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# DETERMINATION OF $^{235}U/^{238}U$ ISOTOPIC RATIOS BY NUCLEAR METHODS

Marina B.A.Vasconcellos and Barbara P.Mazzilli

Radiochemistry Division
Instituto de Pesquisas Energéticas e Nucleares
Comissão Nacional de Energia Nuclear
Caixa Postal 11049 - São Paulo - SP
Brasil



## ABSTRACT

The determination of $^{235}U/^{238}U$ isotopic ratios is extremely important in nuclear technology.

Although it is reckoned that very precise and accurate isotopic analyses of uranium can be performed by mass spectrometry, nuclear methods can give their contribution as well.

Neutron activation analysis followed by high resolution gamma-ray spectrometry using solid state Ge(Li) detectors utilizes the ratio between peaks of $^{239}Np$ and fission products of $^{235}U$ to measure $^{235}U/^{238}U$ ratios in samples with several enrichments in $^{235}U$. Due to the possibility of using several ratios between peaks, the precision of the method can be greatly improved.

The method of passive gamma-ray spectrometry, in which the natural radioactivity of uranium is measured can also be utilized to determine $^{235}U/^{238}U$ ratios. In this case, the ratios of the areas of several peaks corresponding to the natural isotopes $^{235}U$ and $^{238}U$ are computed.

In the present work, an application of the method of

multiple peak ratios was introduced for the case of passive gamma-ray spectrometry. The results were compared to those obtained by neutron activation analysis and to those obtained by other authors.

In the case of activation analysis, an average precision of down to 0.1% and an average accuracy of 3% were attained. For passive gamma-ray spectrometry, the corresponding values were 1.0% and 2.6%.

The measurements were carried out in standards containing several $^{235}U/^{238}U$ ratios.

# DETERMINAÇÃO DE RAZÕES ISOTÓPICAS $^{235}U/^{238}U$ POR MÉTODOS NUCLEARES

Marina B.A. Vasconcellos e Barbara P.Mazzilli

Divisão de Radioquímica
Instituto de Pesquisas Energéticas e Nucleares
Comissão Nacional de Energia Nuclear
Caixa Postal 11049 - São Paulo - SP
Brasil

RESUMO

A determinação de razões isotópicas $^{235}U/^{238}U$ é de extrema importância para a tecnologia nuclear.

Embora se reconheça que resultados muito precisos e exatos sejam obtidos por espectrometria de massa, os métodos nucleares também podem dar sua contribuição.

O método de análise por ativação com nêutrons seguido de espectrometria de raios gama de alta resolução em detectores de estado sólido de Germânio-Lítio utiliza as razões entre os picos do $^{239}Np$ e dos produtos de fissão do $^{235}U$ para medir as razões isotópicas $^{235}U/^{238}U$ em amostras com diversos graus de enriquecimento em $^{235}U$. Devido à possibilidade de utilizar um número bastante grande de razões entre picos, a precisão do método pode ser grandemente aumentada,como já foi demonstrado por alguns autores.

O método de espectrometria de raios gama passiva, em que a radioatividade natural de amostras contendo urânio é medida, pode também ser utilizado para determinar razões $^{235}U/^{238}U$, calculando-se as razões entre as áreas dos picos correspondentes aos isótopos naturais $^{235}U$ e $^{238}U$.

No presente trabalho, introduziu-se uma aplicação do método das múltiplas razões entre picos para o caso da espectrometria de raios gama passiva e comparou-se os resultados obtidos com os da análise por ativação e também com os resultados obtidos por outros autores.

No caso da análise por ativação, obteve-se uma precisão média de até 0,1% e uma exatidão de 3% e para a espectrometria de raios gama passiva, uma precisão média de 1,0% e uma exatidão de 2,6%.

As medidas foram feitas em padrões contendo diversas razões $^{235}U/^{238}U$.

# DETERMINATION OF $^{235}U/^{238}U$ ISOTOPIC RATIOS BY NUCLEAR METHODS

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Radiochemistry Division

Instituto de Pesquisas Energéticas e Nucleares

Comissão Nacional de Energia Nuclear

São Paulo - Brasil

## 1. INTRODUCTION

The determination of the $^{235}U/^{238}U$ isotopic ratios is of great importance in nuclear technology. It is reckoned that precise and accurate isotopic determination of uranium is usually carried out by mass spectrometry. Nevertheless, this method requires highly specialized and expensive equipment. In nuclear laboratories it is often more convenient and cheaper to use other available methods of analysis. Among the existing nuclear methods for the $^{235}U/^{238}U$ ratio determination, neutron activation followed by high resolution gamma-ray spectrometry and passive gamma-ray spectrometry can give satisfactory results. The purpose of the present work is to compare these two methods and decide which one gives the most precise and accurate results.

The method of neutron activation in which several peak ratios between $^{239}Np$ and some of the fission products of $^{235}U$ are computed can give very precise results, as related by Mantel et al[1] and by John et al[2].

In the present work, this calculation procedure was applied also to natural radioactivity measurements (passive gamma-ray spectrometry), by determining several ratios between peaks corresponding to $^{235}U$ and to $^{238}U$.

The precision and accuracy of the two methods were evaluated and compared to the results obtained by Mantel et al[1] and by John et al[2].

## 2. DETERMINATION OF THE $^{235}U/^{238}U$ ISOTOPIC RATIO BY THERMAL NEUTRON ACTIVATION ANALYSIS FOLLOWED BY HIGH-RESOLUTION GAMMA-RAY SPECTROMETRY

### 2.1. Principle of the Method

The activation of uranium with thermal neutrons gives origin,

among others, to the following nuclear reactions:

$$^{238}_{92}U\ (n,\gamma)\ ^{239}_{92}U\ (T_{1/2} = 23.54\ m) \xrightarrow{\beta^-} {}^{239}_{93}Np\ (T_{1/2} = 2.35\ d)$$

$$^{235}_{92}U\ (n,\ fission) \longrightarrow F.P. + 2.5\ ^{1}_{o}n$$

where F.P. = fission products

The first transuranium element, $^{239}Np$, as well as many of the fission products of $^{235}U$, are gamma emitters and give origin upon activation to well identifiable species. The use of high-resolution $\gamma$-ray detectors could, therefore, allow the separation and determination of many $\gamma$-ray peaks present in the same matrix, even if the corresponding energies are close together. As, in this case, all the species can be determined separately in a single gamma spectrum, many of the common sources of error, such as flux variation, self shielding, sample weight, chemical yield and counting geometry, can be avoided.

In Table 1 the energies and half-lives of several gamma-ray peaks of $^{239}Np$ and fission products identified in irradiated uranium standards are presented.

TABLE 1 - Energy and Half-Life of Several Gamma-Ray Peaks Obtained in the Spectrum of Irradiated Uranium

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

The area ratio between two identifiable gamma-ray peaks corresponding to $^{239}Np$ and to a fission product will therefore be proportional to the $^{235}U/^{238}U$ atom ratio in the analyzed sample. Of course, the precision of such a method of analysis is greatly increased if we use the average of several ratios between the areas of $^{239}Np$ and fission product peaks. In this case, the only error present is due to counting statistics and to the peak integration. The idea of using several ratios between the area of $^{239}Np$ and fission product peaks was already described by different authors[1-4].

Vasconcellos et al[5] and Lima et al[6] have used the method of the peak ratios of $^{239}Np$ and of the fission products to calculate the $^{235}U$ isotopic abundances in geological samples, in search for an "Oklo Phenomenon" in the Northeastern regions of Brazil.

## 2.2. Experimental

### 2.2.1. Preparation of the Standards for Irradiation

Since just a few uranium standards of well known $^{235}U$ isotopic composition were available, new mixtures were prepared in order to obtain sufficient experimental points for the calibration curves.

The solutions were prepared by dissolution of the standards in 1:1 $HNO_3$, and addition of water in order to obtain a final concentration of about 10 mg of uranium/ml. By mixing these standards solutions, fourteen final solutions with different isotopic ratios were obtained, according to Table 2.

TABLE 2 - $^{235}U/^{238}U$ isotopic Ratios Used to Obtain the Calibration Curves in the Neutron Activation Method

| Standard | $^{235}U/^{238}U$ Composition | Origin of the Standards |
|---|---|---|
| 1 | 0.005297 | CNEN* |
| 2 | 0.007254 | CNEN* |
| 3 | 0.01014 | NBS |
| 4 | 0.01931 | Mixture |
| 5 | 0.02081 | NBS |
| 6 | 0.03143 | NBS |
| 7 | 0.04028 | Mixture |
| 8 | 0.05278 | NBS |
| 9 | 0.07607 | Mixture |
| 10 | 0.1145 | Mixture |
| 11 | 0.1566 | Mixture |
| 12 | 0.1924 | Mixture |
| 13 | 0.25126 | NBS |
| 14 | 0.9997 | NBS |

* Standards analyzed by mass spectrometry in the "Comissão Nacional de Energia Nuclear".

### 2.2.2. Irradiation and Counting

For the irradiation of the standards, convenient aliquots of the uranium solutions were pipetted into small polyethylene containers especially made for activation analysis, supplied by the Free University of Amsterdam. The solutions pipetted were then dried under an infra-red lamp prior to the irradiation. The total uranium and the $^{235}U$ masses irradiated ranged from 1 to 5 mg and from 25 to 200 µg, respectively.

Each group of standards were introduced into the same polypropylene vial for irradiation and were irradiated for 30 minutes. The irradiations were carried out in a pneumatic tube of the IEA-R1 reactor, at a thermal neutron flux of $4.3 \times 10^{11} n/cm^2 s$ and a rapid neutron flux of

$1.6 \times 10^{11} n/cm^2 s$.

The gamma-spectra of $^{239}Np$ and of the fission products were recorded by using a solid state Ge(Li) detector, model 8001-1022V, with a resolution of 2.9 keV for the 1332 keV peak of $^{60}Co$. The detector was coupled to a 4096 channel Model 5410A Hewlett-Packard analyzer and to a Hewlett - Packard 2100A minicomputer for data reduction.

The cooling times varied from 20 to 50 hours, depending upon the experiment, although they were usually close to 25 hours. The counting times, on the other hand, varied between 20 to 50 minutes. The distance between sample and detector and the respective time of measurement were chosen such that the dead time of the system would not exceed 10%.

## 2.3. Results and Discussion

The standard samples of well known isotopic composition, as well as the sample to be analyzed were prepared, irradiated and counted as described above. The next step was then to choose the best $^{239}Np$ and fission product peaks to use for the evaluation of the ratios. A similar study has already been carried out by Mantel et al[1], in order to investigate the influence of Compton scattered higher energy gamma-rays from fission products on the $^{239}Np$ peaks. They compared the ratios of the principal peak areas of pure $^{239}Np$ with those obtained from uranium samples with different $^{235}U$ composition. They concluded that the ratios involving the 105, 118,210 and 278 keV peaks show no systematic variation with the $^{235}U$ content, up to a concentration of 5% $^{235}U$.

The results obtained in the present work for the ratio between these peak areas confirm that they can be chosen as representative of the amount of $^{238}U$ in samples containing up to about 10% $^{235}U$. The ratios between the principal fission product peaks and the $^{99}Mo$ 140 keV peak were also evaluated for samples of different $^{235}U$ contents, to investigate the presence of any possible influence of the $^{239}Np$ amount. The results obtained show no systematic variation of the ratios with the $^{235}U$ content even in concentrations up to 16%.

After correction for decay, the calculation of the ratios between all the net areas of fission product peaks ($^{99}Mo$-140 keV, $^{143}Ce$-293 keV, $^{133}I$-530 keV, $^{91}Y$-556 keV, $^{97}Nb$-658 keV, $^{132}I$-668 keV and 773 keV)

and those of $^{239}Np$ (105, 110, 210 and 270 keV) was carried out.

The isotopic composition of each sample was evaluated from the calibration curves constructed by linear regression from the above mentioned ratios and from the values of enrichment of the standards. This procedure yielded 20 values of isotopic composition for each analyzed sample. The next step was to evaluate the mean enrichment (x) according to John et al[2], and the standard deviation of this mean ($\sigma x$). In order to get a better precision, the values of x and $\sigma_x$ were used for excluding the outlayers from the set of averaged data. A new mean enrichment ($x_1$) and a new standard deviation ($\sigma_{x1}$) 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 an weighted mean of enrichment ($\omega \pm \sigma_\omega$), by defining an ampirical 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 $\omega_i$ of the interval.

$$\omega - \frac{\sigma_\omega}{\sqrt{\frac{p_i}{\Sigma p_i}}} < \omega_i < \omega + \frac{\sigma_\omega}{\sqrt{\frac{p_i}{\Sigma p_i}}}$$

Finally, the accuracy of the method was evaluated for each

mean according to the equation:

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

where x is the mean enrichment mentioned above and $\mathfrak{x}$ is the same value for the respective standard.

A computer routine was developed for these calculations. The results achieved in two distinct experiments are summarized in Table 3, where $\bar{\sigma}_x$, $\bar{\sigma}_{x1}$, $\bar{\sigma}_\omega$, $\bar{\sigma}_{\omega 1}$ and $\bar{\Delta}$ stand for the mean values of $\sigma_x$, $\sigma_{x1}$, $\sigma_\omega$, $\sigma_{\omega_1}$ and $\Delta$, calculated from individual results found for all the n samples analyzed.

Our method proved to be applicable for the determination of the $^{235}U/^{238}U$ isotopic composition (x) in the range $0.005297 < x < 0.25126$ which corresponds to $^{235}U$ abundances up to 20.013%.

We can see from the data of Table 3 that the precision of the method is improved when the weighted mean, $\omega$, is used. Of course, this precision can be further improved by averaging over a number of ratios greater than 28.

Indeed, for the two experiments, the mean standard deviation improved of about 12% to 34% when the new weighted mean of enrichment ($\omega_1$) was used instead of the arithmetic mean of enrichment (x). For example, it can be observed in Table 3 that $\bar{\sigma}x$ is 1.0%, while $\bar{\sigma}\omega_1$ is 0.88% for experiment 1; and that $\bar{\sigma}_x$ is 0,67%, while $\bar{\sigma}_{\omega_1}$ is 0,44% for experiment 2.

The precision achieved of at least 1.0%, considering the mean values of standard deviations of the means for all the n samples ($\bar{\sigma}_x$), is in good agreement with the results of John et al[2].

Mantel et al[1] obtained a precision of 0.6% for the standard deviation of the mean ($\sigma_x$), considering a sample of natural uranium. In our experiments we obtained precisions even better (0.1%, for instance, for the 0.25126 $^{235}U/^{238}U$ isotopic composition in experiment 1), when dealing with higher concentration ratios.

Nevertheless, the accuracy of the method did not prove to be as good as expected ($\bar{\Delta}$ equal to 3.0 and 5.5 for experiments 1 and 2, respectively). No apparent reason was found for this fact.

## Study of the Reproducibility of the Method

Five groups of uranium standards were irradiated at different days in order to study the reproducibility of the method. As variations can occur in the reactor neutron flux, the irradiations were carried out always in the same week's day and at the same hour. The irradiations during the first day of the reactor operation were avoided as well as those imediately after the reactor had reached the criticality, the chosen time falling always after 11 am.

The results obtained for the analysis of the NBS standard, with $^{235}U/^{238}U$ atomic ratio equal to 0.03143, using these five groups of uranium standards are summarized in Table 4.

TABLE 4 - Analysis of NBS standard ($^{235}U/^{238}U$ atomic ratio = 0.03143) using five groups of calibration curves irradiated at different days.

| | $\sigma_x$% | $\sigma_{x1}$% | $\sigma_\omega$% | $\sigma_{\omega_1}$% |
|---|---|---|---|---|
| Group 1 | 1.8 | 1.1 | 1.8 | 1.2 |
| Group 2 | 1.1 | 0.7 | 1.0 | 0.7 |
| Group 3 | 2.7 | 1.8 | 2.5 | 1.4 |
| Group 4 | 0.8 | 0.6 | 0.9 | 0.5 |
| Group 5 | 2.0 | 1.2 | 2.0 | 1.1 |

$^{235}U/^{238}U$ isotopic composition of the standards used in each group of experiment.

Group 1 0.005297, 0.007254, 0.01931, 0.03143, 0.04028, 0.07607, 0.1145, 0.1566

Group 2 0.005297, 0.007254, 0.01931, 0.03143, 0.04028, 0.07607, 0.1145, 0.1566, 0.1924, 0.25126

Group 3 0.005297, 0.007254, 0.03143, 0.05278, 0.1145, 0.25126, 0.9997

Group 4 0.007254, 0.01014, 0.01931, 0.02081, 0.03143, 0.04028, 0.05278, 0.07607, 0.1145

Group 5 0.005297, 0.007254, 0.03143, 0.05278, 0.1145, 0.25126.

From Table 4 it is seen that the reproducibility of the method is adequate.

Table 3 - Analysis of the Precision and the accuracy of the Method

Experiment 1

| Isotopic composition of the standard | mean enrichment x | relative error $\Delta_x$% | relative standard deviation $\sigma x$% | new mean enrichment xl | relative error $\Delta_{xl}$% | relative standard deviation $\sigma_{xl}$% |
|---|---|---|---|---|---|---|
| 0.005297 | 0.004824 | 8.9 | 2.3 | 0.004800 | 9.4 | 1.4 |
| 0.007254 | 0.006905 | 4.3 | 1.6 | 0.006910 | 4.7 | 1.2 |
| 0.03143 | 0.03160 | 0.54 | 0.66 | 0.03164 | 0.67 | 0.41 |
| 0.05270 | 0.05440 | 3.1 | 0.82 | 0.05368 | 1.7 | 0.34 |
| 0.1145 | 0.1124 | 1.8 | 0.59 | 0.1128 | 1.5 | 0.27 |
| 0.25126 | 0.25147 | 0.08 | 0.09 | 0.25144 | 0.07 | 0.05 |
| | * | $\bar{\Delta}_x$% | $\bar{\sigma}_x$% | | $\bar{\Delta}$xl% | $\bar{\sigma}$xl% |
| | | 3.1 | 1.0 | | 3.0 | 0.61 |

Table 3 - Analysis of the Precision and the accuracy of the method (cont.)

Experiment 1

| weighted mean enrichment $\omega$ | relative error $\Delta\omega\%$ | relative standard deviation $\sigma\omega\%$ | new weighted mean enrichment $\omega 1$ | relative error $\Delta\omega 1\%$ | relative standard deviation $\sigma\omega 1\%$ |
|---|---|---|---|---|---|
| 0.004800 | 9.4 | 2.2 | 0.004800 | 9.4 | 2.2 |
| 0.006800 | 5.0 | 1.6 | 0.006860 | 5.4 | 1.6 |
| 0.03166 | 0.73 | 0.63 | 0.03165 | 0.70 | 0.52 |
| 0.05424 | 2.8 | 0.76 | 0.05368 | 1.7 | 0.47 |
| 0.1126 | 1.7 | 0.55 | 0.1128 | 1.5 | 0.39 |
| 0.25140 | 0.06 | 0.09 | 0.25143 | 0.07 | 0.08 |
| | $\bar{\Delta}\omega\%$ | $\bar{\sigma}\omega\%$ | | $\bar{\Delta}\omega 1\%$ | $\bar{\sigma}\omega 1\%$ |
| | 3.3 | 0.97 | | 3.1 | 0.88 |

Table 3 - (cont.)

Experiment 2

| Isotopic composition of the standard | mean enrichment x | relative error Δx% | relative standard deviation σx% | new mean enrichment x1 | relative error Δx1% | relative standard deviation σx1% |
|---|---|---|---|---|---|---|
| 0.007254 | 0.005941 | 18.1 | 2.1 | 0.006000 | 17.3 | 1.7 |
| 0.01014 | 0.00879 | 13.3 | 1.3 | 0.00887 | 12.5 | 0.71 |
| 0.01931 | 0.01937 | 2.9 | 0.33 | 0.01987 | 2.9 | 0.25 |
| 0.02081 | 0.02188 | 5.1 | 0.29 | 0.02188 | 5.1 | 0.22 |
| 0.03143 | 0.03215 | 2.3 | 0.41 | 0.03224 | 2.6 | 0.27 |
| 0.04028 | 0.04012 | 0.39 | 0.47 | 0.03981 | 1.2 | 0.30 |
| 0.05278 | 0.05197 | 1.5 | 0.41 | 0.05168 | 2.1 | 0.28 |
| 0.07607 | 0.07947 | 4.5 | 0.47 | 0.07920 | 4.1 | 0.32 |
| 0.1145 | 0.1124 | 1.8 | 0.28 | 0.11254 | 1.7 | 0.20 |
| | * | $\bar{\Delta}x\%$ 5.5 | $\bar{\sigma}x\%$ 0.67 | | $\bar{\Delta}x1\%$ 5.5 | $\bar{\sigma}x1\%$ 0.47 |

Table 3 - (cont.)

Experiment 2

| weighted mean enrichment $\omega$ | relative error $\Delta\omega\%$ | relative standard deviation $\sigma\omega\%$ | new weighted mean enrichment $\omega 1$ | relative error $\Delta\omega 1\%$ | relative standard deviation $\sigma\omega 1\%$ |
|---|---|---|---|---|---|
| 0.006030 | 16.9 | 2.0 | 0.006030 | 16.9 | 1.6 |
| 0.00888 | 12.4 | 1.2 | 0.00892 | 12.0 | 0.61 |
| 0.01991 | 3.1 | 0.33 | 0.01992 | 3.2 | 0.24 |
| 0.02189 | 5.2 | 0.26 | 0.02184 | 4.9 | 0.23 |
| 0.03213 | 2.2 | 0.41 | 0.03219 | 2.4 | 0.29 |
| 0.04011 | 0.42 | 0.47 | 0.03981 | 1.2 | 0.29 |
| 0.05182 | 1.8 | 0.38 | 0.05157 | 2.3 | 0.25 |
| 0.07915 | 4.0 | 0.44 | 0.07910 | 4.0 | 0.31 |
| 0.1127 | 1.6 | 0.26 | 0.1127 | 1.6 | 0.18 |
| | $\bar{\Delta}\omega\%$ | $\bar{\sigma}\omega\%$ | | $\bar{\Delta}\omega 1\%$ | $\bar{\sigma}\omega 1\%$ |
| | 5.3 | 0.64 | | 5.4 | 0.44 |

* The figures indicated in this line stand for the mean value of the corresponding data of the same column.

## 3. DETERMINATION OF THE $^{235}U/^{238}U$ ISOTOPIC RATIO BY PASSIVE GAMMA-RAY SPECTROMETRY

### 3.1. Principle of the Method

The alpha decay of many of the natural isotopes and daughters of uranium (also thorium and transuranic elements, like plutonium) 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. For example, $^{235}U$ decays to $^{231}Th$ through the emission of an alpha particle, with a half life of $7.1 \times 10^8$ years and 95% of the decays leave the $^{231}Th$ nucleus in approximately 10 different excited states. These excited states decay through different de-excitation modes, emitting gamma-rays at about 30 different discrete energies. This spectrum of gamma-rays is unique to $^{235}U$ decay.

A similar situation occurs in the decay of $^{238}U$ and its daughters. So, it can be easily foreseen that the determination of $^{235}U/^{238}U$ isotopic ratios can be accomplished by computing the ratios between $\gamma$-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 already been performed by some authors. Cesar and Mafra[7] calculated $^{235}U$ enrichments in $UO_2$ and $U_3O_8$ pellets with enrichments varying from 0.4% to about 20% in $^{235}U$. The authors measured the 185.7 keV peak of $^{235}U$ in the samples, with a solid state Ge(Li) detector, using as standards $UO_2$ and $U_3O_8$ pellets of natural abundance (0.720% $^{235}U$). The importance of using thick samples for measuring $\gamma$-rays in this energy range was pointed out and the critical distance for $UO_2$, $U_3O_8$ and uranyl nitrate were calculated.

Pacak and Obrusnik[8] measured $^{235}U$ and $^{238}U$ contents in fuel elements with 10 and 80% w.w. enrichment, using the 185.7 keV line for the quantitative determination of $^{235}U$, while for the $^{238}U$ content only the 1001.4 keV line of the $^{234}Pa$ daughter could practically be used.

Hemon et al[9] performed analysis of uranium isotopic abundances by fine gamma spectrometry before and after activation, on ore samples from Oklo.

Rowson and Hontzeas[10] have determined the $^{235}U/^{238}U$ isotopic ratio on uranium chemical precipitates by gamma-spectroscopy. Measurements were performed of the $^{235}U$ 185.7 keV peak and of the 92.5 keV doublet of the $^{234}Th$ daughter. Interferences normally encountered by using the latter peak removed by approximating the spectrum in the region of the $^{234}Th$ doublet by a series of Cauchy functions.

Noxham[11] analyzed a sample of the Oklo deposit containing about 0.51 atom percent of U, by a gamma-ray spectrometer system, using a high-purity planar Ge detector. The $^{238}U$ was determined from its daughter's ($^{234}Th$) 63.3 keV photopeak, the $^{235}U$ was determined from its 143.8 and 163.4 keV photopeaks. The ratios of these photopeaks were compared with that from a standard having normal uranium isotopic content.

In the present work, the method of multiple peak ratios intoduced by Mantel[1] for the neutron activation method was applied to the determination of $^{235}U/^{238}U$ isotopic ratios by passive gamma-ray spectrometry using solid state Ge(Li) detectors.

For $^{235}U$, the 144, 164, 186 and 205 keV peaks of $^{235}U$ were used, while for $^{238}U$, the 258, 766 and 1001 keV peaks of the $^{234m}Pa$ daughter ($t_{1/2}$ = 1.18 min) were utilized.

## 3.2 Experimental

The experimental work consisted of measuring the radioactivity of nitrate solutions of NBS isotopic standards with several $^{235}U/^{238}U$ ratios. The measurements were performed by using the same solid state Ge(Li) detector as described in item 2.2.2 of the neutron activation procedure. The measurement periods had to be very long, due to the low intensity of the peaks of $^{235}U$, and $^{238}U$, and varyied between 540 and 1120 minutes.

In Table 5, the $^{235}U/^{238}U$ isotopic ratios of the several standards used to obtain the calibration curves are presented.

TABLE 5 - $^{235}U/^{238}U$ isotopic ratios used to obtain the calibration curves in the passive gamma-ray spectrometry method.

| Standard | $^{235}U/^{238}U$ composition | Origin of the standards |
|---|---|---|
| 1 | 0.005297 | CNEN* |
| 2 | 0.007254 | CNEN* |
| 3 | 0.01014 | NBS |
| 4 | 0.02081 | NBS |
| 5 | 0.05270 | NBS |
| 6 | 3.166 | NBS |

* Standards analyzed by mass spectrometry in the "Comissão Nacional de Energia Nuclear".

The nitrate solutions of the NBS standards were measured in plastic containers of 4.4 cm diameter and the height of the liquid was of 4.5 cm.

Cesar and Mafra have calculated the critical distance for solutions of uranyl nytrate to be of 2.30 cm, for the 136 keV peak of $^{235}U$. So, it was considered that the height of 4.5 cm was sufficient for the self-absorption of the gamma-rays measured to be considered as saturated.

Moreover, the height of the liquid was always the same for all the standards measured.

### 3.3 Results and Discussion

The isotopic composition of each sample was evaluated from the calibration curves constructed by linear regression from the above mentioned ratios and from the values of enrichment of the standards. This procedure yielded 12 values of isotopic composition for each analyzed sample, since this was the number of peak ratios obtained by combining the 144, 164, 186 and 205 keV peaks, for $^{235}U$, with the 258, 766 and 1001 keV peaks, for $^{238}U$.

The statistic treatment applied to the data was similar to the one developed by John et al[2] and described in item 2.3 of the present work.

In Table 6 are presented the values of the $^{235}U/^{238}U$ ratios obtained, together with the relative standard deviations, σx, σxl, σω, σωl and the relative errors, Δx, Δxl, Δω and Δωl, all in %.

It can be observed in Table 6 that the relative error, Δ, and the relative standard deviations, σ, decrease with increasing $^{235}U$ abundance. The best values were obtained for very enriched samples (Δx and σx = 0 for $^{235}U/^{238}U$ = 3.166 or 75% in $^{235}U$).

The relative standard deviations had a significant improvement by employing the statistical treatment of John et al[2]. For example, the value of σx was 0.8% for the $^{235}U/^{238}U$ ratio equal to 0.05278 while $\sigma\omega_1$ was 0.09% for the same enrichment.

## 4. Conclusions

In conclusion, it can be said that both nuclear methods studied, neutron activation analysis and passive gamma-ray spectrometry, for the determination of $^{235}U/^{238}U$ isotopic ratios, can give satisfactory results.

By using the method of multiple peak ratio computation and employing the statistical treatment of the data recommended by John et al, the following conclusions were drawn:

### 4.1. Neutron activation method

- The neutron activation method proved to be applicable for the determination of the $^{235}U/^{238}U$ isotopic composition in the range from 0.005297 to 0.2516, which corresponds to slightly depleted uranium (~0.5%) to an enrichment of about 20% in $^{235}U$.

- The precision achieved, of at least 1.0%, considering the mean values of standard deviations of the means for all the n samples, $\bar{\sigma}x$, is in good agreement with the results of John et al[2].

- Mantel et al[1] obtained a precision of 0.6% for the standard deviation of the mean, σx, for natural uranium. In the present work, a precision of 0.1% was achieved for the standard enriched in 20%.

- The accuracy of the method did not prove to be as good as expected ($\bar{\Delta}\omega_1$ equal to 3.1 and 5.4 for experiments 1 and 2).

## 4.2 Passive gamma-ray spectrometry

- The passive gamma-ray spectrometry method proved to be applicable in the interval of $^{235}U/^{238}U$ ratios from 0.005297 to 3.166 (slightly depleted uranium to uranium enriched to 75%).

- The precision achieved was of at least 1.6% (value of $\bar{\sigma}x$).

- The relative errors, $\Delta\omega_1$(%), varyied from 10.4%, for natural uranium, to 0% for the uranium enriched to 75%.

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