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Determination of uranium in human head hair of a Brazilian populational group by epithermal neutron activation analysis

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Hair analysis is extensively used in forensic sciences, assessment of occupational or environmental exposure and in some cases also for clinical and nutritional studies. Hair has a series of advantages in relation to other biomonitors, like blood and urine, since it is very easy to collect, very stable at room temperature and it represents not only instantaneous concentrations, but it can reveal the exposure along a given period of time. The assessment of environmental or occupational exposure to uranium is generally done by means of urine analysis, although a few papers have described attempts to use hair as a biomonitor. In the present work, epithermal neutron activation analysis has been used to establish base-line concentrations for a Brazilian populational group, living in Sao Paulo and not exposed to uranium, either environmentally or occupationally. For quality control, the reference materials Pine Needles NIST 1575 and Basalt USGS BCR-1 were used. The concentrations obtained for the control population studied up to now varied from about 2 to 50 ng·g^{-1}.

Introduction

The assessment of occupational or environmental exposure to uranium and its compounds is generally carried out by analysis of urine. On the other hand, as pointed out by KARPAS[1] diurnal fluctuations in "spot samples" make it difficult to estimate the extent of the internal dose received. According to the same author, if urine samples are not collected in a short time after accidental exposure or if the samples are not representative due to collection logistics, the calculations of the internal dose based only on analysis of urine may be misleading. Consequently, the study of hair as a possible biomonitor for uranium exposure is proposed.

BYRNE[2] has developed a very sensitive radiochemical neutron activation analysis technique for an exploratory study of uranium levels in hair, urine and blood of non-exposed and occupationally exposed individuals. For the controls, the typical values found in hair, urine and blood were 10 ng·g^{-1}, 10 and 5 ng·l^{-1}, respectively.

GONNEN et al.[3] have determined uranium in human hair samples of a population residing in the South of Israel, using acid digestion and FIAS-ICP-MS in order to establish the level of the element in a so-called "normal" population. The range of uranium concentration in the initial study group was from 10 to 180 ng·g^{-1} and the mean and median values of the entire study population were 62 and 50 ng·g^{-1} in hair, respectively. The differences between male and female, smokers and non-smokers and people below and above 45 years of age were examined. The only statistically significant difference was found in the latter group, according to the authors.

OUGH et al.[4] have examined uranium levels in urine and hair of Canadian forces personnel who served in the Gulf War and in Kosovo, in search for the presence of depleted uranium in these samples. The total uranium concentrations were analyzed by ICP-MS and by INAA. Isotopic assays could not be made in urine, due to the very low concentration of uranium, but it was possible to do it in hair samples of 19 of the veterans participating in the test. The isotopic hair assays were scattered around the natural ^{238}U/^{235}U ratio of 137.8, so not characterizing the presence of depleted uranium.

In Brazil, some authors have utilized hair as a biomonitor for several elements, potentially toxic or important for nutrition, using very sensitive analytical methods, such as instrumental neutron activation analysis (INAA), or inductively coupled plasma mass spectrometry (ICP-MS). Hair analysis has a series of advantages in relation to other biomonitors, since it is very easy to collect, very stable at room temperature and it represents not only instantaneous concentrations, but it can reveal the exposure along a given period of time. SAIKI et al.[5] have determined the concentrations of the elements Al, As, Br, Ca, Cd, Cl, Co, Cu, Fe, Hg, K, Mg, Mn, Na, Sb, Sc, Se, V and Zn using INAA with thermal neutron activation in a Brazilian population living in São Paulo. Due to the low concentrations of uranium found in hair and to interferences of other elements, it was not possible in this work to determine the concentrations of uranium in hair of the Brazilian population.

CARNEIRO et al.[6] established reference intervals for twenty minor and trace elements in human hair of a Brazilian population living in the city of Rio de Janeiro (N = 1775), using ICP-MS as analytical method.

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The elements determined were Ag, Al, As, Ba, Cd, Hg, Ni, Pb, Sb, Ca, Co, Cu, Fe, Mg, Mn, Mo, P, Sr, V and Zn, but no data were presented for uranium concentrations in hair.

In the present work, epithermal neutron activation analysis (ENAA) was used for the determination of uranium in hair of a Brazilian populational group living in the city of São Paulo, Brazil, not exposed to uranium either occupationally or environmentally. It is known that several nuclides that have high resonance activation integrals compared to their thermal activation cross sections can be more favorably determined by epithermal neutron activation than by corresponding activation in the total reactor neutron spectrum. Uranium is one of the elements that are favored by ENAA, together with thorium and others, such as Rb, Cs, Sr, Sb, Ta.

The first aim of the present work was to establish a base-line concentration for uranium in the hair of a Brazilian populational group, in order to allow a comparison with the results found in other countries and with populations living in areas with high natural contents of monazitic sands, in Brazil. Later, the work can be extended to comparison with the uranium concentrations in hair of individuals occupationally exposed to uranium, such as miners and workers of uranium plants.

For quality control of the analytical data, the Certified Reference Materials NIST 1575 Pine Needles and USGS BCR-1 Basalt were analyzed, in the same experimental conditions as the hair samples.

Experimental

Sample collection and preparation

The group selected for the establishment of the control population was of individuals residing in the city of São Paulo, not exposed to uranium occupationally or environmentally. Most of them were students from the University of São Paulo, adults, male and female.

The hair samples were collected from the occipital part of the head, with stainless steel scissors, according to the protocol recommended by the International Atomic Energy Agency (IAEA).[7] It is important to collect the samples always from the same region of the head, mainly for comparative studies, since variations can occur in the same individual according to the region of the head.

The samples were then cut in small fragments of about 2 mm and then submitted to washing using a 2% solution of Triton X100, a non-ionic detergent, followed by MilliQ water and p. a. acetone.[5] After the washing procedure, the samples were placed in filter paper for drying at room temperature.

Irradiation and counting

About 250 mg of the hair samples, together with synthetic standards of uranium, prepared in the laboratory, by pipetting 3.992 micrograms of the uranium solution on analytical filter paper were irradiated at the IEA-R1 Nuclear Research Reactor of IPEN/CNEN-SP.

The samples and standards were irradiated in cadmium capsules of 1 mm thickness, in order to shield the thermal neutron spectrum and allow the epithermal neutron irradiation, which is favorable for the uranium analysis. The irradiation time was of 16 hours.

After about 4 days waiting time, to allow the decay of interfering activities, the samples were measured, for 50000 seconds, in a gamma-ray spectrometer, containing of an hyperpure germanium detector coupled to associated electronics, for gamma-ray spectrum collection. The resolution of the detector was of 1.80 keV, for the 1332 keV peak of ^{60}Co.

VISPECT2 software was used for analysis of the gamma-ray spectrum. The analysis of uranium was made by measuring the radioisotope ^{239}Np, formed in the (n,γ) reaction of ^{238}U, followed by beta-decay of ^{239}U. The peaks used for analysis were the 106 and 278 keV peaks of ^{239}Np.

Results and discussion

Table 1 presents the results obtained for the analysis of uranium in the Certified Reference Material NIST 1575 Pine Needles, by epithermal neutron activation analysis. Six determinations were made. The values found for the relative standard deviation (3.9%) and for the relative error, (7.5%) as compared to the certified value can be considered as good for this level of concentration of uranium.

In Table 2 are the results for the analysis of uranium by ENAA of the Reference Material BCR-1. The values found for the relative standard deviation, 7.0%, and for the relative error, 0.55%, are also very good.

These reference materials were analyzed because, of the several hair reference materials that are available, the concentrations of uranium are not reported or not certified.

In Table 3 are presented the results obtained up to now for the individuals of the Brazilian control population. It can be observed that many of the samples analyzed present very low concentrations of uranium, like samples C-19 and C-13. The population studied is quite homogeneous, being constituted mainly of young females in their 20 s. The mean U concentration of the population is of 15.4 ng·g^{-1}, the median is 10.7 ng·g^{-1} and the range is from 2.1 to 49.8 ng·g^{-1}.

Table 1. Concentrations of uranium obtained for the CRM NIST 1575 Pine Needles by epithermal neutron activation analysis

Aliquot	U, ng·g^{-1}
01	19.2 ± 0.6*
02	17.9 ± 0.6
03	19.8 ± 0.8
04	18.5 ± 0.8
05	19.7 ± 0.6
06	18.6 ± 0.6
Mean ± SD:	18.9 ± 0.7
RSD, %:	3.9
RE, %:	7.5
Certified value:	20.0 ± 0.4

RSD: Relative standard deviation.
RE: Relative error.
* Uncertainty calculated considering counting statistics.

Table 2. Concentrations of uranium obtained in the Reference Material USGS BCR-1 Basalt by epithermal neutron activation analysis

Aliquot	U, ng·g^{-1}
01	1616.3 ± 6.7
02	1785.0 ± 10.9
Mean ± SD:	1701 ± 119
RSD, %:	7.0
RE, %:	0.55
Certified value:	1710 ± 160

RSD: Relative standard deviation.
RE: Relative error.

Table 3. Concentrations of uranium obtained in hair of a Brazilian control population by epithermal neutron activation analysis

Sample code	Gender of the donor	Age, years	Uranium concentration, ng·g^{-1}
C-3	Female	21	12.6 ± 1.7
C-5	Female	26	5.9 ± 0.7
C-9	Female	25	5.1 ± 0.8
C-10	Female	20	17.1 ± 1.5
C-11	Female	17	22.5 ± 1.5
C-13	Female	43	3.2 ± 0.4
C-15	Female*	42	39.8 ± 0.5
C-16	Female	18	20.8 ± 1.1
C-19	Male	40	2.1 ± 0.5
C-20	Female	41	4.3 ± 0.6
C-21	Male	32	10.4 ± 0.1
C-24	Female*	42	31.9 ± 0.8
C-25	Female	21	4.7 ± 1.4
C-26	Female	20	8.0 ± 2.3
C-27	Female	Not informed	7.8 ± 1.0
C-28	Female	20	10.7 ± 1.6
C-29	Female	48	49.8 ± 2.3
03	Female	24	38.5 ± 1.4
17	Male	22	11.7 ± 1.3
18	Female	22	7.3 ± 1.2
19	Male	47	10.7 ± 1.3
24	Female	61	13.8 ± 1.3
		Mean:	15.4
		Range:	2.1 – 49.8

* Donor whose hair was collected twice in different days.

BYRNE,[2] using a very sensitive radiochemical method for uranium analysis in hair, with a limit of detection from 1–2 pg·g^{-1} found typical values of 10 ng·g^{-1}, for a control population in Slovenia, which is close to the value of the median found for the Brazilian population.

GONNEN[3] has found a mean of 62 ng·g^{-1} and a range from 10 to 180 ng·g^{-1} for a population residing in the South of Israel and not occupationally exposed to uranium, which values are much higher than those found for the Brazilian control population studied.

Conclusions

From the results obtained for the analysis of uranium in reference materials by epithermal neutron activation analysis, it can be concluded that the method applied gave satisfactory results as regards the relative standard deviation and the relative error.

The comparison between these values found by GONNEN et al.[3] and BYRNE[2] for populations in Europe seem to point out that the concentrations of uranium in hair of a Brazilian control population are very low. There seems to be a tendency of higher concentration with aging, but a larger number of data is necessary to confirm this.

To obtain lower limits of detection, a radiochemical separation for uranium could be applied.

It would be interesting to compare values for uranium in hair and urine of Brazilian individuals, to study if there is a correlation.

Future work will include analysis of uranium in hair of Brazilian individuals living in a region with high natural content of monazite sands. Also it would be interesting to compare the results of the control population with individuals who are exposed occupationally to uranium, such as miners and workers of uranium plants.

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