium decays very slowly by emitting an alpha particle (1). Uranium in different forms and in combination with thorium/plutonium is used as nuclear fuel. From nuclear fuel to reprocessing and disposal, uranium undergoes several transformations within the nuclear fuel cycle, including concentration, purification, isotope enrichment, metallurgical processing, and recovery of precious elements such as Pu (2). Uranium has a line-rich emission spectrum and is expected to interfere during the determination of analytes at the trace levels due to its multi-electronic nature. Spectral interference caused by the line-rich spectrum of actinides, especially uranium, is a well known problem in the determination of trace-metal impurities and rare earths (REEs) in nuclear fuels using atomic emission spectrometric methods. Therefore, it is required to separate the major matrix (i.e., uranium) from the ana-

ABSTRACT

A method was developed for the determination of critically important rare earth elements (Sm, Eu, Gd, and Dy) at the ppm level in nuclear-grade uranium samples without separation from the major matrix using high-resolution ICP-AES. For this purpose, a commercially available high-resolution ICP sequential spectrometer was used, modified in our laboratory to enable analysis of radiotoxic samples within an alpha containment facility. The elemental lines identified as free from uranium interference for the analytes were Sm at 332.12 nm, Eu at 420.51 nm, Gd at 379.64 nm, and Dy at 353.17 nm. The studies carried out revealed that 0.05 µg/mL of each of the analytes can be determined without any significant interference in the presence of 400 µg/mL of uranium. In another experiment, it was demonstrated that these four rare earth analytes could also be determined at 50 µg/mL each in the presence of 400 µg/mL americium. The detection limits were calculated as the concentrations corresponding to signals equal to the blank signal plus three times its standard deviation. The repetitive analyses showed that the precision was better than 2% RSD. The method has high potential for the assay of trace amounts of rare earths in uranium and americium samples.

lytes without loss of the analytes even at trace levels. Though physical separation methods can be used, such as the d.c. arc carrier distillation technique, they may increase the chance of contamination during handling and require

appreciable time for the analysis of the samples. The relative standard deviation of the d.c. arc carrier distillation technique is poor, about 15–20%. Hence, it necessitates having an ICP-AES-based methodology for the direct determination of trace level rare earth constituents, without using any separation method. Secondly, the determination of impurities in uranium at various stages of the nuclear fuel cycle is important for quality control and achievement of chemical and metallurgical requirements (3). The increased concentration of metallic impurities may alter the metallurgical characteristics of the fuel; for instance, the transition temperature between the different uranium metal phases (4). Therefore, the concentration of the metallic impurities in the fuel must be below the maximum permissible levels specified to obtain the required density for the pellets. The impurities, metallic and nonmetallic, which are incorporated with the fuel during various fuel fabrication procedures, have to be under specified limits for safe and efficient operation of the reactors (5, 6). These materials have to undergo stringent quality control before they can be used in the power generation as fuels. Uranium- and plutonium-based nuclear fuels are required to conform to stringent specifications with regard to the trace metallic constituents, even at sub-ppm levels. Since they have an important bearing on the fuel performance, in particular B, Cd, and Gd, they have a very high neutron absorption cross-section in the quality control of nuclear materials such as uranium samples, which in turn, can affect neutron economy of the reactor fuel (7-8).

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No single technique appears to be ideally suited to estimate all of the metallic and rare earths present as impurities. A number of analytical protocols have been used for the elemental characterization of fuels, depending upon the target analytes and concentration range of impurities, required precision, sample preparation, and time of analysis. These methods include inductively coupled plasma mass spectrometry (ICP-MS), X-ray fluorescence spectrometry (XRF), instrumental neutron activation analysis (INAA), inductively coupled plasma atomic emission spectrometry (ICP-AES), d.c. arc carrier distillation atomic emission spectrometry (d.c. arc-AES), graphite furnace atomic absorption spectrometry (GF-AAS), and recently high performance chromatography inductively coupled plasma mass spectrometry (HPLC-ICP-MS) (9-11). Among these techniques, AES is widely accepted due to its capability for multi-element analysis with reasonable precision, accuracy, and compatibility for radiotoxic elements. Inductively coupled plasma atomic emission spectrometry measurement is one of the powerful analytical methods. Therefore, among the spectroscopic methods which are routinely employed for trace metal characterization of nuclear fuels, ICP-AES is most established and preferred due to being a powerful multi-element analytical technique. In view of its rapidity, high sensitivity, good precision, large linear dynamic range, relative freedom from matrix effects, it provides reasonable detection limits for the simultaneous determination of common as well as rare earth impurities in a uranium/plutonium matrix. However, the trace metal characterization of uranium/plutonium by ICP-AES requires quantitative separation of the matrix as a pre-requisite because of the severe spectral interference caused by the line-rich

spectrum of the actinides, which have multi-electron configurations, and the inability of the optical instrument to resolve the same as discussed above. The extent of spectral interferences encountered during the analysis depends on the resolution of the spectrometer. A typical ICP-AES spectrometer, having practical resolution of the order of 0.03 nm, is known to tolerate 5–10 µg/mL residual U/Pu/Am/Th during the determination of the analytes at sub-ppm levels. On the other hand, a high-resolution spectrometer, with a practical resolution of 0.005 nm, offers higher tolerance for residual amounts of the actinides (12,13). Therefore, with the acquisition of a high-resolution ICP sequential spectrometer and its subsequent adaptation for the determination of radiotoxic elements in a glove box environment, feasibility studies have been carried out to examine the tolerance limits in the presence of the matrix for rare earth determination.

Murthy et al. (14) described an ICP-AES method for the determination of five rare earth elements (Ce, Sm, Eu, Gd, and Dy) separated from 10 g of uranium by means of cellulose column extraction. They studied the effect of trace amounts of uranium, iron, calcium, and aluminum on the rare earths and reported recoveries in the range of 96 to 102%. Seshagiri et al. (15) reported the determination of Dy, Eu, Gd, Sm, and Th in uranium by ICP-AES after their separation by solvent extraction from hydrochloric acid medium, with a 20% trioctylamine solution in xylene. These authors revealed that their method could be used for the determination of Dy and Eu down to 0.20 µg/mL, Gd to 0.05 µg/mL, Sm to 0.1 µg/mL, and Th to 0.20 µg/mL. More recently, Bose Roopa (16) reported the ICP-AES determination of rare earths and yttrium in uranium-, thorium-, and zirconium-

rich matrices after solvent extraction separation. The report further mentioned that an antipyretic agent, 1-phenyl 2, 3-dimethyl-5-pyrazolone (antipyrine), was used for the efficient, rapid, and single-stage extraction of thorium and uranium present in milligram levels and allowed the estimation of individual rare earths at µg levels by ICP-AES. In the present work, the studies aimed at the determination of rare earths in the presence of a uranium matrix. Therefore, Sm, Eu, Gd, and Dy were determined without separating from uranium using high-resolution inductively coupled plasma atomic emission spectrometry (HR-ICP-AES).

EXPERIMENTAL

Instrumentation

A Jobin Yvon Ultima (France) high-resolution sequential ICP atomic emission spectrometer with radial viewing configuration was used for this study. By virtue of having a holographic grating with 3600 grooves/mm and 4320 grooves/mm rulings, the spectrometer provides a practical resolution of <0.005 nm and a continuous coverage of the widest spectral range of 200–800 nm. This is ideally suited for the determination of rare earths in uranium (17). The argon plasma source is powered with a solid state 40.68 MHz R.F. generator system that offers frequency stabilization, automatic initiation of inductively coupled plasma, and reflected power regulation. Any small variation in plasma impedance is overcome by its auto-tuning. The R.F. generator is located inside the bench cabinet forming a single entity. The generator is fully isolated against R.F. leakage and electromagnetic interference. It has a self-closed loop cooling water system for the R.F. coil. The composite light emission from the plasma source is focused onto the slit of the concave grating spectrometer with a Czerny-Turner

mounting, which disperses light into individual wavelength. A photomultiplier tube measures the intensity of the light emerging from the exit slit. In order to extend the wavelength coverage below 200 nm, the optical path between plasma and spectrometer is provided with a gas flushing arrangement, while the spectrometer needs to be operated in a nitrogen-filled environment. The spectrometer unit and plasma source are computer-controlled and the system can be programmed to monitor the individual analytical wavelengths sequentially.

Glove Box Adaption of the HR-ICP-AES

The commercially available ICP emission spectrometers cannot be readily employed for the analysis of radioactive-based nuclear fuel samples due to their inadaptability to handle radiotoxic materials as stated earlier. The analysis of radioactive samples necessarily requires extensive modifications in the otherwise custom-built experimental facilities available commercially. Such modifications have to be carried out without affecting the basic performance features in any way. The basic instrumental facility to analyze radiotoxic samples incorporated ICP torch assembly, peristaltic pump, and other sample handling accessories within the glove box. For an optical spectrometer coupled to a very sensitive analytical technique such as ICP-AES, it is an involved affair and needs maximum care. The high-resolution ICP sequential spectrometer was modified extensively to enable analysis of the radiotoxic samples within an alpha containment glove box facility. The glove box adaptation of the spectrometer assembly involved detachment of the plasma housing from the main unit and relocating the same inside a specially designed glove box with all the service points such as gas inlet, water cooling, and electrical connections re-

installed. A heat exchanger was installed inside the glove box for the efficient removal of excess heat generated due to running of the plasma. The glove box has a circular quartz window fitted in an aperture on one side for transmitting the plasma radiation to the spectrometer, while on the other side the box is connected to a standard-sized single module glove box to facilitate chemical work pertaining to sample preparation, dilution, etc. The glove box assembly has been checked for leak tightness and was connected to a suction point to maintain the required negative pressure. A schematic diagram of the glove box with the spectrometer has been provided in earlier papers (18,19). The specifications and operating condition of the instrument and the plasma source are given in Tables I and II, respectively.

Preparation of Working Standards and Synthetic Samples

Quartz ware was used for preparing the working standards and samples. All equipment, such as flasks, beakers, glass rods, etc., were thoroughly cleaned with 4M HNO₃, followed by washing with quartz double-distilled (Q.D.D.) water. Suprapur® HNO₃ (E. Merck, Darmstadt, Germany) and Q.D.D. water were used for appropriate dilutions, and final solutions to be fed into the ICP were maintained at 0.5 M acid. Uranium oxide (U₃O₈) was dissolved in 0.5 M HNO₃ to prepare a high concentration master standard. Individual stock solutions for four rare earths (Sm, Eu, Gd, and Dy) were prepared at the 1 mg/mL concentration level. Then, a series of rare earth solutions was prepared in the concentration range of 0–10 µg/mL with a fixed uranium concentration of 400 µg/mL. In addition, a set of standards was prepared containing 0.05–10 µg/mL of Sm, Eu, Gd, and Dy in the presence of Am at 400

µg/mL concentration. A synthetic sample of rare earths at 0.05 µg/mL concentration in the presence of 50 µg/mL Am was also prepared. To check the effect of Am on rare earths, a matrix blank with Am at the same level as that in the sample was prepared. Optimization of the ICP-AES experimental parameters was carried out to obtain maximum analyte signals. Initially, a two-point standardization for rare earth determination was carried out using a reagent blank and 10 µg/mL of rare earths alone as the low and high standard, respectively. The rare earth solutions in the range 0–1 µg/mL with and without 400 µg/mL uranium were then analyzed and the results recorded in both absolute intensity and the concentration modes. Using the working curve obtained for each of the four rare earths, the concentration of rare earths in a set of samples was determined to study the linearity of the analytical response. In a similar manner, experiments were carried out for the determination of rare earths in an Am sample.

RESULTS AND DISCUSSION

Peak Search and Profile of Spectral Lines

A detailed spectral scan of rare earth and uranium lines ranging from 250–500 nm was carried out by aspirating rare earth and uranium solutions into the plasma. The instrumental parameters such as forward power, flow rate of the argon gas, and signal integration time were optimized for positioning the analytical lines with appropriate sensitivity on the photomultiplier tube to obtain the optimum signal-to-noise ratio. As mentioned earlier, uranium/ameridium have multi-electron configurations and severe spectral interference caused by the line-rich spectrum. This necessitated a chemical separation method or a high-resolution sequential spectrometer to resolve

TABLE I
Instrumental and Operating Parameters for the ULTIMA HR-ICP-AES

Optical design	1.0 M Czerny Turner
Grating	Holographic, ion-etched original grating
Groove density	4320 gr/mm and 2400 gr/mm
Grating size	110 x 110 mm
Spectral range	160 to 800 nm
Resolution	0.005 nm in the first order
R.F. Generator	
Operating Frequency	40.68±0.02 MHz
Design	Solid State, Crystal Control
r.f. power	Computer Controlled
Load coil	Three-turn copper tubing (1/8 in o.d.)
Automation	Computer-programmable r.f.power and shutdown of plasma
Safety Interlocks	Argon, water, plasma compartment door, reflected power and exhaust
Sample Introduction	
Torch design	Completely de-mountable, quick-changed kits
Plasma geometry	Single view, radial observation
Plasma viewing height	Simultaneous radial observation of entire Normal Analytical Zone
Patented sheath gas	Computer-controlled, sheath flow of argon around aerosol prior to 3 mm injector tube; optimizes residence time for group I & II elements and allows for analysis of high dissolved solid samples
Pump	Dual channel (nebulizer, drain) 12 roller computer-controlled
Nebulizer	Pneumatic concentric
Spray chamber	Glass
Detectors	Two patented high dynamic range detectors
Instrument control	Spectralink which contains microprocessors
Observation zone	16 mm above top induction coil
Software	V5 for Windows® 95 and Image Navigator for spectrum acquisition and semi-quantitative analysis

TABLE II
ULTIMA HR-ICP-AES Operating Condition for the Determination of REEs

Argon gas:	Plasma gas flow	12 L/min
	Cooling gas flow	0.2 L/min
	Nebulizer pressure	3 bar
	Nebulizer flow	0.85 L/min
Pressure of the manometer		6 bar
R.F. power	Continuously adjustable from 800–1550 kW in the plasma	

the analytical spectral lines. In our studies, an HR-ICP-AES-based methodology for the direct determination of rare earth (Sm, Eu, Gd, Dy) constituents was developed without any separation. The rare earth-containing uranium solutions were fed into the plasma and interference-free spectral lines were identified. In the beginning, the analytical lines of the rare earths were examined using individual stock solution for any background analytical intensity recorded with each of them. Based on these data, four analytical lines (Sm-332.12 nm, Eu- 420.51 nm, Gd- 379.64 nm, and Dy-353.17 nm) were chosen for further studies. These four spectral lines were found to be suitable with sufficient separation, high intensity, and interference-free in nature. For U and Am, good spectrally separated and sufficiently intense lines were identified. The analytical lines at 424.437 nm and 283.236 nm were chosen for U and Am, respectively.

Rare Earth Determination in Presence of Uranium

It was of interest to examine the highest amount of uranium that would still enable determination of the rare earths. Optimization of the experimental ICP-AES parameters was carried out with a 10-µg/mL concentration of rare earth elements to obtain the maximum analyte signal. Subsequently, high purity uranium solutions in 0.5 M nitric acid in the concentration range 0–1000 µg/mL were fed to the ICP and a total of eight analytical lines were examined for any background analytical intensity recorded at each one of them. The analytical lines monitored were Sm 332.12 and 442.44 nm, Eu-393.12 and 420.51 nm, Gd-335.05 and 379.64 nm, and Dy-353.17 and 364.54 nm. From these studies, four interference-free analytical lines (Sm-332.12 nm, Eu-420.51 nm, Gd-379.64 nm, and Dy-353.17 nm)

were chosen for further studies. Two-point standardization for rare earth determination was carried out using a reagent blank and 10 $\mu\text{g/mL}$ of rare earths alone as the low and high standard, respectively. The rare earth solutions in the range 0–1 $\mu\text{g/mL}$, with and without 400 $\mu\text{g/mL}$ uranium, were then analyzed using the working curve obtained for each of the four rare earths.

Figure 1 shows the profile of the spectral lines of the rare earths with and without a uranium matrix. The analysis of uranium-containing rare earth solutions in the concentration range of 0.05–1.0 $\mu\text{g/mL}$ showed very good results. The blank subtracted estimates agree closely with the added concentrations. The upper limit of 400 $\mu\text{g/mL}$ of U solution for the determination of rare earths at 0.05 $\mu\text{g/mL}$ is of special significance as it has shown greater tolerance for the presence of the matrix. Therefore, the stringent requirement of quantitative separation of the matrix for ICP-AES determination of rare earths can be reduced significantly.

Figure 2 shows the calibration curves for the determination of rare earths, Sm at 332.12 nm, Eu at 420.51 nm, Gd at 379.64 nm, and Dy at 353.17 nm. The detection limit obtained is based on the concentration corresponding to the signal obtained for the blank plus three times the standard deviation in the determination of the signal for the blank, while the sensitivity is defined as the slope of the analytical working curve. The precision of the determination is based on 10 replicate analyses of the sample. The precision obtained for the repetitive analyses was <2% RSD. The near constant contribution due to 400 $\mu\text{g/mL}$ of the uranium blank showed that the signal is due to the non-specific signal for uranium per se. Table III lists the data obtained for the four rare earths with and

Fig. 1. Profiles for Sm at 332.12 nm, Eu at 420.51 nm, Gd at 379.64 nm, and Dy at 353.17 nm spectral lines with uranium and without uranium matrix.

Fig 2. Calibration curves for the determination of Sm, Eu, Gd, and Dy.

without uranium. The RSD values of the rare earths were compared with values available in the literature (10, 20–22), which have shown variations from 3–10 %.

Analysis of Uranium Solution

Several spectrometric methods were developed for the determination of trace amounts of uranium in a different matrix. The need for sensitive and reliable analytical methods to detect low-level concentrations of uranium is important

TABLE III
Rare Earth Determination With and Without Uranium

Amount added ($\mu\text{g/mL}$)	REEs Determined ($\mu\text{g/mL}$)							
	Dy		Eu		Gd		Sm	
	with U*	w/o U	with U*	w/o U	with U*	w/o U	with U*	w/o U
0.05	0.05	0.04	0.05	0.04	0.03	0.04	0.04	0.04
0.1	0.09	0.1	0.09	0.1	0.07	0.1	0.08	0.1
0.5	0.48	0.48	0.48	0.5	0.46	0.49	0.43	0.5
1.0	0.99	0.98	1.01	1.03	0.97	0.99	0.97	1.02
Values from Literature		(% RSD)				References		
Sm, Em, Gd, Dy		3–10%				(10, 20, 21, 22)		
Sm, Em, Gd, Dy		about 2%				Present work		

*Blank-subtracted values.

for various areas such as in environmental, biological and radioactive waste samples (23). An analytical spectrum for uranium was studied using 10 $\mu\text{g/mL}$ uranium solution. Based on the recordings, the background-free and mutually interference-free line at 424.437 nm was identified as the analytical line. The profile of the spectral line is shown in the Figure 3. The reagent blank and the well-characterized uranium standard with 10 $\mu\text{g/mL}$ concentration were used for two-point standardization. Using the calibration curve, determination of the uranium concentration in a set of uranium samples was carried out.

The concentration of uranium was kept constant at 400 $\mu\text{g/mL}$ in both the standard and the sample. ICP-AES measurements were made in peak intensity mode. The uranium concentrations were determined after obtaining the respective calibration plots for uranium. Uranium was determined up to 399 ± 2 $\mu\text{g/mL}$ concentration in 0.5 M HNO_3 solution. The precision of the determination at the lowest detection limit was better than 2% RSD.

Rare Earth Determination in Presence of Americium

The determination of rare earths in a power reactor-grade Pu containing approximately 0.3 to 0.8% Am was not feasible with the ICP spectrometer in our laboratory with a grating of 2400 rulings/mm. This is due to the fact that the chemical separation of the matrix only separates Pu, leaving behind Am with the rare earths. Therefore, attempts were made to utilize a the high-resolution ICP spectrometer with a grating of 4320 rulings/mm by spectrally isolating the rare earth emission lines from the Am lines, thereby reducing the interference of the Am line on the determination of the rare earths. An earlier experience reported on the determination of rare earths at 0.05 $\mu\text{g/mL}$ in the presence of 400 $\mu\text{g/mL}$ of uranium using this spectrometer came in handy when planning the experiment with Am where the interference-free spectral line of Am was identified as 283.236 nm (24). The profile of the Am spectral line is shown in Figure 4. A two-point standardization for the rare earth determination was carried out using a reagent blank and 10 $\mu\text{g/mL}$ of rare earths alone as the low and high standard, respectively. The rare earth solutions of 0.05 $\mu\text{g/mL}$, with and without the presence of

Fig. 3. Profile of uranium spectral line.

Fig. 4. Emission profile of the 283.236 nm spectral line of americium.

50 µg/mL Am, were analyzed using the working curve obtained for each of the four rare earths. No significant interference was observed due to the presence of Am up to 50 µg/mL on the determination of the four rare earths at 0.05 µg/mL. A matrix blank of 50 µg/mL of Am was monitored for its contribution at the analytical channels. It was found that the four rare earths were determined at the 0.05 µg/mL level in the presence of 50 µg/mL Am, with a precision better than 2% RSD.

In short, a method has been developed for the determination of critically important rare earths in uranium/ameridium without requiring any physical/chemical separation from the major matrix using a commercially available high-resolution ICP-AES sequential spectrometer.

CONCLUSION

The present method was successfully employed for the determination of Sm, Eu, Gd, and Dy of radioactive samples. A glove box-adapted high-resolution ICP sequential spectrometer was fruitfully utilized. Initially, the interference-free analytical lines of Sm at 332.12 nm, Eu at 420.51 nm, Gd at 379.64 nm, and Dy at 353.17 nm were identified. All of these analytical lines were used for the determination of the rare earths with and without uranium using a working curve for each of the elements. The method was found to be satisfactory. The precision of method was nearly 2% RSD. The studies carried out offered the following advantages:

(a) The rare earth elements of Dy, Eu, Gd, and Sm were quantitatively determined at 0.05 µg/mL each in the presence of 400 µg/mL uranium matrix.

(b) The rare earth elements of Dy, Eu, Gd, and Sm were quantita-

tively determined at 50 µg/L each in the presence of 400 µg/mL of americium.

(c) The determination of uranium was carried out using the 424.437 nm line.

(d) An interference-free Am spectral line at 283.236 nm was identified.

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REFERENCES

- H. S. Dang, V. R. Vullat, and R. C. Sharma, *Health Phys.* 68, 328 (1995).
- D. Prat, R. Compano, M. Granados and E. Miralles, *J. Chromatogr. A* 746, 239 (1996).
- J. Wang, X. J. Liu, and C. P. Wang, *J. Nucl. Mater.* 374 (1), 79 (2008).
- S. K. Gupta, S. K. Thulasidas, P.J. Purohit, Goyal Neelam, and S.V. Godbole, *At. Spectrosc.* 35(1), 43 (2014).
- Hansjoachim Matzke, *J. Chem. Soc. Faraday Trans.* 86(8), 1243 (1990).
- K.C. Radford and J.M. Pope, *J. Nucl. Mater.* 116, 305 (1983).
- Mary Gopalkrishnan, K. Radhakrishnan, P.S. Dhami, V.T. Kulkarni, M.V. Joshi, A.B. Patwardhan, A. Ramanujam, and J.N. Mathur, *Talanta* 44, 169 (1997).
- Alexandre Luiz de Souza, Marycel Elena Barboza Cotrim, and Maria Aparecida Faustino Pires, *Microchem. J.* 106, 194 (2013).
- G.V. Ramanaiah, *Talanta* 46, 533 (1998).
- R.K. Malhotra and K. Satyanarayana, *Talanta* 50, 601 (1999).
- Kazunori Shinotsuka and Mitsuru Ebihara, *Anal. Chim. Acta* 338, 237 (1997).
- Anna Szymczycha-Madeja, *Arabian J. Chem.* (2014), DOI: 10.1016/j.arabjc.2014.05.031
- Parviz N. Soltanpour, Greg W. Johnson, Stephen M. Workman, J. Benton Jones, Jr., and Robert O. Miller, *Adv. in Agron.* 64, 27 (1998).
- P. S. Murty and Ramon M. Barnes, *J. Anal. At. Spectrom.* 1, 145 (1986).
- T. K. Seshagiri, Y. Babu, M. L. Jayanth Kumar, A.G.I. Dalvi, M.D. Sastry, and B.D. Joshi, *Talanta* 31, 773 (1984).
- Roopa Bose, National Conference on Science Technology and Applications of Rare Earths, (Munnar, India, 19-20 August 2011).
- S.K. Thulasidas, Mithlesh Kumar, B.A. Dhawale, B. Rajeswari, and A.G. Page, DAE-BRNS Nuclear and Radiochemistry Symposium, Mumbai, India, NUCAR-2003, (February 10, 2003), Page 361.
- S.K. Thulasidas, Mithlesh Kumar, B.A. Dhawale, B. Rajeswari, and V. Natarajan, *At. Spectrosc.* 35(2) (2014) 147-153.
- S. K. Thulasidas, Mithlesh Kumar, B. Rajeswari, B.A. Dhawale, S.V. Godbole, and V. Natarajan, *J. Instrumentation Science & Technology*, 43, 125 (2015).
- M.J. Kulkarni, A.A. Argekar, J.N. Mathur, and A.G. Page, *Anal. Chim. Acta* 370, 163 (1998).
- S.J. Buchanan and L.S. Dale, *Spectrochim. Acta, Part B: At. Spectrosc.* 41(3), 237 (1986).
- A.A. Argekar, M.J. Kulkarni, J.N. Mathur, and A.G. Page, *Talanta* 56, 591 (2002).
- Juracir S. Santos, Leonardo S.G. Teixeira, Walter N.L. dos Santos, Valfredo A. Lemos, Jose M. Godoy, and Sérgio L.C. Ferreira, *Anal. Chim. Acta* 674, 143 (2010).
- Arijit Sengupta and V. C. Adya, *J. Radioanal. Nucl. Chem.* 299, 2023 (2014).