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Rapid and non-destructive determination of uranium and thorium by gamma spectrometry and a comparison with ICP-AES

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Abstract A rapid, simple and non-destructive method was developed for the determination of thorium, uranium by gamma ray spectrometry (high purity Ge detector) in thorium–uranium mixture. Using the calibration curves, thorium and uranium were analyzed in synthetic samples with RSD ~2 %. Inter element effect suggested that 583 and 185.7 keV gamma lines are more suitable for the determination of Th and U, respectively in a mixture of Th–U. The newly developed method was validated by routinely employed method using synthetic samples. An ICP-AES based method was developed for the determination of uranium and thorium for comparison purpose.

Keywords Thorium · Uranium · Gamma spectrometry · ICP-AES

Introduction

In a country like India, due to the unavailability of high quality uranium resources, the nuclear power production depends on the utilization of thorium resources in a three-stage nuclear energy programme using thorium fuel cycle [1]. The thorium fuel cycle uses the naturally abundant isotope of thorium, ^{232}Th, as the fertile material. In the reactor, ^{232}Th is transmuted into the fissile artificial uranium isotope ^{233}U which is the nuclear fuel. Unlike natural uranium, natural thorium contains only trace amounts of fissile material (such as ^{231}Th), which are insufficient to initiate a nuclear chain reaction. Additional fissile material or another neutron source is necessary to initiate the fuel cycle. In a thorium-fueled reactor, ^{232}Th absorbs neutrons eventually to produce ^{233}U. This parallels the process in uranium breeder reactors whereby fertile ^{238}U absorbs neutrons to form fissile ^{239}Pu. Depending on the design of the reactor and fuel cycle, the generated ^{233}U either fissions in situ or is chemically separated from the used nuclear fuel and formed into new nuclear fuel. The thorium fuel cycle claims several potential advantages over a uranium fuel cycle, including thorium's greater abundance, superior physical and nuclear properties, better resistance to nuclear weapons proliferation [2, 3] and reduced plutonium and actinide production [3]. Therefore, it is required to develop simple, rapid and non-destructive technique to determine thorium and uranium in a thorium–uranium mixture at each stages of fuel fabrication.

The investigation of flooding processes in former underground mines, where uranium was leached in situ with dilute sulfuric acid, requires the activity determination of several radionuclides of the ^{238}U, ^{235}U and ^{232}Th decay chains in waters of various origin. Commonly used methods for determination of uranium and thorium include direct γ-ray measurements [4], γ-ray measurements after chemical separation [5, 6], α-particle spectrometry [7–9], radon emanation, liquid scintillation counting [10, 11], α- or β- particle counting methods with proportional counter [6], inductively coupled plasma atomic emission spectroscopy [12, 13] and mass spectrometry. The measurement of ^{238}U activity in samples by the high resolution γ-ray spectrometry is generally based on the quantification of the more intense γ-ray peaks either at 63.3 keV (3.8 %) or at ~92.6 keV (doublet: ~4.8 %) of ^{234}Th [14–16]. Recently,

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a relatively weaker intense but a cleaner high energy peak at 1001.0 keV (~0.84 %) of $^{234\text{m}}$Pa is also preferably used for measuring ^{238}U activity [17, 18], especially in uranium ore, processed uranium materials and also environmental samples.

In the present study, an attempt was made to develop a methodology for the determination of thorium and uranium in a thorium–uranium mixture. The method was found to be simple, rapid and non-destructive. No significant interference was observed from uranium on thorium determination and vice versa. The method was validated using synthetic samples and the analytical results were compared with that of the routinely employed method. ICP-AES being multi-elemental, sensitive and routinely employed analytical technique [19–23] due to desired analytical performance has been employed here for comparison purpose.

Generally thorium is determined by complexometric titration using ethelene diamine tetra acetic acid (EDTA). Though the method is very accurate and precise (RSD ~2 %), it does not tolerate interference of any other complexing anions such as fluorides, carbonates which are normally used for the dissolution of refractory thorium oxide (ThO$_2$) [24]. In a three stage nuclear work programme in a country like India, bulk of thorium with different proportions of natural uranium is used as reactor fuel materials. Therefore, in the present investigation, gamma spectrometric determination of thorium, uranium and thorium–uranium mixture was studied using high purity germanium (HPGe) detector.

Experimental

The working standard of thorium in the concentration range 100–200 mg/g and the working standard of uranium in the concentration range 60–170 mg/g and the mixture were counted at a fixed geometry using a high purity germanium detector coupled to a 4 k—multi channel analyzer. The resolution of the detector 2 keV for the 1332 keV gamma line of ^{60}Co. Depending upon the concentration, counting time ranged from 5000 to 10,000 s. The area under peaks corresponding to the energies 63.3, 185.7, 238.0, 583.0 and 1001.0 keV were calculated after subtracting the linear Compton baseline. The count rates in the peak regions were plotted against the thorium and uranium concentration respectively to study the correlation. The concentrations of the working standards of thorium and uranium and their gamma energy counts, relative to these, have been used for the estimation of respective concentrations in the mixtures.

ICP-AES based analyses were carried out using Spectro-Arcos spectrometer with both DC Arc and ICP as excitation source and charged coupled device (CCD) as detector systems. The instrumental specifications and optimized experimental parameters were given elsewhere [23]. The samples were analyzed after proper peak search, auto attenuation and multi point calibration. Quartz double distilled water and supra pure nitric acid were used for dilution. The method was validated with working reference materials obtained from inter laboratory comparison experiment involving different laboratories of Department of Atomic Energy (DAE), India.

Results and discussion

Determination of thorium

In the present paper attempt was made to determine Th using gamma energies emitted by the daughter ^{212}Pb at 238 keV gamma line (γ abundance ~43.6 %) and daughter ^{208}Tl at 583 keV gamma line (γ abundance 30.9 %). Calibration curves were established for Th using these lines and were presented in Fig. 1. The sensitivity of Th using 238 keV γ line (0.05 cps/mg/g) was found to be better than that of 583 keV line (0.016 cps/mg/g). High intercept of 238 keV line make the detection limit of this line poorer (0.41 mg/g) than that of 583 keV line (0.04 mg/g). A series of synthetic samples was prepared with concentration ranging from 0.01 to 500 mg/g. It was observed that using both the lines Th can be determined successfully with a RSD ~2 %. Table 1 summarizes the analytical results for the determination of Th using the γ lines of its daughters specified above. The methodology for the determination of thorium by using 911 keV gamma line of

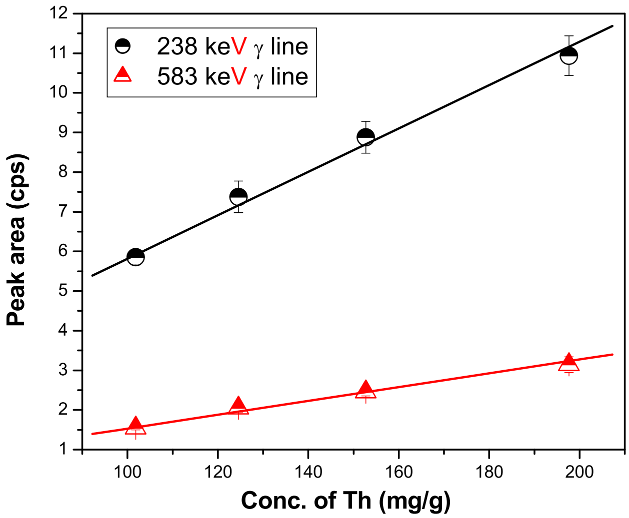

Fig. 1 Calibration curves for determination of Th using 238 keV γ line of ^{212}Pb and 583 keV γ line of ^{208}Tl

Table 1 Determination of Th using 238 keV γ line of ^{212}Pb and 583 keV γ line of ^{208}Tl

^{232}Th conc. (mg/g)	238 keV of ^{212}Pb	583 keV of ^{208}Tl
0.05	BDL	0.042 ± 0.003
0.1	BDL	0.098 ± 0.005
0.5	0.53 ± 0.05	0.51 ± 0.02
1	0.98 ± 0.03	1.0 ± 0.1
5	4.8 ± 0.2	4.9 ± 0.1
10	10.1 ± 0.2	10.2 ± 0.2
100	99 ± 1	100.0 ± 4
200	201 ± 2	205 ± 5
500	496 ± 1	505 ± 7
Detection limit (mg/g)	0.41	0.004
Sensitivity (cps/(mg/g))	0.05	0.016

^{228}Ac and 1079 keV gamma line of ^{212}Bi as the high energy gamma lines are less influenced by interference from other gamma energies [25].

Equation (1) and (2) depicted the nuclear reactions which lead to the formation of ^{212}Pb and ^{208}Tl responsible for the emission of the γ lines that were used for the determination of thorium.

$$^{232}_{90}\mathrm{Th} + n \rightarrow {}^{233}_{90}\mathrm{Th} \xrightarrow{\beta-} {}^{233}_{91}\mathrm{Pa} \xrightarrow{\beta-} {}^{233}_{92}\mathrm{U} + n \longrightarrow {}^{239}_{92}\mathrm{U} + 2n \tag{1}$$

$$^{232}_{92}\mathrm{U} \xrightarrow{\alpha} {}^{228}_{90}\mathrm{Th}(68.9\mathrm{a}) \xrightarrow{\alpha} {}^{224}_{88}\mathrm{Ra}(1.9\mathrm{a}) \xrightarrow{\alpha} {}^{220}_{86}\mathrm{Rn}(3.6\mathrm{d}) \xrightarrow{\alpha} {}^{216}_{84}\mathrm{Po}(55\mathrm{s}) \xrightarrow{\alpha} {}^{212}_{82}\mathrm{Pb}(0.15\mathrm{s}){}^{212}_{82}\mathrm{Pb}(0.15\mathrm{s}) \xrightarrow{\beta-} {}^{212}_{83}\mathrm{Bi}(10.64\mathrm{h}) \xrightarrow{\alpha} {}^{208}_{81}\mathrm{Tl}(61\mathrm{m}) \tag{2}$$

In the present case, a systematic study was carried out for the determination of natural uranium by gamma energies emitted by daughter ^{234}Th at 63.3 keV (γ abundance 4.8 %) and by daughter ^{234m}Pa at 1001 keV (γ abundance 0.84 %) as well as by ^{235}U gamma energy (γ abundance 57.2 %). Figure 2 presented the calibration curves for the determination of uranium using the above mentioned lines while Table 2 summarizes the analytical results for the determination of uranium in different synthetic samples. At 63.3 keV, correlation between count rate and concentration of uranium was found to be non-linear due to the interference from other gamma energies or prominence of self attenuation at low energy. Count rates of uranium are very low at 1001 keV, but still the correlation between count rate and the concentration of uranium is as good as that of 1001 keV, since 1001 keV energy is less attenuated by other gamma energies. Apart from this, 185.7 keV energy gamma line showed better analytical performance with detection limit 0.58 mg/g and the sensitivity 0.011 cps/mg/g, than the other. The suitability of various gamma lines have been evaluated in literature for the determination of ^{238}U in environmental samples [26]. ^{234}Th and ^{234m}Pa generally formed from ^{238}U by α decay.

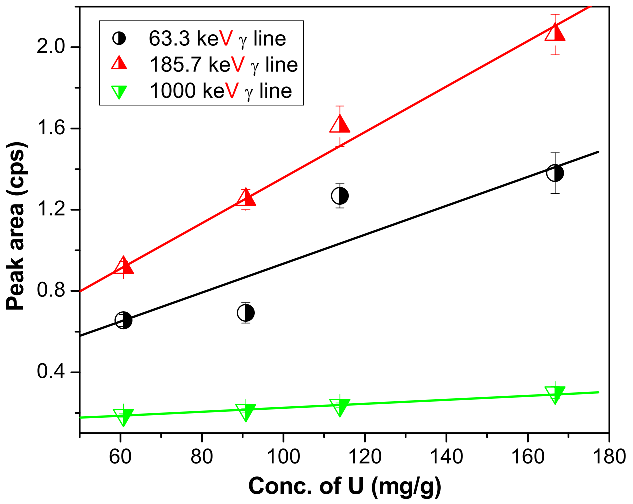

Fig. 2 Calibration curves for determination of U using 63.3 keV γ line of ^{234Th}, 1001 keV γ line of ^{234m}Pa and 1001 keV γ line of ^{234m}Pa

Inter element effect

The effect of the determination of thorium on uranium and vice versa is extremely important for a real sample of U–Th mixture. Five synthetic samples (identified as S1–S5) with various concentrations of uranium and thorium in U–Th mixture were taken for this purpose. From the calibration curves (obtained from pure U and Th) the area under the mentioned peaks were calculated for both U and Th in synthetic sample. If there is any inter element interference present in the synthetic samples, the measured area under the mentioned peaks (in terms of counts per second) will be different than the calculated area (in terms of counts per second). Tables 3 and 4 summarizes the analytical results obtained from actual counting and its comparison with the calculated values for thorium and uranium, respectively. No significant interference was observed (except 1001 keV) for all the mentioned gamma lines for the determination of both thorium and uranium. It was also noticed that for thorium determination 583 keV gamma line appeared to be better than the other with observed count rate within ±2 % of expected count rate. In case of uranium, 185.7 keV gamma line appeared to be more suitable than that of other with observed count rate within ±2 % of the expected count rate.

Table 2 Determination of U using using 63.3 keV γ line of ^{234Th}, 1001 keV γ line of ^{234m}Pa and 1001 keV γ line of ^{234m}Pa

U conc. (mg/g)	63.3 keV of ^{234}Th	1001 keV of ^{234m}Pa	185.7 keV of ^{235}U
1	BDL	BDL	1.0 ± 0.1
5	3.6 ± 0.4	4.9 ± 0.1	5.0 ± 0.1
10	13.1 ± 0.5	10.1 ± 0.1	9.9 ± 0.2
100	121.0 ± 4	97 ± 4	98 ± 1
200	233.0 ± 7	205 ± 8	198 ± 4
500	546.0 ± 8	505 ± 7	501 ± 3
Detection limit (mg/g)	2.0	2.15	0.58
Sensitivity (cps/(mg/g))	0.004	0.0011	0.011

Table 3 Comparison of calculated Th count rate with the experimentally observed count rate in Th–U mixtures

Synthetic samples	238 keV γ line		583 keV γ line	
	Calculated (cps)	Observed (cps)	Calculated (cps)	Observed (cps)
S1	10.935	9.935	3.142	3.079
S2	9.639	9.061	2.77	2.801
S3	8.729	7.609	2.508	2.467
S4	7.147	6.516	2.054	2.024
S5	5.789	5.557	1.663	1.686

Table 4 Comparison of calculated U count rate with the experimentally observed count rate in Th–U mixtures

Synthetic samples	63.3 keV γ line		185.7 keV γ line		1001 keV γ line	
	Calculated (cps)	Observed (cps)	Calculated (cps)	Observed (cps)	Calculated (cps)	Observed (cps)
S1	0.357	0.269	0.624	0.615	0.091	0.15
S2	0.555	0.398	0.969	0.982	0.141	0.117
S3	0.693	0.489	1.212	1.221	0.176	0.219
S4	0.934	0.688	1.633	1.603	0.238	0.234
S5	1.142	0.817	1.995	2.009	0.29	0.279

ICP-AES methods

To compare the results obtained by gamma spectrometric method, an ICP-AES based methodology was developed for the determination of uranium and thorium after establishing proper calibration curves. Table 5 and 6 summarizes the analytical performance of the analytical lines of uranium and thorium, respectively. Four analytical lines of uranium were chosen for the present study namely 385.958, 409.041, 367.007 and 279.394 nm. The detection limits of uranium using these lines was found to follow the trend: 385.958 < 409.041 < 367.007 < 279.394 nm. 385.958 nm line was found to be the most sensitive analytical lines while 409.041 nm was the least one. Comparable sensitivity was observed for the rest two lines chosen for the present case. The linear dynamic range for 385.958 and 409.041 nm line was found to be up to 1000 mg/L while the same for 367.007 and 279.394 nm line was up to 700 and 850 mg/L, respectively. The analytical performance revealed that 385.958 nm line of uranium is the best line for its determination.

Similar study was carried out for thorium by establishing calibration curves for the identified analytical lines: 401.913, 283.730, 274.716 and 283.231 nm. The overall detection limits of thorium were found to be more than one order of magnitude better than that of uranium (due to the high background intensity of uranium). The detection limits of all the lines were comparable while the sensitivity followed the trend: 401.913 > 283.730 > 283.231 > 274.716 nm. Based on the analytical performance Th 401.913 nm line was found to be the best for its determination.

Validation of the methodology using synthetic samples

Synthetic samples were prepared and uranium and thorium were analyzed using gamma spectrometric method

Table 5 Analytical performance of different analytical lines of uranium by ICP-AES

Uranium	385.958 nm	409.041 nm	367.007 nm	279.394 nm
Detection limits (mg/L)	0.02	0.09	0.12	0.34
Sensitivity (counts/(mg/L))	9000	800	1500	1200
Linear dynamic range (mg/L)	0.02–1000	0.09–1000	0.12–700	0.34–850

Table 6 Analytical performance of different analytical lines of thorium by ICP-AES

Thorium	401.913 nm	283.730 nm	274.716 nm	283.231 nm
Detection limits (mg/L)	0.001	0.001	0.003	0.002
Sensitivity (counts/(mg/L))	64,000	39,000	16,000	34,000
Linear dynamic range (mg/L)	0.001–1000	0.001–1000	0.003–950	0.002–970

Table 7 Determination of thorium in synthetic samples

Synthetic sample	S6	S7	S8
Amount of Th (mg/g)	1.0	10	100
Titrimetric determination (mg/g)	0.97 ± 0.05	10.9 ± 0.7	102 ± 4
X-ray fluorescence (mg/g)	1.3 ± 0.4	10.2 ± 0.3	100 ± 3
ICP-AES (mg/g)	1.1 ± 0.05	9.97 ± 0.4	97 ± 4
238 keV γ line (mg/g)	1.01 ± 0.04	9.7 ± 0.6	97 ± 4
Using 583 keV γ line (mg/g)	0.98 ± 0.05	10.3 ± 0.5	100 ± 3

Table 8 Determination of uranium in synthetic samples

Synthetic sample	S9	S10	S11
Amount of U (mg/g)	200	50	5
Davies & Gray method (mg/g)	203 ± 5	48 ± 2	5.2 ± 0.5
X-ray fluorescence (mg/g)	201 ± 6	52 ± 3	5.3 ± 0.3
ICP-AES (mg/g)	197 ± 5	52 ± 5	4.7 ± 0.2
Using 63.3 keV γ line (mg/g)	193 ± 5	57 ± 3	4.1 ± 0.5
Using 185.7 keV γ line (mg/g)	198 ± 3	50 ± 2	4.9 ± 0.3
Using 1001 keV γ line (mg/g)	202 ± 3	47 ± 3	5.2 ± 0.3

developed in this study. The analytical results were compared with the routinely employed method i.e. Davies & Gray method for uranium [27] and titrimetric determination for thorium [28]. Tables 7 and 8 summarizes the analytical results. It was observed that the analytical results of gamma spectrometric method are comparable with the routinely employed method (for uranium Davies & Gray method was employed while for Th complexometric titration was used) with RSD <5 %. Using 385.958 nm analytical line of uranium and 401.913 nm line of thorium, the analyses were done for the synthetic samples by ICP-AES. The analytical results obtained by gamma spectrometric study compared well with the ICP-AES technique also. The main advantage of the present method over conventional methods lies in its simplicity and non-destructive nature. X-ray absorption florescence (XRF), being a routinely employed method was also employed for the comparative study and the analytical results obtained by newly developed method found to be in good agreement with other analytical techniques.

Conclusions

A simple, rapid and non-destructive, gamma spectrometric method was developed for the determination of thorium and uranium content in a thorium–uranium mixture using γ energy at 583 keV for thorium and 185.7 keV for uranium. The detection limit for thorium using 583 keV γ line was found to be 0.04 mg/g while that for uranium using 185.7 keV γ line was 0.58 mg/g. Both these lines were found to be interference free in Th–U matrix. The newly method was validated using synthetic samples and was compared with the routinely employed methods for the determination of thorium and uranium. An ICP-AES based method was developed to compare the analytical results obtained by gamma spectrometry and was found to be satisfactory. Since, ^{212}Pb obtained from both ^{232}U and ^{232}Th, was not considered for the estimation to avoid interference.

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