APPLICATION OF THERMAL IONIZATION MASS SPECTROMETRY IN THE NUCLEAR FUEL CYCLE*

JORGE EDUARDO DE SOUZA SARKIS, MAURÍCIO HIROMITU KAKAZU AND ISABEL MORENO DA SILVA SOUZA

INSTITUTO DE PESQUISAS ENERGÉTICAS E NUCLEARES - CNEN/SP
SÃO PAULO - P.O.BOX 11.049 - BRASIL

Mass spectrometry plays a key role in the analysis of nuclear and geological materials. Our efforts in the area of thermal ionization mass spectrometry can be divided in three general areas: measurements of the isotopic composition, determination of elements in various materials and measurements of the nuclear parameters.

Different methods have been developed for the isotopic analysis of U, Pu, B, Li, Cd and rare earths with an external precision in the range of ±0,2 to ±0,5%.

The isotopic concentrations measurements of uranium and plutonium in nuclear irradiated fuel, uranium in waste solution of process and uranium in geological samples were performed by using the isotopic dilution mass spectrometry with a precision in the range of ±0,5 to ±2% depending on the concentration of the element to be determined.

The burnup of nuclear irradiated fuels was obtained by the method of stable fission product ^{148}Nd as well as the heavy atom variation technique with a precision of about ±3% in both case.

The integrated neutron flux of the IEA-R1 reactor was studied by the measurement of the change of isotopic composition of cadmium and gadolinium before and after an irradiation period. The results indicate that the flux values (10^{13} n/cm² s) obtained using the variation in the isotopic ratio $^{114}Cd/^{113}Cd$ present a standard deviation of the order of ±15%, whereas values calculated using $^{158}Gd/^{157}Gd$ show a deviation of about ±5%.

For accurate results a calibration programm is performed by

analysing isotopic standard reference materials of known isotopic composition in order to establish a given set of conditions which must be reproduced in the same way during the routine analysis. The analyses were performed by using a single foccusing magnetic type sector field mass spectrometer TH5 by Finnigan Mat, equiped with a Faraday cup detector.

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INTRODUCTION

The thermal ionization mass spectrometry technique has been used extensively at IPEN since 1976 as an accurate technique to determined both isotopic composition and total concentration of chemical elements in nuclear and geological materials.

The isotopic analyses are carried out by using a single focusing thermoionic mass spectrometer VARIAN MAT TH5 with an ion source designed for either single, dual or triple filament operation, wich can operate at accelerating voltages up to 10kV. The mass separation of the ions is effected in the magnetic sector field up to 13,4 k gaus with 21,4cm radius and with a deflection angle of 90^{o}. The ion detection is carried out either through a Faraday cup detector or 23- stage electron multiplier system, which allows measurements of the ion intensity current range from 10^{-17}A to 10^{-9}A. The magnetic field, peak jump unity, and the processing of the results are automatically controlled by an on-line desk-top computer adapted to the instrument [1].

The data aquisition consists in integrating four measurements on top of each peak with eight scans in each of the three runs. Each peak intensity is integrated with time and the integration period used depending on the intensity. It normally is set in the ranges from 3 to 7 seconds. At the beginning, and the end, of each cycle the background is measured and the intensities of each peak are corrected by subtraction. The minor isotope intensity ionic current must be at least two times higher than the background. The signal drift is corrected through the linear interpolation method [2]. The isotope ratios are calculated from the corrected intensities with respect to the main isotope.

The data are processed and from each run of 10 ratios the isotopic ratios, atom percent, weight percent, the mean ratio and standard deviation as well as the intensities of each isotope and the background noise are calculated and printed.

Each run of isotopic ratios is checked for the presence of outliers ($\pm 2\sigma$). In case that more than 30% of the data are rejected the whole measurements must be repeated.

THE CALIBRATION OF THE MASS SPECTROMETER

The isotopic ratio obtained through thermal ionization mass

spectrometer results in a measured ratio which does not correspond to the true or accurate ratio. The main factor affecting the isotopic ratio uncertainty are the non linearity of the ion current measuring system and the isotope fractionation that occurs during the surface ionization process. For accurate results it is necessary to perform a calibration by analysing isotopic reference materials of known isotopic composition in order to establish a given set of conditions such as: chemical preparation procedure, loading procedure of the sample on the evaporating filament, measuring procedure, which must be reproduced in the same way during routine analysis.

The figure 1 shows a typical graphical control during uranium analysis. The measurements were performed by using a Faraday cup detector, and uranium sample size of 10µg.

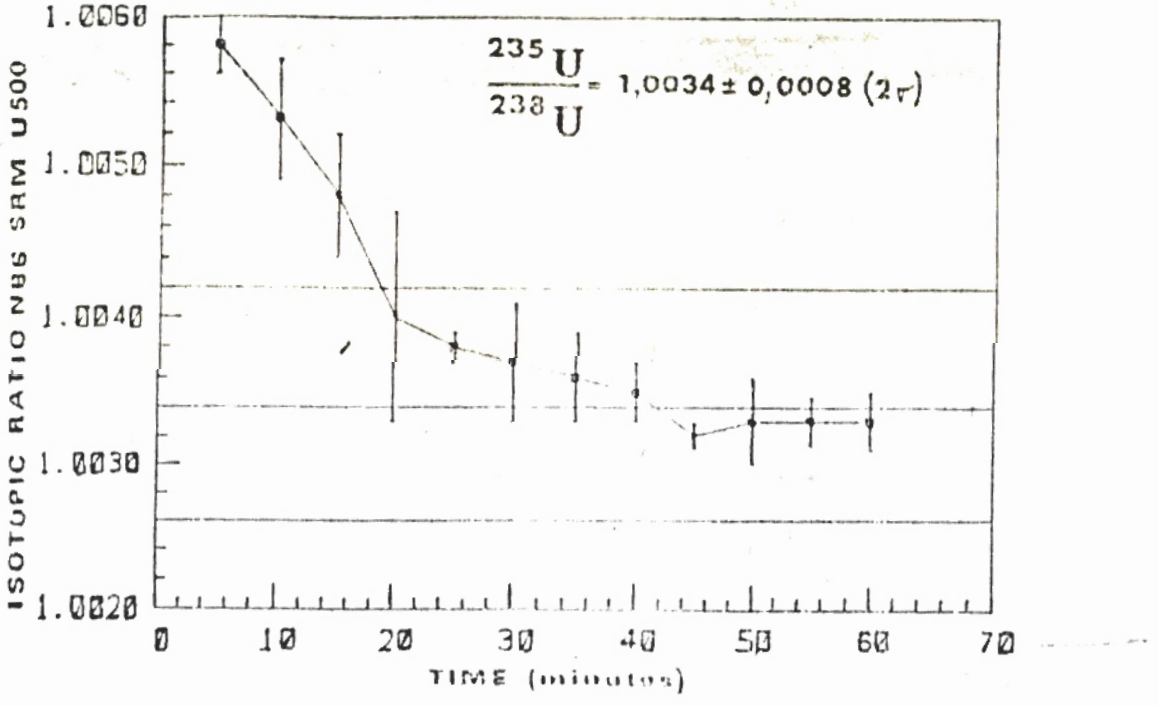

FIGURE 1. CONTROL OF ISOTOPIC FRACTIONATION DURING ANALYSIS

The calibration standard used for determining of bias is NBS SRM U500. For such sample ($^{235}U/^{238}U \approx 0,9997$) a possibility of existing nonlinearity in the recording system can be neglected [3].

The bias factor (B) is calculated by dividing the certified value of the standard, T_{500}, by the measured value, R_{500}, of the standard.

$$B = T_{500}/R_{500}$$

The results obtained in the last four years are presented in table 1 and figure 2.

TABLE 1. CONTROL OF BIAS 1987-1990

YEAR	R_{500} $^{235}U/^{238}U$	BIAS B
1987	1,0032	0,9965
1988	1,0032	0,9965
1989	1,0035	0,9962
1990	1,0034	0,9963
MEAN	1,0033	0,9964
±SD%	±0,02	±0,02

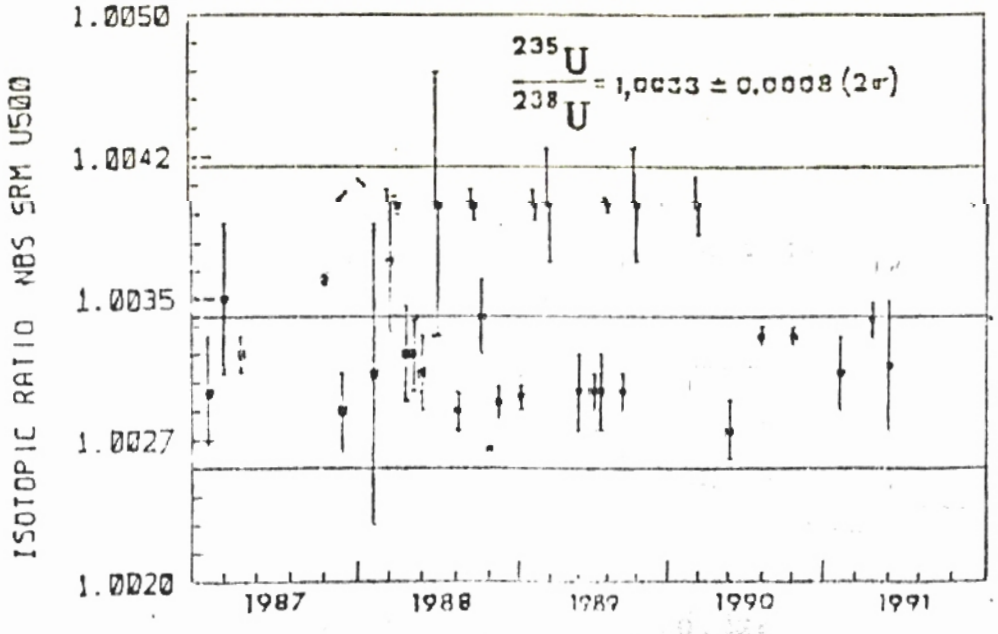

FIGURE 2. CONTROL OF BIAS - PERIOD: 1987-1991

The mean value of the isotopic ratio obtained with different loadings (1,0033 ± 0,0008) are in good agreement with the internal analysis (1,0034 ± 0,0008) present of on figure 1.

The linearity of the measurement mass spectrometer was determined over the ratio range of 0,01 to 186,7 by measuring the $^{235}U/^{238}U$ of other NBS SRM standards under analytical identical conditions.

The table II presents the calibration coefficient, K, and the percent deviation for each standard. As it can be observed the K values for the differents SRM standards are highly in accordance with themselves. It shows the highly reproducibility in the sample preparation and the linearity of the recording system.

TABLE II. SYSTEM LINEARITY

NBS SRM U	$^{235}U/^{238}U$ MEASURED VALUE (M)	$^{235}U/^{238}U$ CERTIFIED VALUE (C)	$\frac{K}{\frac{M}{C} * B}$	$\frac{A}{\frac{K-1}{K} * 100}$
010	0,01016	0,01014	0,9984	-0,1603
020	0,02084	0,02081	0,9978	-0,2205
030	0,03146	0,3143	0,9974	-0,2607
050	0,05293	0,05278	0,9992	-0,0801
100	0,1135	0,1136	0,9955	-0,4497
200	0,2525	0,25126	1,0013	0,1298
500	1,0033	0,9997	1,0000	
750	3,1699	3,1662	0,9944	-0,5632
970	186,727	186,772	0,9962	-0,3814

Based on these values a statistical estimate of the overall accuracy of the system calibration, AC, can be calculated by the expression[3]:

$$AC = \sqrt{\frac{\Sigma \quad A'}{N - 1}} = 0,32\%$$

ISOTOPIC COMPOSITION ANALYSIS

Several parameters have to be considered with development of a method for the measurements of the isotopic composition of a particular element by thermal ionization mass spectrometry such as: chemical preparation procedure of the sample, sample size, the loading and convertion procedure of the sample on the evaporation filament and the measurement procedure. The reproduction of these procedures is essential to obtain reproducible values of the isotopic ratio for different runs.

Isotopic analysis of various elements are carried out in our laboratory using single and dual filament ionization cartridge, table III.

In order to measure the enrichment in UF_6 samples a system for the gass transfer and collection was mounted [4]. After sampling and hydrolysis, the isotopic analysis is performed through the same method used for the solid samples.

The filament materials used are rhenium and tantalum ribbon both with 0,0015" x 0,030" and from Rembar Co., USA. In order to eliminate some impurities before the use the filaments are preheated at 3,5A for about 30 minutes under 10^{-6} Torr vaccum. The samples are loaded by 10µL Eppendorf micropipets in a programmable dryer unit similar to the one developed by Gramlich and Schidler [5].

In order to calibrate temperature versus current during the loading procedures different chemical compounds were loaded on filament and the current was increase until to reach the melting point of each compound, figure 3.

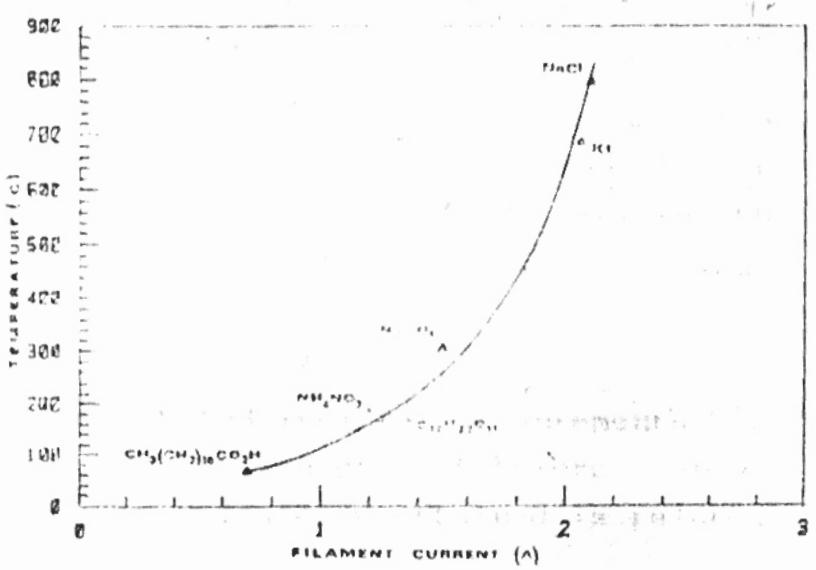

FIGURE 3. TEMPERATURE VERSUS CURRENT

THE ISOTOPIC DILUTION MASS SPECTROMETRY TECHNIQUE

The isotopic dilution mass spectrometry technique (IDMS), has been largely used for the determination of small concentrations of uranium and other elements in various media such us: nuclear irradiated fuels, geological samples (ores, rocks and sediments rivers) as well as waste solutions of chemical process, tables IV and V.

The principle of the IDMS is to add a known amount of the analysed sample solution to a known amount of a spike solution with a very well known isotopic composition. After homogeneous mixing and semiquantitative separation of the element of interest the altered isotopic composition is measured.

The concentration of the nuclide x in a sample may be calculated by the general formula[9].

$$x = \frac{Wsp}{Wsa} \left(\frac{Mxy - Txy}{1 - Mxy/Sxy}\right)$$ where:

y - denotes the concentration of the nuclide y in the spike solutions;

Wsp, Wsa - denote the weight aliquots of the spike and sample solution respectively;

Mxy, Txy, Sxy - denote the isotope ratio between the nuclides x and y measured in the mixture, spike and sample solution respectively.

BURNUP MEASUREMENT'S

The determination of burnup in irradiated nuclear fuels were performed through the ^{148}Nd[9] and heavy atom method[23].

The principle of the ^{148}Nd method is simply that the number of atom of this nuclide devided by its fission yield represents the number of fissions in a irradiated sample. Dividing this value by the number of the heavy atoms present in the begining of the irradiation gives the relative fissions which multiplying by 100 gives the percentage of atoms fissioned.

The heavy atom method includes measurements of the quantity of fissionable nuclide present before and after an irradiation period. The difference obtained is related to the

number of fissions which occured and consequently to the atom per cent fission.

For the chemical processing and handling of the samples a laboratory was installated with glove boxes and equipments for radiation monitoring and protection[9].

DETERMINATION OF THE INTEGRATED NEUTRON FLUX OF THE IEA-R1 REACTOR

The determination of the integrated neutron flux of the IEA-R1 reactor was performed through the change of isotopic ratios of cadmium and gadolinium during an irradiation period.

The results indicated that the fluence values obtained using the variation in the isotopic ratio $^{114}Cd/^{113}Cd$ presented a standard deviation of the order of 15% whereas the values calculated using $^{158}Gd/^{157}Gd$ show a deviation of about 5%. The fluence values calculated by the two methods agree within about 10%[16,17].

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TABLE III. ISOTOPIC ANALYSIS PROCEDURES

SAMPLE	LOADING CONDITIONS FILAMENT TYPE SAMPLE SIZE	ISOTOPIC RATIO	PRECISION EXT (%)	PRECISION INT (%)	REF
U	SINGLE - Re 5 - 10µg 0,5N NHO_3 + saccharose	$^{235}U/^{238}U$	0,3	0,3	6,7
	DUAL - Re 1 - 10µa 0,5N NHO_3	(0,99967)	0,2	0,1	8,11
Pu	DUAL - Re ≅ 0,5µg 0,5N NHO_3	$^{239}Pu/^{240}Pu$ (2,7561)	0,5	0,3	9,10
B	SINGLE - Ta 8 - 10µg	$^{10}B/^{11}B$ (25,25)	0,5	0,2	
B_4C	DIRECT FUSION WITH Na_2CO_3		0,2	0,1	12
H_3BO_3	SINGLE - Ta 7 - 10µg 0,1M NaOH + SACCHAROSE	$^{10}B/^{11}B$ (0,2457)	0,4	0,4	13,14
Li	DUAL - Re 0,05 - 0,5µg Li_2CO_3	$^{6}Li/^{7}Li$ (0,08137)	0,4	0,2	24
Nd	DUAL - Re 0,1 - 1µg 0,5M HNO	$^{148}Nd/^{150}Nd$ (2,1017)	0,2	0,1	9,10
Cd	SINGLE - Re 1µg HCℓ+0,75M H_3PO_4 + SILI-CA GEL	$^{119}Cd/^{110}Cd$ (0,9649)	0,5	0,3	16 17
Gd	DUAL - Re 1µg 0,5M HCℓ + AQUADAG	$^{156}Gd/^{160}Gd$ (0,9361)	0,5	0,3	
	DUAL - Re 1µg 0,5M HNO_3 + AQUADAG		0,2	0,02	14

TABLE IV. ISOTOPIC CONCENTRATION ANALYSIS

ELEMENT	MATRIX	TRACE	SAMPLE SIZE DISSOLUTION CHEMICAL SEPARATION PRECISION	REF
U	GEOLOGICAL SAMPLES	^{235}U	2 - 1290 ppm U 0,5mL $HClO_4$ + 15mL HF CONC. (UNDER PRESSURE 120°C) DOWEX 1 X 8 200-400 MESH (10M HCℓ + ASCORBIC ACID) 0,9 - 2%	6
		^{235}U + ^{233}U	2 - 9850 ppm U 5mL HNO_3 CONC. + 10mL HF 40% DOWEX 1 X 8 200-400 MESH 8M HCℓ DOWEX 1 X 8 200-400 MESH (6N HCℓ + 7% HI) 1N HCℓ 0,4 - 0,6%	18 19 20
	SEDIMENT RIVERS	^{233}U	4 - 75 ppm U CALCINATION 450°C 5mL HNO_3 CONC. + 10mL HF 40% DOWEX 1 X 8 100-200 MESH 6M HCℓ + ascorbic acid + METHANOL 0,5 - 1%	21
	WASTE SOLUTIONS	^{233}U	2 - 10 ppm U 10M HCℓ DOWEX 1 X 8 200-400 MESH 0,1M HCℓ	14
Li	GEOLOGICAL SAMPLES	^{6}Li	≅ 35 ppm Li 0,5mL $HClO_4$ + 15mL HF CONC. (UNDER PRESSURE 120°C) HEATING TO ELIMINATE HF 0,1N HC + methanol 50% DOWEX 50W (0,1N HCℓ + methanol 50%) 0,01N HCℓ + methanol 80% 0,1%	15
	$UO_2(NO_3)_2$		≅ 2 ppm Li HEATING TO DRYNESS 1N $NH_4Cℓ$ AG 50W X 8 200-400 MESH 1N $NH_4Cℓ$ ≅ 2%	

TABLE V. NUCLEAR IRRADIATED FUEL ANALYSIS

ELEMENT	MATRIX	TRACE	CHEMICAL TREATMENT SAMPLE SIZE DISSOLUTION CHEMICAL SEPARATION (PRECISION)	REF
U	NUCLEAR IRRADIATED FUELS	^{239}U	≅9µg ^{235}U / ≅1µg ^{239}Pu 8M HNO_3 + HF CONC. HEATING 80°C TO DRYNESS 8M HNO_3 DOWEX 1 X 8 200-400 MESH 4mL 8M HNO_3 → waste 2mL 8M HNO_3 → U (≅ 0,5%)	9 10
Pu		^{242}Pu	4mL 8M HNO_3 1mL 5M HNO_3 0,2mL 0,95M HNO_3 → waste 2mL 0,95M HNO_3 → Pu (≅ 0,8%)	
Nd		^{150}Nd	≅ 0,07µg ^{148}Nd 10mL HCℓ DOWEX 1 X 8 200-400 MESH (U, Pu → retained) fission products, Am, Cm + HEATING TO DRYNESS 0,05M HCℓ DOWEX 50W (α-HIBA 0,25M) pH = 4,6 α-HIBA 0,25M, pH = 4,6 (≅ 1%)	