

A COMPARATIVE STUDY OF SOME NUCLEAR METHODS FOR $^{235}\text{U}/^{238}\text{U}$
ISOTOPIC RATIOS DETERMINATION

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In the present work, a comparative study is made among nuclear methods for $^{235}\text{U}/^{238}\text{U}$ ratios determination: activation analysis followed by high-resolution gamma-ray spectrometry, delayed neutron counting, passive gamma-ray and alpha spectrometry. Activation analysis followed by high-resolution gamma-ray spectrometry yielded a relative standard deviation down to 0.1% and a relative error of about 1% for standards of uranium enriched to 14%. Passive gamma-ray spectrometry using Ge(Li) detectors yielded a relative error down to 0.1% for enriched uranium and values even lower for the standard deviation. Passive gamma-ray spectrometry using Low Energy Photon Detector (LEPD) yielded a precision of 0.2% and a still better accuracy for enriched standards. In the case of alpha spectrometry, a relative error down to 0.5% and a precision of about 1% were obtained, also for enriched uranium standards. Delayed neutron counting allowed a relative standard deviation of about 7% and a relative error of about 2%, for standards of depleted uranium.

Introduction

The determination of $^{235}\text{U}/^{238}\text{U}$ isotopic ratios is of great importance in nuclear technology. It is normally assumed that precise and accurate isotopic analysis of uranium has to be carried out by mass spectrometry. In nuclear laboratories, on the other hand it can be more convenient and less expensive to use other available methods of analysis.

In the present work, a comparative study is made among some nuclear methods for $^{235}\text{U}/^{238}\text{U}$ ratios determination, such as: activation analysis followed by high-resolution gamma-ray spectrometry, delayed-neutron counting, passive gamma-ray and alpha spectrometry.

The methods were studied by using uranium isotopic standards from the Compagnie Generale de Matieres Nucleaires (COGEMA) from Pierrelatte, France.

The precision (in terms of the standard deviation) and the accuracy (in terms of the relative error) of the four methods studied are compared, as well as their range of applicability. Also a comparison is made with the results obtained by Mantel et al. /1/ and by John et al. /2/, who also worked with neutron activation analysis followed by high-resolution gamma-ray spectrometry.

Materials and methods

1. Thermal Neutron Activation Analysis Followed by High Resolution Gamma-ray Spectrometry

As was described by Mantel et al and by other authors /1-6/, thermal neutron activation analysis followed by high resolution gamma-ray spectrometry can be used successfully for the determination of $^{235}\text{U}/^{238}\text{U}$ isotopic ratios, by calculating the ratios between the areas of the peaks corresponding to the fission products of ^{235}U and to ^{239}Np , formed by activation of ^{238}U .

The precision of the method can be greatly improved by using the average of several peak ratios obtained in the gamma spectra. Lima et al /6/ have applied this procedure to the determination of $^{235}\text{U}/^{238}\text{U}$ ratios in rocks, in search for an "Oklo Phenomenon" in Brazil.

In the present work, the calibration curves constructed by linear regression from the peak ratios and from the values of enrichment of the standards were established by using uranium isotopic standards from the Compagnie Generale de Matieres Nucleaires, COGEMA (France).

The uranyl nitrate solutions of these U_3O_8 standards were prepared by dissolution with 1:1 HNO_3 and dilution with water, in order to obtain a final concentration from about 2 to 10 mg U/mL.

Convenient aliquots of these solutions, containing from 1 to 5 mg of total uranium, were pipetted into small polyethylene containers and dried under an infra-red lamp.

Irradiations were performed in the IEA-R1 reactor, for periods of 30 minutes, at a thermal neutron flux of $4.3 \times 10^{11} \text{ n cm}^{-2} \text{ s}^{-1}$.

The gamma-spectra of ^{239}Np and of the fission products were measured by using a solid state Ge(Li) detector, model 8001-1022V, with a resolution of 2.9 keV for the 1332.5 keV of ^{60}Co . The detector was coupled to a 4096 channel Hewlett-Packard model 5410A analyzer and to a Hewlett-Packard 2100A minicomputer for data reduction. Counting times varied between 1200 and 3000s.

After correction for decay, the calculation of the ratios between all the net areas of fission product peaks: $^{99\text{m}}\text{Tc}$ - 140 keV, ^{143}Ce -293 keV, ^{133}I -530 keV, ^{91}Sr - $^{91\text{m}}\text{Y}$ -556 keV, ^{97}Nb -658 keV, ^{132}Te - ^{132}I -668 and 773 keV and those from ^{239}Np (106, 118, 210 and 278 keV) was carried out. The areas were calculated by the method of Covell /7/.

2. Passive Gamma-ray Spectrometry

The alpha decay of many of the natural isotopes and daughters of uranium is accompanied by the emission of gamma-rays, as the excited nuclei formed lose energy and decay to the ground state or to a closely lying isomeric state.

These gamma-rays originate from the decay of ^{235}U , ^{238}U and daughters, so it can be easily foreseen that the determination of $^{235}\text{U}/^{238}\text{U}$ ratios can be accomplished by computing the ratios between γ -ray peaks corresponding to each one of these two isotopes or their daughters in the spectra.

The determination of uranium isotopic ratios or ^{235}U enrichments by the use of passive gamma-ray spectrometry has been reported by other authors /8-12/.

In the present work, the method of multiple peak ratios introduced by Mantel et al /1/ for the neutron-activation method was applied to the determination of $^{235}\text{U}/^{238}\text{U}$ isotopic ratios by passive gamma-ray spectrometry using solid state Ge(Li) and hyperpure Ge detectors (LEPD_j).

The experimental work consisted of measuring the radioactivity of solid U_3O_8 standards from COGEMA (France). The counting geometry was identical for all standards.

The measurements were performed by using the same solid state Ge(Li) detector already described in item 1 and an ORTEC hyperpure Ge detector, model 1013-1620, with a resolution of 600 eV for the 121.9 keV peak of ^{57}Co . Counting times varied between 30,000 and 54,000s, for both detectors.

For ^{235}U , the 144, 164, 186 and 205 keV peaks of ^{235}U were chosen, while for ^{238}U , the 258, 766 and 1001 keV peaks of the $^{234\text{m}}\text{Pa}$ daughter were utilized, when a Ge(Li) detector was used.

In the case of hyperpure Ge detector, for ^{235}U the 84 keV peak of ^{231}Th , the 90 and 105 keV (X rays) and the 143, 163, 185 and 201 keV γ -rays of ^{235}U were chosen. For ^{238}U , the 63 and 93 keV peaks of ^{234}Th were used.

3. Delayed-neutron Counting

The determination of the $^{235}\text{U}/^{238}\text{U}$ isotopic ratios by delayed-neutron counting is performed by means of a linear relation obtained when several uranium standards with various enrichments are irradiated and measured with

and without thermal neutron shielding. This relation, according to Cavallari et al /13/, can be expressed by the equation:

$$\frac{R}{K} = B - \left(\frac{R - K}{K} \right) \frac{1}{\eta} D$$

Where R/K varies linearly with $(R - K)/K\eta$ 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 for irradiations, with and without cadmium shielding.

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

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

Since the variables $\left(\frac{R - K}{K}\right)$ and $\frac{R}{K}$ have both the same magnitude of error, the method proposed by Wald /14/ was adopted to adjust the curve that fits the experimental points.

The calibration curve was obtained with solutions prepared from COGEMA U_3O_8 isotopic standards pipetted on to filter paper.

Pairs of identical standards were packed into polyethylene envelopes. One standard of each pair was irradiated covered with a filter for thermal neutrons and the other one uncovered. A composite cadmium and boron carbide filter

was chosen for the determination of $^{235}\text{U}/^{238}\text{U}$ ratios. A polyethylene holder was used to fix the position of the standards and samples inside the polypropylene irradiation rabbits.

Irradiations were carried out in the IEA-R1 research reactor, in a position where the neutron flux had the following intensities: thermal flux = $4.4 \times 10^{11} \text{ n cm}^{-2} \text{ s}^{-1}$; epithermal flux = $4.0 \times 10^{10} \text{ n cm}^{-2} \text{ s}^{-1}$; fast flux = $1.6 \times 10^{11} \text{ n cm}^{-2} \text{ s}^{-1}$. A more detailed description of this neutron detection and counting system has been presented elsewhere /15,16/.

Irradiation, decay and counting times were always of 60, 20 and 60 seconds respectively.

4. Alpha-spectrometry

The determination of the $^{235}\text{U}/^{238}\text{U}$ isotopic ratios by this method consists in obtaining the ratio between alpha activities, one corresponding to the peaks of ^{235}U and the other to the peaks of ^{238}U .

If we consider that the ratios of these activities is proportional to the $^{235}\text{U}/^{238}\text{U}$ isotopic ratio, it is possible to calculate the isotopic ratio of an unknown sample comparing it to the ratio obtained for an isotopic uranium standard.

The sources were prepared for alpha-measurements by electrodeposition such as described by Donnan and Dukès /17/. A brass-lucite cell with a conical shape was used. The cathode was a stainless steel disk (25 mm diameter x 0.3 mm thickness) polished to a mirror surface. The anode was a platinum wire (1 mm diameter). The distance between the electrodes was 5 mm.

An aliquot of a uranyl nitrate solution prepared from COGEMA standards containing between 17 to 170 μg uranium was added to the cell that con-

tained 4 mL of a saturated NH_4Cl solution with a pH of 1.0. The electrolysis was carried out at a constant current of 1.25 A (current density of 1.5 A cm^{-2}) for about 60 minutes. Before the current was discontinued, 1 mL of concentrated NH_4OH was added. Then the disk with electrodeposited uranium was removed from the cell, rinsed with distilled water and ethyl alcohol and dried for 20 minutes under an infrared lamp.

The alpha particles were measured with an ORTEC alpha spectrometer model 576, with a ruggedized surface barrier detector of 300 mm^2 active area. During the counting period, the chamber pressure was kept at 4×10^{-2} Torr.

The detector pulses were analyzed by means of an ORTEC model 6240 B multichannel analyzer, in an alpha particle energy range of 4 to 6 MeV. The resolution of the detector for $E_\alpha = 5.48 \text{ MeV}$ of ^{241}Am varied from 30 to 50 keV, depending on the distance between source and detector. The counting time was typically 50,000 seconds.

For isotopic ratios calculation, the peaks corresponding to the energies of 4.20 MeV of ^{238}U and 4.40 MeV of ^{235}U were considered. To calculate the area of the peak, a particular number of channels was selected in such a way that this selection was not interfered by any other nuclide in the same spectrum.

Results

In Table 1 are presented the results of the determination of $^{235}\text{U}/^{238}\text{U}$ isotopic ratios of the COGEMA standards, by neutron activation followed by high resolution gamma-ray spectrometry.

The isotopic composition of each sample was evaluated from the calibration curves constructed by linear regression from the peak ratios obtained and from the values of enrichment of the standards. This procedure yielded 28 values of isotopic composition for each analyzed sample, in the case of acti-

Table 1
Results of the determination of $^{235}\text{U}/^{238}\text{U}$ isotopic ratios by
activation analysis followed by high-resolution gamma-ray spectrometry

Isotopic Composition of the standard ($^{235}\text{U}/^{238}\text{U}$)	Mean Enrichment (x) ($^{235}\text{U}/^{238}\text{U}$ measured)	Relative Error $\Delta_x\%$	Relative Standard Deviation $\sigma_x\%$	New weighted Mean Enrichment ω_1	Relative Error $\Delta_\omega\%$	Relative Standard Deviation $\sigma_{\omega_1}\%$
0.002038	0.00222	8.8	1.7	0.00214	5.0	0.6
0.007258	0.00752	3.8	1.2	0.00734	1.2	0.8
0.01335	0.01379	3.3	1.1	0.01351	1.2	0.6
0.02700	0.02814	4.2	1.1	0.02773	2.7	0.7
0.07704	0.08241	7.0	0.8	0.08184	6.2	0.5
0.16846	0.1658	1.6	0.2	0.1661	1.4	0.1

vation analysis followed by high resolution γ -ray spectrometry. The next step was to evaluate the mean enrichment (x) according to John et al /2/, and the standard deviation of this mean (σ_x). In order to get a better precision, the values of x and σ_x were used for excluding the outliers from the set of averaged data. A new mean enrichment (x_1) and a new standard deviation (σ_{x_1}) were then obtained by considering just the x_i values within the interval

$$x - \sigma_x < x_i < x + \sigma_x$$

To further optimize the precision of the method, John et al /2/ calculated a weighted mean of enrichment ($\omega \pm \sigma_\omega$), by defining an empirical formula:

$$P_i = \frac{1}{|1 - r| \cdot 3 + 0.03}$$

where p_i is the weight of the i^{th} result, r is the correlation coefficient of the calibration curve used for the calculation of the i^{th} value.

This formula is such that the p_i value will fall down from 33.33 for $r = 1$ to about 1.5 for $r = 0.8$, it giving, therefore, a greater weight to the best calibration curves.

Following the same procedure as for the simple mean, a new weighted mean enrichment ($\omega_1 \pm \sigma_{\omega_1}$) was calculated by excluding the values of ω_i outside the interval.

$$\omega - \frac{\sigma_{\omega}}{P_i} < \omega_i < \omega + \frac{\sigma_{\omega}}{P_i}$$

$$\frac{P_i}{\Sigma P_i}$$

Finally, the accuracy of the method was evaluated for each mean according to the equation:

$$\Delta = \left| \frac{x - \mu}{x} \right| \cdot 100$$

where x is the mean enrichment mentioned above and μ is the same value for the respective standard.

A computer routine was developed for these calculations.

In the Tables of results, are presented the values of the mean enrichment, x , of the relative errors, $\Delta x\%$, of the relative standard deviations, $\sigma x\%$, and the values corresponding to the "new weighted mean enrichment", ω_1 and the respective relative error, $\Delta \omega\%$ and relative standard deviation, $\sigma \omega_1\%$.

In Tables 2 and 3, the results of the isotopic ratios determined by passive gamma-ray spectrometry, using Ge(Li) and hyperpure Ge(LEPD) are presented. The same treatment of the data as explained above was applied.

Table 2
Results of the determination of $^{235}\text{U}/^{238}\text{U}$ isotopic ratios by
passive gamma-ray spectrometry, using a Ge(Li) detector

Isotopic Composition of the Standard ($^{235}\text{U}/^{238}\text{U}$)	Mean Enrichment (x) ($^{235}\text{U}/^{238}\text{U}$ measured)	Relative Error $\Delta_x\%$	Relative Standard Deviation $\sigma_x\%$	New weighted Mean Enrichment ω_1	Relative Error $\Delta_{\omega_1}\%$	Relative Standard Deviation $\sigma_{\omega_1}\%$
0.002038	0.00163	19.9	9.7	0.00188	7.7	3.2
0.007258	0.00694	4.4	1.6	0.00702	3.3	1.0
0.01335	0.01256	5.9	0.6	0.01241	7.0	0.2
0.02700	0.02870	6.3	1.2	0.02856	5.8	0.7
0.16846	0.1683	0.1	0.03	0.1683	0.1	0.01

Table 3
Results of the determination of $^{235}\text{U}/^{238}\text{U}$ isotopic ratios by
passive gamma-ray spectrometry, using an hyperpure Ge detector (LEPD)

Isotopic Composition of the Standard ($^{235}\text{U}/^{238}\text{U}$)	Mean Enrichment (x) ($^{235}\text{U}/^{238}\text{U}$ ratio measured)	Relative Error $\Delta_x\%$	Relative Standard Deviation $\sigma_x\%$	New weighted Mean Enrichment ω_1	Relative Error $\Delta_{\omega_1}\%$	Relative Standard Deviation $\sigma_{\omega_1}\%$
0.007258	0.00655	9.7	3.8	0.00664	8.5	3.0
0.01335	0.01468	9.9	2.1	0.01454	8.9	1.4
0.02700	0.02851	5.6	1.6	0.02786	3.2	1.7
0.07704	0.07730	0.3	0.8	0.07664	0.5	0.8
0.16846	0.1680	0.2	0.2	0.1684	0.04	0.2

Table 4
Results of the determination of $^{235}\text{U}/^{238}\text{U}$ isotopic ratios by
alpha spectrometry

Isotopic Composition of the Standard ($^{235}\text{U}/^{238}\text{U}$)	$^{235}\text{U}/^{238}\text{U}$ Ratios Measured	Relative Error $\Delta x\%$	Relative Standard Deviation $\sigma x\%$
0.002038	0.002530	19.4	21.9
0.007255	0.007523	10.4	8.1
0.01335	0.01461	10.0	2.6
0.02700	0.02570	4.8	1.5
0.07704	0.07722	2.3	1.0
0.16846	0.1676	0.5	1.6

Table 5
Results of the determination of $^{235}\text{U}/^{238}\text{U}$ isotopic ratios by
delayed neutron counting

Isotopic Composition of the Standard ($^{235}\text{U}/^{238}\text{U}$)	$^{235}\text{U}/^{238}\text{U}$ Ratios Measured	Relative Error $\Delta x\%$	Relative Standard Deviation $\sigma x\%$
0.002038	0.00200	1.9	7.5
0.007258	0.00706	2.8	8.1
0.01335	0.0129	3.7	7.8
0.02700	0.0248	8.2	13.7
0.07704	0.0693	10.0	8.2

In Table 4, the results of the $^{235}\text{U}/^{238}\text{U}$ ratios as obtained by alpha spectrometry measurements are presented. In this case it was not possible to apply the statistical treatment of the data proposed by John et al /2/, since only one measurement was performed for each point. The relative standard deviation, $\sigma_x\%$ and the relative error, $\Delta_x\%$, calculated for each point are presented.

In Table 5, the results of the isotopic ratios determination by delayed-neutron counting are presented.

Discussion

The four methods discussed in the present work were studied in the range of $^{235}\text{U}/^{238}\text{U}$ isotopic ratios between 0.002038 and 0.16846, which corresponds to an interval between depleted uranium (about 0.2% ^{235}U) and uranium enriched to about 14%.

For all methods except delayed-neutron counting, the relative errors and relative standard deviations were generally much better in the case of enriched uranium standards. In the case of activation analysis and high resolution gamma-ray spectrometry (Table 1), for example, the relative error $\Delta x\%$ decreased from 8.8% for depleted uranium to 1.6% for uranium enriched to 14%. The relative standard deviation, $\sigma x\%$, decreased from 1.7 to 0.2% in the same interval. The same can be said about $\Delta \omega_1\%$ and $\sigma \omega_1\%$. In Table 3 also we can observe that for passive gamma-ray spectrometry with LEPS detectors the relative error $\Delta x\%$ fell from 9.7 to 0.2% and the relative standard deviation $\sigma x\%$ from 3.8 to 0.2%. Similar comments can be made about Table 2. This could in principle be attributed to improved counting statistics for the peaks of ^{235}U in the enriched standards.

Comparing the results of the four methods, we can conclude that the best performances were those of activation analysis and passive gamma-ray spectrometry, followed by alpha spectrometry and delayed-neutron counting.

Relative standard deviations of 0.1% were obtained for the most enriched standards, in the case of activation analysis and even lower values in the case of passive gamma-ray spectrometry, with Ge(Li) as well as with Ge detectors.

Mantel et al. /1/ obtained a precision of 0.6% for the relative standard deviation, for the method of activation analysis applied to a sample of natural uranium. In our case, we obtained a precision of 0.8%, also for natural uranium.

The statistical treatment developed by John et al /2/ and applied in the present work resulted generally in better values for the relative errors and relative standard deviations, as can be observed in Tables 1, 2 and 3.

In the case of alpha spectrometry (Table 4), good accuracy and precision for the $^{235}\text{U}/^{238}\text{U}$ ratios were achieved for enriched uranium standards. It can be observed that a precision of 1.6% and an accuracy of 0.5% were obtained for uranium enriched to 14%. It is to be noted, on the other hand that the relative standard deviation and the relative error correspond to a single determination, because the procedure is too time-consuming to obtain a large set of data. For depleted or natural uranium standards, the difficulty resides in obtaining alpha activities for ^{235}U with good counting statistics. Besides, it is difficult to resolve the ^{235}U peak, since the low energy tail of ^{234}U extends into the region of the ^{235}U and ^{238}U spectrum.

For delayed neutron counting, the results were not so good as for the other methods. The best values for the standard deviation and relative error, 7.5% and 1.9% respectively, were obtained for standards of depleted uranium. For highly enriched uranium the method is not supposed to be applicable, since the simplification introduced by Cavallari et al. /13/ as to the fission of ^{235}U with fast neutrons cannot be applied.

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References

1. M. MANTEL, J. GILAT, S. AMIEL, *J. Radioanal. Chem.*, 2 (1969) 395.
2. G. JOHN, J. SEDLÁČEK, J. P. RAMLAK, *Radiochem. Radioanal. Letters*, 53 (1982) 263.
3. W. J. DEWET, J. TURKSTRA, *J. Radioanal. Chem.*, 1 (1968) 379.
4. J. FRÁNA, M. VOLIECKY, J. KRISTAK, *Radiochem. Radioanal. Letters*, 1 (1969) 41.
5. M. B. A. VASCONCELLOS, M. J. A. ARMELIN, R. FULFARO, F. W. LIMA, São Paulo, Instituto de Pesquisas Energéticas e Nucleares, September 1981 (IPEN-Pub. 33).
6. F. W. LIMA, M. B. A. VASCONCELLOS, M. J. A. ARMELIN, R. FULFARO, V. J. FULFARO, B. B. BRITO NEVES, *J. Radioanal. Chem.*, 71 (1982) 311.
7. D. F. COVELL, *Anal. Chem.*, 31 (1959) 1785.
8. M. F. CESAR, O. Y. MAFRA, São Paulo, Instituto de Energia Atômica, December 1974 (Informação IEA No. 42).
9. P. PACAK, J. OBRUSNIK, *Jad. Energ.*, 25 (1979) 378.
10. G. HEMON, A. MANET, *Proc. Symp. on the Oklo Phenomenon*, Libreville, Gabon, 23–27 June, 1975, p. 437.
11. J. A. ROWSON, S. A. HONTZEAS, *Nucl. Instrum. Methods*, 154 (1978) 541.
12. R. M. MOXHAM, *J. Res. U.S. Geol. Surv.*, 4 (1976) 589.
13. F. CAVALLARI, M. TERRANI, S. TERRANI, *Nucl. Instrum. Methods*, 79 (1970) 69.
14. A. WALD, *Ann. Math. Stat.*, 11 (1940) 284.
15. M. B. A. VASCONCELLOS, M. J. A. ARMELIN, R. FULFARO, F. W. LIMA, São Paulo, Instituto de Pesquisas Energéticas e Nucleares, August 1980 (IPEN-Pub. 17).
16. M. J. A. ARMELIN, M. B. A. VASCONCELLOS, *J. Radioanal. Nucl. Chem.*, 100 (1986) 37.
17. M. Y. DONNAN, E. K. DUKES, *Anal. Chem.*, 36 (1964) 392.