BR8917459

ISSN 0101-3084

CNEN/SP

ipen Instituto de Pesquisas Energéticas e Nucleares

DETERMINATION OF $^{235}U/^{238}U$ AND $^{234}U/^{238}U$ ISOTOPIC RATIOS BY ALPHA SPECTROMETRY

Mitiko Saiki

IPEN - PUB -- 204

PUBLICAÇÃO IPEN 204 SETEMBRO/1988

SÃO PAULO

PUBLICAÇÃO IPEN 204 SETEMBRO/1988

DETERMINATION OF $^{235}U/^{238}U$ AND $^{234}U/^{238}U$ ISOTOPIC RATIOS BY ALPHA SPECTROMETRY

Mitiko Saiki

DEPARTAMENTO DE FÍSICA E QUÍMICA NUCLEARES

CNEN/SP
INSTITUTO DE PESQUISAS ENERGÉTICAS E NUCLEARES
SÃO PAULO – BRASIL

Série PUBLICAÇÃO IPEN

INIS Categories and Descriptors

B11.10

ALPHA SPECTROSCOPY
COGEMA PIERRELATTE
ELECTRODEPOSITION
ISOTOPE RATIO
URANIUM
URANIUM 234
URANIUM 235
URANIUM 238
US NBS

IPEN - Doc - 3072

Publicação aprovada pela CNEN em 10/05/88.

Nota: A redação, ortografia, conceitos e revisão final são de responsabilidade do(s) autor(es).

DETERMINATION OF $^{235}U/^{238}U$ AND $^{234}U/^{238}U$ ISOTOPIC RATIOS BY ALPHA SPECTROMETRY

Mitiko Saiki

ABSTRACT

Alpha spectrometry has been applied to the determination of $^{235}U/^{238}U$ and $^{234}U/^{238}U$ isotopic ratios in uranium standard reference materials from COGEMA and NBS. The sources were prepared by electrodeposition on stainless steel and the alpha activities measured with a ruggedized detector.

In the $^{235}U/^{238}U$ isotopic ratio determination, the best results were obtained with the standards enriched in ^{235}U. A relative error down to 0.5% (COGEMA standard) and a precision of about 1% (NBS and COGEMA standards) were obtained for uranium standards enriched in ^{235}U.

A precision down to 0.8% (COGEMA standard) and a relative error of about 1% (NBS and COGEMA standards) were obtained in the $^{234}U/^{238}U$ ratio determinations for standards containing high percentages of ^{234}U and ^{238}U atoms.

DETERMINAÇÃO DAS RAZÕES ISOTÓPICAS $^{235}U/^{238}U$ E $^{234}U/^{238}U$ PELA TÉCNICA DE ESPECTROMETRIA ALFA

RESUMO

No presente trabalho foram determinados as razões isotópicas $^{235}U/^{238}U$ e $^{234}U/^{238}U$ nos padrões de urânio da COGEMA e NBS, pela técnica de espectrometria alfa. Para a contagem das partículas alfa os padrões de urânio foram dissolvidos e eletrodepositados em discos de aço inoxidável.

Nas determinações das razões $^{235}U/^{238}U$ os melhores resultados foram obtidos com padrões enriquecidos de ^{235}U, obtendo-se resultados com erros relativos de até a 0,5% (padrão COGEMA) e uma precisão de cerca de 1% (padrões NBS e COGEMA).

No caso das determinações das razões $^{234}U/^{238}U$ foram obtidos resultados com uma precisão de até 0,3% (padrão COGEMA) e erro relativo de até 1% (padrões NBS e COGEMA) para padrões com alto teor de ^{234}U e ^{238}U.

INTRODUCTION

The knowledge of uranium isotopic composition is of great importance in nuclear investigations for the analysis of several kinds of sample containing depleted or enriched uranium. Gladney et al[8] determined $^{235}U/^{238}U$ ratios in natural waters to examine the level of environmental contamination from facilities handling depleted or enriched uranium. Bakhtiar et al[1] determined $^{234}U/^{238}U$ and $^{235}U/^{238}U$ ratios in rainwater to study uranium fallout from the nuclear powered satellites and volcanic eruptions. Ganopathy[7] determined $^{235}U/^{238}U$ ratios in reagent grade uranium from commercial sources and concluded that they had quite different ratio values from natural uranium due to the presence of uranium depleted in ^{235}U. Barnes et al[2] have observed the variable isotopic composition of uranium compounds on NBS standards . Recently,Roy et al[10]determined depletion factors of ^{235}U and ^{234}U in nine commercially available uranium compounds and they also concluded that many of these compounds present different isotopic compositions from that presented by natural uranium. Because of this variable uranium isotopic composition in commercial compounds of uranium,the inadvertent use of such compounds in nuclear investigations can lead to erroneous results.

Besides determination of $^{234}U/^{238}U$ ratios have given useful information to geochemists in the interpretation of radiohydrogeological anomalies[3,9,12]. The existence of $^{234}U/^{238}U$ disequilibrium ratio has wide applicability in studies related to geochemical exploration, marine chemistry, age dating and hydrology.

In a previous paper[13], a comparative study of the re-

sults of $^{235}U/^{238}U$ ratio determinations obtained by nuclear methods such as activation analysis, delayed neutron counting, passive gamma-ray and alpha spectrometry was reported.

This study is now extended to the $^{234}U/^{238}U$ ratio determinations as well as to the $^{235}U/^{238}U$ ratio determinations in other uranium standards, to evaluate the precision and accuracy of the results obtained by alpha spectrometry.

These determinations were carried out in the uranium isotopic standards from the Compagnie Generale de Matierés Nucleaires (COGEMA) from Pierrelatte, France and from National Bureau of Standards (NBS), US.

The electrodeposition procedure described by Donnan and Dukes[6] was adopted to prepare the thin and uniform sources of uranium required for alpha spectrometry.

EXPERIMENTAL

Source Preparation

The electrodeposition procedure adopted is described in the previous paper[13]. Briefly, the sources were electrodeposited onto stainless steel disks (25 mm diameter) polished to a mirror surface. The anode was a platinum wire (1 mm diameter). The electrolytical solution consisted of the uranium standards solution containing from 17 to 170 µg of U and a saturated NH_4Cl solution presenting pH value equal to 1.0. The total volume of the solution for electrodeposition was 5.0 mL and the distance betwwen the electrodes was 0.5cm. The eletrolysis was carried out for about 1 h using a current density of 1.5 A cm^{-2}. One minute before turning off the current, 1 mL of concentrated NH_4OH solution was added to the

solution. The solution was discarded and the cell was rinsed with distilled water. The cell was dismounted and the disk was rinsed with water and ethyl alcohol. Before counting the disk was dried under an infra red lamp.

Counting of the Uranium Sources

For alpha particle spectrometry, an ORTEC alpha spectrometer model 576 with a ruggedized surface barrier detector of 300 mm^2 active area was used. This detector was used connected to an ORTEC model 6240B multichannel analyzer. The system was calibrated in an alpha particle energy range of 4 to 6 MeV. The resolution of the detector for $E\alpha$ = 5.48 MeV of ^{241}Am varied from 30 to 50 keV, depending on the distance between source and detector. The counting time was of about 50,000 seconds and all the sources were measured in the same geometry in the chamber kept at a 4 x 10^{-2} Torr pressure. One of these spectra is shown in Fig.1.

Isotopic Ratio Calculation

For determining the isotopic ratios, the peaks corresponding to the energies of 4.20 MeV of ^{238}U, 4.40 MeV of ^{235}U and 4.70 MeV of ^{234}U were considered. To calculate the peak area, a particular number of channels was selected in a way that this selection was not interfered by any other nuclide in the same spectrum. The method of Covell[5] was used to calculate the area of photopeak.

The calibration curve was constructed by linear regression using the peak area ratios and the corresponding isotopic ratios. Fig.2 shows a typical calibration curve used for $^{234}U/^{238}U$ ratio determinations.

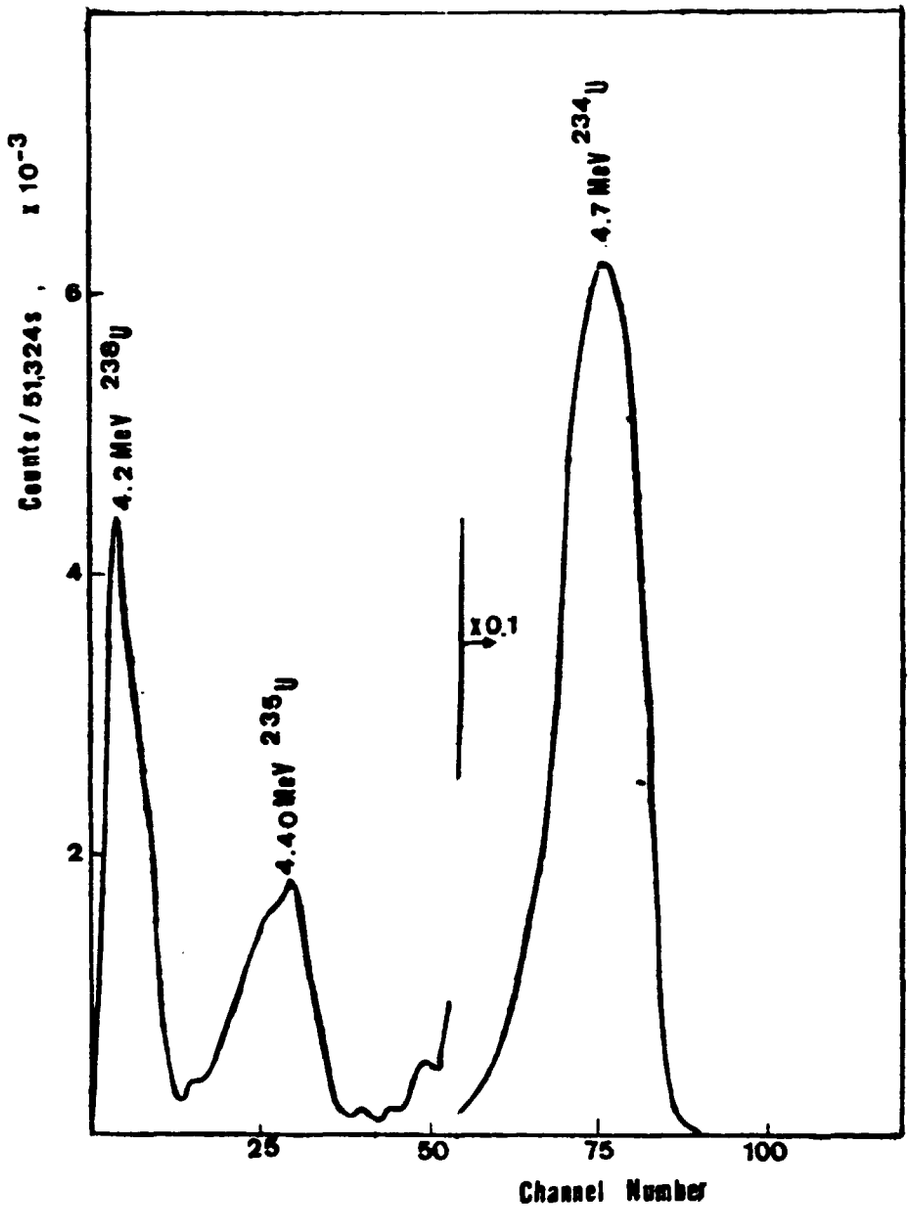

Fig.1 - Typical alpha spectrum of the COGEMA standard containing 7.15% of ^{235}U.

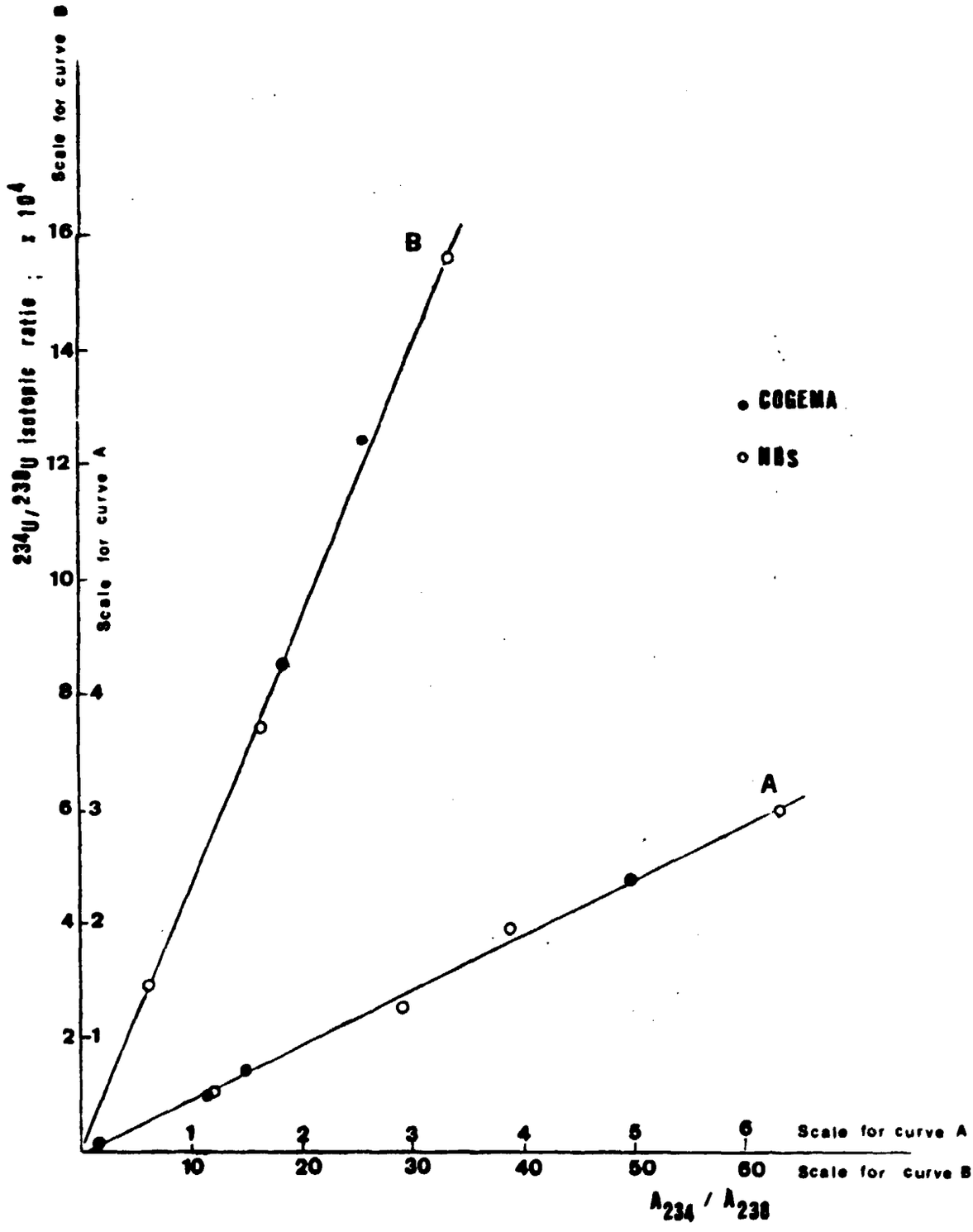

Fig.2 - Activity ratio of ^{234}U and ^{238}U as a function of $^{234}U/^{238}U$ isotopic ratio.

To determine the isotopic ratio of an unknown sample from its spectrum, the photopeak ratio is calculated and its isotopic ratio can be read on this curve or calculate using the parameters of calibration equation. The standard deviation values obtained for these parameters are used in the evaluation of the precision.

RESULTS AND DISCUSSION

Results of $^{235}U/^{238}U$ and $^{234}U/^{238}U$ ratio determinations in the uranium standards from COGEMA and NBS are presented in Table 1 and 2, respectively. Comparing our results of the isotopic ratios with those calculated using certified values of ^{234}U, ^{235}U and ^{238}U isotopic abundances we can conclude that there is, generally, a good agreement between these results.

In the $^{235}U/^{238}U$ ratio determinations, a good accuracy and precision were achieved for uranium standard enriched in ^{235}U. It can be seen (Tables 1 and 2) that a precision (standard deviation) varying from 0.8 to 9.4% and an accuracy (relative errors) from 0.5 to 8.8% were obtained for the standards with ^{235}U atom percent higher than 3.0%.

In the case of $^{234}U/^{238}U$ ratio determinations a precision varying from 0.8 to 4.0% and an accuracy from 1.0 to 6.7% were obtained with standards containing atom percents of ^{234}U and ^{238}U higher than 0.007 and 50% respectively.

For standards containing low percentage of ^{235}U atom (depleted or natural uranium) or low percentage of ^{238}U atom, the main difficulty consisted in obtaining alpha activities for ^{235}U and ^{238}U with good counting statistics. Another dif-

TABLE I - RESULTS OF $^{235}U/^{238}U$ AND $^{234}U/^{238}U$ ISOTOPIC RATIOS IN THE COGEMA STANDARDS

COGEMA Standards Nr.	Atom percent (certified) [4]		$^{235}U/^{238}U$ Ratios				$^{234}U/^{238}U$ Ratios			
	% ^{235}U	% ^{234}U	Certified Values	This Work (*)	Δs, %	ΔE, %	Certified Values x 10^4	This Work x 10^4	Δs, %	ΔE, %
001	0.2034	0.0008	0.002038	0.00253±0.00055	21.9	19.4	0.08016	0.0945±0.0061	6.5	17.9
006	0.7202	0.0055	0.007255	0.00657±0.00053	8.1	10.4	0.55402	0.5625±0.0586	10.4	1.5
010	1.3170	0.0070	0.01355	0.0146 ± 0.0004	2.6	10.0	0.70939	0.7022±0.0069	1.0	1.0
013	2.6282	0.0232	0.02700	0.0257 ± 0.0004	1.5	4.8	2.30319	2.359 ± 0.095	4.0	1.0
017	7.1473	0.0793	0.07704	0.0772 ± 0.0007	1.0	2.3	8.54771	8.700 ± 0.140	1.6	1.8
020	14.402	0.1063	0.16846	0.1676 ± 0.0026	1.6	0.5	12.4339	12.0484±0.102	0.8	2.8

(*) Results already presented in previous paper [13]

Δs - Relative standard deviation

ΔE - Relative error

TABLE 2 - RESULTS OF $^{235}U/^{238}U$ AND $^{234}U/^{238}U$ ISOTOPIC RATIOS IN THE NBS STANDARDS

NBS Standard	Atom percent (certified)[11]			$^{235}U/^{238}U$ Ratios				$^{234}U/^{238}U$ Ratios			
	% ^{235}U	% ^{234}U	% ^{238}U	Certified Values x 10^2	This Work x 10^2	As, %	ΔE, %	Certified Values x 10^4	This Work x 10^4	As, %	ΔE, %
U-010	1.0037	0.00541	98.984	1.014	1.17±0.32	27.3	15.4	0.5466	0.540±0.059	10.9	1.2
U-020	2.038	0.0125	97.933	2.081	2.18±0.28	12.9	4.7	1.2764	1.362±0.052	3.8	6.7
U-030	3.046	0.0190	96.915	3.143	2.865±0.001	0.05	8.8	1.9605	1.876±0.043	2.3	4.3
U-050	5.010	0.0279	94.315	5.273	5.58 ± 0.53	9.4	5.7	2.9395	3.042±0.126	4.1	3.5
U-100	10.190	0.0676	89.704	11.360	11.99 ± 0.68	5.6	5.5	7.5359	7.899±0.098	1.2	4.8
U-200	20.813	0.1246	79.651	25.126	24.51 ± 0.42	1.7	2.4	15.643	15.483±0.139	0.9	1.0
U-500	49.696	0.5189	49.711	99.97	100.77±0.82	0.8	0.8	104.22	106.32±2.48	2.3	2.0
U-750	75.357	0.5923	23.801	316.6	311.1 ± 4.8	1.5	1.7	248.85	207.01±6.30	3.0	16.8

ficulty was to solve the ^{235}U and ^{238}U peaks since the low energy tail of ^{234}U extends into the region of ^{235}U and ^{238}U spectrum.

To improve the counting statistics of ^{235}U and ^{238}U activities we tried to increase the mass of uranium to be electrodeposited. Nevertheless it was observed that a mass of uranium upper than 170 μg change the isotopic radio due to self-absorption of alpha particles caused by the increase of the sample thickness.

On the other hand it is important to note that the results presented in this paper correspond to a single determination. We believe that our results of accuracy and precision can be improved by using replicate samples obtaining a larger set of data.

ACKNOWLEDGMENTS

This work was partially supported by Financiadora de Estudos e Projetos (FINEP).

REFERENCES

1. BAKHTIAR, S.N.; SALAYMEH, S.; KUROBA, P.K. Uranium fallout from the nuclear powered satellites and volcanic eruptions. J.Radioanal.Nucl.Chem., Articles, 100(1): 57-63, 1986.

2. BARNES, I.L.; GARNER, E.L.; GRAMLICH, J.W.; MOORE, L.J.; MUROHY, T.J.; MACHLAN, L.A.; SHIELDS, W.R.; TATSUMOTO, M.; KNIGHT, R.J. Determination of lead, uranium, thorium and thallium in silicate glass standards

materials by dilution mass spectrometry. Anal. Chem., 46(6):880-5, 1973.

3. BONOTTO, D.M. Aplicação dos dados do fracionamento isotópico $^{234}U/^{238}U$ nos problemas geoquímicos dos aquíferos de Águas da Prata. São Paulo, 1983. (Dissertação de mestrado, Univ. São Paulo, Instituto Astronômico e Geofísico) (INIS-BR-383).

4. ETALON isotopique de l'uranium. Pierrelate, Fr., CEA, 1983. (Certificat de garantie).

5. COVELL, D.F. Determination of gamma abundance directly from the total absorption peak. Anal. Chem., 31:1785--90, 1959.

6. DONNAN, M.Y. & DUKES, E.K. Carrier technique for quantitative electrodeposition of actinides. Anal. Chem., 36(2): 392-4, 1964.

7. GANAPATHY, R. Reagent grade uranium salts: isotopic composition by neutron activation. J.Radioanal. Chem., 44:199-206, 1978.

8. GLADNEY, E.S.; PETERS, R.J.; PERRIN, D.R. Determination of Uranium-235/Uranium-238 ratio in natural waters by chelex 100 ion exchange and neutron activation. Anal. Chem., 55:976-7, 1983.

9. JOSHI, L.U.; ZINGDE, M.D.; ABIDI, S.A.H. Anomalous behaviour of uranium isotopes in backwater sediments of Zuari River. J.Radioanal.Chem., 79(2):317-33, 1983.

10. ROY, L.C.; BRETTON, L.; COTE, J.E.; TURCOTTE, J. On the depletion of ^{235}U and ^{234}U in commercially available uranium compounds: A survey using low energy ray spectrometry. J.Radioanal.Nucl.Chem., Letters, 118(5): 305--12, 1987.

11. SHIELDS, W.R. The evaluation of the accuracy of isotopic analysis by thermal ionization from 2% to 0.02%. In: INTERNATIONAL ATOMIC ENERGY AGENCY. Nuclear materials

management: proceedings of a symposium on held... in Vienna, 30 Aug-3 Sept, 1965. Vienna, 1966 pg. 737-46. (Proceedings series).

12. SZY, D.; SEBESSY, L.; BALINT, G. Determination of the isotope ratio $^{234}U/^{238}U$ with a scintillation - spectrometer. J.Radioanal.Chem., 7:57-65, 1977.

13. VASCONCELLOS, M.B.A.; ARMELIN, M.J.A.; FIGUEIREDO, A.M. G.; MAZZILLI, B.P.; SAIKI, M. A comparative study of some nuclear methods for $^{235}U/^{238}U$ isotopic ratios determination. J.Radioanal.Nucl.Chem ,Articles, 113 (2):357-70, 1987.