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PUBLICAÇÃO IPEN 33
IPEN - Pub - 33

SETEMBRO/1981

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CENTRO DE OPERAÇÃO E UTILIZAÇÃO DO REATOR DE PESQUISAS - COURP
ÁREA DE RADIOQUÍMICA

INSTITUTO DE PESQUISAS ENERGÉTICAS E NUCLEARES
SÃO PAULO - BRASIL

Série PUBLICAÇÃO IPEN

INIS Categories and Descriptors

811

URANIUM 235: Rocks

ROCKS: Brazil

BRAZIL: Rocks

OKLO PHENOMENON: Activation analysis

ACTIVATION ANALYSIS: Uranium 235

ACTIVATION ANALYSIS: Thermal neutrons

URANIUM 235: Mass spectroscopy

COURP-ARQ

Received in March 1981.

Approved for publication in August 1981.

Writing, orthography, concepts and final revision are of exclusive responsibility of the Authors.

**DETERMINATION OF THE ISOTOPIC ABUNDANCE OF ^{235}U IN ROCKS IN
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Maria B. A. Vasconcellos ^(**), Maria José A. Armelin ^(**),
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ABSTRACT

Isotopic analyses of uranium are generally carried out by mass spectrometry, with a precision better than 1%.

In nuclear laboratories it is often necessary to perform rapid determinations of ^{235}U isotopic abundances. Thermal neutron activation analysis by delayed neutron counting or by high resolution gamma-ray spectrometry can be applied for this purpose, although with less precision than by mass spectrometry.

In this work, delayed neutron counting and gamma-ray spectrometry were used for the determination of the isotopic abundance of ^{235}U in rocks from the Northeastern region of Brazil.

In the case of the application of delayed neutron counting, the rocks were analyzed non-destructively. When high resolution gamma-ray spectrometry was applied, a pre-irradiation chemical separation had to be performed, by extraction of uranium with tributylphosphate.

By both methods employed the results for the isotopic abundance of ^{235}U can be considered as equal to the natural value of 0.702%, for the rocks under study. The precision attained by gamma-ray spectrometry was better than that by delayed neutron counting.

I - INTRODUCTION

The determination of the isotopic abundance of ^{235}U is of great importance in nuclear technology, as well as in any research work in which the analysis of samples enriched or depleted in ^{235}U is required.

The isotopic analysis of uranium is generally carried out by mass spectrometry, with a precision well below 1% but requires expensive equipment and skilled personnel.

In nuclear laboratories, on the other side, it is frequently necessary to perform such analysis using other methods and available equipment.

Among the nuclear methods for ^{235}U isotopic abundance determination, thermal neutron activation analysis, followed either by delayed neutron counting or by high resolution gamma-ray spectrometry can be applied with good results.

(*) Paper presented at the XXI Brazilian Congress of Chemistry, held by the Brazilian Association of Chemistry in Porto Alegre, RGS, Brazil from 26 to 31 October 1980.

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Delayed neutron counting has been applied by Amiel⁽¹⁾ for the determination of the isotopic composition of some NBS uranium standards with various enrichments. A precision of 0.3% relative to counting statistics is claimed by the author.

Thermal neutron activation analysis followed by high resolution gamma-ray spectrometry was used by De Wet and Turkstra⁽²⁾, for the analysis of uranium standard solutions with several $^{235}\text{U}/^{238}\text{U}$ ratios from natural uranium to highly enriched material. The results obtained were compared to the ones determined by mass spectrometry for the same samples and an agreement of 5% in almost all cases was found. Only in the case of natural uranium analysis the results were not satisfactory and the error rose to 30%.

Mantel⁽⁸⁾ introduced a considerable improvement in the determination of $^{238}\text{U}/^{235}\text{U}$ ratios by gamma-ray spectrometry. Instead of using one or two peaks of the radioisotope ^{239}Np and comparing it to one of the fission products peaks, the author calculated a series of ratios between various peaks, which considerably decreased the error of analysis. Within a range of $^{238}\text{U}/^{235}\text{U}$ ratios from 20 to 200, the ratio of the two uranium isotopes could be determined with a precision of at least 0.6%, which approaches the one obtained by mass spectrometry.

The mentioned authors performed the isotopic analysis in pure uranium standards, which eliminates a number of interferences that show up when dealing with real samples.

The proposition of the present work is to determine the isotopic abundance of ^{235}U in some rocks from the Northeastern region of Brazil, by the methods discussed. The results obtained will be part of a geological study related to the eventual localization of fossil nuclear reactors in Brazilian territory, in the region corresponding to a possible connection with the African continent, in the Proterozoic Period. This fact is related to the discovery, in 1972, in an uranium mine at Oklo, in the Republic of Gabon, in the western coast of Africa, of the remain of a natural nuclear fission reactor. In this reactor, a spontaneous fission chain reaction occurred at approximately two billion years ago with a burn-up of ^{235}U and the abundance of ^{235}U varied from the natural value of 0.7202% down to 0.29⁽⁵⁾. Many of the stable products which are characteristic of the nuclear fission of uranium were identified in the veins that contained the depleted uranium, although they were absent elsewhere in the ore body.

In the case of the application of thermal neutron activation analysis followed by delayed neutron counting to the determination of the isotopic abundance of ^{235}U in the rocks analysed, it was not necessary to carry out a previous chemical separation of uranium, because the interferences of all the natural elements except thorium are practically non-existent.

When high resolution gamma-ray spectrometry was applied, it was considered convenient a separation of uranium prior to irradiation, in order to eliminate possible interfering radioisotopes that present peaks, of energies close to those of ^{239}Np and of the ^{235}U fission products.

Three rocks from the Northeastern Brazilian region were analyzed: one, containing 230 ppm of U_3O_8 , from the so-called "Estância Area", located in the state of Sergipe and two fragments of calc-silicate rocks containing uranium mineral with 1.5 and 2.3% in U_3O_8 , respectively, from the Gneissic Migmatitic complex, Panelas Area, in the state of Pernambuco.

Other rocks from the same region were not analyzed for the ratio $^{235}\text{U}/^{238}\text{U}$ because they presented very low concentration of uranium, of only a few parts per million. These concentrations were also determined by neutron activation analysis.

II – EXPERIMENTAL

II.1 – Sample Preparation

The rock samples were broken in fragments of about 0.5 cm, first by using a hammer and then

in a porcelain mortar. The final grinding was carried out in a SPEX mixer-mill with steel balls, in which the material was reduced to a fine powder, of granulometry lower than 150 mesh.

II.2 -- Determination of the Isotopic Abundance of ^{235}U by Delayed Neutron Counting Thermal Neutron Activation Analysis

II.2.1 -- Principle of the Method

When a heavy nuclide ($Z \geq 90$) undergoes fission, a small fraction of the fission products decays by neutron emission. This phenomenon is known as delayed neutron emission, in contrast with the emission of prompt neutrons, which takes place simultaneously with the process of fission.

Slow neutrons can induce fission in only a limited number of nuclides - eg., ^{233}U , ^{235}U , ^{239}Pu while fission of other nuclides, such as ^{238}U and ^{232}Th can occur only by the action of fast neutrons. The fission thresholds and cross sections of different nuclides provide differences in fissionability, with respect to different neutron energy ranges in various nuclides, which enables one to discriminate against some nuclides. Since fission, especially by thermal neutrons, is so specific and characteristic of the minor constituent of uranium, ^{235}U , delayed neutron emission may be a good criterion for measuring the isotopic composition of uranium⁽¹⁾.

Delayed neutron counting activation analysis as applied to uranium is carried out by irradiating a sample in a nuclear reactor for a period of time ranging from seconds to minutes, rapidly removing the sample to a neutron counting facility, allowing the counter to collect counts for a period of time and recording the collected counts. A blank sample and a standard sample are then treated precisely as was the test sample. The standard sample should contain a known quantity of ^{235}U , what can be achieved by using natural uranium with known isotopic composition.

When the isotopic compositions are different for uranium in the test and standard samples, the total uranium in the test sample can be obtained by the equation⁽³⁾:

$$U_t = U_s \cdot \frac{f_{s_s}}{f_{s_t}} \times \frac{T - BG}{S - BG} \quad (1)$$

where U is the total amount of uranium; f_s is the percentage of ^{235}U ; T and S are the total delayed neutron counts obtained upon irradiation of sample and standard, respectively. Background counts (BG) corresponding to the blank sample, which consists of an empty irradiation container, must be discounted. Sub-indexes t and s indicate, respectively, **test** and **standard**.

On the other hand, irradiations of the sample inside a cadmium foil enable one to determine the total uranium in the test sample, according to an equation similar to equation (1), but in this case counts are related only with delayed neutrons emitted by fission products of ^{238}U ⁽³⁾:

$$U_t = U_s \cdot \frac{f_{s_s}}{f_{s_t}} \times \frac{T_{Cd} - BG}{S_{Cd} - BG} \quad (2)$$

where f_n is the percentage of ^{238}U ; T_{Cd} and S_{Cd} are the total delayed neutron counts obtained with cadmium cover for test sample and standard, respectively.

The purpose of the cadmium foil is to shield the sample from the thermal neutron flux (4.3×10^{11} neutrons/cm².s), thereby reducing the fission rate of the ^{235}U in the sample, while the rate of fissions of ^{238}U is practically not affected, since it is fissioned by fast neutrons, which are not

absorbed significantly in the cadmium shield. The fissions of ^{235}U caused by epithermal neutrons can be neglected since at the irradiation position used in the IEA-R1 reactor, the fast neutron flux (1.6×10^{11} neutron/cm².s) is higher than the epithermal neutron flux (3.6×10^{10} n/cm².s). We must also take into account the fact that the cadmium cross section at the epithermal energy range is about twice its cross section in the fast neutron region.

Combining equations (1) and (2), and defining $(S - BG)/(T - BG) = K_1$ and $(S_{\text{Cd}} - BG)/(T_{\text{Cd}} - BG) = K_2$; and considering that $f_{s_t} + f_{n_t} = 100$ if the isotopic abundance of ^{234}U (0.0055%) is neglected, the following expression for the isotopic percentage of ^{235}U in the test sample is obtained.

$$f_{s_t} = \frac{f_{s_s} K_2}{f_{n_s} K_1 + f_{s_s} K_2} \times 100 \quad (3)$$

The application of expression (3) is more adequate when the isotopic abundances of sample and standard have close values.

11.2.2 – Preparation of Samples and Standards for Irradiation

Samples were prepared by weighing a small amount (about 25 to 380 mg) of the rock powders in polyethylene envelopes for the irradiation in the total neutron flux. An identical mass was also weighed for irradiation in an epithermal and rapid neutron flux, by wrapping the plastic envelopes containing the samples in cadmium foils of 1 mm thickness.

The standards utilized were certified uranium ores from the International Atomic Energy Agency having the natural percentage of ^{235}U (0.7202%) (4).

In the case of the rock that contained a lower concentration of uranium (ES – 30 C, 230 ppm U_3O_8), the IAEA ore with 0.039% U_3O_8 (IAEA S-13), Pechblenda, Lot n° 449 was utilized. In the case of the calc-silicate rocks containing uranium mineral (1.5 to 2.3% U_3O_8) the IAEA ore with 0.527% U_3O_8 (IAEA S-7, Pechblenda, Lot n° 43) was used.

The weighing of the standards was carried out similarly to the preparation of the test samples.

11.2.3 – Irradiations

To make sure that samples and standards were submitted to practically the same neutron flux, the irradiations were performed in the following sequence: bare sample, sample in cadmium shielding; bare standard, standard in cadmium shielding; bare polyethylene blank, blank in cadmium shielding.

Countings were performed in a neutron counting facility consisting of six BF_3 neutron detectors embedded in a paraffin cylinder and coupled to an electronic counting system. The detection and counting system is described with more details elsewhere (10).

Irradiation time was of 1 minute, delay time between the end of irradiation and the beginning of counting was of 20 seconds, and counting time, 1 minute.

11.2.4 – Results

The results of the determinations of the isotopic percentage of ^{235}U by delayed neutron counting activation analysis are presented in Tables 11.2.1, 11.2.2 and 11.2.3.

Only three of the rocks received were analyzed for the ^{235}U percentage, since the others contained amounts of uranium of only a few parts per million, which prevented the determination by a purely instrumental technique, requiring a chemical concentration of the uranium in the sample.

Table II.2.1

Determination of the Isotopic Abundance of ^{235}U in the Rock ES-30C, of the Estância Group, by Delayed Neutron Counting

Sample	% ^{235}U
1	0.763
2	0.627
3	0.701
4	0.773
5	0.760
6	0.700
7	0.744
8	0.611
9	0.778
10	0.590
Mean	0.705

Standard Deviation (s) = 0.0715
 Relative Standard Deviation = 10.1%
 Confidence Limits* = 0.705 ± 0.051

Table II.2.2

Determination of the Isotopic Abundance of ^{235}U in the Chalc-Silicate Rock Containing Uranium Mineral (nº 1), of the Gneissic-Migmatitic Complex, Panelas Area by Delayed Neutron Counting

Sample	% ^{235}U
1	0.751
2	0.763
3	0.694
4	0.690
5	0.692
6	0.667
7	0.704
8	0.823
9	0.683
10	0.776
11	0.720
12	0.666
13	0.707
14	0.770
Mean	0.722

Standard Deviation = 0.0471
 Relative Standard Deviation = 6.5%
 Confidence Limits = 0.722 ± 0.027

$$\text{*Confidence Limits} = \bar{x} \pm \frac{st}{\sqrt{n}}$$

t taken from Fischer's Tables at 95% Confidence Level.

Table II.2.3

Determination of the Isotopic Abundance of ^{235}U in the Chalc-Silicate Rock Containing Uranium Mineral (nº 2), of Gneissic-Migmatitic Complex, Panelas Area by Delayed Neutron Counting

Sample	% ^{235}U
1	0.703
2	0.783
3	0.757
4	0.773
5	0.712
6	0.699
7	0.649
8	0.771
9	0.687
10	0.764
11	0.734
12	0.712
13	0.629
14	0.753
Mean	0.723

Standard Deviation = 0.0473

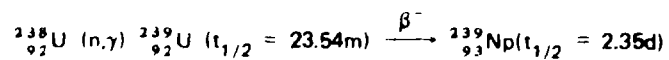
Relative Standard Deviation = 6.5%

Confidence Limits = 0.723 ± 0.027

II.3 – Determination of the Isotopic Abundance of ^{235}U by Thermal Neutron Activation Analysis and High Resolution Gamma-Ray Spectrometry

II.3.1 – Principle of the Method

The activation of uranium with thermal neutrons gives origin to the following main nuclear reactions



F. P. = fission products

The first transuranium element, ^{239}Np , as well as many of the fission products of uranium, are gamma emitters and, consequently, they can be analyzed by gamma-ray spectrometry.

With the use of Ge(Li) solid state detectors, the resolution of the many peaks of the complex mixture of fission products formed became feasible.

Besides the quantitative determination of many elements present in trace concentrations, the method of thermal neutron activation, analysis followed by high resolution gamma-ray spectrometry allows also the determination of the isotopic ratios of some elements. This can be accomplished provided that two or more of the isotopes of these elements give origin, upon activation to well identifiable species.

This is the case for the activation of uranium, since the radioisotopes ^{239}Np , originated from ^{238}U , and several of the fission products of ^{235}U have many easily identifiable total absorption peaks in the gamma-ray spectrum obtained with a Ge(Li) solid state detector. In Table II.3.1, the energies of the main peaks identified in the spectra recorded in the present work are presented.

Table II.3.1

Energies of the Main Gamma-Rays Identified in the Spectra of Irradiated Uranium

Radioisotope	Half-life	Gamma-Ray Energies keV) *
^{239}Np	2.35d	61, 99, 106, 118, 210, 228 278, 285, 316, 334
$^{99}\text{Mo} - ^{99\text{m}}\text{Tc}$	66.2h - 6.02h	140, 181
$^{132}\text{Te} - ^{132}\text{I}$	78.0h - 2.38h	668, 773
^{143}Ce	33.7h	293
$^{91}\text{Sr} - ^{91\text{m}}\text{Y}$	9.67h - 50.3m	556
^{133}I	20.3h	530
$^{97}\text{Zr} - ^{97}\text{Nb}$	17.0h - 72.0m	658, 743

* Values taken from: Erdtmann, G., Soyka, W., Die γ -Linien der Radionuklide, Jül - 1003 - AC, April 1974.

The ratios between the areas of two peaks corresponding to one of the fission products of ^{235}U and the other corresponding to one of the peaks of ^{239}Np , will be proportional to the $^{235}\text{U}/^{238}\text{U}$ atom ratio in the sample analyzed. If a standard containing uranium with a known $^{235}\text{U}/^{238}\text{U}$ ratio is irradiated simultaneously with the sample and its gamma spectrum recorded in the same conditions as the sample, the isotopic percentage of ^{235}U in the sample can be calculated, provided that the percentage of ^{234}U , of 0.0055% is neglected.

Considering only one peak ratio, we would have, for test sample and for standard:

$$R_t = \left(\frac{A_1}{A_2} \right)_t = K \left(\frac{f_s}{f_a} \right)_t \quad (1)$$

$$R_s = \left(\frac{A_1}{A_2} \right)_s = K \left(\frac{f_s}{f_a} \right)_s \quad (2)$$

where A_1 and A_2 are the areas of two peaks corresponding, respectively, to one of the fission products and to ^{239}Np and f_s/f_a is the atom ratio between the two isotopes of uranium.

Dividing equations (1) and (2), we have:

$$\frac{R_t}{R_s} = \frac{(A_1/A_2)_t}{(A_1/A_2)_s} = \frac{(f_s/f_a)_t}{(f_s/f_a)_s} \quad (3)$$

When a standard or natural uranium is used, equation (3) can be written as:

$$\frac{R_t}{R_s} = \frac{(A_1/A_2)_t}{(A_1/A_2)_s} = \frac{(f_s/f_a)_t}{0.007254} \quad (4)$$

If we neglect the contribution of ^{234}U and consider:

$$f_{s_t} + f_{a_t} = 100 \quad (5)$$

(6) The isotopic abundance of ^{235}U in test sample is calculated by combining (4) and (5) giving

$$f_{s_t} = 0.7254 \times \frac{A_{1_t} \cdot A_{2_s}}{A_{1_s} \cdot A_{2_t} + A_{1_t} \cdot A_{2_s}} \quad (6)$$

Formula (6) is valid for samples of low enrichment or low depletion since the assumption that the amount of ^{234}U is too low as compared to the amounts of ^{235}U and ^{238}U , is valid only for those samples.

In order to improve the precision of the method, several ratios between total absorption peaks of the fission products and of ^{239}Np can be used instead of only one, and the average of the various ^{235}U percentages obtained through the above expressions can be calculated.

For the calculation of the peak ratios used in the present work, the areas of the 106, 118, 210, 228 and 278 keV peaks of ^{239}Np were chosen. As to the fission products, the following peaks were used: 140 keV (^{99}Mo - ^{99m}Tc), 668 and 773 keV (^{132}Te - ^{132}I), 293 keV (^{142}Ce), 530 keV (^{133}I), 743 keV (^{97}Zr - ^{97}Nb). These peaks were considered to be the most convenient, since they were practically interference free and the corresponding activities were high enough for the purposes. The 556 keV peak, of ^{91}Sr - ^{91m}Y was not identified in all the samples and standards, due to the relatively short half-life (9.7 h) of ^{91}Sr . Combining all these peaks 30 ratios are obtained.

Since there was a time interval of at least 30 minutes between the countings of samples and standards, corrections for peak decay were applied.

11.3.2 – Preparation of Samples and Standards for Irradiation

Since the determination of the ^{235}U isotopic abundance was carried out in rocks, which generally present a very complex composition, it was decided to perform a simple chemical separation of uranium, prior to irradiation, to avoid too many interferences in the gamma spectra. Samples and standards (IAEA certified uranium ores) whose mass varied between 10 to 500 mg, according to their uranium content, were attacked with a HF-HNO_3 mixture, to which some drops of H_2SO_4 were added. The mixture was slowly heated in a sand bath and evaporated to dryness. The residue was taken up in 5 ml of 0.7 N HNO_3 , with gentle heating, until a clear solution was obtained.

The solutions were transferred to 60 ml separatory funnels. A drop of metacresol purple indicator was added to each funnel, and by dropwise addition of a solution of 50% NH_4OH , the pH was adjusted to the yellow form of the indicator (pH = 2.8). After addition of 15 ml of aluminum nitrate salting solution, 5 ml of a 10% solution of tributylphosphate (TBP) in iso-octane were pipetted. The funnels were stoppered and shaken for 60 seconds, in order to extract the uranyl ion.

After allowing the phases to separate, the aqueous phase was discarded. The uranium was then back-extracted from the organic phase into another aqueous phase, of 5% $(\text{NH}_4)_2\text{CO}_3$ solution. Two back-extractions were performed, with 5 ml portions of this solution and 10 minute agitation, according to the procedure recommended by Sato⁽⁹⁾.

The two aqueous phases obtained were then mixed and slowly evaporated to dryness. The residue was taken up in approximately 0.25 ml of 50% HNO_3 .

The solutions obtained for samples and standards were pipetted, with a micropipette, on rectangles of approximately 5 cm^2 area of Whatman n° 40 filter paper. After drying under an infra-red lamp, the rectangles were folded and introduced into polyethylene envelopes, especially manufactured for irradiation in the IEA-R1 swimming pool reactor.

For each group of two samples treated, one standard was simultaneously processed in exactly the same way.

11.3.3 – Irradiation and Counting

Each group of two samples and one standard was placed inside an aluminum can, for irradiation under a thermal neutron flux of 5×10^{12} neutrons/cm².s, for an 8 hour period.

After a delay time that varied between 2 and 5 days after the end of irradiation, countings were carried out using a solid state ORTEC Ge(Li) Detector, Model 8001 – 1022V, with a resolution of 4.2 keV for the 1332 keV peak of ^{60}Co . The detector was coupled to a 4096-channel Hewlett-Packard analyser. Counting time varied between 20 and 50 minutes.

The assignment of the energies of the several peaks in the gamma spectrum and the calculation of the corresponding areas was performed by means of a Hewlett-Packard minicomputer, using a program in Basic Language, FALA⁽⁷⁾, specially developed for the analysis of gamma-ray spectra.

11.3.4 – Spectra

In Figure 3.1, the gamma-ray spectrum obtained upon irradiation and counting of a sample

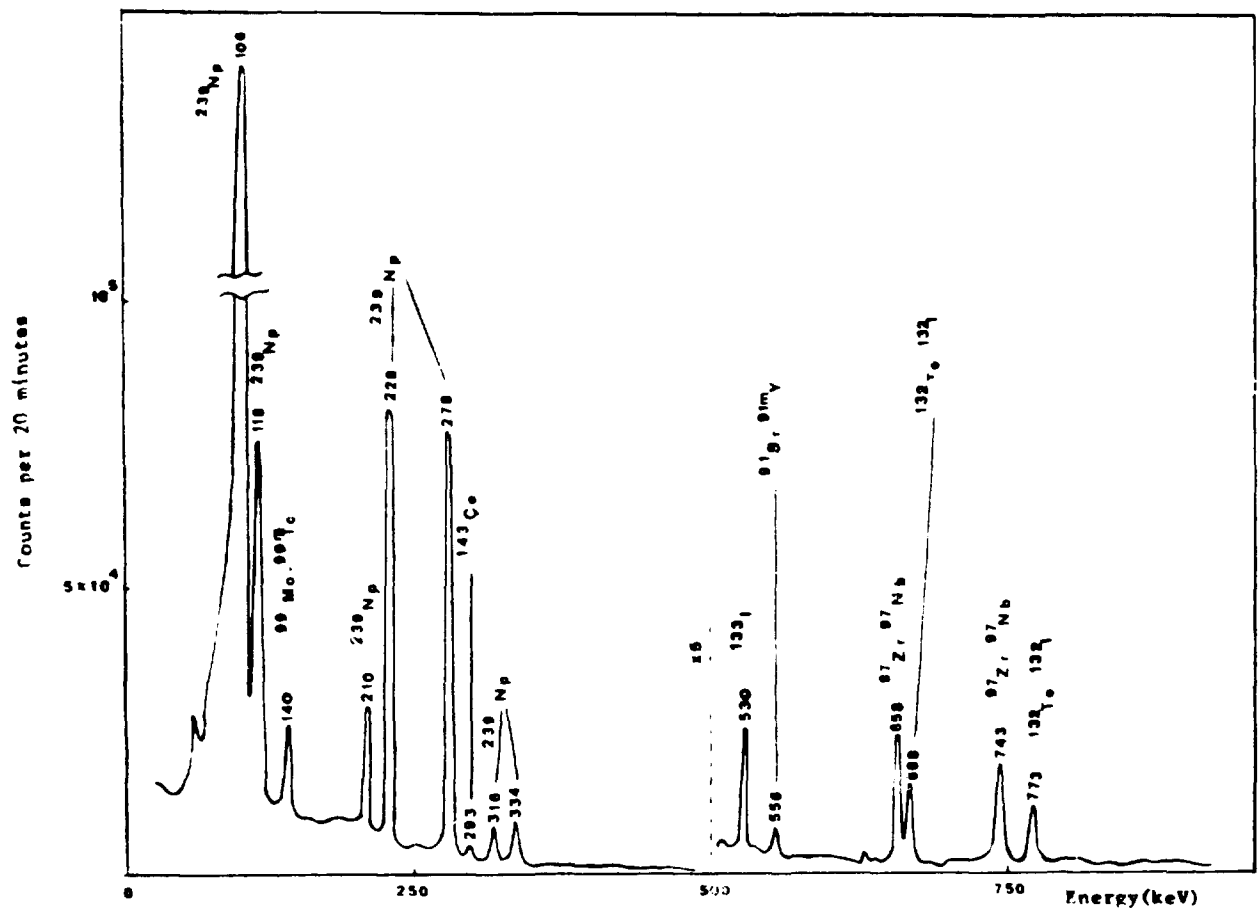


Figure 3.1 – Gamma-ray spectrum of the chalc-silicate rock containing uranium mineral (n° 1).

of the calc-silicate rock containing uranium mineral, n° 1, from the Gneiss-Migmatitic Complex, is presented.

In this spectrum, the peaks of ^{239}Np and of the fission products ^{99}Mo - ^{99m}Tc , ^{132}Te - ^{132}I , ^{143}Ce , ^{91}Sr - ^{91}Y , ^{133}I and ^{97}Zr - ^{97}Nb can be observed.

II.3.5 – Results

In Tables II.3.2, II.3.3 and II.3.4, the results obtained for the determination of the ^{235}U isotopic percentage by the method of thermal neutron activation analysis and high resolution gamma-ray spectrometry, are presented.

III – DISCUSSION AND CONCLUSIONS

The results presented in Tables II.2.1 to II.2.3 and II.3.2 to II.3.4 for the isotopic abundance of ^{235}U in the rocks analysed, by both methods, can be considered as equal to the value of 0.7202% taken as natural. This conclusion was drawn by application of a t-test on the means obtained with a confidence level of 95%. The relative error was calculated by the expression:

$$e_{rel} = \frac{\bar{x} - \mu}{\mu}$$

where μ is the "true value"... Only in the case of the analysis of rock ES-30C by the method of delayed neutron counting, the error was of 2.1%. Taking 0.7202% as the "true value" for the isotopic percentage of ^{235}U we would have in almost all cases a relative error lower than 1%.

The low relative errors attained show that the two methods are adequate for the analysis of the isotopic abundance of ^{235}U , considering the purpose of the present work, although not approaching the precision and accuracy of mass spectrometry.

On the other hand, if we compare the methods of delayed neutron counting and gamma-ray spectrometry, it is obvious that the second presented a precision, of about 2%, among replicate analysis, better than the first method, whose reproducibility was between 6 and 10%. This fact can be attributed to the low delayed neutron countings obtained, due to the not very high neutron flux (4.3×10^{11} neutrons/cm².s) available in the irradiation position used. Amiel⁽¹⁾ obtained reproducibility of 0.3% based on counting statistics only, but the level of neutron counting involved was much higher and he based the calculation only on the countings obtained by irradiation the samples on the total neutron flux, not considering the countings obtained with cadmium shielding, which are much lower. If we calculate the precision obtained in the present work on the same basis, the relative standard deviation goes down to 3%.

Chemical separation of uranium, by means of extraction with tributyl phosphate (TBP), previously to irradiation, showed itself as very convenient, due to its speed and efficiency. It is not necessary that the separation be quantitative, since the measurements of the peaks corresponding to both ^{235}U and ^{238}U are carried out in the same sample. It is important only that the separated uranium be as free of interferences as possible. Francois⁽⁴⁾ showed, in a study of uranium extraction with TBP, in the presence of a great number of ions, that only Bi(III), Ce(IV) and Th(IV) were extracted in significant amounts. Of these elements only cerium could give origin, by activation with thermal neutrons, to a peak, at 145 keV, close to the 140 keV of the fission product ^{99}Mo .

Table II.3.2

Determination of the ^{235}U Isotopic Abundance of Rock ES-30C, from the Estância Area, by the Method of Activation Analysis and Gamma-Ray Spectrometry

Sample	% ^{235}U
1	0.727
2	0.729
3	0.694
4	0.721
5	0.695
6	0.716
Mean	0.714

Standard Deviation = 0.0155

Relative Standard Deviation = 2.2%

Confidence Limits = 0.714 ± 0.016

Table II.3.3

Determination of the Isotopic Abundance of ^{235}U in the Chalc-Silicate Rock Containing Uranium Mineral (nº 1), from the Gneissic-Migmatitic Complex, Panelas Area, by the Method of Activation Analysis and Gamma-Ray Spectrometry

Sample	% ^{235}U
1	0.732
2	0.736
3	0.723
4	0.722
5	0.712
6	0.726
Mean	0.725

Standard Deviation = 0.00848

Relative Standard Deviation = 1.2%

Confidence Limits = 0.725 ± 0.009

Table II.3.4

Determination of the Isotopic Abundance of ^{235}U in the Chalc-Silicate Rock Containing Uranium Mineral (nº 2), from the Gneissic-Migmatitic Complex, Panelas Area, by the Method of Activation Analysis and Gamma-Ray Spectrometry

Sample	% ^{235}U
1	0.743
2	0.740
3	0.694
4	0.703
5	0.724
6	0.713
Mean	0.719

Standard Deviation = 0.0198
 Relative Standard Deviation = 2.7%
 Confidence Limits = 0.719 ± 0.021

In the case of the method of high resolution gamma ray spectrometry, counting statistics is also the limiting factor of the precision.

By using the same sample for comparing the activities corresponding to fission products of ^{235}U and the activity due to ^{239}Np , many of the other common causes of errors in activation analysis, such as flux variation, self-absorption, weighing errors, different counting geometry of sample and standard etc are eliminated and high precision should be attainable. It was observed that the fission product peaks (180 and 530 keV), which presented the lowest counting levels, and, consequently, poorest counting statistics, lead to the less accurate results.

One problem that arises in the application of this method is that the activity corresponding to the total absorption peak of ^{239}Np is much higher than the activity due to the fission products of ^{235}U . Due to this fact, it becomes necessary, many times, to perform the countings at a farther distance from the detector, to avoid an excessive dead time caused by the high activity of ^{239}Np . With this procedure, the countings due to the fission product peaks are reduced and consequently counting statistics becomes poorer.

The advantage of the method of counting of delayed neutrons is the very short time of analysis. A complete cycle of irradiation, delay time and counting, lasts less than 3 minutes for each sample. To improve the precision of the determinations, a concentration of uranium, prior to irradiation, could be performed in order to obtain a higher neutron count rate. But in this case, the characteristic of speed of analysis would be lost.

ACKNOWLEDGEMENTS

These analytical procedures are part of an extended paper "Search for an Oklo Phenomenon in Brazil", by F. W. Lima, Marina B. A. Vasconcellos, Maria José A. Armelin, V. Fulfaro, B. B. Brito Neves, R. Fulfaro. The authors of the present paper are grateful to Dr. Brito Neves and Professor V. Fulfaro for providing the uranium samples.

RESUMO

As análises isotópicas de urânio são normalmente realizadas por espectrometria de massa, com a qual se obtém uma precisão melhor do que 1%.

Em laboratórios nucleares, por outro lado, muitas vezes se torna necessária a realização de um tal tipo de análise, utilizando-se recursos disponíveis ao pesquisador.

Dois métodos nucleares se destacam dentre os aplicáveis à finalidade descrita: a análise por ativação com nêutrons térmicos seguida de contagem de nêutrons retardados de fissão e a análise por ativação seguida de espectrometria de raios gama de alta resolução.

Ambos os métodos têm sido utilizados para determinação da fração isotópica do ^{235}U geralmente em padrões contendo urânio puro.

No presente trabalho, esses métodos foram aplicados à determinação da percentagem isotópica de ^{235}U em rochas oriundas da região Nordeste do Brasil, mais precisamente dos Estados de Sergipe e Pernambuco.

No caso da aplicação do método de análise por ativação e contagem de nêutrons retardados de fissão, as rochas analisadas não destruíram-se. Quando se empregou a análise por ativação seguida de espectrometria de raios gama de alta resolução, foi necessária uma extração prévia do urânio, realizada com tributilfosfato (TBP) diluído em iso-octano, seguida de retro-extração em carbonato de amônio.

Por meio de ambos os métodos empregados, obtiveram-se valores para a fração isotópica do ^{235}U que podem ser considerados iguais ao valor tabelado para o urânio natural, de 0,7202%. A precisão obtida com o método de espectrometria de raios gama foi superior à alcançada com o método que utiliza a contagem de nêutrons retardados de fissão.

REFERENCES*

1. AMIEL, S. Analytical applications of delayed neutron emission in fissionable elements. *Analyt. Chem.*, 34:1683-92, 1962.
2. DE WET, W. J. & TURSTRA, J. The determination of $^{235}\text{U}/^{238}\text{U}$ ratios by activation analysis utilizing high resolution γ -spectrometry. *J. Radioanalyt. Chem.*, 1:379-87, 1968.
3. DYER, F. F.; EMERY, J. F.; LEDDICOTTE, G. W. A comprehensive study of the neutron activation analysis of uranium by delayed neutron counting. Oak Ridge, In Oak Ridge National Lab., Oct. 1962. (ORNL-3342).
4. FRANÇOIS, C. A. Rapid spectrophotometric determination of submilligram quantities of uranium. *Analyt. Chem.*, 30:50-3, 1958.

(*) Bibliographic references related to documents belonging to IPEN Library were revised according with NB-66 of Associação Brasileira de Normas Técnicas.

5. INTERNATIONAL ATOMIC ENERGY AGENCY. Analytical quality control group. Certificates. Uranium Ores. March 1975. 2p.
6. INTERNATIONAL ATOMIC ENERGY AGENCY. *Le phenomene d'Oklo: compte rendu d'un colloque sur... et tenu a Livreville, Gabon 23-27 Juin, 1975*. Vienna, 1975.
7. LIMA F. W. & ATALLA, L. T. A program in Basic language for analysis of gamma-spectra using on-line minicomputers. *J. Radioanalyt. Chem.*, 20:769-77, 1974.
8. MANTEL, M.; GILAT, J. ; AMIEL, S. Isotopic analysis of uranium by neutron activation and high resolution gamma ray spectrometry. *J. Radioanalyt. Chem.*, 2:395-407, 1969.
9. SATO, T. The back-extraction of uranyl nitrate from TBP solution. *J. Inorg. Nucl. Chem.*, 7:147, 1958.
10. VASCONCELLOS, M. B. A.; ARMELIN, M. J. A.; FULFARO, R.; LIMA, F. W. *A comparative study of some methods for the determination of uranium, used at the Instituto de Pesquisas Energéticas e Nucleares*. São Paulo, Instituto de Pesquisas Energéticas e Nucleares, August, 1980. (IPEN Pub-17).

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