Determination of Uranium Isotopic Ratio ($^{235}\text{U}/^{238}\text{U}$) Using ICP-AES

S.K. Thulasidas, Mithlesh Kumar*, B.A. Dhawale, B. Rajeswari, and V. Natarajan
Radiochemistry Division, Bhabha Atomic Research Centre
Trombay, Mumbai-400 085, India

INTRODUCTION

Uranium is the heaviest naturally occurring element on earth. It is comprised of three natural isotopes: ^{234}U ($t_{1/2} \approx 2.5 \times 10^5$ years), ^{235}U ($t_{1/2} \approx 7.0 \times 10^8$ years), and ^{238}U ($t_{1/2} \approx 4.5 \times 10^9$ years), having relative natural isotopic abundances of 0.0054%, 0.720%, and 99.275%, respectively. The most common isotopes of uranium are ^{238}U and ^{235}U , which have a wide area of applications (1-3). The natural abundance ratio of the isotopes ($^{235}\text{U}/^{238}\text{U}$) is to be expected at 0.00725 and is useful in determining any artificial nuclear activities. Information on the enrichment level in the nuclear fuel at any given time is very important for its proper utilization in the nuclear fuel cycle. Precise measurement of the isotopic composition of uranium is necessary for the nuclear industry as well as in the environmental and earth sciences (4). Uranium isotopic measurements can be made using either alpha-spectrometry for ^{234}U , ^{238}U , and to a lesser extent ^{235}U , or by a mass spectrometric technique for ^{235}U , ^{234}U , and ^{238}U . However, ^{234}U is found to be at very low concentration levels in natural uranium. The methods such as inductively coupled plasma mass spectrometry (ICP-MS), electrothermal vaporization-ICP-MS, thermal ionization mass spectrometry (TIMS), and extractive electrospray ionization (EESI) mass spectrometry (MS) have been used for isotopic measurement of uranium from natural samples (5-10). TIMS provides the highest precision, normally with 0.2% at the 95% uncertainty level compared with approximately

ABSTRACT

Studies have been carried out on the determination of the ^{235}U and ^{238}U isotopes in a set of uranium samples using an inductively coupled plasma atomic emission spectrometer and employing a high resolution holographic grating with practical resolution of <0.005 nm. The analytical profiles of the individual lines with sufficient separation and intensity were recorded with regard to the absence of both interference and background. The most suitable spectral lines were identified as 424.412 nm and 424.437 nm for ^{235}U and ^{238}U , respectively. Peak area calculations for both the ^{235}U and ^{238}U spectral peaks and to plot the ratio of $^{235}\text{U}/^{238}\text{U}$ peak area versus ^{235}U concentration were carried out to know the trend. Determinations of ^{235}U in a set of nominally enriched uranium samples were obtained using the calibration curve. The ^{235}U concentration at an enrichment level even at 0.72% in natural uranium could be determined with a precision better than 2%. The results obtained for the samples were found to be in close agreement with the values found by mass spectrometry. The high speed of analysis achieved suggests the utility of the present method for use in performing a quick survey of the uranium samples for their isotopic constituents.

1-2% for ICP-MS. Isotopic compositions are normally accomplished by using mass spectrometric techniques known for their accuracy and precision. The high sensitivity of inductively coupled plasma mass spectrometry (ICP-MS) allows the determination of ^{235}U and ^{238}U and

their isotopic ratio in uranium samples. Nevertheless, it frequently requires tedious, time-consuming sample preparation in addition to the very high cost of analysis. Chunxiao et al. (10) reported isotopic ratio ($^{235}\text{U}/^{238}\text{U}$) determination by extractive electrospray ionization mass spectrometry (EESI-MS) for the quantitative assay in uranyl nitrate sample solutions. The advantages of the method are high reproducibility, fast analysis speed, acceptable accuracy, and only requiring a widely available ion-trap MS instrument. The fast detection of uranium isotopes shows potential applications of EESI-MS in nuclear research laboratories and the nuclear energy industry. In another report, Sahoo et al. (4) discussed the $^{235}\text{U}/^{238}\text{U}$ isotopic ratio determination in soil samples by using thermal ionization mass spectrometry. The method should be applicable to a wide range of environmental and geological applications which are limited due to sample size or for which higher precision is required. These researchers developed a procedure to measure $^{235}\text{U}/^{238}\text{U}$ to better than 0.2% at two standard deviations.

A fast analytical method to verify the composition of fuel is required during fuel fabrication, whereas accurate and precise data are needed for chemical quality assurance and certification. The isotopic effect in the emission spectrum of the same element with different mass numbers can be effectively studied by isotopic assay through resolving the fine structure using a high-resolution ICP spectrometer, which should have the capability to resolve very close analyte peaks. The ICP-AES methodology is very simple and can be adopted for rapid analysis at intermediate stages

*Corresponding author.
E-mail: mitblesb010757@gmail.com

of a process such as nuclear fuel production. It has high sensitivity, large dynamic range, exceptional stability, and relative freedom from matrix effects. The present work on the determination of uranium isotopic composition by ICP-AES involved identification of interference-free analytical lines for the simultaneous determination of different uranium lines and to study the spectral interference of ^{235}U and ^{238}U on the analytical lines of all other trace metallic constituents. Reports on the determination of the isotopic composition of uranium are scanty. Some authors have determined the $^{235}\text{U}/^{238}\text{U}$ ratios, which would involve a large spectral shift. In the early eighties, ICP-AES was used as spectral excitation/ionization source for the determination of uranium (11-13). Since then, this source has been used to determine individual U isotopes using high-resolution instruments (14-16). Dhumwad et al. (17) reported the determination of $^{235}\text{U}/^{238}\text{U}$ ratios using two instruments with a different resolution and two different lines for measurement of the two isotopes. A recent literature report (18) refers to the use of a 1.5 M spectrometer with 2400 grooves/mm grating for the determination of the $^{235}\text{U}/^{238}\text{U}$ isotopic ratio in (U-Zr) alloy. The determination of the $^{235}\text{U}/^{238}\text{U}$ isotopic ratio in U-Zr alloys by ICP-AES has been shown to be accurate, precise, and rapid.

The present results deal with the determination of ^{235}U using ICP-AES even at the natural abundance level. However, commercially available ICP emission spectrometers cannot be readily employed for the analysis of ^{239}Pu - and ^{233}U -based nuclear fuels due to their non-adaptability to handle radiotoxic materials. Several literature reports refer to the use of a Direct Reading spectrometer for the analysis of radiotoxic samples. The authors of this study present the work in radioactivity containment facilities

pertaining only to the use of the ICP-AES technique. It can be seen from these reports that the ICP-AES instrument has been suitably modified for glove-box containment so as to analyze radiotoxic materials. The design of the ICP enclosure and its installation were mainly governed by some criteria such as total containment of radiotoxic materials in solution as well as in aerosol form, ease of operation during servicing, and permissible radioactive exposure levels to the operator (19).

EXPERIMENTAL

Instrumentation

High Resolution ICP-AES

The present experiments were carried out using a Jobin-Yvon Ultima high-resolution inductively coupled plasma atomic emission spectrometer (ICP-AES). The high-resolution sequential spectrometer has a 0.5 M focal length and is equipped with concave holographic gratings of 3600 grooves/mm and 4320 grooves/mm. The optical configuration with 4320 grooves/mm grating gives a practical resolution of $<0.005\text{ nm}$ and a continuous coverage of the widest spectral range of 200–800 nm, which is ideally suited for the analysis of uranium isotopes. The specifications and operating conditions of the instrument are listed in Table I.

The instrument has been set up with the facility to analyze radiotoxic samples by incorporating an ICP torch assembly, peristaltic pump, and other sample handling accessories within the glove box. The glove box of the spectrometer assembly was adapted and involved detachment of the plasma housing from the main unit and relocating it 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 efficient removal

of the excess heat generated during the 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 was checked for leak tightness, which connected to a suction point to maintain the required negative pressure. The specially made glove box for the present work is shown in Figure 1. Details of the instrumentation are discussed elsewhere (19).

A thermal ionization mass spectrometer (TIMS) (Finigan Mat-261 Instrument, Bremen, Germany), equipped with nine Faraday cup detectors, was employed for an independent cross-check. The ratio of $^{235}\text{U}/^{238}\text{U}$ was analyzed using a double filament assembly made out of high purity Re filaments. Data acquisition was carried out using the static mode of the ion beam collection process using the multi-Faraday cup detector system. The instrument has built-in software for carrying out data acquisition and an on-line isotopic ratio measurement system (20, 21).

Procedure for Reagents and Standard Preparation

Quartz ware was used for preparing the standards and the samples. All equipment, flasks, and beakers, etc., were thoroughly cleaned with 4M HNO_3 , followed by washing with quartz doubly distilled (Q.D.D.) water, and drying before any experimental use. Suprapur® HNO_3 (E. Merck, Darmstadt, Germany) and Q.D.D. water were used for making 0.5M HNO_3 . Appropriate amounts of well-characterized uranium powder with 10% enriched ^{235}U were dissolved in 8M HNO_3 to prepare a stock solution. This was further diluted

with 0.5M HNO₃ to obtain a 20 mg/L concentration of uranium, which served as the higher standard for ²³⁵U during the calibration studies.

The ²³⁵U (10% enriched) sample solution was divided into parts. The first part of the sample was used for carrying out the ICP-AES analysis. The remaining portions of the sample were appropriately diluted and used for mass spectrometric analysis.

TABLE I
Specifications and Operating Conditions of 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, continuously adjustable from 800–1550 W in the plasma
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-change kit
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	ICP-AES is equipped with a Spectralink, containing microprocessors
Software	V5 for Windows® 95 and Image Navigator for spectrum acquisition and semi-quantitative analysis
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 Manometer	6 bar

The peak search and profiles of the ²³⁵U and ²³⁸U spectral lines were studied using a 10% enriched uranium solution and a natural uranium solution, respectively. Based on these studies, background-free and interference-free lines of 424.412 and 424.437 nm for ²³⁵U and ²³⁸U, respectively, were identified as the analytical lines for further studies. Optimization of the experimental parameters related to ICP-AES was carried out to obtain maximum analyte signals with a 20 mg/L uranium sample. A two-point standardization was carried out using 0.5M HNO₃ as the common lower standard of both isotopes, while 10% ²³⁵U and natural uranium (the appropriate correction for the ²³⁵U content in it) were used as the higher standards for ²³⁵U and ²³⁸U, respectively. The concentration of uranium was kept constant at 20 mg/L in both the standards and the samples. Using the calibration curve, the concentration of ²³⁵U was determined in a set of samples.

RESULTS AND DISCUSSION

Peak Search and Profile of Spectral Lines

Figure 2 shows the profiles of the ²³⁵U and ²³⁸U spectral lines recorded on 20 mg/L (10% enriched ²³⁵U). A detailed spectral scan of the uranium spectral lines ranging from 250–500 nm was carried out by feeding the uranium solution into the plasma. The instrumental parameters such as forward power, plasma torch, flow rate of 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. It is reported that uranium has multi-electron configurations and severe spectral interference caused by the line-rich spectrum. Therefore, it was necessary to use a high-resolution

Fig. 1. Schematic diagram of glove box with spectrometer: (a) Spectrometer, (b) Heat exchanger, (c) Funnel, (d) ICP enclosure, (e) Transparent quartz window, (f) ICP torch, (g) Cyclonic spray chamber, (h) Water connection, (i) Argon gas connections, (j) Connections to active main suction valve at the ceiling, (k) Connections to the adjacent glove box, (l) Tesla discharge assembly, (m) Provision for inactive sampling.

Fig. 2. Resolved spectral line profiles of ^{235}U and ^{238}U .

sequential spectrometer to resolve the spectral lines. Initially, the lines of four uranium wavelengths at 385.958, 424.398, 424.412, and 424.437 nm were recorded as reported in the literature for different uranium isotopes (14,22). Based on these data, background-free and mutual interference-free lines of 424.412 and 424.437 nm for ^{235}U and ^{238}U , respectively, were identified for further investigation. These spectral lines were the most suitable pair of lines with sufficient separation, high intensity, and interference-free in nature. Good spectral separation and sufficiently intense line intensity for the ^{235}U isotope even at the natural abundance level was observed.

Analysis of ^{235}U Samples

Since the ICP is an extremely high temperature source, Doppler broadening is prevalent which leads to reduced separation of the analytical lines. This is all the more relevant in the context of isotopic shifts, which are very small. The theoretical line separation between the ^{235}U and ^{238}U lines of 424.412 and 424.437 nm, respectively, is thus difficult to achieve in practice, unless the resolution of the optical spectrometer is extremely good. This aspect is precisely explored in the present studies, since the practical resolution offered by the spectrometer optics is <0.005 nm with a 4320 grooves/min holographic grating. In addition to this, due to the high temperature of the plasma and matching of the samples and standards, the physical interferences can be minimized but spectral interference plays a significant role. In this context, ICP-AES measurements are made in the peak intensity mode. Attempts were made to explore the linearity of the ^{235}U and ^{238}U analytical lines. The blank reading was subtracted from all measurements. The concentration of ^{235}U and ^{238}U was determined after obtaining the respective calibration plots for these isotopes. It was

found that the calibration curves obtained for the analytical lines were linear throughout the concentration range. The analytical lines of ^{235}U and ^{238}U could be successfully utilized for the determination of ^{235}U by ICP-AES. In addition to peak intensity measurements, peak area measurements were also carried out for these two isotopes using the following equation:

$$\text{Peak area} = \sum C - \left\{ \frac{C_{(F)} + C_{(L)}}{2} \right\} \times n$$

where:

$\sum C$ = Counts of all channels taken

$C_{(F)}$ = Counts_(First)

$C_{(L)}$ = Counts_(Last)

n = Total number of channels

A plot of the ratio of the $^{235}\text{U}/^{238}\text{U}$ peak area versus the ^{235}U concentration estimated in the peak intensity mode shows a linear progression (see Figure 3). It is evident from the figure that the points lie quite close to a linear fit. Table II lists the concentrations of ^{235}U obtained by the present ICP-AES method in comparison to those obtained by the mass spectrometric technique. The detection limits of both uranium analytical lines were evaluated on the basis of the concentration corresponding to the intensity of the absolute value of the blank at that specified wavelength plus three times the standard deviation of the measurement ($x + 3\sigma$). The detection limit of uranium was calculated for both

analytical lines and was found to be better for 424.437 nm due to the sensitivity of the line in comparison to 424.412 nm. The precision of the determination, as calculated from the repetitive analyses of an intermediate range concentration of ^{235}U (10% value), was found to be 1–2% RSD. In comparison to the mass spectrometric method, the precision may appear poor, but the present method has the advantage of high speed of analysis (it requires typically only a couple of minutes per sample) and a simple sample preparation procedure which makes it easily applicable to real samples.

Figure 4 shows the intensity profiles of ^{235}U at different enrichment levels as compared to natural uranium (NU) at 3%, 10%, 15%, and 20%. As seen from the figure, even at the natural abundance level (0.7%) there is an adequate intensity for ^{235}U to enable its determination. The large linear dynamic range of ICP-AES enables the determination over a wide range of concentrations.

The performance and the accuracy of the method were also evaluated by analyzing two synthetic samples by ICP-AES. For this purpose, well-characterized uranium solutions with a 10% ^{235}U enrichment and natural uranium for the determination of the ^{235}U and ^{238}U isotopes were used. Blank correction was carried out using 0.5M HNO_3 . The feasibility of determining ^{235}U by ICP-AES was established successfully. The results are comparable with the values of the synthetic samples as seen in Table III.

Analysis of Real Samples

For an independent cross-check, a small portion of the ^{235}U -enriched sample was used for mass spectrometric analysis. The analysis of ^{235}U was carried out by isotope dilution thermal ionization spectrometry. The sample was loaded onto the

Fig. 3. Plot of peak ratio versus concentration of ^{235}U .

TABLE II
Comparison of Concentration of ^{235}U
by Present ICP-AES Method and MS Method

Peak Area of $^{235}\text{U}/^{238}\text{U}$	Conc. Ratio of $^{235}\text{U}/^{238}\text{U}$	^{235}U Conc. by ICP-AES (in %)	MS Values for ^{235}U Conc.
0.013	0.0079	0.077	-
0.04	0.0388	2.94	3.1
0.112	0.1474	10.2	10.7
0.192	0.2305	15.7	15.8
0.277	0.3291	20.9	20.8

high-purity rhenium filament in a double filament assembly (23). The ionization and vaporization filaments were heated to obtain sufficient UO^+ ions. The temperature of the ionization filament was increased slowly by monitoring the signal strength and was maintained at a constant level for the different analyses during the mass spectrometric experiments. A single Faraday cup detector was used and the intensities of the different ions of uranium were monitored at the m/z values of 235. The intensities of the different ions were monitored by varying the heating current of one of the filaments and keeping the other filament at constant temperature. The atom ratio of $^{235}\text{U}/^{238}\text{U}$ was obtained by using the UO^+ ion and this ratio was used as an input for the data reduction by the interfering element correction approach. Data acquisition was carried out

using the static mode of ion beam collection in the multi-Faraday cup detector system. The estimate obtained for ^{235}U after applying the appropriate multiplication factors was found to be similar to the ICP-AES results, confirming the validity of the method developed.

As shown in Table II, the results obtained in the present method are comparable with those obtained by the mass spectrometric technique.

CONCLUSION

A commercially available high-resolution ICP sequential spectrometer assembly has been modified extensively to enable analysis of radiotoxic samples with an alpha containment facility. It was subsequently utilized successfully to obtain spectral lines of ^{235}U and ^{238}U with sufficient separation, high intensity, and an interference-

free nature at 424.412 and 424.437 nm, respectively. The studies carried out here have revealed a significant resolution of the two isotopic lines of uranium for ^{235}U and ^{238}U , thereby enabling quantitative analysis of uranium. An isotopic composition of uranium (^{235}U) with an enrichment level in the range of 0.7–20% and a precision of 2% RSD or better was observed. In comparison to the mass spectrometric method, the precision may, however, be poor; but the present method has the advantage of high speed of analysis and using a simplified sample preparation which makes it easily applicable to real samples.

ACKNOWLEDGMENT

The authors are grateful to Dr. A. Goswami, Head, Radiochemistry Division, BARC, for his keen interest, encouragement, and constant support during the course of this work. The authors also are thankful to Shri A.R. Parab of the Fuel Chemistry Division, BARC, for providing the thermal ionization mass spectrometric analysis data.

Received January 25, 2014.

Fig. 4. Intensity profiles of ^{235}U at different enrichment levels.

TABLE III
Typical Analysis Results of Synthetic Samples

Control Samples	Expected Amount (%)	^{235}U (424.412 nm)	Expected Amount (%)	^{238}U (424.437nm)
Sample 1	0.72	0.77±0.13	99.28	98.00±0.10
Sample 2	10.01	10.70±0.09	99.28	98.01±0.13

REFERENCES

1. J.K. Gibson and J. Marcalo, Coord. Chem. Rev. 250, 776 (2006).
2. G.S. Groenewold, A. K. Gianotto, K. C. Cossel, M. J. Van Stipdonk, D. T. Moore, N. Polfer, J. Oomens, W. A. de Jong and L. Visscher, J. Am. Chem. Soc. 128, 4802 (2006).
3. S. Handley-Sidhu, M. J. Keith-Roach, J. R. Lloyd, and D. J. Vaughan, Sci. Total Environ. 408, 5690 (2010).
4. S.K. Sahoo, H. Yonehara, K. Kurotaki, K. Fujimoto, and Y. Nakamura, J. of Radioanalytical and Nuclear Chem. 252, 241 (2002).
5. J.H. Chen and G. J. Wasserburg, Anal. Chem. 53, 2060(1981).
6. K.L. Ramakumar, S. Jeykumar, R. M. Rao, L. Gnanayyan, and H. C. Jain, J. Radioanal. Nucl. Chem. 190, 121(1995).
7. R.N. Taylor, I. W. Croudace, P. E. Warwick, and S. J. Dee, Chem. Geol. 144, 73(1998).
8. S. Ritcher, A. Alonso, W. De Bolle, R. Wellum, P. D. P.Taylor, Intern. J. Mass Spectrom. 193, 9 (1999).
9. S.K. Sahoo and A. Masuda, Proc. Japan Acad. 76, 151(2000).
10. Chunxiao Liu, Bin Hu, Jianbo Shi, Jianqiang Li, Xinglei Zhang, and Huanwen Chen, J. Anal. At. Spectrom. 26, 2045 (2011).
11. A.G. Page, S.V. Godbole, K.H. Madraswala, M.J. Kulkarni, V.S. Mallapurkar and B.D. Joshi, Anal. Letters 16,1005 (1983).
12. E. Mainka and H.G. Muller, EUA-6629, p.89 (1979).
13. Osamu Fujino, Shigeo Umetani, Eiji Ueno, Kazunori Shigeta, and Takashi Matsuda, Anal. Chim. Acta 420, 65 (2000).
14. A.B. Patwardhan, V.T. Kulkarni, K. Radhakrishnan, A. Ramanujam and A.G. Page, Anal. Lett. 27, 2377 (1994).
15. K. Radhakrishnan, V.T. Kulkarni, A.B. Patwardhan, A. Ramanujam and A.G. Page, J. Anal. At. Spectrom. 14, 1889 (1999).
16. M.C. Edelson and V.A. Fassel, 3rd Annual Symp. on Safeguards & Nuclear Materials Management, Karlsruhe, Germany (May 6-8, 1981).
17. R.K. Dhumwad, A.B. Patwardhan, M.V. Joshi, V.T. Kulkarni and K. Radhakrishnan, Proc. Radiochemistry & Radiation Chemistry Symp., Kalpakkam, India, RA-16 (Jan. 1989).
18. Phillip S. Gooddall and Stephen G. Johnson, J. Anal. At. Spectrom. 11, 57 (1996).
19. S.K. Thulasidas, Mithlesh Kumar, B.A. Dhawale, B. Rajeswari and A.G. Page, NUCAR-03, Held at Mumbai, India (Feb. 10, 2003).
20. S.K. Aggarwal and D. Alamel, Internatl. J. of Mass Spectrom. 241, 83 (2005).
21. D. Alamelu, P.S. Khodade, P.M. Shah, and S.K. Aggarwal, Internatl. J. of Mass Spectrom. 239, 51 (2004).
22. Michael Krachler and Paul Carbol, J. Anal. At. Spectrom. 26, 293 (2011).
23. D. Alamelu, P.S. Khodade, P.M. Shah, and S.K. Aggarwal, Int. J. Mass Spectrom. 239, 51 (2004).