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DETERMINATION OF THORIUM IN HUMAN URINE BY NEUTRON ACTIVATION

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A routine procedure for the determination of thorium in urine of workers has been developed by the neutron activation method. The technique suggested by Dang, et. al. has been modified in order to reduce the costs involved and the sample processing time. The samples were irradiated in the MIT (Massachusetts Institute of Technology - Boston) reactor, in a thermal neutron flux of 8 x 10^{12} n.cm^{-2}.s^{-1} for 3½ hours. Thorium-232 was determined by counting ^{233}Pa.

Brazil has one of the largest deposits of thorium, distributed mainly in beaches of monazite sand and in certain regions of the state of Minas Gerais. In Brazil, thorium is an important contaminant, especially in industries that explore the monazite sand, and in gas mantle plants.

The Instituto de Pesquisas Energéticas e Nucleares of São Paulo has a staff of 70 people engaged in a pilot facility for the purification of thorium. Presently nearly two tons of thorium sulfate are processed per month in order to obtain thorium nitrate. This product is sold to Brazilian industries. The internal monitoring of workers has been carried out by means of thorium analysis in excreta samples using alpha spectrometry.

This paper describes the development of neutron activation analysis (NAA) for improving the internal monitoring program. According to the literature NAA is one of the most sensitive techniques for determination of thorium in body fluids.

The method reported by Dang, et. al. has been slightly modified in order to make it suitable for routine monitoring of thorium-exposed workers.

Experimental

Sample preparation

The standard solution was prepared by diluting an analytical grade thorium nitrate obtained from the National Institute of Standards and Technology (NIST, USA).

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The urine samples used, for establishment of the methodology, were collected from volunteers of the University of Utah ERTL not exposed to thorium. Each sample consisted of 1 liter of urine stored in polyethylene containers. The samples were transferred to a beaker. Concentrated HNO_3 (10% by volume) and a known amount of ^{232}Th were added to these urine samples. The solution was then digested at low heat for 2 hours. After cooling, calcium phosphate was precipitated by the addition of ammonium hydroxide until the precipitation was complete.

The solution was heated for 1 hour, centrifuged, and the supernate discarded. The dense precipitate was washed with water, dissolved in concentrated HNO_3, and heated to 500°C for 1 hour to destroy the residual organic matter.

The white residue was dissolved in 1 N HCl. Calcium oxalate was precipitated by adding a saturated solution of oxalic acid and adjusting to pH 3-4 with NH_4OH. The calcium oxalate precipitate, which carried Th quantitatively, was washed with water, filtered, dried, and sealed for irradiation. A blank was prepared by following the same procedure.

Sample irradiation

Neutron bombardment of ^{232}Th produced the isotope ^{233}Th, a beta-gamma emitter with a half-life of 23.3 minutes. Thorium-233 decays to ^{233}Pa, a beta-gamma emitter with a half-life of 27.4 days. The following reaction takes place:

$$^{232}Th\ (n, \gamma)\ ^{233}Th \xrightarrow{\beta^-} {}^{233}Pa$$

To eliminate the necessity of absolute determination and calibration of various parameters such as flux density, slow neutron capture cross-section, and counter efficiency, ^{232}Th standards were prepared and irradiated in parallel with the samples.

The samples were packed in a polyethylene vial and irradiated for 4 hours at the Massachusetts Institute of Technology (MIT), Nuclear Reactor Laboratory, operating at 4.8 MW at a thermal neutron flux of ~ $10^{13} n.cm^{-2}.s^{-1}$.

Radiochemical separation

After irradiation, the samples were cooled for a week, thereby eliminating the activity of short-lived interfering radionuclides such as ^{24}Na, ^{38}Cl, and ^{82}Br.

The samples were then digested in concentrated HNO_3 and separated by co-precipitation of the ^{233}Pa activity, first with MnO_2 and then with $BaSO_4$. The details of the chemical procedure are described elsewhere.[1]

Activity measurements

The purity of the final ^{233}Pa source was confirmed by gamma spectrometry. A HPGe detector, model GEn-10195, with 11% efficiency was used, coupled to a 1024 channel EG&G ORTEC analyzer to measure the activity of ^{233}Pa. Each decay is accompanied by a 100% abundant 311.8 keV gamma ray.

Results and discussion

The gamma activity from ^{233}Pa is generally used[4] because the longer half-life of ^{233}Pa provides greater convenience in working time and allows the cooling off after irradiation of high-activity, short-lived interfering nuclides. The accuracy of the method was checked by adding known amounts of thorium to the samples to be analyzed. This was done over a range of concentrations. The results obtained are presented in Table 1.

The initial results showed that the method can be utilized to measure 5 to 82 ng of ^{232}Th with good recovery (mean = 89%). The background was found to be about 5 ng of ^{232}Th per liter of normal and synthetic urine.

These limits, although higher than those reported by Dang, et al., shows that this technique, including our modifications, is sufficiently sensitive for measuring thorium in human urine at the recording level and well below the annual limit of intake (ALI) as defined in ICRP 54 when one liter of urine is analyzed. Therefore, the method can be applied for routine measurement of samples from occupationally-exposed workers.

TABLE 1

Th measurement in spiked urine samples

Sample Number	Th Added (ng)	Th Measured (ng)	Yield (%)
1	5.06	5.14 + 0.21	101.5 + 4.1
2	4.98	3.36 + 0.33	67.5 + 6.5
3	11.15	10.04 + 0.4	90.0 + 3.6
4	10.96	9.92 + 0.40	90.5 + 3.6
5	28.69	23.1 + 4.8	80.5 + 3.9
6	58.30	52.6 + 2.0	90.2 + 1.8
7	81.98	82.6 + 3.9	100.8 + 4.8

TABLE 2

Recording levels of ^{232}Th in 1 liter urine samples

(occupational exposure per ICRP 54)

Class W, T = 120d

	Bq/L	pCi/L	ng/L
ALIxT/365	8.0×10^{-4}	1.56×10^{-2}	143
DIL	2.4×10^{-4}	4.68×10^{-3}	42.9
RL	0.8×10^{-4}	1.56×10^{-3}	14.3

Class Y, T = 120d

	Bq/L	pCi/L	ng/L
ALIxT/365	1.0×10^{-4}	2.73×10^{-3}	25.0
DIL	3.0×10^{-5}	8.18×10^{-4}	7.5
RL	1.0×10^{-5}	2.73×10^{-4}	2.5

Table 2 lists the recording levels, derived investigation levels, and levels at which an ALI would be inferred for routine monitoring at 3 intervals per year (120 days) in urine, expressed as Bq/L, pCi/L and nanograms/liter, both for class W and Y compounds.

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