

**A COMPARATIVE STUDY OF SOME METHODS FOR THE DETERMINATION  
OF URANIUM USED AT THE INSTITUTO DE PESQUISAS  
ENERGÉTICAS E NUCLEARES**

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**INIS Categories and Descriptors**

**B11**

**ACTIVATION ANALYSIS: Uranium**

**DELAYED NEUTRON: Uranium**

**SPECTROPHOTOMETRY: Uranium**

**EPITHERMAL NEUTRON: Uranium**

**TBP: Uranium**

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

**A COMPARATIVE STUDY OF SOME METHODS FOR THE DETERMINATION  
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Marina B. A. Vasconcellos<sup>(\*\*)</sup>, Maria José A. Armelin<sup>(\*\*)</sup>,  
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**ABSTRACT**

The choice of analytical methods to be adopted for uraniferous materials depends much on the nature or kind of material to be analyzed (several types of ores, biological materials) and it is practically impossible to adopt a general method, especially in respect to the accuracy, precision and sensitivity to be attained.

In the present work, a comparative study is made of some of the methods employed at the IPEN for the analysis of uranium. The methods chosen were: epithermal neutron activation analysis, delayed neutron counting activation analysis and spectrophotometric analysis with dibenzoylmethane.

For the study of the three methods cited, six reference ores of the International Atomic Energy Agency were analyzed.

The results obtained for the analysis of the standard ores agreed well between themselves in most cases. The method which presented best precision and accuracy, in the case of the samples analyzed, was the delayed neutron counting method, with an average precision and accuracy of the order of 2%. In the spectrophotometric analysis, an average precision and accuracy of about 3% was obtained and 5% for epithermal neutron activation analysis. The total errors, which include the precision and the accuracy, were inferior to 25% in practically all cases, which allows the inclusion of the methods in the "Excellent" category, according to McFarren's<sup>(12)</sup> statistical criterion.

**I - INTRODUCTION**

The determination of uranium in several materials, especially geological materials, is becoming more and more important, due to the growing use of this metal for the generation of energy in nuclear reactors and to the decreasing in the uranium reserves. An ore with a concentration of 120 ppm of uranium is already considered as economically exploitable<sup>(3)</sup>.

For these reasons, the employment of analytical methods that are sufficiently precise, accurate and sensitive is necessary. The speed of analysis is also of great importance, especially in the case of routine analysis, for geological prospection, in which the number of determinations is very large.

On the other hand, some discrepancies have been noticed between the results obtained by different methods for the determination of uranium in several materials. Even in the data presented by the International Atomic Energy Agency, some differences can be observed between the uranium concentrations determined in some standard ores, by methods such as spectrophotometry with dibenzoylmethane or arsenazo, fluorimetry, radiometric analysis and X-ray fluorescence analysis<sup>(9)</sup>.

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(\*\*) COURP - Área de Radioquímica

(\*\*\*) COURP - Área de Física Nuclear

Some works have already been published in which several methods of uranium analysis have been compared, such as epithermal neutron activation analysis and spectrophotometry in the work of Mainka et al<sup>(10)</sup> and several different techniques (mass spectrometry, delayed neutron counting, alpha spectrometry, gamma-ray spectrometry, total beta counting, fission track registration and radiometry) in the work of Stuckless et al<sup>(15)</sup>. Matsuda<sup>(11)</sup> studied three methods of non-destructive analysis of uranium (gamma-ray spectrometry, X-ray fluorescence and delayed neutron counting) and compared them with a volumetric method. Garrett and Lynch<sup>(8)</sup> studied the method of delayed neutron counting and compared it with fluorimetric analysis, in the geochemical prospection of uranium in lake sediments in Canada.

On the other hand, in the mentioned publications, detailed comparative studies of the precision, accuracy and sensitivity of the several methods employed were not made, with the application of adequate statistical tests.

For this reason, in the present work it was decided to make a comparative study of some of the methods for the determination of uranium employed at the Instituto de Pesquisas Energéticas e Nucleares. The methods chosen were: epithermal neutron activation analysis, delayed neutron counting activation analysis and spectrophotometric analysis with dibenzoylmethane.

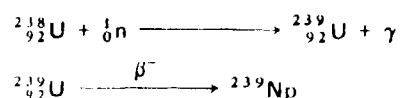
For the study of the three methods cited, six standard ores of the International Atomic Energy Agency were analyzed.

## II – METHODS EMPLOYED

A brief presentation will be made of the several methods employed for the determination of uranium.

### II.1 – Epithermal Neutron Activation Analysis

The activation of uranium with neutrons gives origin, among others, to the nucleus reaction:



${}_{92}^{239}\text{U}$  is a radioactive isotope, of 23.54 minutes half life, which emits, besides beta radiation, gamma radiation with an energy of 74 keV. This radiation can be utilized for qualitative and quantitative analysis of uranium, by means of a gamma spectrometer.

Since most elements are activated by thermal neutrons, a more selective activation is obtained for uranium, as well as for some other heavy elements, by placing the sample to be analyzed in a cadmium shielding of convenient thickness, so as to shield the thermal neutrons, of lower energy.

By means of this procedure, a "cleaner" gamma spectrum can be obtained, that is, spectrum with less interference.

In many cases, epithermal neutron activation analysis can be purely instrumental, but depending on the ratio between the concentrations of uranium and of some interfering elements, such as thorium and some rare earths, a post irradiation chemical separation may become necessary.

The procedure employed in the present work for epithermal neutron activation analysis is described by Atalla and Lima<sup>(11)</sup>.

## II.2 – Activation Analysis by Delayed Neutron Counting

Delayed neutrons are emitted in the fission of  $^{235}\text{U}$ , besides prompt neutrons, which are emitted at the moment of fission itself. These delayed neutrons are originated from neutron rich, beta emitter fission products.

Six groups of so-called delayed neutron precursors have been identified in the fission of  $^{235}\text{U}$  by thermal neutrons, with half-lives ranging from 0.230 to 55.72 seconds.

The detection and counting of the delayed neutrons, by means of an assembly of  $\text{BF}_3$  detectors coupled to an adequate electronic system, allows a quantitative analysis of the uranium content, since the number of delayed neutrons emitted is proportional to the amount of uranium present.

Only the possible interference of thorium, which also undergoes fission, must be considered, especially if this element is present in concentrations much higher than uranium. The frequency with which uranium and thorium are found together in Brazilian minerals makes the simultaneous determination of these two elements very important to us.

The method of activation analysis by delayed neutron counting allows very rapid determinations, which makes it specially suited for routine analysis. A great number of systems have been developed in several countries for the analysis of uranium by delayed neutron counting, as the recent review by Binney and Scherpelz<sup>(2)</sup> shows.

## II.3 – Spectrophotometric Analysis with Dibenzoylmethane

This method is based on the formation of a bright-yellow complex between uranyl ion,  $\text{UO}_2^{2+}$  and dibenzoylmethane (DBM). Quantitative determinations can be accomplished by measuring the absorbance of this complex at 395 nanometers.

Some cations and anions can interfere in the determination of uranium and for this reason it is usual to make a previous extraction of uranium from contaminant elements. In the present work, it was decided to adopt the extraction of uranium with tributylphosphate (TBP) diluted in iso-octane, as recommended by Francois<sup>(7)</sup>. Some cations, as Bi(III), Ce(IV) and Th(IV) are also extracted by TBP in sufficient amounts so as to become interferences. In these cases, it is possible to resort for instance, to the complexation of Bi(III) with disodium versenate and of Th(IV) with acetate ion and to the reduction of cerium to the trivalent state with sodium sulfite.

## III – EXPERIMENTAL PART

### III.1 – Preparation of the Uranium Standards

The uranium standards were prepared as following:

Uranium oxide,  $\text{U}_3\text{O}_8$  was calcinated at  $850^\circ\text{C}$ , for about one hour. A weighed amount of the oxide was then dissolved in 1:1  $\text{HNO}_3$ , with gentle heating. After evaporating to dryness, the residue was taken up in 1:20  $\text{HNO}_3$ . The solution was taken to volume, so as to obtain a stock solution with 10 mg  $\text{U}_3\text{O}_8$ /ml, which was diluted according to necessity.

In the case of the spectrophotometric analysis, the uranyl nitrate solution was utilized as such. For the epithermal neutron activation analysis and for the analysis by delayed neutron counting, aliquots of the solution were pipetted on pieces of filter paper (Whatman nº 40) of about  $1\text{ cm}^2$  area and dried under an infrared lamp.

### III.2 – Preparation of Samples for Analysis

The ore samples, in the case of the non-destructive analysis, were simply weighed in small polyethylene bags especially prepared for this purpose.

For the spectrophotometric analysis, it was necessary to dissolve the ores in the first place. The weighed material was transferred to a platinum crucible and a mixture of HF, HNO<sub>3</sub> and some drops of H<sub>2</sub>SO<sub>4</sub> was added. The mixture was heated in a sand bath, evaporating to dryness. The treatment was repeated once or twice according to the solubility of the ore.

The residue was finally taken up in 0.7N HNO<sub>3</sub>, with gentle heating. The solution was taken to volume in 50 ml flasks, with 0.7 HNO<sub>3</sub> also. For the analysis, 5 ml aliquots were pipetted.

### III.3 – Irradiation and Counting

#### III.3.1 – Epithermal Neutron Activation Analysis

The samples and standards were irradiated in cadmium cylinders of 1 mm thickness, 10 mm external diameter and 20 mm high. The cylinders were put in polypropylene irradiation vials and transported to the irradiation position by means of a pneumatic system. The irradiation time varied between 15 seconds and 1 minute, according to the uranium content of the ores.

The thermal neutron flux in the irradiation position was of  $5 \times 10^{11}$  neutrons/cm<sup>2</sup>.s and the cadmium ratio in this position was of 4.5, for gold.

After irradiation, samples and standards were removed from the cadmium shields and put separately in counting tubes. The countings were done with the aid of a well-type sodium iodide scintillation detector, coupled to a 400 channel pulse-height analyzer, TMC Model 404-6. The counting times varied between 4 and 10 minutes and the cooling times between 10 and 30 minutes.

The quantitative analyses were made by integrating the area under the 74 keV peak of <sup>239</sup>U. The Compton effect was subtracted by the method of Covell<sup>(4)</sup>, as can be seen in Figure 3.1.

The areas obtained for samples and standards were compared by means of the classical expression of activation analysis.

#### III.3.2 – Activation Analysis by Delayed Neutron Counting

The samples and standards were sent to the irradiation position by means of the pneumatic system already mentioned. Contrary to the epithermal neutron activation analysis, the irradiations of samples and standards were done separately, due to the very short half-lives of the delayed neutron precursors (0.230 to 55.72 seconds).

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

The delayed neutrons emitted by the fissioned <sup>235</sup>U were counted by means of a system of six BF<sub>3</sub> detectors, 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, amplifier, monochannel analyzer, scaler and timer. In Figure 3.2, a scheme of the neutron detection and counting system can be seen.



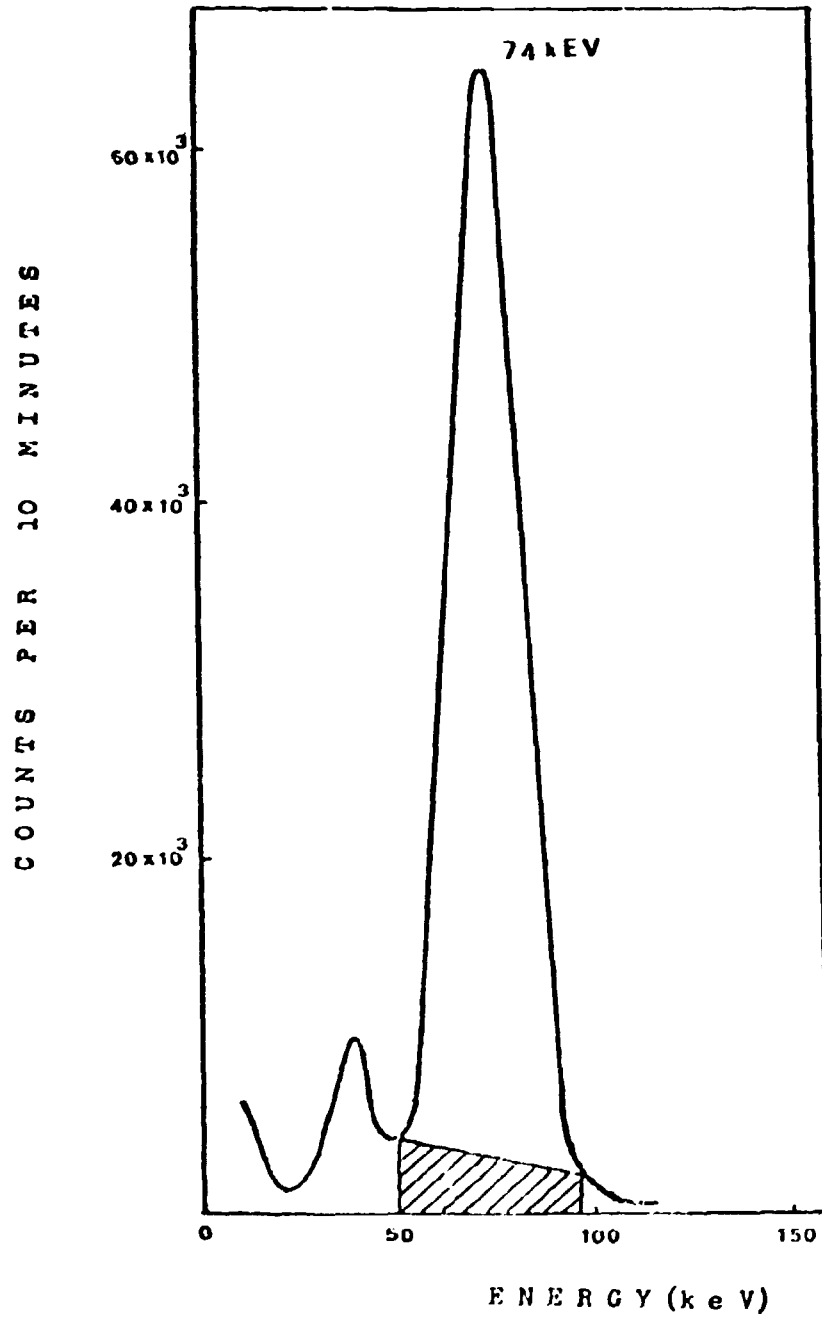


Figure 3.1 - Gamma ray spectrum of  $^{239}\text{U}$

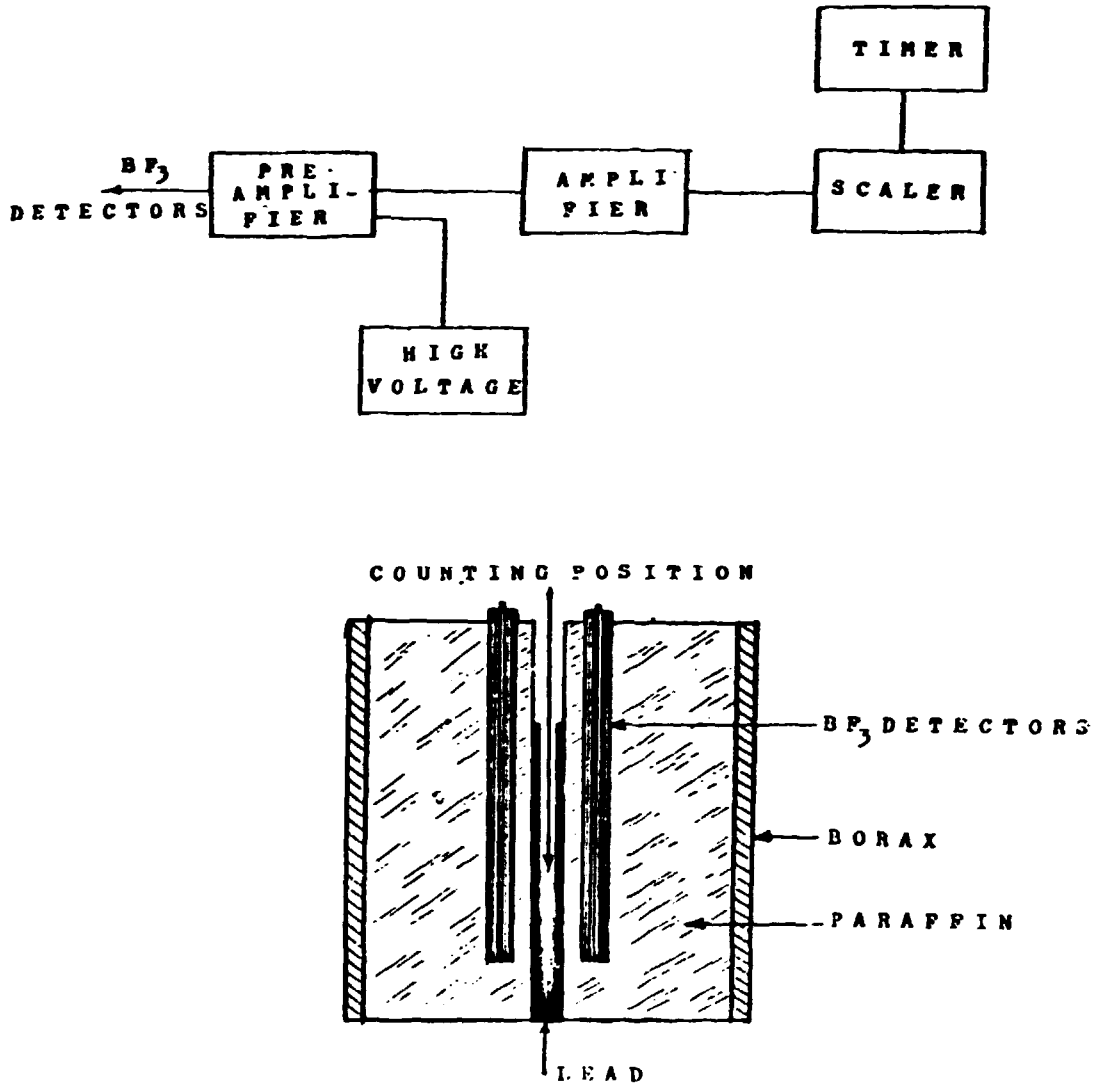


Figure 3.2 - Sistem of neutron detection and counting

For the quantitative analysis of uranium, the integral counts registered by the scaler were used. The counts obtained for the sample were compared to the counts of the standard, after subtracting the background from both, for the quantitative analysis of uranium.

In order to subtract the interference of thorium, irradiations were performed with and without a cadmium shielding. Since  $^{235}\text{U}$  is fissioned by the action of thermal neutrons and  $^{232}\text{Th}$  by fast neutrons, the irradiation in cadmium leads to the activation mainly of thorium, together with  $^{238}\text{U}$ . The double irradiation allows the setting of a simple system of equations, from which one can obtain the real concentration of uranium, without the interference of thorium.

#### III.4 – Procedure in the Spectrophotometric Analysis

After dissolving the ores, as described under III.2, 5 ml aliquots of the solutions were pipetted into separatory funnels. Sodium sulfite was added, to reduce Ce(IV) to Ce(III). After adjusting the pH with  $\text{NH}_3$  or  $\text{HNO}_3$ , using metacresol purple as indicator, glacial acetic acid was added, to complex thorium. The uranium present was then extracted with TBP diluted in iso-octane, using aluminum nitrate as salting agent.

The aqueous phase was rejected and 2 ml of the organic phase were pipetted into 25 ml volumetric flasks. The volume was completed with the so-called "chromogenic reagent", prepared by mixing a 1% solution of dibenzoylmethane in acetone with pyridine and acetone. The solutions were kept in the dark for at least one hour. Simultaneously with the samples, two uranium standards (uranyl nitrate solution) of known uranium content and a blank (distilled water) were processed as described.

The absorbances of samples and standards were read at 410 nanometers against the blank, in 10 mm cells. Although the wavelength of maximum absorbance was 395 nanometers, the measurements were done at 410 nanometers, to avoid the interference of thorium or other tetravalent cations which can be coextracted with uranium and also form complexes with dibenzoylmethane, absorbing below 410 nanometers.

#### IV – ORES OF THE INTERNATIONAL ATOMIC ENERGY AGENCY ANALYZED

- 1) IAEA S-12, Pechblenda, Lot nº 102  
%  $\text{U}_3\text{O}_8$  0.014 (average of three methods)
- 2) IAEA S-13, Pechblenda, Lot nº 449  
%  $\text{U}_3\text{O}_8$  0.039 (average of three methods)
- 3) IAEA S-8, Pechblenda, Lot nº 4  
%  $\text{U}_3\text{O}_8$  0.141 (average of four methods)
- 4) IAEA S-2, Torbernite  
%  $\text{U}_3\text{O}_8$  0.313
- 5) IAEA S-1, Torbernite  
%  $\text{U}_3\text{O}_8$  0.471 (average of three methods)
- 6) IAEA S-7, Pechblenda, Lot nº 43  
%  $\text{U}_3\text{O}_8$  0.527 (average of three methods)

#### V – RESULTS

In the following tables, the results obtained for the analysis of the standard IAEA ores by the methods of epithermal neutron activation analysis, activation analysis by delayed neutron counting and spectrophotometry with dibenzoylmethane are presented.

Table V.1

Results of the Analysis of the Standard Ores of the International Atomic Energy Agency, by Epithermal Neutron Activation Analysis

IAEA Ore	Ore n° 1	Ore n° 2	Ore n° 3	Ore n° 4	Ore n° 5	Ore n° 6
Sample Number	% U <sub>3</sub> O <sub>8</sub>	% U <sub>3</sub> O <sub>8</sub>	% U <sub>3</sub> O <sub>8</sub>	% U <sub>3</sub> O <sub>8</sub>	% U <sub>3</sub> O <sub>8</sub>	% U <sub>3</sub> O <sub>8</sub>
1	0.0172	0.0384	0.134	0.297	0.475	0.497
2	0.0155	0.0396	0.127	0.282	0.457	0.375*
3	0.0168	0.0348	0.145	0.316	0.431	0.516
4	0.0166	0.0363	0.132	0.318	0.444	0.560
5	0.0159	0.0369	0.134	0.311	0.421	0.553
6	0.0177	0.0388	0.127	0.320	0.462	0.538
7	0.0162	0.0339	0.147	0.307	0.446	0.489
8	0.0160	0.0390	0.136	0.298	0.463	0.498
9	0.0172	0.0436	0.134	0.319	0.467	0.494
10	0.0165	—	—	0.311	0.511	0.495
11	—	—	—	—	0.457	—
Average	0.0166	0.0379	0.135	0.308	0.459	0.515
Standard Deviation	6.85 x 10 <sup>-4</sup>	0.00289	0.00694	0.0122	0.0239	0.0277
Relative Std. Dev.	4.1%	7.6%	5.1%	4.0%	5.2%	5.4%
Relative Error	18.6%	2.8%	4.2%	1.6%	2.5%	2.3%
Total** Error	28.4%	14.8%	14.0%	7.8%	10.1%	10.5%
Confidence Limits	0.0166 ± 0.0005	0.0379 ± 0.0022	0.135 ± 0.005	0.308 ± 0.009	0.459 ± 0.016	0.515 ± 0.022

\* Rejected value

\*\* See VI.4 and references (12) and (16)

— Experiment not carried out

Table V.2

Results of the Analysis of the Standard Ores of the International Atomic Energy Agency,  
by Delayed Neutron Counting Activation Analysis

IAEA Ore	Ore nº 1	Ore nº 2	Ore nº 3	Ore nº 4	Ore nº 5	Ore nº 6
Sample Number	% U <sub>3</sub> O <sub>8</sub>	% U <sub>3</sub> O <sub>8</sub>	% U <sub>3</sub> O <sub>8</sub>	% U <sub>3</sub> O <sub>8</sub>	% U <sub>3</sub> O <sub>8</sub>	% U <sub>3</sub> O <sub>8</sub>
1	0.0145	0.0382	0.138	0.301	0.455	0.514
2	0.0146	0.0367	0.146	0.312	0.440	0.498
3	0.0142	0.0384	0.142	0.297	0.470	0.525
4	0.0138	0.0379	0.138	0.316	0.467	0.533
5	0.0142	0.0385	0.137	0.315	0.465	0.531
6	0.0146	0.0386	0.142	0.310	0.470	0.563
7	0.0147	0.0369	0.140	0.309	0.463	0.554
8	0.0148	0.0383	0.136	0.311	0.455	0.520
9	0.0143	0.0390	0.139	0.314	0.483	0.496
10	0.0146	0.0375	0.144	0.310	0.477	0.511
Average	0.0144	0.0380	0.140	0.309	0.465	0.525
Standard Deviation	$3.04 \times 10^{-4}$	$7.50 \times 10^{-4}$	0.00307	0.00605	0.0122	0.0217
Relative Std. Dev.	2.1%	2.0%	2.2 %	2.0%	2.6%	4.1 %
Relative Error	2.9%	2.6%	0.71%	1.1%	1.3%	0.38%
Total Error	8.0%	6.4%	4.4 %	4.0%	5.2%	8.2 %
Confidence Limits	0.0144 $\pm$ 0.0002 $\pm$	0.0380 $\pm$ 0.001 $\pm$	0.140 $\pm$ 0.002 $\pm$	0.309 $\pm$ 0.004 $\pm$	0.465 $\pm$ 0.009 $\pm$	0.525 $\pm$ 0.014 $\pm$

Table V.3

Results of the Analysis of the Standard Ores from the International Atomic Energy Agency by Spectrophotometric with Dibenzoylmethane

IAEA Ore	Ore nº 3	Ore nº 4	Ore nº 5	Ore nº 6
Sample Number	% U <sub>3</sub> O <sub>8</sub>	% U <sub>3</sub> O <sub>8</sub>	% U <sub>3</sub> O <sub>8</sub>	% U <sub>3</sub> O <sub>8</sub>
1	0.132	0.310	0.456	0.516
2	0.128	0.311	0.460	0.499
3	0.127	0.308	0.468	0.517
4	0.133	0.295	0.449	0.496
5	0.133	0.300	0.436	0.499
6	0.145	0.300	0.442	0.519
7	0.145	0.288	0.453	0.548
8	0.137	0.293	0.459	0.536
9	0.132	0.298	—	—
10	0.143	—	—	—
11	0.147	—	—	—
12	0.142	—	—	—
Average	0.137	0.300	0.453	0.516
Standard Deviation	0.00708	0.00795	0.0103	0.0186
Relative Std. Dev.	5.2%	2.6%	2.3%	3.6%
Relative Error	2.8%	4.1%	3.8%	2.1%
Total Error	10.0%	9.2%	7.9%	7.1%
Confidence Limits	0.137 ± 0.004	0.300 ± 0.006	0.453 ± 0.008	0.516 ± 0.016

— Experiment not carried out

## VI – STATISTICAL TESTS APPLIED

To make the comparative study between the results obtained by the three methods applied to the analysis of the IAEA ores, some statistical tests were applied, to allow a non-subjective evaluation of the data. For the application of these tests, the concepts of Nalimov's textbook were followed<sup>(13)</sup>.

### VI.1 – F-test

The F-test permits the comparison of the variances of two methods, that is, it allows one to decide if the methods are equally precise or not.

### VI.2 – Comparison of Methods by the Differences between Results

By means of this test, it is possible to decide if the mean values obtained by two different methods can be considered as equal, independently of the fact of the respective variances being equal or not.

### VI.3 – t-test

A t-test permits the comparison of the mean obtained by a given method with the result considered as the "true value". In the case of the present work, the results of the IAEA for the concentration of uranium in the standard ores were considered as the "true values".

### VI.4 – Calculation of the Total Errors

According to the statistical criterion developed by McFarren<sup>(12)</sup> and complemented by Eckschlager<sup>(6)</sup> the total error of an analytical method can be calculated by the expression:

$$\text{Total error} = \frac{d_A + 2s}{\mu}$$

where:

$d_A$  = absolute value of the difference between the mean and the true value

$s$  = standard deviation

$\mu$  = "true" value

According to this criterion, analytical methods can be classified in three categories:

- a – Excellent: when the total error is less than 25%
- b – Acceptable: when the total error is greater than 25% but less than 50%
- c – Unacceptable: when the total error is greater than 50%.

## VII – DISCUSSION OF THE RESULTS AND CONCLUSIONS

### VII.1 – Precision

The variance analysis, using the F-test for the methods taken two by two, allows us to draw the following conclusions:

**a -- Activation by Epithermal Neutrons vs Delayed Neutron Counting**

In practically all cases, the precision of the method of delayed neutron counting can be considered as superior to the precision of the epithermal neutron activation analysis (ENAA).

In the case of ore nº 1, the relative standard deviation for the ENAA was anomalously high (18.6%). This could be attributed to some interference in the peak of 74 keV of  $^{239}\text{U}$ , although the half-life obtained for this peak was compatible with the tabulated value.

**b – Delayed Neutron Counting vs Spectrophotometry**

Only for ore nº 3 the spectrophotometric method was less precise than the delayed neutron counting method. In the other cases, the reproducibility can be considered as the same.

**c – Activation by Epithermal Neutrons vs Spectrophotometry**

Only for ore nº 5 the spectrophotometric method could be considered as superior to epithermal neutron activation in terms of precision. In all other cases, the reproducibility of the two methods can be considered as statistically equal.

The smaller variances between the three methods were the ones obtained in the analysis by delayed neutron counting. By means of the F-test employed, this method shows itself as clearly superior to epithermal neutron activation analysis but not so much in relation to the spectrophotometric analysis.

**VII.2 – Comparison between the Means Obtained**

Employing the statistical test of the differences between the results of the three methods, we observe that, in practically all cases there is an agreement between the means obtained, if we compare the methods two by two.

The results of this comparison are summarized in Table VII.1:

**Table VII.1**

Comparison between the means obtained with the three methods employed in the analysis of the samples of the IAEA

Ore nº	Epithermal neutrons vs delayed neutrons	Epithermal neutrons vs spectrophotometry	Delayed neutrons vs spectrophotometry
1	–	*	*
2	+	*	*
3	+	+	+
4	+	+	+
5	+	+	+
6	+	+	+

+ The averages can be considered as equal

– The averages cannot be considered as equal

\* Analysis not carried out by the spectrophotometric method



### VII.3 – Accuracy

In order to evaluate the accuracy of the methods, the average of the results given by the IAEA were considered as the true values for the uranium concentration of the ores.

The result of the t-test applied to decide if the averages obtained by the methods employed can be considered as equal to the IAEA averages are presented in Table VII.2.

**Table VII.2**

Comparison between the means obtained by the three analytical methods employed and the IAEA results for the standard ores

Ore nº	Epithermal neutrons	Delayed neutrons	Spectrophotometric Method
1	–	–	*
2	+	–	*
3	–	+	+
4	+	+	–
5	+	+	–
6	+	+	+

– The averages are different from the IAEA averages

+ The averages are equal to the IAEA averages

\* Analysis not carried out

From the results presented in the Table, it can be observed that there was a tendency to a better agreement between the averages obtained in the present work and the results of the IAEA in the case of the ores with a greater concentration of uranium.

On the other side, there was not a marked superiority of any one of the three methods in respect to the agreement with the results of the Agency.

Only in the case of the spectrophotometric method, the results obtained for ores 4 and 5 seem to be somewhat low, but no apparent reason was found for this fact.

### VII.4 – Total Errors

The total errors were, in practically all cases, inferior to 25%, which allows one to place the three methods studied in the "Excellent" category, according to McFarren's criterion<sup>(12)</sup>. Only in the case of the analysis of ore nº 1, by epithermal neutron activation analysis, the total error was superior to 25%, which means it should be included in the "Acceptable" category.

### VII.5 – Sensitivity

For each one of the methods of analysis employed, a different criterion had to be used to calculate the sensitivity, as is explained below:

### VII.5.1 – Epithermal Neutron Activation Analysis

In order to evaluate the sensitivity of the method, Currie's<sup>(5)</sup> criterion was applied, by which we can calculate the determination limit  $L_Q$ , given by the expression:

$$L_Q = 50 \left\{ 1 + \left[ \frac{\mu_B}{12.5} \right]^{1/2} \right\}$$

where  $\mu_B$  is the background detected by the equipment and experimentally determined.

In the case of the present work, the value determined for  $\mu_B$  was of 998, for a counting time of 10 minutes. From the expression above, the value of  $L_Q$  calculated was of 500 impulses.

Considering that the counting obtained for a standard containing 2.2  $\mu\text{g}$  of uranium, irradiated for 10 minutes and counted also for 10 minutes, after a cooling time of 7 minutes, was of 584 563 impulses, we can calculate the minimum mass of uranium which can be quantitatively determined as:

$$m_Q = 0.0019 \mu\text{g}$$

This mass corresponds to an approximate concentration of 0.02 ppm of uranium, for a sample of 100 mg, which was about the biggest mass irradiated in the epithermal neutron activation employed.

### VII.5.2 – Delayed Neutron Counting Activation Analysis

According to Binney and Scherpelz<sup>(2)</sup>, we can calculate the minimum level of detection of this method by the expression:

$$\text{MLD} = 3 \sqrt{B} / \text{net number of counts per unit mass}$$

where B is the background count for a given time interval.

If we take as a value for B the average of several experimental determinations, which was 56, we will obtain for MLD a value of 0.56  $\mu\text{g}$  of natural uranium. This mass corresponds to a concentration of 1.1 ppm in a sample of 500 mg.

Greater masses of samples were not irradiated to avoid working with high doses of gamma radiation and also because with large samples the geometry would be very different from the geometry of the uranium standards.

### VII.5.3 – Spectrophotometric Analysis with Dibenzoylmethane

According to Sandell<sup>(14)</sup>, the sensitivity of the spectrophotometric method can be considered as the concentration of the analyzed element which gives an absorbance reading of 0.001, using a cell of 1.00 cm. In the case of the present work we would have, according to this criterion, a sensitivity of 0.015 ppm of uranium. Yoe et al<sup>(16)</sup> found a sensitivity of 0.013 ppm of uranium, adopting Sandell's criterion.

## VII.6 – Conclusions

The comparative study made between the methods of epithermal neutron activation analysis, delayed neutron counting activation analysis and spectrophotometric analysis with dibenzoylmethane allows one to draw the following conclusions:

In relation to precision, the best results, in the case of the analysis of the IAEA ores, were obtained with the method of delayed neutron counting.

As to the averages obtained by the three methods for the analysis of the IAEA ores, in almost all cases there was a good agreement between them.

The agreement between the results of the three methods and the results given by the IAEA was better in the case of the ores with a higher concentration of uranium.

In respect to the total errors, in practically all cases they were inferior to 25%, which allows the classification of the three methods in the "Excellent" category.

As to the sensitivity, the following values were obtained:

Epithermal neutron activation analysis	0.02 ppm of uranium
Delayed neutron counting activation analysis	1.1 ppm of uranium
Spectrophotometric analysis with dibenzoylmethane	0.015 ppm of uranium

These data show that the sensitivity of epithermal neutron activation and of spectrophotometric method were of the same order. In the case of delayed neutron counting, it would be necessary to work with a higher neutron flux, to obtain a comparable sensitivity.

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## RESUMO

A escolha de métodos de análise a serem adotados para materiais uraníferos depende muito da natureza ou tipo do material a ser analisado (diversos tipos de minérios, material biológico, elementos combustíveis nucleares, material para estudos de Ecologia etc.), sendo praticamente impossível a adoção de um método universal, especialmente no que diz respeito à exatidão, precisão e sensibilidade.

No presente trabalho fez-se um estudo comparativo entre alguns dos métodos de determinação de urânio empregados no Instituto de Pesquisas Energéticas e Nucleares. Os métodos escolhidos foram: análise por ativação com nêutrons epitérmicos, análise por ativação por contagem de nêutrons retardados de fissão e análise espectrofotométrica com dibenzolmetano.

Para o estudo dos três métodos citados, fez-se a análise de seis minérios padrões da Agência Internacional de Energia Atômica, cujo teor de urânio já foi determinado por vários métodos.

Os resultados obtidos para a análise de minérios padrões foram de modo geral concordantes entre si. O método que apresentou melhor precisão e exatidão, no caso das amostras analisadas, foi o de contagem de nêutrons retardados, com uma precisão e exatidão médias de cerca de 2%, seguido da análise espectrofotométrica, com cerca de 3% e da análise por ativação com nêutrons epitérmicos, com precisão e exatidão médias em torno de 5%. Os erros totais, que

incluem a precisão e a exatidão ~~inferiores~~ inferiores a 25% em praticamente todos os casos, o que permite incluir os métodos na categoria de "excelentes", de acordo com o critério estatístico de McFarren<sup>(12)</sup>.

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