

Alpha spectrometry enriched uranium urinalysis results from IPEN

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Abstract. IPEN (Instituto de Pesquisas Energéticas e Nucleares) manufactures the nuclear fuel for its research reactor, the IEA-R1. The CCN (Centro do Ciclo do Combustível) facility produces the fuel cermets from UF₆ (uranium hexafluoride) enriched 19.75% in ²³⁵U. The production involves the transformation of the gaseous form in oxides and silicates by ceramic and metallurgical processing. The workers act in more than one step that involves exposition to types F, S and M compounds of uranium. Until 2003, only fluorimetric analysis was carried out by the LRT (Laboratório de Radiotoxicologia – IPEN) in order to evaluate the intake of uranium, in spite of the sub estimation of the ²³⁴U contribution to the internal doses. Isotopic uranium determination in urine by alpha spectrometry is the current method to monitoring the contribution of ²³⁴U, ²³⁵U and ²³⁸U. Alpha spectrometry data of 164 samples from 84 individuals separate in three categories of workers: routine work group; special operation group and control group. The samples were analyzed to know if the isotopic composition excreted by urinary tract corresponds with the level of enrichment and isotopic composition of the plant products. Results show that is difficult to estimate these intakes of ²³⁴U and ²³⁵U since these isotopes alpha activities are below the limit of detection or minimum detectable activity (MAD) of this method in most part of the samples. Only in 22 samples it was possibly to measure the three radionuclides. Not expected high contribution of ²³⁴U activity was found in samples of the control group. No result over the ²³⁴U and ²³⁵U MAD was found in the samples from the special operation group. Only in 5 samples from the routine group the levels of ²³⁵U was higher than the levels of others groups. In a complementary study, 3 solid samples of UF₆, U₂O₈ and U₃Si₂ from the CCN plant were analyzed to determine the isotopic uranium composition in these salts, since this composition varies with the amount of any of the isotopes in the original ores. Considering the results from workers urine and salts measurements, the LRT studies the options to introduce a more sensitive method to estimate the intake of ²³⁴U and ²³⁵U.

KEYWORDS: *Uranium isotopes, Alpha spectrometry, Bioassay*

1. Introduction

IPEN (Instituto de Pesquisas Energéticas e Nucleares) manufactures the nuclear fuel for its research reactor, the IEA-R1. The CCN (Centro do Ciclo do Combustível) facility produces the fuel cermets from UF₆ (Uranium hexafluoride) enriched to 19.75% in ²³⁵U. The production involves the transformation of the gaseous form of the enriched Uranium in oxides and silicates by ceramic and metallurgical processing. The workers act in more than one step involving exposition to types F, S and M compounds of Uranium. Until 2003, only fluorimetric analysis was carried out by the LRT (Laboratório de Radiotoxicologia – IPEN) in order to evaluate the intake of Uranium, in spite of the sub estimation of the ²³⁴U contribution to the internal doses.

The laboratory ability to measure Uranium in urine impacts the assessment of internal doses. Therefore, isotopic Uranium determination in urine by Alpha spectrometry has been the current method since 2003 to monitoring the contribution of ²³⁴U, ²³⁵U and ²³⁸U.

In this work, Alpha spectrometry data of 146 samples from 84 individuals separate in three categories of workers: routine work group; special operation group and control group were analyzed to study the relation between the isotopic composition of the enriched Uranium from production plants and the Uranium isotopic composition excreted by urinary tract.

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Data of the yearly compositions of the processed material for the facilities are not available. Alternatively, samples of the last batch processed in 2005 were analyzed by Alpha spectrometry after radiochemical separation to estimate the contribution in activity of the three most relevant isotopes: ^{234}U , ^{235}U and ^{238}U .

2. Methodologies

2.1. Determination of Uranium isotopes by Alpha spectrometry

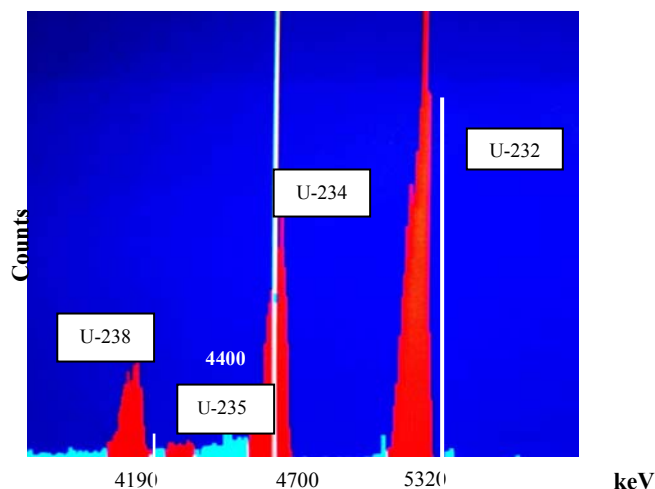
2.1.1. Urine samples

The urine samples for Uranium enriched analysis were the collection of all the urine excreted during a 24-h period. The pretreatment of the samples were made in the same way to all the urine samples for all radionuclides determinations [1]. Samples of more than 1liter were mixed and one aliquot of 1000ml was analyzed.

The urine was spiked with a purified ^{232}U tracer, mineralized by hot concentrated nitric acid and oxygen peroxide, precipitated with ammonium hydroxide as phosphate, the supernatant liquid removed with a transfer pipet vacuum system. The precipitate was centrifuged, washed until all the ammonium traces were removed, dissolved with nitric acid, evaporated to dryness on a hot plate to a white powder residue. The residue was recovered with HCl 8M and percolated through two different ion-exchange columns. The Uranium eluate (HCl 0.5M medium) was evaporated to dryness, dissolved with concentrated nitric acid and dried until chlorides were removed. The residue was recovered with ammonium sulfate and electroplated on a polished steel disk and annealing over a hot plate. The electroplated Uranium source was measured by Alpha spectrometry in an Ortec EG&G Alpha Spectrometer System assembled with Alpha Spectrometer 576A, Multichannel Analyzer ADCAM 918A and a vacuum pump (Edwards). Analysis of spectra was performed with Maestro 3.2 software package (Ortec). The counting time was 60000s.

Fig. 1 shows a typical urine sample Alpha spectrum where is possible to identify the four principal Uranium isotopes that contribute to high values of the internal dose when incorporated: ^{234}U , ^{235}U and ^{238}U because they have hazardous progenies. ^{232}U is the tracer to determine chemical recovery and radiometric counting efficiency in the sample measuring.

Figure 1: Alpha spectrum of a urine sample where it is to possible identify the four principal Uranium isotopes that contribute to high values of internal dose. U-232 is the tracer to determine chemical recovery and radiometrical counting efficiency.



2.1.2. Uranium products: UF₆, U₂SiO₃ and U₂O₃ samples

The following methods of separation of Uranium from the products UF₆, U₂SiO₃ and U₂O₃ samples were employed before the ion-exchange step of the Alpha spectrometric analysis.

UF₆: 1.1559g containing 0.7815g of U was treated with concentrated sulfuric acid to remove fluorides on a covered Teflon beaker on a hot plate. Concentrated nitric acid was added to the residue, evaporated until dryness and recovered with a minimum of de-ionized water, then transferred to a volumetric balloon of 500ml and completed with 1M chloridric acid. The resulting UF₆ solution concentration was [U]=1.56E-04g/ml.

U₂SiO₃: 0.5224g containing 0.4831g of U was treated with “aqua regia” under reflux in a covered Teflon beaker in a hot plate. Concentrated nitric acid was added to the residue, evaporated until dryness and recovered with a minimum of de-ionized water, transferred to a volumetric balloon of 500ml and completed with 1M chloridric acid. The resulting U₂SiO₃ solution concentration was [U]=9.66.E-04g/ml.

U₂O₃: 0.4007g containing 0.3640g of U was treated with “acqua regia” under reflux in a covered Teflon beaker in a hot plate. Concentrated nitric acid was added to the residue, evaporated until the dryness and recovered with a minimum of deionized water, transferred to a volumetric balloon of 500ml and completed with 1M chloridric acid. The resulting U₂SiO₃ solution concentration was [U]=7.20.E-04g/ml.

Aliquots of 1ml of each solution were analyzed in triplicate. The aliquots were spiked with purified ²³²U tracer, evaporated on a hot plate and recovered with HCl 8M and percolated through the ion exchange columns and followed the same subsequent step employed to measure the urine samples.

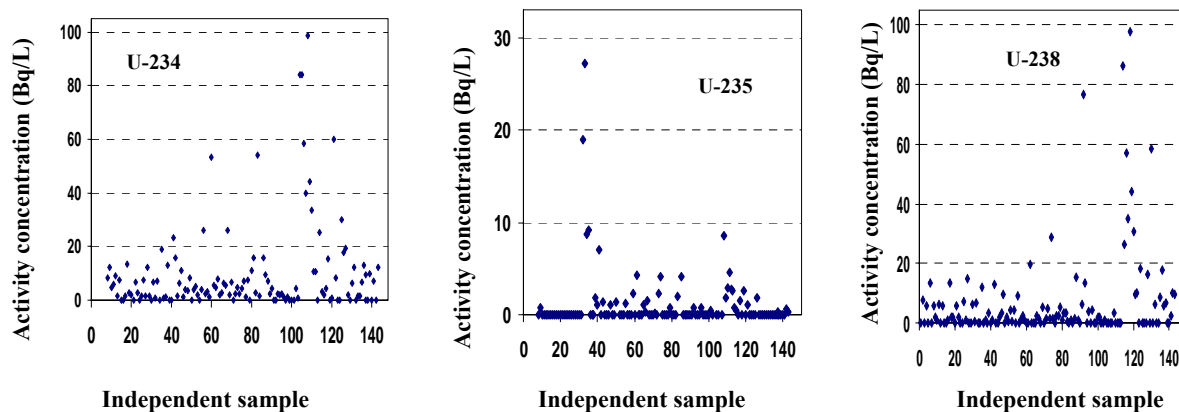
The UF₆, U₂SiO₃ and U₂O₃ samples time of counting was 20000s in the counting system described above.

3. Results and discussion

3.1. Results of urine samples analysis

The results of the Uranium isotopes Alpha spectrometry urinalyses from the IPEN workers made during the period 2003-2005 are summarized in the Fig. 2.

Figure 2: Distribution of Uranium isotopes activity concentration in the urine samples from workers of IPEN



A few number of high values increased the mean Uranium isotopes activity concentration. The most remarkable discrepant results are in the measurement of the ^{234}U : 8/145 results increase the mean value from $(7.74\text{E}+00\pm 8.30\text{E}+00)\text{Bq/L}$ to $(3.57\text{E}+01\pm 2.32\text{E}+02)\text{Bq/L}$. In the ^{235}U case, only 6/145 results increase the mean concentration value from $(1.56\text{E}+00\pm 1.18\text{E}+00)\text{Bq/L}$ to $(5.82\text{E}+00\pm 1.63\text{E}+01)\text{Bq/L}$. In the ^{238}U case, 8/145 results increase the mean value from $(1.10\text{E}+00\pm 1.84\text{E}+01)\text{Bq/L}$ to $(5.05\text{E}+00\pm 4.72\text{E}+00)\text{Bq/L}$.

^{234}U activity found in samples of the control group was higher than expected. No result over the ^{234}U and ^{235}U MDA (minimum detectable activity) was found in the samples from the special operation group who manipulated the highest amounts of enriched Uranium.

Fig. 3, 4 and 5 show the ratio between the three isotopes activity concentration $^{234}\text{U}/^{235}\text{U}$, $^{234}\text{U}/^{238}\text{U}$, $^{235}\text{U}/^{238}\text{U}$, in each worker urine sample. These relations were also increased by discrepant high values: $^{234}\text{U}/^{235}\text{U}$ mean ratio value increase from $(1.04\text{E}+01\pm 1.29\text{E}+01)$ to $(1.95\text{E}+01\pm 1.03\text{E}+01)$; $^{234}\text{U}/^{238}\text{U}$ from $(1.97\text{E}+00\pm 9.80\text{E}-01)$ to $(2.04\text{E}+00\pm 2.30\text{E}+00)$ and $^{235}\text{U}/^{238}\text{U}$, from $(4.20\text{E}-01\pm 4.30\text{E}-01)$ to $(2.94\text{E}+00\pm 2.61\text{E}+00)$.

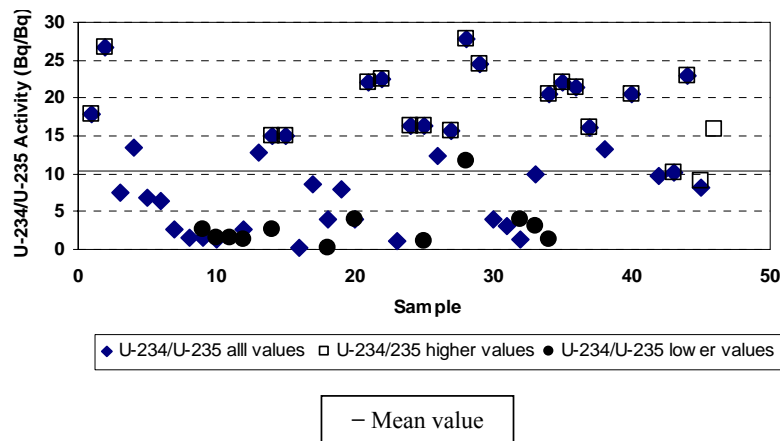


Figure 2. $^{234}\text{U}/^{235}\text{U}$ activity concentration ratio in urine samples from 43 IPEN workers.

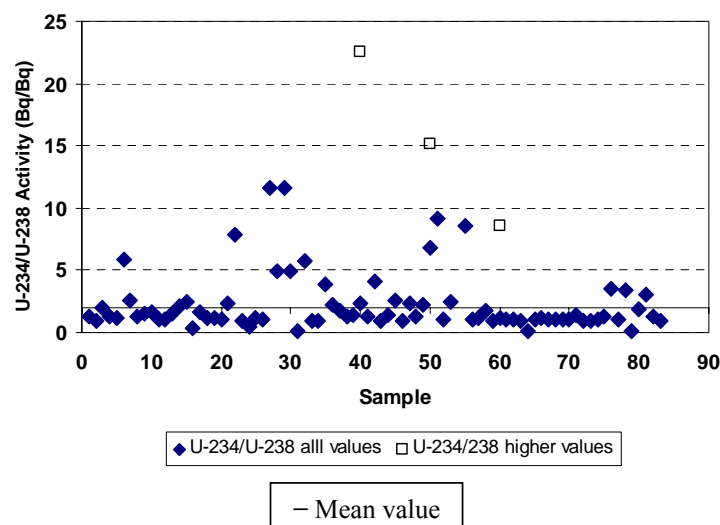


Figure 3. $^{235}\text{U}/^{238}\text{U}$ activity concentration ratio in urine samples 84 from IPEN workers.

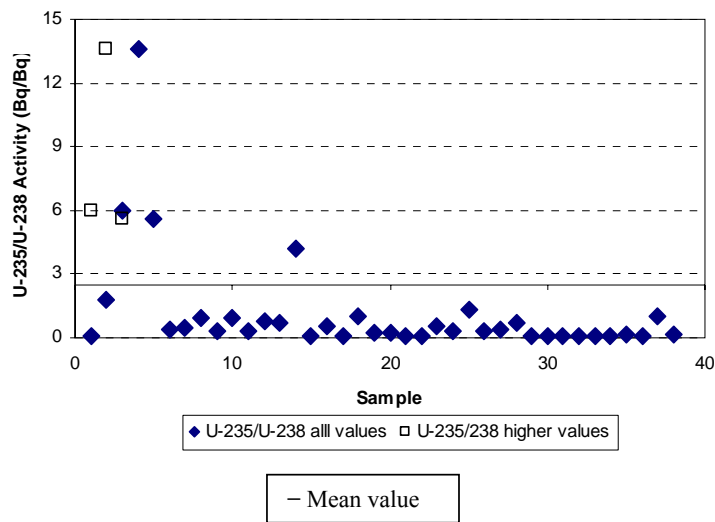


Figure 4. $^{235}\text{U}/^{238}\text{U}$ activity concentration ratio in urine samples from 39 workers of IPEN.

3.2. Results of Uranium samples analysis

The counting results of the Uranium isotopes Alpha spectrometry from the UF_6 , U_2SiO_3 and U_2O_3 samples were very difficult to resolve and had interference of the ^{226}Ra in the ^{234}U region.

Figure 5 is a spectrum of a UF_6 sample. The progeny radionuclides as ^{226}Ra , ^{210}Po , ^{222}Rn and ^{218}Po ($E_{\alpha_{\text{max}}}=4784, 5304, 5489$ and 6000) interfere in the resolution of the Uranium isotopes energy peaks.

The estimation of the integrate square under the peaks was made as described by Carvalho and Oliveira [2] using the typical resolution values at full width at one quarter of the maximum (FW1/4M).

The final isotopic concentration in the UF_6 , U_2SiO_3 and U_2O_3 samples, measured as activity by Alpha spectrometry, were determinate considering the chemical recovery of the ^{232}U tracer and the Alpha detection system efficiency.

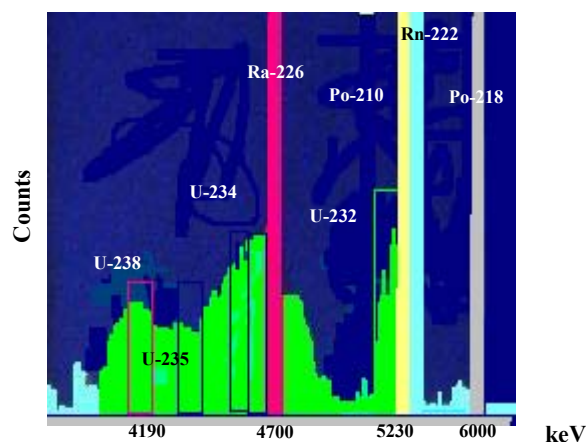


Figure 5. UF_6 sample Alpha spectrum with the radionuclides of ^{238}U progeny interfering in the resolution of the ^{232}U , ^{234}U and ^{235}U isotopes.

Table 1 shows the values of Uranium composites samples measured and the expected theoretical values considering the literature [3]. Values of ^{234}U concentration in a 20% Uranium enriched varies from 1672 to 2047.[B]. The total ^{234}U considered in the calculation was the maximum value expected (2063ppm), increased by around 13ppm of ^{234}U due to the ^{238}U decay, since their concentration process.

Table 1. Results of the Uranium isotopes Alpha spectrometry from the UF_6 , U_2SiO_3 and U_2O_3 samples.

Uranium isotope	Sample chemical form	Theoretical concentration activity in Bq/sample (A)	Measured concentration activity in Bq/sample (B)	(A)/(B) Ratio
^{234}U	UF_6	4.21E+08	2.64E+08	1.59E+00
^{235}U		1.20E+06	1.01E+07	1.19E-01
^{238}U		5.25E+06	6.39E+06	8.22E-01
^{234}U	U_2O_3	3.10E+08	4.13E+08	7.50E-01
^{235}U		1.18E+06	1.58E+07	7.50E-02
^{238}U		7.49E+06	9.98E+06	7.50E-01
^{234}U	U_2SiO_3	3.19E+08	5.90E+08	5.40E-01
^{235}U		1.22E+07	2.26E+07	5.40E-01
^{238}U		7.69E+06	1.43E+07	5.39E-01

As seen in Table 2, comparing the isotopic ratios between uranium composites and urine samples the best concordance was given considering theoretical uranium compounds isotopic composition and all the urine samples measured.

These ratios results: $^{234}\text{U}/^{238}\text{U}$ (4.14E+01 and 1.97E+00); $^{234}\text{U}/^{235}\text{U}$ (2.62E+01 and 1.04E+01) and $^{235}\text{U}/^{238}\text{U}$ (1.58E+00 and 4.20E-01), would be compared with theoretical isotopic ratios of natural Uranium: $^{234}\text{U}/^{238}\text{U}$ (1.03E+000; $^{234}\text{U}/^{235}\text{U}$ (2.20E+01) and $^{235}\text{U}/^{238}\text{U}$ (4.70.E-02) found in the literature. [4]

It was difficult to conclude definitely whether an exposure to enriched Uranium had occurred or not. In 21 samples, it was possible to calculate the $^{235}\text{U}/^{238}\text{U}$ ratio and the values exceeded those expected for natural Uranium. From these values 15 were given by the not exposed personnel (control group) and 6 were given by the routine, 4 of them from the same worker.

Table 2. Comparison between $^{234}\text{U}/^{238}\text{U}$, $^{234}\text{U}/^{235}\text{U}$ and $^{235}\text{U}/^{238}\text{U}$ Uranium isotopes ratios measured in the UF_6 , U_2SiO_3 , U_2O_3 and urine workers samples with theoretical values for enriched and natural Uranium.

Uranium isotopes ratio	Theoretical rate in uranium enriched samples ^a (A)	Measured rate in uranium enriched samples ^b (B)	(A)/(B) Ratio	Theoretical rate in natural Uranium ^c	Measured rate in urine workers samples ^d	Measured rate in urine workers samples ^e
$^{234}\text{U}/^{238}\text{U}$	4.14E+01	5.14E+01	8.05E-01	1.03E+00	2.04E+00	1.97E+00
$^{234}\text{U}/^{235}\text{U}$	2.62E+01	7.20E+01	3.64E-01	2.20E-01	1.95E+01	1.04E+01
$^{235}\text{U}/^{238}\text{U}$	1.58E+00	7.13E-01	2.22E+00	4.70E-02	2.94E+00	4.20E-01

a Considers the same isotopic composition for all samples.

b Mean values of all chemical forms of Uranium samples measurements.

c...From <http://wise-uranium.org/rdfi68.html>. [4]

d Considers the mean values of all the 146 measurements..

e Excludes discrepant values.

3. Conclusion

Considering that the results from workers urine and uranium compounds measurements could be misinterpreted, the LRT studies the options to introduce a complementary method to estimate the intake of ^{234}U and ^{235}U using the $^{235}\text{U}/^{238}\text{U}$ ratios determined in a future study. The ^{238}U will be also determined by INAA (instrumental neutron activation analysis) and compared with alpha spectrometry in the next urine samples measurements.

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