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AN EVALUATION OF THE DELAYED NEUTRON COUNTING METHOD FOR SIMULTANEOUS ANALYSIS OF URANIUM AND THORIUM AND FOR $^{235}U/^{238}U$ ISOTOPIC RATIO DETERMINATION*

M. J. A. ARMELIN, M. B. A. VASCONCELLOS

Radiochemistry Division,
Instituto de Pesquisas Energéticas e Nucleares – CNEN/SP,
Caixa Postal 11049
05499 – São Paulo, SP (Brasil)

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This paper describes an evaluation of activation analysis by delayed neutron counting to determine uranium and thorium simultaneously in geological materials and to measure $^{235}U/^{238}U$ isotopic ratios. A procedure to isolate the thorium before the irradiation was studied and adapted for use when the interference of uranium makes the nondestructive thorium analysis impossible. $^{235}U/^{238}U$ ratios were determined in standards with ^{235}U abundances from about 0.5 to 93%, in milligram size samples. Discussion on precision, accuracy and total error of the method is presented.

Introduction

The use of delayed neutrons of fission in analytical measurements was introduced in 1957 by ECHO and TURK.[1] AMIEL[2] showed that the method could be applied to all fissionable nuclides when they are exposed to a neutron flux, showing the possibility of the method to determine the $^{235}U/^{238}U$ ratio in a sample which contains uranium. In the same year, DYER and LEDDICOTTE[3] published a study about the application of the method for uranium analysis in various kinds of materials. GALE[4] made an evaluation of the influence of high energy gamma-radiation on delayed neutron counting and applied the method to geochronological problems and meteorite study.

The literature shows that this method has been the object of many studies which improved the sensitivity of analysis through the use of several counting and activation cycles.[5] In some cases, the development of automated systems[6,7] to put the samples in and get them out of the reactor irradiation sites allowed hundreds of uranium analysis to be done in a single day.

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There are many studies using different techniques to discriminate a fissil and fertile nuclide, in order to determine their ratio. One of these techniques is based on the difference among the fission cross section of several nuclides according to the incident neutron energy.

The energy of the incident neutron is changed by covering or not the sample with material capable of absorbing lower energy neutrons. CAVALLARI et al.[8] utilized this technique in a thermal reactor for the activation of milligram size samples. In other cases, researchers[9] utilized a 14 MeV neutron generator to active samples and neutrons of different energies obtained by surrounding the neutron source with various combinations of moderating materials to reduce the neutron energy.

In the present work, special attention was given to the simultaneous determination of uranium and thorium, to be carried out on a routine basis. In the case of Brazilian ores, which are rich in thorium, it is important to discount the interference of thorium in uranium analysis, as well as to determine the element itself.

A fast and quantitative procedure was adapted to separate the thorium from uranium before the determination of thorium concentration by counting the delayed neutrons produced in fission, for the cases in which the interference of uranium does not allow the instrumental analysis of thorium.

The determination of $^{235}U/^{238}U$ ratios was made through a calibration curve built with standards of different enrichments in ^{235}U. The calibration curve was defined by means of standards with abundances varying between 0.5% and 93% in ^{235}U.

A study was made to assess the precision, accuracy and efficiency of the method and also, an evaluation of the interference of uranium on the precision and accuracy of thorium analysis was carried out.

Experimental

Preparation of samples and standards for irradiation

Two samples of identical mass were weighed inside polyethylene envelopes, one to be irradiated when covered by a neutron filter and the other to be irradiated without the filter. Cadmium was used as filter for uranium and thorium analysis while composite cadmium and boron carbide was chosen as filter for the determination of $^{235}U/^{238}U$ ratio.

The standards consisted of standard uranium ores certified by the International Atomic Energy Agency (IAEA), or were prepared of standard solutions which

were obtained from oxides of the elements (U_3O_8 or ThO_2, provided by NBS), pipetted on a filter paper or silica gel matrix.

Pairs of identical standards were packed into polyethylene envelopes. One standard of each pair was irradiated covered with a filter and the other one uncovered. The standards were always reutilized because the delayed neutrons decay rapidly and because the burnup of fissionable nuclide is negligible with each short irradiation.

A polyethylene holder was used to fix always in the same position the standards and samples inside the irradiation polypropylene containers (rabbits).

Detection and measurement system

Irradiations were carried out in the IEA-R1 research reactor, in a position where the neutron flux had the following intensities: thermal flux = $4.4 \cdot 10^{11}$ n $\cdot$ cm^{-2} $\cdot$ s^{-1}; epithermal flux = $4.0 \cdot 10^{10}$ n $\cdot$ cm^{-2} $\cdot$ s^{-1}; fast flux = $1.6 \cdot 10^{11}$ n $\cdot$ cm^{-2} $\cdot$ s^{-1}.

At the Radiochemistry Division of IPEN-CNEN/SP, a system for the determination of U, Th and $^{235}U/^{238}U$ ratios close to the natural abundance[10] has been working since 1978. In this system delayed neutrons emitted by the fissionable nuclides were counted by means of six BF_3 detectors, enriched to about 90% ^{10}B, connected in parallel and immersed in a paraffin cylinder, which acts as a neutron moderator. The detector assembly was coupled to an electronic counting system made up of pre-amplifier, monochannel analyzer, scaler and timers. A more detailed description of this neutron detection and counting system was presented elsewhere.[11]

Irradiation, decay and counting times were always 60, 20 and 60 seconds, respectively. This sequence of operations corresponds to a complete cycle of irradiation and counting. In some cases this cycle was sucessively repeated many times in order to improve the sensitivity of the method.

Experimental procedure for destructive thorium analysis

Rock samples were attacked with a 1 : 1 mixture of concentrated HNO_3 and concentrated HF and the final solution was taken to almost dryness. The residue was taken up in a minimum volume of concentrated HNO_3 and the resulting solution was centrifuged. The supernatant solution was taken to almost dryness for elimination of HNO_3. The silica centrifugation residue was washed with 5M HNO_3 containing about 2g of $Al(NO_3)_3 \cdot {}_9H_2O$, at a temperature of approximately 70 °C.

The residue resulting from the washing process was centrifuged again and the remaining solution was added to that obtained in the first centrifugation. Washing

residues and further centrifugation operation, as described above, were repeated several times.

After this procedure, a suitable volume of methanol was added to the final solution, which was then ready to be percolated in the wet resin. Before percolation, 0.6mg of this resin was conditioned in a 0.4 cm diameter column, by passing a solution containing one volume of 5M HNO_3 and nine volumes of methanol. The resin used was Bio-Rad Ag 1X4, 200–400 mesh.

Thorium was completely retained by the resin as a result of the percolation process. The last step was the transfer of the resin to polyethylene envelopes in order to proceed with the irradiation and measurement in the conditions of analysis already described.

Results

Analysis of uranium and thorium

Sensitivities, limits of detection and limits of determination for uranium and thorium analysis. The sensitivities, limits of detection and limits of determination in the conditions studied for uranium and thorium analysis are shown in Table 1.

The limits of detection were calculated according to KAISER's[12] criterion, and the determination limits from LONG and WINEFORDNER's criterion.[13] Detection limits and determination limits were calculated for 1.5 g samples.

Table 1
Sensitivities, limits of detection and limits of determination for uranium and thorium analysis

	Natural uranium			Thorium		
	Number of cycles					
	1	2	3	1	2	3
Sensitivity, counts/μg	43.4	86.7	117.2	0.52	1.06	1.51
Detection limits, ppm	0.31	0.22	0.20	25	18	15
Determination limits, ppm	1.0	0.72	0.65	85	59	51

Detection limits and determination limits were calculated for a 1.5 g sample.

Nondestructive and simultaneous analysis of uranium and thorium. The accuracy and the precision of the method, under pre-defined experimental conditions were studied by means of the analysis of geological samples provided by the IAEA, through an intercomparison program for uranium and thorium analysis. After publication of the results of the intercomparison by the IAEA[14] it was possible to calculate the accuracy of the method. Results obtained in this study are shown in Table 2.

Evaluation of the interference of uranium on the precision and accuracy of non-destructive analysis of thorium and vice versa. Since the method is much more

Table 2
Results for the nondestructive and simultaneous analysis of uranium and thorium in IAEA thorium ores

Sample	U, ppm	Relative error, * %	Th, %	Relative error, %
S-14	(26 ± 2)	10.3	0.067 ± 0.007	9.8
S-15	(80 ± 4)	5.9	0.372 ± 0.018	2.5
S-16	(433 ± 5)	2.7	1.71 ± 0.08	1.8

Means and standard deviations for 6 determinations.
*Relative error compared to the certified value published by the IAEA.[14]

sensitive for the determination of uranium than of thorium, the precision of uranium analysis is very little affected by the presence of thorium in the sample. The precision is much more dependent on the weighing errors and counting statistics. This is the same conclusion that was arrived at by MILLARD et al.[15]

In the present work, it was considered that counting statistics is the main source of error in the precision of uranium and thorium analysis. Also it was considered that the accuracy of uranium analysis is independent of the presence of thorium in the sample, but a reliable result for thorium depends on the sample U/Th ratio.

Depending on the U/Th ratio in the sample and on the neutron flux conditions (thermal on fast neutron flux), there can exist a strong preponderance of the counting that comes from uranium, compared to the one that arises from thorium fission. This can occur even when the sample is irradiated in a neutron filter, which causes a kind of masking of thorium and false results for thorium, even when it has a concentration in the sample of the order of the determination level indicated in Table 1.

An evaluation of the U/Th ratio in the sample as a function of multiples(N) of the minimum determinable mass of thorium (MDT = 127 μg Th) with one irradiation cycle was made with the sensitivity data from Table 1.

It was considered that the thorium contribution to the total counts for the samples is equal to at least 3σ of the counting of uranium when the sample is irradiated in a cadmium filter. In this way, a calculation was made of the maximum U/Th ratio (R) acceptable to have thorium determined with an expected confidence level of 95%. The relation between R and multiples N of the minimum determinable mass in the experimental conditions of the present work is given by the linear function:

$$R = 2.05N.$$

So it can be concluded that the accuracy of the results for thorium analysis depends on the U/Th ratio in the sample.

Destructive analysis of thorium in geological materials. As in some cases uranium interferes in the determination of thorium through the nondestructive analysis method, a method, developed by KORKISCH[16] for the chemical separation of thorium and uranium, was chosen and adapted to solve this interference problem.

The experimental procedure was described in Experimental. This procedure was tested with simulated samples obtained from an ore in which thorium and uranium were not found by convetional activation analysis methods. 10 mg of uranium and 4.96 mg of thorium were added to this ore. Table 3 shows the fractions of thorium and uranium retained by the resin.

In order to verify the accuracy of uranium and thorium determination by this procedure, the IAEA thorium ore, S-16, was analyzed according to it. This

Table 3
Separations yields for thorium and uranium in a Bio Rad AG 1 × 4 resin, in a HNO_3 - methanol medium

Thorium sorbed in resin, %	Uranium sorbed in resin, %
100.7	0.009
95.8	0.11
103.8	0.44

Table 4
Results for destructive and instrumental analysis of thorium in the S-16 IAEA ore

Destructive analysis		Non-destructive analysis	
Th %	Relative error, %	Th %	Relative error, %
(1.72 ± 0.08)	2.4	(1.71 ± 0.08)	1.8

Means and standard deviation for 6 determinations.

ore had already been analyzed by instrumental analysis and Table 4 shows the mean result and the standard deviation for six thorium determinations. Also the results of instrumental analysis are presented for the sake of comparison.

Nondestructive analysis of the $^{235}U/^{238}U$ isotopic ratio

For the determination of the $^{235}U/^{238}U$ ratio, it was assumed that the sample contained only uranium as fissionable nuclide. If the sample contains various fissionable nuclides, they must be previously separated.

Pairs of standards and samples were irradiated and counted. In each pair, one of them was irradiated covered by a neutron filter and the other uncovered. A composite cadmium and boron carbide was used as filter for the isotopic ratio determination.

A calibration curve was drawn using the values obtained by the counting of delayed neutrons which are observed for uranium standards with known isotopic percentage of uranium. The calibration curve was defined through standards with abundance varying between 0.5% and 93% of ^{235}U. This curve, according to CAVALLARI et al.,[8] may be expressed by the following equation:

$$\frac{R}{K} = B - \frac{R-K}{K}\frac{1}{\eta} D.$$

where R/K varies linearly with (R-K)/K and η is the ratio to be determined, which is the relation (N_{T235}/N_{T238}) between the total number of ^{235}U atoms and the total number of ^{238}U atoms. R and K are obtained through the counting of delayed fission neutrons.

R is the ratio between two countings of delayed fission neutrons, the first when the standard or sample is irradiated without a neutron filter and the second when the standard or sample is covered with a filter for the irradiation.

K is the ratio between two countings of delayed fission neutrons, the first when a thorium standard is irradiated without a neutron filter and the second when the standard is covered with a filter for the irradiation. K is the factor which reflects the decrease of counting of delayed neutrons caused by the filter.

The standards used to get the calibration curve were prepared from standard solutions which were obtained from U_3O_8 provided by NBS with known isotopic abundances of uranium. The solutions were pipetted over silica gel powder.

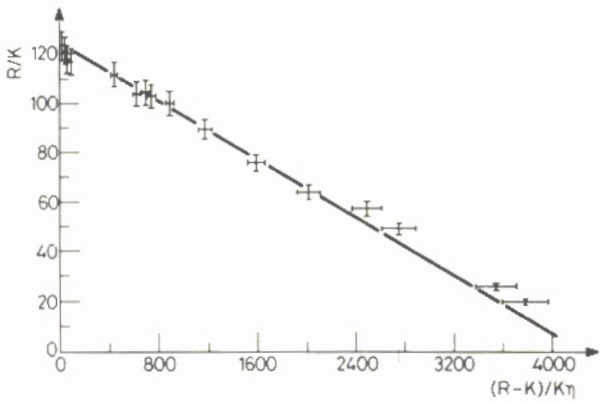

Fig. 1 Calibration curve for $^{235}U/^{238}U$ ($0.519 < \%^{235}U < 93$) ratio determinations

Each point in the curve is the mean of 7 measurements of R. Figure 1 shows the experimental points observed and the standard deviations corresponding to each point.

As the variables $(R - K)/K$; R/K) have both the same magnitude of error, the method proposed by WALD[17] was adopted to adjust the curve that fits the experimental points.

The equation found for the curve was:

$$R/K = (121.4 \pm 1.3) - (0.02658 \pm 0.00127)\,(R - K)/K\eta.$$

Precision, accuracy and efficiency of the method for determination of $^{235}U/^{238}U$ ratio was evaluated through measurements with samples of known isotopic composition.

Table 5 shows the results of the analysis of known samples.

Table 5
Results for analysis of $^{235}U/^{238}U$ ratio

Sample	Irradiation	η_{exp},*** 10^3	Relative error, %	Total error,**** %
IAEA ore*	SI**	7.6 ± 0.48	2.7	15.7
	N/SI	7.8 ± 0.50	5.4	18.9
Standard (Matrix: SiO_2)	SI	7.8 ± 0.47	5.4	18.1
	N/SI	7.9 ± 0.51	6.8	20.5
Standard (Matrix: filter paper)	SI	7.9 ± 0.50	6.8	20.3
Standard (Matrix: SiO_2)	SI	30.9 ± 2.7	2.8	19.7
	N/SI	29.4 ± 2.4	7.5	22.9
Standard (Matrix: filter paper)	SI	35.0 ± 3.1	10.1	29.6
	N/SI	35.2 ± 3.1	10.7	30.3
Standard (Matrix: SiO_2)	SI	74.7 ± 11.9	2.5	33.6

*IAEA S-7, Pitchblende, Lot nº · 43 with 0.527% of U_3O_8.
**SI and N/SI, irradiation made simultaneously or not with irradiations of standards, respectively.
***Mean of 6 determinations.
****Total error calculated by the criterion of McFARREN.[18]

Discussion

Considering the experimental procedure adopted, it was concluded that among the possible sources of error that affect the accuracy of the results, the following may be considered as negligible: sample preparation and standard preparation; reproducibility of sample position in relation to reactor core; variation of neutron flux in the rabbits; measurement of irradiation, decay and counting times; high count rates due to counting losses by coincidence.

In the case of uranium and thorium analysis, the source of error considered significant was the counting statistics, when samples presented low concentration of uranium and thorium. The error arising from counting statistics in the precision of the analysis (Table 2) is larger in the S-14 sample where the concentration of uranium and thorium are lower.

The destructive analysis for thorium is the alternative solution for the cases in which concentration of uranium in the sample is such that it generates a serious interference as well as when thorium has a concentration below the detection limit for the method. In this last case separation and concentration of thorium in the sample is mandatory.

The separation method chosen fits the requirements for the solution of this case. In the medium used (90% methanol–10% 5M nitric acid) the anionic resin shows a high affinity for thorium, making possible the quantitative separation of milligrams of thorium with a small mass of resin, which may be easily packed for the delayed neutron counting system. In addition, the tendency of uranium to be sorbed by anion exchange resin as nitrate complex is minimum in this medium, reducing the amount of solution required to wash the column and increasing the speed of the process.

It was found, by analysis of the IAEA sample S-16, that the results obtained with destructive and nondestructive methods are very consistent and can be considered as statistically identical within a confidence level of 95%.

As results obtained for the samples provided by the IAEA were all within the the concentration range recommended by the IAEA, one concludes that the method studied in this work has an accuracy as good as other analytical methods commonly used for analysis of uranium and thorium.

For the case of the determination of $^{235}U/^{238}U$ ratio, the error in the experimental points for the calibration curve (Figure 1) are about 5%. The main contribution to this error is counting statistics. Another source of error comes from the fact that sets of measurements were performed during many days and there may be variations in the neutron flux (thermal and fast) from one day to another. The impossibility of reducing those errors in available experimental conditions restrains the method to obtain acceptable results for samples with low enrichment in ^{235}U (^{235}U abundance $< 10\%$).

The MACFARREN[18] criterion was used to define the applicability and the total error of the method. According to this criterion, the method proved to be excellent for $^{235}U/^{238}U$ determination in samples within the natural range of uranium isotopic percentage and gave acceptable results (total error $< 50\%$) for measuring enriched uranium materials up to 10% in ^{235}U.

The difference in physical form between standard and sample and the irradiation of samples and standards in different periods did not affect the analytical results significantly. So, after the construction of the calibration curve, it can be used many times to quickly obtain the results. This method is nondestructive and demands minimum handling of the sample.

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References

1. M. W. ECHO, E. H. TURCK, Determination of ^{235}U by delayed neutron counting, Oak Ridge, Tn. TID-7531, 1959, p. 157.
2. S. AMIEL, Anal. Chem., 34 (1962) 1683.
3. F. F. DYER, J. F. EMERY, G. W. LEDDICOTTE, A Comprehensive Study of the Neutron Activation Analysis of Uranium by Delayed Neutron Counting, ORNL-3342 Art., 1962.
4. N. H. GALE, Proc. Symp. Radioactive dating and methods of low level counting, in Monaco, 2–10 March, 1967, p. 431.
5. K. W. MACMURDO, W. W. BOWMAN, Nucl. Instr. Methods, 141 (1977) 299.
6. M. C. B. SMIT, The determination of uranium in geological material by delayed neutron counting, PEL-248, 1976.
7. R. J. ROSENBERG, V. PITKANEN, A. SORSA, J. Radioanal. Chem., 37 (1977) 169.
8. F. CAVALLARI, M. TERRANI, Nucl. Instr. Methods, 79 (1970) 69.
9. H. O. MENLOVE, R. W. AUGUSTSON, D. B. SMITH, Nucl. Technol., 10 (1971) 366.
10. F. W. LIMA, M. B. A. VASCONCELLOS, M. J. A. ARMELIN, R. FULFARO, V. J. FULFARO, B. B. B, NEVES, J. Radioanal. Chem., 71 (1982) 311.
11. M. B. A. VASCONCELLOS, M. J. A. ARMELIN, R. FULFARO, F. W. LIMA, A comparative study of some methods for the determination of uranium used at the Instituto de Pesquisas Energéticas e Nucleares, IPEN Pub-17, 1980.
12. H. KAISER, Anal. Chem., 42 (1970) 26A.
13. G. L. LONG, J. D. WINEFORDNER, Anal. Chem., 55 (1983) 712A.
14. L. PSZONICKI, A. N. HANNA, O. SUSCHUNY, Report on intercomparisons S-14, S-15 and S-16 of the determination of uranium and thorium in thorium ores. Vienna, IAEA, (IAEA/RL/101), 1983.
15. H. T. MILLARD Jr., B. A. KEATEN, J. Radioanal. Chem., 72 (1982) 489.
16. J. KORKISCH, F. TERA, Anal. Chem., 33 (1961) 1264.
17. A. WALD, Ann. Math. Stat., 11 (1940) 284.
18. E. F. McFARREN, R. J. LISHKA, J. H. PARKER, Anal. Chem., 42 (1970) 358.