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Simultaneous Analysis of Uranium and Thorium by the Delayed Fission Neutron Counting Method

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Abstract

A small modification in the procedure of Amiel's delayed neutron counting method is attempted for the simultaneous determination of uranium and thorium in geological samples. This analytical procedure is found to hold good accuracy over the wide range of concentration ratio of two elements. Details of the development and evaluation of the method are described. The sensitivity obtained from the method is less than 0.1 μg for uranium and it is about 5μg for thorium.

요 약

Amiel의 지발중성자 계측법을 사용한 분석과정을 다소 수정하여 지질학적 시료중의 우라늄 및 토륨의 동시 정량을 시도하였다. 본 분석과정은 넓은 범위의 두원소의 함량비에서 정확하게 적용할 수 있었다. 개발과정중 수행한 세부사항을 기술하였으며 나아가 본 분석법을 평가하였던 바 우라늄의 감도는 0.1μg 이하였고 토륨의 감도는 약 5μg 이었다.

1. Introduction

Analysis of trace quantities of uranium and thorium in complex matrices has been subject to extensive research and development because accurate content of these elements is necessary for the identification and demarcation of regions having their reserves of economic value. A number of analytical methods are currently in use for the analysis of uranium[1] and thorium[2] in various geological samples. Most of these methods are time-consuming and require elaborate chemical processing in order to eliminate blank and/or matrix interferences prior to measurements.

The basic requirements of the analytical procedure to be adopted for geological survey

programs are that it is highly sensitive, fast, reliable and preferably nondestructive. Neutron irradiation, followed by delayed fission neutron counting, first introduced by Echo and Turk[3] and investigated further by Amiel[4], was found to satisfy adequately most of these basic requirements.

For the uranium assay Amiel irradiated samples without cadmium cover and determind uranium content by comparing the activities thus obtained from samples with those from uranium standards. When thorium content is much high compared with uranium, thorium, however, interferes in the uranium assay. In order to eliminate this interference of thorium in the uranium assay, Reddy and Sanker Das[6] irradiated samples with a thermal neutron flux of which the thermal to fast neutron ratio was approximately 13.

In this work each sample containing uranium and thorium is irradiated with and without cadmium cover for the uranium content using a mixed neutron flux of which the thermal to fast neutron ratio is approximately 4. When the sample is irradiated without cadmium cover ^{235}U and ^{238}U as well as thorium are fissioned by this mixed neutron flux. On the other hand when the same sample is irradiated with cadmium cover, ^{238}U, thorium and very smaller amount of ^{235}U as compared with the irradiation without cadmium cover are fissioned by fast neutrons. The counting differences between the counts obtained with cadmium cover and the counts obtained without cadmium cover are pure thermal neutron responses due to the fission of ^{235}U. This counting differences obtained from analytical samples are compared with those obtained similarly from uranium standards in order to determine uranium content. The fast neutron responses due to thorium fission among the total fast neutron responses are deduced by subtracting the fast neutron responses due to uranium fission, which are obtained from pure thermal responses due to ^{235}U fission described above and cadmium ratio of uranium, from the total fast neutron responses due to fission of uranium and thorium. The fast neutron responses due to thorium fission thus obtained from samples are compared with those obtained similarly from thorium standards to determine thorium contents.

As the results of this modification the present method is found to hold good accuracy over more wide range of concentration ratio of two elements than in previous Amiel's method. Statistical error estimations as well as details of the development and the evaluation of this technique are also described.

2. Experimental

Preparation of Samples and Standards; The sample for analysis was normally ground to pass the 200 mesh sieve. A 100-200 mg portion of the sample was accurately weighed and sealed by heating in a small polyethylene bag for irradiation.

A stock solution of uranium was prepared by dissolving 0.210 g of A.R. grade $UO_2(NO_3)_2.6H_2O$ in 5 ml of 0.1 N nitric acid and diluting with distilled water to 100 ml in a volumetric flask. A stock solution of thorium was prepared similarly from thorium nitrate, which was previously standardized by igniting to oxide and weighing. Those stock solutions were further diluted to prepare several standard solutions containing various amounts of each elements, few micrograms to milligrams per ml. An 100λ aliquot of the standard solutions was evaporated to dryness on a small polyethylene bags by heating.

Facilities; Irradiation was carried out by the pneumatic transfer system of TRIGA Mark III reactor. The position of irradiation

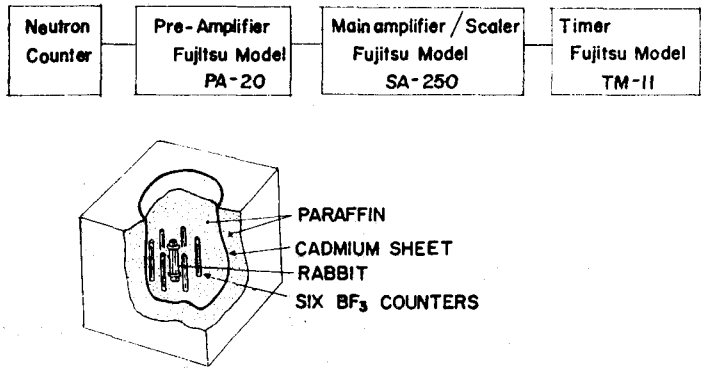

Fig. 1. Delayed neutron detecter and associated electronics.

is located at the face of the reactor core. At the power level of 1 MW, the thermal neutron flux was 1.0×10^{13} neutrons cm^{-2} sec^{-1} and the unmoderated fission flux was 2.6×10^{12} neutrons cm^{-2} sec^{-1} at the irradiation position. Samples can be received for counting within 6—8 sec after the end of irradiation.

For the simultaneous determination of uranium and thorium, an accurately weighed portion of a sample that was sealed in a polyethylene bag was first irradiated without cadmium cover to obtain mostly the thermal neutron responses on uranium. An another portion of the same sample was second irradiated with cadmium cover of 0.5mm thickness in order to obtain a summed fast neutron responses on uranium and thorium. The polyethylene rabbits that were used for the transfer of sample to the irradiation position had a dimension of 110 mm length $\times$ 16 mm I.D..

Details of neutron detector assembly and associated electronics are represented schematically in Fig. 1. The detector consists of six boron trifluoride proportional counters, 96% enriched boron 10 (N. Wood Model G-10-20), each 20″ length$\times$1″ in diameter. Each counter was inserted into an aluminum tube (2.6cm I.D.) that was embedded in a block of a paraffin wax moderator (60 cm length and 27 cm in diameter) so as to form a ring of 8cm radius by 6 counters. The moderator was surrounded by 0.75 mm thick cadmium foil, followed by an additional 6 cm thick layer of borated paraffin to serve as external neutron shield. For the access of samples, an extra aluminum tube was introduced along the coaxial axis of the ring formed by 6 counters. The polyethylene rabbit which contained the irradiated sample was inserted half way along the tube for the neutron counting.

The counters were operated in parallel from a common regulated high voltage source (~3000 volts). The pulses from the counters were fed through a current sensitive preamplifier (gain 3/10) and a nonoverload amplifier (gain 400) into a scaler. Discrimination level of 25 μA of input signal could effectively reduce the contribution from gamma rays.

The efficiency of the counting assembly was checked using a standard RaD-Be source and was found to be 6—8%. However, the detection efficiency for delayed neutrons was higher and found to be around 13%, when deduced from the data presented by Amiel[4] and measured thermal neutron flux of the irradiation site.

Procedures for irradiation and measurement; Sealed samples in a polyethylene bags, which were either covered by cadmium or not, inserted into rabbits to a fixed position. The rabbits were transferred pneumatically to the irradiation site of TRIGA Mark III by pressing the 'send' button. A stop-watch turned on simultaneously to control the irradiation time. At the end of irradiation, the rabbits were received by pressing the 'return' button. Another stop-watch turned on simultaneously to control the delay time before starting the count. The rabbit was quickly collected and transferred to the counting assembly. Periods of 60 sec were adopted for irradiation and counting, respectively, with the delay time of 20 sec in the present work according to the recommendation[4].

System background; Under normal operating conditions, the counting assembly has a room background of 4—5 cpm and there was no significant change in this value. A background count of $48\pm6(1\sigma)$ cpm was obtained after 20 sec delay by following the experimental conditions, *i.e.*, by irradiating an empty rabbit for 1 min., transfering to the counting position, and etc.

Comments on the analysis of uranium and thorium in mixtures; When a portion of a mixed sample is first irradiated by a mixed neutron flux without cadmium cover, not only is occured the fission of ^{235}U by thermal neutron but also those of ^{238}U and thorium by fast neutron. When another portion of the same sample is second irradiated with cadmium cover, only the fissions of ^{238}U and thorium occur because the thermal neutron is discriminated out.

Since delayed neutrons are emitted from

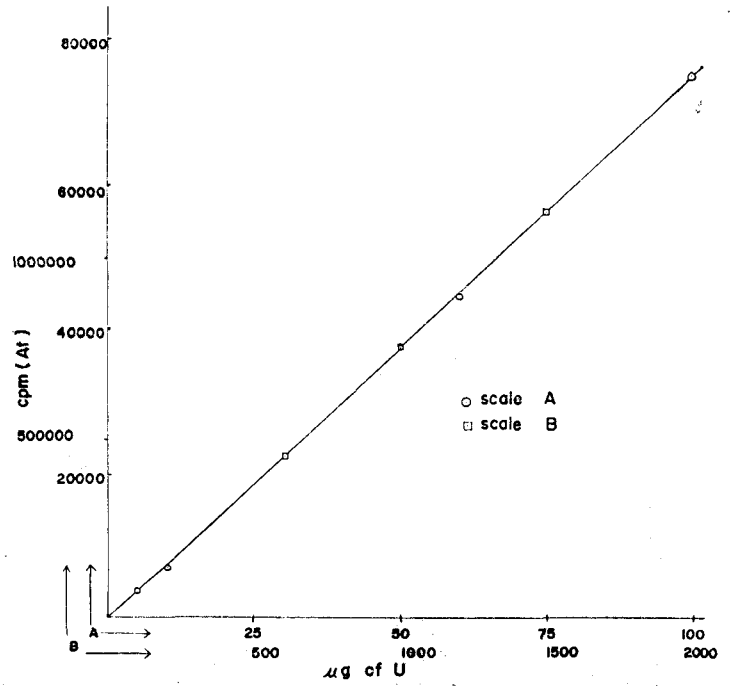

Fig. 2. Calibration curve of 1~1,000μg standard uranium samples. (Irrad. time 1min.; power level 2MW; counted for 1 min. after 20 sec delay.)

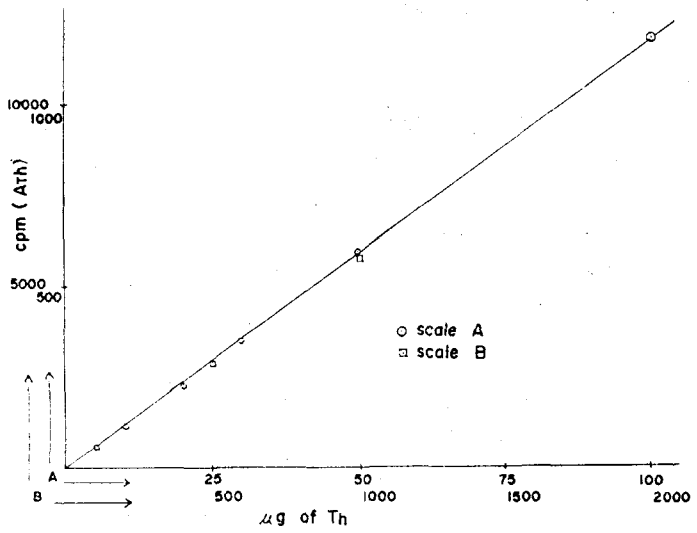

Fig. 3. Calibration curve of 1~1000μg standard thorium samples (Irrad. time 1min.; power level 2MW; counted for 1min. after 20 sec delay)

fission precursors by both thermal and fast neutrons when irradiating samples without cadmium cover, the following additivity holds in counting rates,

$$A=A_t+A_f, \qquad (1)$$

where A is the total counting rate which is due to ^{235}U, ^{238}U and thorium components, A_t the counting rate from ^{235}U component, A_f the counting rate from both ^{238}U and thorium components, *i.e.*, total fast neutron response. When the mixed sample is irradiated with cadmium cover, only the total fast neutron response A_f is taken and given by Eq. 2,

$$A_f=A_{Th}+A_{U-238}, \qquad (2)$$

where A_{Th} and A_{U-238} are the counting rate from thorium and uranium components, respectively. The thorium component A_{Th} can be given by Eq. 3, which is deduced from Eq. 2,

Table 1. Delayed neutron activities of uranium standard, irradiated at 1 MW for 1 min., counted for 1 min, 20 sec after end of irrad.

μg of U	Net count without Cd cover	Net count with Cd cover	At	$A_t/\mu g$	CR
1	363	25	338	338	14.6
5	1,850	130	1,720	343	14.3
10	3,695	274	3,421	342	13.6
30	11,050	809	10,241	341	13.6
60	22,331	1,619	20,712	345	13.8
100	36,329	2,595	33,734	337	14.0
300	108,970	8,457	100,513	335	12.9
600	217,731	15,984	202,827	338	13.6
1,000	363,925	26,105	339,022	339	13.9
				average 340±3.2	13.8±0.5

Table 2. Delayed neutron activites of thorium standard. irradiated at 1 MW for 1 min, counted for 1 min, 20 sec after end of irrad.

μg of Th	Net count without Cd cover (A)	Net count with Cd cover (A_{Th})	$A_{Th}/\mu g$	CR
10	58.0	56.0	5.60	1.03
20	115	109	5.47	1.05
30	175	167	5.57	1.05
50	296	284	5.74	1.04
100	1,600	578	5.76	1.04
500	2,854	2,713	5.42	1.05
1,000	5,620	5,495	5.47	1.02
		average	5.57±0.14	1.04±0.01

$$A_{Th}=A_f-A_t\times\frac{1}{CR-1,} \qquad (3)$$

where CR is cadmium ratio of uranium.

Calibration; Calibrations were established using respective standard samples of uranium and thorium as follows. Each standard solution of uranium and thorium was twice irradiated for 1 min., *i.e.*, first with cadmium cover and second without cadmium cover. The sample was counted for 1 min. after 20 sec delay. The counting rate from ^{235}U, A_t, and the counting rate from thorium, A_{Th}, were deduced using Eq. 1 and 3, respectively. The counting rates were resulted in linear curves over a wide range of quantities and concentrations as shown in Fig. 2 and 3 and Table 1 and 2.

Analysis of uranium and thorium in mixtures; Mixtures were irradiated and counted according to the procedures as described above. The counting rate from ^{235}U, A_t, and the counting rate from thorium, A_{Th}, were deduced using Eq. 1 and 3, respectively. Uranium content in mixed samples was determined by comparing the counting rate A_t with the corresponding values obtained from the uranium standards, while thorium content was determined by comparing the counting rate A_{Th} with the corresponding values of thorium standards.

Table 3. Analysis of uranium and thorium in sample (U, ppm)

Sample	Present method		Colorimetric method	
	Uranium	Thorium	Uranium*	Thorium**
AlC—7	66.0	266	60	270
〃 —24	61.5	111	60	132
〃 —25	54.0	355	50	357
〃 —45	66.5	97	70	99
〃 —48	172.0	303	200	305
〃 —49	417.0	173	400	180
〃 —69	250.0	69	280	72
No.—1	176.0	223	195	250
〃 —5	116.0	388	93.3	396
〃 —6	97.5	590	102	610

* Results were presented by Korea National Geological Servey.

** Results were obtained by the method described in Ref. (5)

Table 4. Uranium content of standard ores

Ores	Uranium content (U_3O_8 %)	
	Reported	Present work
Low grade pitchblende (3—A)	4.29	4.54 ±0.14
Phosphate Rock (No.1)	0.029	0.030±0.001
Carnotite (No.4)	0.18	0.187±0.005
Torbernite (S—1)	0.471	0.489±0.003
Torbernite (S—2)	0.313	0.313±0.008
Carnotite (S—3)	0.418	0.438±0.016
Uraninite (S—4)	0.375	0.375±0.003

3. Results and Discussion

The results of measurements of uranium and thorium in several samples which were

supplied from Korean National Geological Survey are presented and compared with those obtained by other methods in Table 3. This table shows a good agreement between results. It is also notable that the present procedure for the simultaneous determination of uranium and thorium holds good accuracy over the wide range of concentration ratio of two elements. On the other hand when Amiel's procedure is applied for the determination of uranium in the geological samples of Table 3, it is found that the errors due to thorium interference in uranium assay are up to about 10%. Standared ores for uranium, available from International Atomic Energy Agency, were analysed by this method, and the results are compared in Table 4 with certified values. It was found from this comparison that the accuracy of the technique was around ±3% for ores. Replicate measurements also showed a good precision of the procedure as shown in Table 4. A major advantage of the procedure is its rapidity in analysis(~5min.) compared to 3—5 hours required per sample for the determinations of both uranium and thorium by conventional colorimetry.

The activity observed for a sample of 1μg of natural uranium was 340 counts and that for 1μg of thorium was 5.57 counts as shown in Table 1 and 2 when followed experimental procedure as mentioned earlier with the reactor power level of 1 MW. Using these values, the sensitivity of uranium or thorium detection and the accuracy of the measurement were calculated by a statistical analysis of the counting data as follows. If the background of an empty rabbit in a 1-minute count is B, then the counting rate from ^{235}U compoment A_f is given by following Eq. 4,

$$A_f=(A+B)-(A_f+B). \quad (4)$$

The standard deviation in the measurement of uranium σ_u is given by following Eq. 5,

$$\sigma_u=(A+A_f+2B)^{\frac{1}{2}}. \quad (5)$$

When the number of counts of A_f in a single measurement is low, it is desirable to repeat the measurement, both of empty rabbit and rabbit with sample, in order to improve counting statistics. If measurements are repeated n times, the fractional error E is given by following equation,

$$E=\frac{\sigma_u}{A_f}=\frac{(\Sigma_n A+\Sigma_n A_f+2\Sigma_n B)^{\frac{1}{2}}}{\Sigma_n A-\Sigma_n A_f}. \quad (6)$$

A calculation of the standard deviations for various uranium content and background level is given in Table 5. It is seen that uranium content level of about 10μg can be analysed whithin the standard deviation of

Table 5. Error estmate in uranium assay, standard deviations(%) for various uranium content and background levels

	Uranium, 10μg. A_t=3,400 counts	Uranium, 1μg. A_t=340 counts			Uranium, 0.1μg. A_t=34 counts			Uranium 0.05μg. A_t=6.8 counts		
B (counts)	50	60	50	40	60	50	40	60	50	40
1	1.86	6.65	6.47	6.35	37.0	34.7	32.1	69.4	64.1	58.4
2	1.31	4.69	4.60	4.50	26.2	24.6	22.6	49.1	45.5	41.5
3	1.07	3.88	3.76	3.68	21.4	20.0	18.5	40.2	37.0	33.9
4	0.925	3.32	3.25	3.18	18.5	17.4	16.8	34.7	32.2	29.3
5	0.829	2.96	2.91	2.85	16.6	15.5	14.3	31.1	28.7	26.2
7	0.702	2.51	2.46	2.42	14.0	13.1	12.1	26.2	24.3	22.2
10	0.588	2.10	2.05	2.01	11.7	10.9	10.1	22.0	20.4	18.5

Table 6. Error estimates of thorium assay in uranium-thorium mixtures

Uranium μg / Thorium μg	1	5	10	50	100	500	1000
	Relative standard deviation, %						
5	36.9	53.3	66.2				
10	20.6	28.4	35.6	70.2	98.3		
50	6.79	7.79	8.94	15.2	20.6	43.4	61.4
100	4.51	4.94	5.38	8.13	10.6	22.1	30.9
500	1.93	1.97	2.02	2.38	2.62	4.71	6.39
1000	1.36	1.37	1.39	1.52	1.66	2.55	3.34

A_{Th}=5.57 counts per μg of thorium
A_t=340 counts per μg of uranium
B=48 counts
Cadmium ratio of uranium=13.8
irrad. time=60 sec, delayed time=20sec,
counting time=60 sec, at a power level of 1 MW.

about 2% even with single measurement, while for the content level of 0.05μg the deviation can be reduced to about 20% with 10 repeated measurements.

When assessing the sensitivity of the thorium measurement, the presence of uranium gives a rise in background and the sensitivity of the thorium assay is calculated as follows. The net count due to thorium A_{Th} is given by following Eq. 7.

$$A_{Th}=(A_f+B)-[(A+B)-(A_f+B)]\frac{1}{CR-1}. \quad (7)$$

The standard deviation in the measurement of thorium σ_{Th} is given by Eq. 8,

$$\sigma_{Th}=\left[\bar{A}_f\left(1+\frac{1}{R^2}\right)+\frac{\bar{A}}{R^2}+\frac{A_f}{R^4}\sigma_{CR}^2\right]^{\frac{1}{2}}. \quad (8)$$

where σ_{CR} is standard deviation obtained when measuring cadmium ratio of uranium, which is given in Table 1. For the Eq. 8, $\bar{A}$ is defined as $(A+B)$, $\bar{A}_f$ as (A_f+B) and R as $(CR-1)$. The fractional error E of a single net count of thorium is given by Eq. 9 and error propagation,

$$E=\frac{\sigma_{Th}}{A_{Th}}=\frac{\left[\bar{A}_f\left(1+\frac{1}{R^2}\right)+\frac{\bar{A}}{R^2}+\frac{A_t}{R^4}\sigma_{CR}^2\right]^{\frac{1}{2}}}{A_f-A_t\times\frac{1}{CR-1}}$$

$$\cong\frac{\left[\bar{A}_f\left(1+\frac{1}{R^2}\right)+\frac{\bar{A}}{R^2}\right]^{\frac{1}{2}}}{A_f-A_t\times\frac{1}{CR-1}}. \quad (9)$$

Calculated errors obtained when analyzing samples of various content of uranium and thorium is given in Table 6 with a background B=48.

Because of the large activity of ^{235}U by thermal neutrons compared to those of ^{238}U and thorium by fast neutrons, the error due to a small presence of thorium is trivial in uranium assay. On the contrary, however, a small presence of uranium give rise to the large error in thorium assay due to about 4 times larger activity of ^{238}U by fast neutrons than thorium. As can be seen in Table 6, for example, the error of thorium assay is about 4.5% when thorium content is about 100μg level with 1μg of uranium in a mixture, while this value is enhanced to about 10.6% with 100μg of uranium in a mixture. Therefore, for samples in which the content of thorium is comparable to that of uranium a series of repeated measurements is preferable to reduce errors.

As the samples and standards were sepa-

rately irradiated and counted, a check on the stability of the reactor flux is essential. The results given in Table 1 are obtained in a typical series of measurements, involving nine sequential irradiations for 40 min. The mean value of 340 counts per minute was obtained per microgram of uranium with a relative standard deviation of 3.0% out of which 2% could be accounted for the counting statistics alone. The mean value of 5.57 counts per minute was obtained per microgram of thorium with a relative standard deviation of 5.0%.

Effect of impurities; For the analysis of uranium the activity due to thorium A_{Th} was observed to be about 60 times smaller than A_i for uranium. In practice, when analyzing uranium, the error due to the possible presence of thorium was negligible. The interference of uranium in the thorium analysis was discussed above.

Errors may be caused due to flux attenuation by elements such as B, Li, Gd, Cd and etc., having high thermal neutron absorption cross section, This effect was reported to be unimportant in most cases[4]. Beryllium can emit neutron by photo-neutron reaction and causes interferences. It was also reported that such effects are unlikely to be important[4].

The only known delayed neutron emitters, apart from fission products, are ^{17}N and ^{9}Li produced by $^{17}O(n,p)\ ^{17}N$ and $^{9}Be(n,p)\ ^{9}Li$ reactions. Because of their short half-lives (4.2 and 0.17 sec, respectively), these will decay to negligible levels under the selected delay time.

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