Analysis of Uranium Bearing Samples for Rare Earth and Other Elements by k_0-Based Internal Monostandard INAA Method

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A k_0-based internal monostandard instrumental neutron activation analysis (IM-INAA) method was applied for the multielement analysis in uranium bearing samples. Spectral interference correction factors in INAA due to neutron induced fission of uranium for La, Ce, Nd, Zr, Ru, and Mo as well as activation of uranium for Sm and Lu were evaluated using elemental standards. The correction factors were validated by standard addition method in a synthetic sample containing known amount of natural uranium. For evaluating the accuracy of the IM-INAA method, the low uranium containing SRM 1633a (coal fly ash) obtained from NIST was used. For method validation of analysis of uranium bearing sample, SRM 1633a spiked with uranium (about 0.05%) was analyzed by IM-INAA method. The standardized IM-INAA method was applied to analyze uranium ore samples obtained from Jaduguda and Bhatin mines, Jharkhand, India for multielement content including U, Th, and rare earth elements (REEs). Chondrite normalized REE patterns were plotted for obtaining Ce and Eu anomalies.

1. Introduction

Instrumental neutron activation analysis (INAA) is a nondestructive isotope specific nuclear analytical technique for simultaneous multielement analysis at major, minor, and trace levels. The method of INAA requires minimal sample preparation and experiences negligible matrix effect due to high penetration power of activating neutrons and the measured γ-radiation. This technique offers high sensitivity and selectivity for the determination of concentrations of a large number of elements including U, Th, and rare earth elements (REEs).[1,2] In fact, INAA is one of the best methods for the determination of concentrations of REEs, in many geological and environmental matrices, due to their favorable nuclear properties like (n, γ) cross section, isotopic abundances and γ-ray abundances.[3-5] However, determination of REEs like La, Ce, and Nd and other elements like Zr, Mo, and Ru by INAA in the samples containing uranium gives higher (enhanced) values due to spectral interference from neutron induced fission of uranium.[6-8] Two other REEs namely Sm and Lu are also interfered due to γ-rays of activation product of uranium (^{239}Np). Thus for uranium bearing samples, appropriate corrections due to spectral interference of uranium have to be made for these elements to obtain the accurate concentration values determined by INAA. The extent of interference (correction factors) can be determined by irradiating known amounts of uranium and elemental standards of interest and comparing the activities formed. Both parametric and experimental correction factors expressed as (M_X/M_U), microgram of the element of interest per microgram of uranium, are reported in literature for the above-mentioned elements.[6-8] In order to apply this correction, the amount of uranium in the sample must be determined first and then multiplied by correction factor (M_X/M_U) which is further subtracted from the measured amount of that element. Thus, for routine as well as faster analysis of samples and to circumvent chemical separation of uranium, it is necessary to standardize a method to estimate these elements by INAA along with other elements.

Determination of concentration of elements including REEs is carried out both by the relative and k_0 methods of NAA. The advantage of k_0-method over relative one is that it uses a single comparator (like ^{197}Au) instead of multielement standards used in relative method. The details of k_0-method of NAA are given in the references.[9,10] Recently, we have developed a k_0-based internal monostandard INAA (IM-INAA) method applicable for the analysis of different shape and size samples.[11-13] The internal monostandard method for analysis of non-standard geometry sample using prompt γ-ray NAA (PGNAA) was initially developed by Sueki et al.[14] This method gives elemental mass ratio with respect to the internal monostandard. A priori knowledge of concentration of the monostandard is used to convert the elemental concentration ratios to their absolute values. The method is geometry independent since it utilizes in-situ relative detection efficiency. The in-situ detection efficiency was determined, in our method, using γ-rays from the activation products of the elements present in the sample to overcome the problem of γ-ray self-attenuation in the sample.[11,12] It has been applied by us for the analysis of large size and non-standard geometry samples like certified reference materials, alloys of nuclear cladding materials like zircaloy and stainless steel and wheat grains.[11-13]

In the present paper, spectral interference contribution due to uranium fission was evaluated by determining correction factors for La, Ce, Nd, Zr, Ru, and Mo in INAA. Elemental standards of these elements and uranium were used to arrive at the correction factors. In the second stage, correction factors were validated by determining the amount of these elements from the uranium sample of 25 μg spiked with known amounts of above-mentioned elements. γ-Ray spectral interference for Sm and Lu due to activation of uranium was also evaluated using pure uranium standard. IM-INAA was used to determine the relative concentrations of elements including U and REEs in this SRM with and without addition of uranium. IM-INAA of SRM 1633a spiked with uranium was used to validate the method for uranium bearing sample, whereas analysis of SRM 1633a only was carried out to evaluate accuracy of the method. The element Fe was chosen as the comparator element, since its activation product (^{59}Fe) does not get contribution from neutron induced nuclear fission of uranium and its

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certified concentration in SRM 1633a is relatively high $(9.4\pm0.1)\%$ having low uncertainty $(\sim1\%)$.[15] Its activation product (^{59}Fe) has a long half-life (44.5 d) which makes it suitable to be a comparator element mostly for medium and long-lived activation products. The standardized method was applied to uranium ore samples, one each from Jaduguda and Bhatin mines, Jharkhand, India for the determination of concentrations of many elements including REEs.

2. Experimental

2.1. Sample irradiation and measurement of radioactivity. Elemental standard solutions of La, Ce, Nd, Ru, Zr, and Mo were prepared using either respective AR grade compounds or pure metal foils and the standard for uranium was prepared using U_3O_8 compound. Accurately weighed elemental standard solutions containing 5 to 200 µg of elements were dried on a filter paper. Standard solutions of elements were transferred by weight onto Whatmann filter paper kept inside the polyethylene pouches sealed from three sides. The solutions were allowed to dry in air or under IR and then polyethylene was sealed before sending for irradiation. These elemental standards were sealed in polyethylene along with uranium standard (about 25–50 µg). The samples of NIST SRM 1633a, SRM spiked with uranium standard and finely ground uranium ores in the mass range of 75–150 mg were used for irradiations. All samples were sealed in polyethylene and irradiated for duration of 5 h in the E8 position of Apsara reactor, Bhabha Atomic Research Centre, Mumbai. Similarly the uranium ore samples were co-irradiated with SRM 1633a. The neutron flux at this position is $\sim5\times10^{11}$ cm^{-2}s^{-1}. After appropriate cooling, the irradiated samples were assayed for γ activity using a 40% relative efficiency HPGe detector coupled to an MCA. The small size samples (75–150 mg) and standards were counted at 10–15 cm distances with respect to the detector to minimize any true coincidence effect. Standard source of γ-rays, ^{152}Eu was used for energy calibration of the detector. The detector system had a resolution of 2.0 keV at 1332 keV peak of ^{60}Co source. The γ-ray spectra were analyzed for peak area determination using peak-fit software PHAST developed at our institute.[16]

2.2. Concentration calculation. When a homogeneous sample is irradiated in a neutron flux, the ratio of mass (m) of an element (x) to mass of the internal comparator element (y) in the sample by k_0-based IM-INAA method[13] is given by,

$$\frac{m_x}{m_y} = \frac{((S\,D\,C)\,(f+Q_0(\alpha)))_y}{((S\,D\,C)\,(f+Q_0(\alpha)))_x} \cdot \frac{P_{Ax}}{P_{Ay}} \cdot \frac{(\varepsilon_\gamma)_y}{(\varepsilon_\gamma)_x} \cdot \frac{k_{0,Au}(y)}{k_{0,Au}(x)} , \quad (1)$$

where P_A is the net peak area under the γ peak of interest, S is the saturation factor $(1-e^{-\lambda t_i})$, D is the decay factor $(e^{-\lambda t_d})$, C is the term used for correcting the decay during counting period and is given by $((1-e^{-\lambda LT})/\lambda)$, t_i, t_d, and LT are durations of irradiation, cooling, and counting times, respectively, f is the thermal to epithermal neutron flux ratio, α is the epithermal neutron shape factor, $Q_0(\alpha)$ is the α corrected Q_0 value,[17] where Q_0 is the ratio of resonance integral (I_0) to the 2200 ms^{-1} (n, γ) cross section (σ_0), ε_γ is the in-situ relative detection efficiency.[12] The α parameter represents the non-ideal epithermal neutron flux distribution $(1/E^{1+\alpha})$ in the irradiation position of a reactor and it was experimentally determined by "Cd-ratio for dual monitor" method using ^{197}Au and ^{94}Zr monitors.[9,10] The f-value was determined by cadmium ratio method using ^{197}Au as the monitor.[10] The thickness of cadmium foil used was 0.84 mm. The f and α values of E8 position of Apsara reactor are 65.6 ± 1.8 and 0.013 ± 0.004, respectively.[13] The $k_{0,Au}$ is a factor for the γ-ray of the activation product of interest with respect to the γ-ray of the activation product of the monostandard, and it is taken from the latest compilation by De Corte and Simonits.[16]

The literature k_0-factors are experimentally determined recommended values for use in k_0-NAA work. Theoretically the k_0-factor is defined as:

$$k_0 = \frac{M^*\theta\gamma\sigma_0}{M\theta^*\gamma^*\sigma_0^*} , \quad (2)$$

where M is the atomic mass, θ is the isotopic abundance and γ is the γ-ray abundance. The symbol "*" refers to the corresponding parameters of the comparator (e.g. ^{197}Au).

2.3. In-situ relative efficiency detection. One of the important input parameters for IM-INAA is the γ-ray detection efficiency. Use of relative efficiency is adequate to determine the concentration ratio as seen in eq 1. While using γ-rays from more than one radionuclide to cover the requisite energy range, the expression for efficiency is given by,

$$\ln \varepsilon_R(E_\gamma) = k_j + \sum_{i=0}^{m} a_i (\ln E_\gamma)^i , \quad (3)$$

where $\varepsilon_R(E_\gamma)$ is the relative detection efficiency of the γ-ray of energy E_γ, a_i's are the coefficients of the polynomial of order m and k_j is a constant characteristic of the j-th nuclide. The radionuclides used for efficiency calibration should have two or more γ-rays to obtain a smooth calibration plot. In our calculations a third order polynomial ($m = 3$) was used. The details of in-situ detection efficiency calibration are given in References 11 and 12.

2.4. Calculation of correction factors due to fission of uranium. Experimental correction factors due to uranium fission for La, Ce, Nd, Ru, Mo, and Zr in µg per µg of uranium were arrived using a comparative method. The correction factor for ^{153}Sm due to uranium fission is very less,[8] so it was not determined in the present work. The correction factors were also calculated theoretically as follows.[8] The activities produced due to activation (A_a) and fission (A_f) in a nuclear reactor are given by,

$$A_a = N(\phi_{th}\sigma_0 + \phi_e I_0)(1-e^{-\lambda t_i}) , \quad (4)$$

$$A_f = N_U(\phi_{th}\sigma_0 + \phi_e I_0)(1-e^{-\lambda t_i})Y_f , \quad (5)$$

where N is the number of target atoms of element of interest, N_U is the number of target atoms of ^{235}U, since fission from ^{238}U is negligible in the irradiation position used, Y_f is the fission yield of the isotope of interest,[8] ϕ_{th} is the thermal neutron flux, ϕ_e is the epithermal neutron flux, σ_0 is the thermal neutron absorption cross section and I_0 is the resonance integral for the (n, γ) reaction in eq 4 and the corresponding cross sections for neutron induced fission are given in eq 5. The relevant nuclear data required for activation (eq 4) were taken from the References 17 and 18, and the data for nuclear fission (eq 5) were taken from Reference 8. In the calculation, the experimentally determined f-value (65.6) was used instead of absolute neutron flux values. The fission interference correction factor (mass of element per mass of uranium, M_X/M_U) is given by,

$$\frac{M_X}{M_U} = \frac{A_f}{A_a} . \quad (6)$$

Interference contribution calculation of ^{140}La is dependent on the cooling time due to its growth from its precursor ^{140}Ba, which is also a fission product. For correcting its interference, eq 6 was multiplied with the factor $(e^{0.36T_d}-1)$, where T_d is the duration of cooling in days.

3. Results and discussion

The correction factors due to uranium fission obtained for different isotopes namely ^{140}La, ^{141}Ce, ^{143}Ce, ^{147}Nd, ^{99}Mo, ^{99}Mo(^{99m}Tc), ^{95}Zr, ^{97}Zr, and ^{103}Ru are given in Table 1. The values of correction factors reported in the table are the mean val-

ues and unweighted standard deviations from four independent experiments. The % uncertainties (%RSD) are 1–5%, except for Nd (10%), which has a lower sensitivity by NAA compared to other REEs studied. The theoretically calculated values along with literature values[7,8] are also given in Table 1. Experimentally determined and theoretically calculated values are in good agreement with literature values. Higher uranium fission correction factors were observed for the nuclides namely ^{97}Zr, ^{95}Zr, ^{99}Mo(^{99m}Tc), ^{99}Mo, and ^{143}Ce due to higher fission yields.[8] It is to be noted that if the concentrations of the elements present in the sample are comparable to uranium concentration, correction due to neutron induced fission of uranium will be significant. Out of these, the correction factor for La is dependent upon the cooling time as ^{140}Ba (12.75 d) decays to ^{140}La (1.68 d). This correction factor for ^{140}La could be minimized by counting the sample with less decay period after irradiation (within a week) so that the correction due to contribution from the decay of ^{140}Ba would be less (within 3%). The determined value of correction factor for ^{140}La (Table 1) is in good agreement with the value reported by Glascock et al.[8] In our work, a decay period of 6 days (correction factor 2%) was maintained through out the work for determining concentration of La in uranium bearing samples. In the second stage, correction factor procedure was validated by determining the amount of these elements from the sample containing 25 µg of uranium and known amounts of La, Ce, Nd, Zr, Mo, and Ru and the results are given in Table 2. A good agreement (within ±4%) between expected values and measured values validated the method of obtaining correction factors. Characteristic γ-rays of the ^{177}Lu (208.4 keV) and ^{153}Sm (103.2 keV) have spectral interference from the 209.8 and 103.8 keV γ-rays of ^{239}Np,

daughter product of ^{239}U. Between these two nuclides, interference for Sm is more severe. γ-Ray spectral interferences were evaluated for the γ-ray peaks of interest using intensity ratios obtained from a neutron activated pure uranium sample. The correction factors obtained for Sm and Lu were 1.9 and 0.3 in terms of intensity ratios of 103.2 keV and 208.4 keV to 277.6 keV for ^{153}Sm and ^{177}Lu to ^{239}Np, respectively.

Table 3 gives the concentration of elements determined in the NIST SRM 1633a along with the certified values. A typical plot of relative γ-ray detection efficiency as a function of energy generated using neutron activated sample of SRM 1633a is given in Figure 1. Ten selected γ-rays (in the range of 121–2754 keV) from four activation products (Figure 1) were used for constructing the relative efficiency curve.[11,12] These peak areas were used to arrive at relative elemental concentrations by the IM-INAA method. All the relative elemental concentrations were converted to their absolute values using the certified concentration of Fe, which was used as the monostandard.[12] The concentration values in Table 3 were arrived from four replicate experiments and the uncertainties quoted are due to standard deviations at ±1σ confidence limit. Since time to time literature values are published, for comparison purpose two such literature values[8,19] are given in this table along with NIST certified or information values.[15,20] The determined elemental concentrations (column 3) of SRM 1633a were within 6% of the certified values[15,20] except for uranium (9.8%). However, our determined concentration of uranium 11.2±0.4 is in good agreement with the literature value of 11.4±0.3.[19] This agreement between determined values and certified ones validated the IM-INAA method. The concentrations of elements namely Th, La, Nd, Sm, Yb, and Lu, whose certified or information

TABLE 1: Uranium fission interference correction factors of elements in INAA

Element	Radio-nuclide	E_γ (keV)	Experimental correction factor	Theoretical correction factor	Ref. 7	Ref. 8
La	^{140}La	1596.5	(0.0027 ± 0.0002) $\times (e^{0.36.T_d}-1)$	0.016	Variable*	(0.0028 ± 0.0002) $\times (e^{0.35893.T_d}-1)$
Ce	^{141}Ce	145.4	0.34±0.01	0.28	0.27	0.287±0.008
	^{143}Ce	293.3	1.35±0.03	1.33	NA	1.35±0.04
Nd	^{147}Nd	531.0	0.20±0.02	0.22	0.23	0.21±0.01
Zr	^{95}Zr	724.2	10.81±0.17	10.6	10.9	11.3±0.2
	^{97}Zr	355.4	29.50±1.10	33.5	NA	26.6±0.9
Mo	^{99}Mo	739.5	1.34±0.05	1.71	NA	1.39±0.05
	^{99}Mo(^{99m}Tc)	140.5	1.47±0.03	1.71	1.6	1.41±0.05
Ru	^{103}Ru	497.1	0.145±0.002	0.14	0.13	0.126±0.003

NA - Not Available, *Cooling time dependent

TABLE 2: Validation of uranium fission correction factors by standard addition method: Estimation of elements in synthetic sample containing natural uranium (25 µg) by INAA

Element	Radio-nuclide	Amount(µg) before correction (A)	Amount (µg) due to uranium (B)	Amount (µg) obtained after correction (C =A–B)	Amount Added (µg) (D)	% difference (C–D)
La	^{140}La	5.725	0.525	5.2±0.1	5.04	3.2
Ce	^{141}Ce	13.8	8.5	5.3±0.2	5.52	-3.9
	^{143}Ce	39.3	33.8	5.5±0.2	5.52	-0.4
Nd	^{147}Nd	53.9	5	48.9±3.9	48.6	0.62
Zr	^{95}Zr	455.3	270.3	185.0±7.4	177.5	4.2
	^{97}Zr	919.5	737.5	182.0±3.6	177.5	2.5
Mo	^{99}Mo	59.7	33.5	26.2±1.0	26.3	-0.4
	^{99}Mo(^{99m}Tc)	63.6	36.8	26.8±0.5	26.3	1.9
Ru	^{103}Ru	60.2	3.6	56.6±1.6	58.5	-3.2

TABLE 3: Determined elemental concentrations (in mg kg⁻¹ unless % is indicated) in NIST SRM 1633a (coal fly ash)

Element	Formed isotope	E_γ (keV)	This work	NIST Certified value [Refs. 15 and 20]	Ref. 8	Ref. 19
Na%	[24]Na	1368.6	0.180±0.006	0.17±0.01	NA	0.20±0.01
K%	[42]K	1524.7	1.97±0.03	1.88±0.06	NA	2.1±0.3
Sc	[46]Sc	889.3	39.6±0.5	(40)	NA	41.8±0.4
Cr	[51]Cr	320.1	195±4	196±6	NA	212±6
Ga	[72]Ga	834.0	60.3±2.8	58±5.8*	NA	NA
As	[76]As	559.1	143±3	145±15	NA	177±4
U	[239]U/[239]Np	277.6	11.2±0.4	10.2±0.8*	10.3±0.3	11.4 ±0.3
Th	[233]Th/[233]Pa	312.1	29.7±1.7	NA	NA	27.5±5
La	[140]La	1596.5	78.4±0.6	NA	74.7±0.7	94±1
Ce	[141]Ce	145.4	186.2±4.6	180.0±12.6*	174±4	184±8
	[143]Ce	293.3	182.6±4.4	180.0±12.6*	174±4	184±8
Nd	[147]Nd	531.0	78.4±3.0	NA	78±4	79±3
Sm	[153]Sm	103.2	15.8±0.6	NA	16.6±0.1	14±2
Eu	[152]Eu	1408.0	4.1±0.1	(4)	3.5±0.04	3.9±0.1
Yb	[169]Yb	198.0	7.40±0.92	NA	7.68±0.09	9.2±0.2
	[175]Yb	396.3	7.89±0.12	NA	7.68±0.09	9.2±0.2
Lu	[177]Lu	208.4	1.27±0.04	NA	1.15±0.02	1.2±0.1

NA- not available; ( ) information value, *Ref. 20
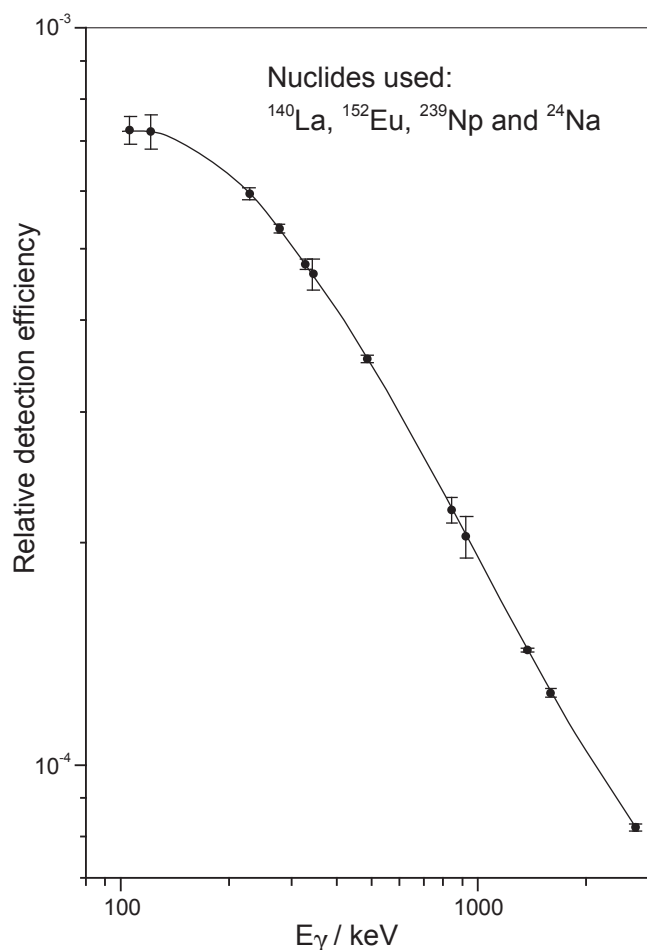
Figure 1. In-situ relative γ-ray detection efficiency using the activation products of SRM 1633a.

TABLE 4: Determined elemental concentrations (in mg kg⁻¹ unless % is indicated) in SRM 1633a spiked with uranium: before and after interference correction

Element	SRM spiked with uranium	SRM only [Table 3, column 4]
Na%	0.185±0.003	0.180±0.006
K%	1.99±0.05	1.97±0.03
Sc	39.1±0.5	39.6±0.52
Cr	203.0±9.6	195±4
Ga	59.7±2.0	60.3±2.8
As	148.0±1 .6	143±3
Th	29.2±1.5	29.7±1.7
U	493±1*	11.2±0.4
La	86.1±0.1 (75.8±0.1)	78.4±0.6
Ce ([141]Ce)	345.7±4.5 (178.0±2.3)	186.2±4.6
([143]Ce)	840.4±5.8 (174.7±1.2)	182.6±4.4
Nd	179.8±7.7 (81.2±3.5)	78.4±3.0
Sm	38.1±2.9 (16.1±1.2)	15.8±0.6
Eu	4.3±0.1	4.1±0.1
Yb ([169]Yb)	7.28±0.39	7.40±0.92
([175]Yb)	8.02±0.09	7.89±0.12
Lu	2.43±0.04 (1.21±0.04)	1.27±0.04

( ) – interference corrected REE concentrations, *uranium concentration in spiked sample

values are not available in NIST catalogue, were determined in the present case. These concentration values agree fairly with the literature values[8,19] given in Table 3. Though contributions from uranium fission to La, Ce, and Nd are very less in this case since concentration of uranium is 11.2 ppm, correction factors were applied to arrive at final concentration values. Table 4 gives the concentrations of the elements in the SRM 1633a spiked with uranium (493 mg kg⁻¹ as the determined value) as well as spectral interference corrected concentrations of specific REEs. The uncertainties quoted in Table 4 (column 2) are due to peak fitting error and counting statistics at ±1σ confidence limit. The amount of uranium was estimated using the 277.6 keV γ-ray of [239]Np. The experimental contributions of γ lines from [239]Np were computed and corrected to arrive at peak areas of 208.4 keV (^{177}Lu) and 103.2 keV ([153]Sm), respectively. It is seen that the values of elemental concentrations determined using purely (n, γ) reactions are found to be unaltered (agreed within ±4%), whereas the concentrations of ele-

TABLE 5: Determined elemental concentration (mg kg⁻¹) in two uranium ore samples by IM-INAA

S.N.	Element	Jaduguda	Bhatin
1	Na	6836±47	5155±46
2	Fe	$(7.1\pm0.3)\times10^4$	$(7.7\pm0.4)\times10^4$
3	Cr	202±2	200±2
4	Co	46.4±1.2	39.6±1.4
5	As	1.6±0.1	2.0±0.1
6	Mn	223±2	228±2
7	K	12097±199	15599±212
8	Sc	14.1±0.3	14.2±0.4
9	Zn	58.6±3.8	65.0±2.5
10	Hf	3.7±0.1	4.35±0.2
11	Rb	120.4±4.8	166.4±6.6
12	Cs	2.83±0.17	2.80±0.11
13	Th	8.2±0.2	9.7±0.3
14	U	577.4±10.7	462.6±8.9
15	La	211.2±1.8	254.1±2.3
16	Ce	337.7±10.1	434.3±17.4
17	Nd	269.5±13.5	325.0±16.3
18	Dy	22.2±1.0	25.4±1.3
19	Sm	14.1±0.4	20.8±0.8
20	Eu	2.11±0.06	2.50±0.06
21	Yb	10.5±0.5	13.3±0.3
22	Lu	2.1±0.1	3.0±0.1
	La*/Lu*	10.4	8.8

La* and Lu* - Chondrite normalized value

Figure 2. Low energy part of the γ-ray spectrum of a neutron activated uranium ore sample from Jaduguda mines.

Figure 3. Chondrite normalized REE patterns in SRM 1633a (coal fly ash): spiked with uranium and uranium interference corrected.

ments, whose activation products have contributions from fission and activation of uranium are enhanced. Discernable enhancement was observed for the isotopes of La, Ce, Nd, Sm, and Lu, which have contributions from fission as well as activation of uranium. The interference corrected values of REEs are in good agreement (within ±5%) with the results obtained for SRM 1633a only (Table 3).

The IM-INAA method was used to determine elemental concentrations in two different uranium ore samples obtained from Jaduguda and Bhatin mines. The element Fe was used as the internal standard. The relative elemental concentrations were converted to absolute values by determining Fe concentration using certified value of Fe in SRM 1633a. Figure 2 shows a typical γ-ray spectrum of the neutron-activated sample of Jaduguda ore. The results of elemental concentrations for 22 elements including 8 REEs were arrived from four replicate experiments and are given in Table 5. The uncertainties quoted in Table 5 are the standard deviations at ±1σ confidence limit and %RSD values are in the range of 1–6%. The concentrations of uranium determined in uranium ores from Jaduguda and Bhatin mines were 577±11 and 463±9 mg kg⁻¹, respectively. Since the uranium concentrations are very high, spectral interference due to uranium was significant. Appropriate corrections (using data in Table 1) were applied to calculate the concentration values of the REEs that are interfered by uranium fission and activation. The concentrations of REEs thus determined were used to analyze possible REE anomaly and fractionation of light REE (LREE) and heavy REE (HREE).

The rare earth elements, La to Lu, are widely utilized as tracers for a range of geological processes because of their strikingly similar electronic configurations that give rise to predictable chemical behavior along the series. Its abundance or pattern in minerals and ores provides fundamental information on the cosmic nucleosynthesis.[4,21,22] It is known that REE patterns in geological samples are influenced by depositional environment. They exhibit a smooth and regular variation with atomic number Z with some striking features of deviation for Ce and/or Eu attributable to the reducing or oxidative environ-
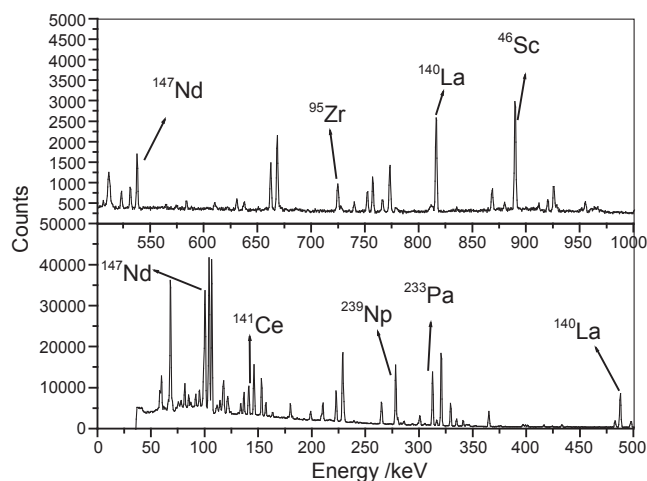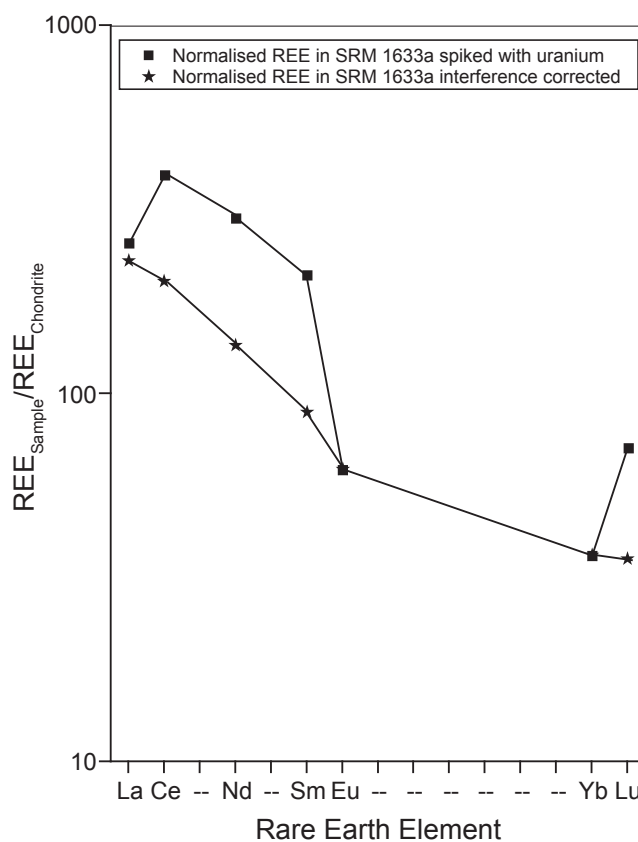
ment at the formation stage or fractionation process.[5,23] The REE patterns are obtained by plotting chondrite normalized REE concentration vs. Z of REE.[4,5,23] The chondrite normalized REE patterns of SRM 1633a spiked with uranium sample were obtained for both uncorrected and corrected for REE contributions due to uranium interference and the plots are given in Figure 3. The chondrite REE concentrations in mg kg⁻¹ are given in parentheses: La (0.33), Ce (0.88), Nd(0.6), Sm (0.181), Eu (0.069), Dy (0.317), Yb (0.20), and Lu (0.034).[24] The connecting lines from one REE to the other in Figure 3 are the eye guides only. The interference corrected pattern of SRM 1633a is in good agreement with the pattern obtained by Glascock et al.[8] except for Sm, showing the validity of the correction factors. Interference correction factor for 103.2 keV of [153]Sm due to γ-ray of [239]Np (103.8 keV) was not carried out by Glascock et al,[8] which is an important correction. Similar way chondrite
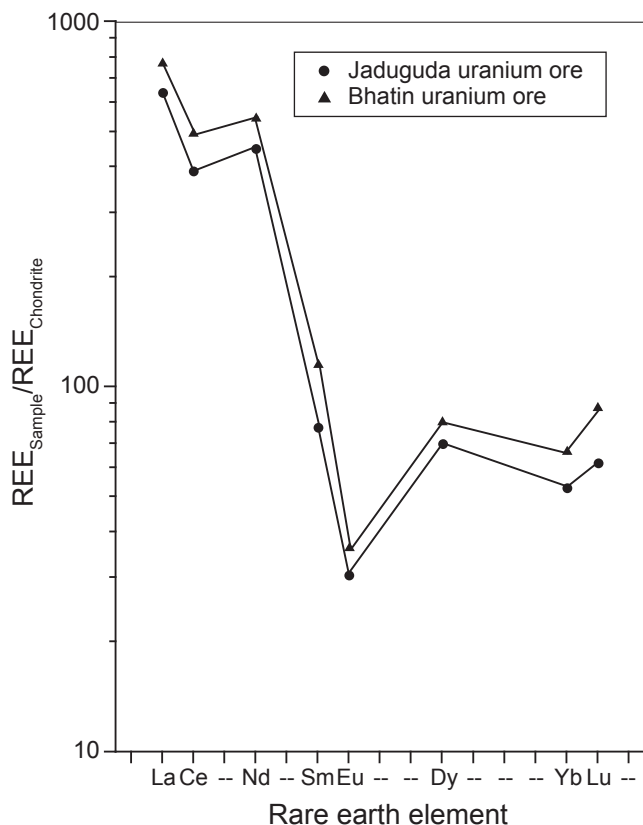
Figure 4. Chondrite normalized REE patterns in uranium ore samples.

normalized REE patterns, using corrected REE values, were obtained for the two uranium ores as shown in Figure 4. The normalized REE patterns for both the ore samples are found to be similar. As observed in Figure 4, REE patterns of the ore sample showed negative Ce as well as Eu anomalies, indicating a reduced depositional environment.[4,5,23] The fractionation of LREE and HREE was obtained for the ore samples from the (La/Lu)* ratio, i.e. [(La $_{sample}$/La $_{Chondrite}$)/(Lu $_{sample}$/Lu $_{Chondrite}$)]. The magnitudes of the (La/Lu)* ratios (Table 5) were > 1 in all the cases suggesting a high enrichment of LREE.

4. Conclusions

Correction factors for elements namely La, Ce, Nd, Zr, Mo, and Ru for the contribution from neutron-induced fission of uranium and for Sm and Lu due to activation of uranium in INAA were determined and validated by standard addition method. The k_0-based IM-INAA method was effectively used for multielement analysis in NIST SRM 1633a, SRM 1633a spiked with uranium and uranium ores containing uranium concentrations in the range of 0.05–0.06%. Using this method, concentrations of 22 elements including 8 REEs in two uranium ore samples were determined. Chondrite normalized REE patterns were used to arrive at the prevalent environment in the ore sites. For routine analysis of uranium bearing sample by INAA, this method is simple, does not need standards for each element, takes care of geometrical effects since it uses in-situ detection efficiency and easy to apply since no chemical separation is required.

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