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# DETERMINATION OF URANIUM AND THORIUM ISOTOPES IN MINERAL SPRING WATERS

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Concentrations levels of uranium and thorium isotopes have been analyzed in the mineral spring waters of a high background region of Brazil: Poços de Caldas and Águas da Prata. The procedure was based on the determination of $^{238}U$, $^{234}U$, $^{232}Th$, $^{230}Th$ and $^{228}Th$ by $\alpha$-spectrometry after separation and purification of the isotopes of interest by using anion-exchange chromatography and preparation of the samples for $\alpha$-measurements by electrodeposition. The concentration varied from <1.1 to 28.4 $mBq.l^{-1}$ and from <1.6 to 141 $mBq.l^{-1}$ for $^{238}U$ and $^{234}U$, respectively. Thorium isotope measurements varied from <0.2 to 1.8 $mBq.l^{-1}$ from <0.3 to 4.9 $mBq.l^{-1}$ and from <0.8 to 19.9 $mBq.l^{-1}$ for $^{232}Th$, $^{230}Th$ and $^{228}Th$, respectively. Calculations of thorium and uranium isotopic activity ratios were carried out giving values ranging from 1.9 to 7.2, from 1.2 to 3.0 and from 7.7 to 15.3 for $^{234}U/^{238}U$, $^{230}Th/^{232}Th$ and $^{228}Th/^{232}Th$, respectively. The effective doses due to the intake of $^{238}U$ and $^{234}U$ present in these waters are expected to reach values up to $1.4 \times 10^{-3}$ mSv $y^{-1}$ and $8.0 \times 10^{-3}$ mSv $y^{-1}$, respectively.

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## INTRODUCTION

This study is part of a large research program to investigate the levels of the natural radionuclides present in mineral spring waters of a highly radioactive region of Brazil: Poços de Caldas plateau.

This area is a deeply weathered alkaline igneous intrusion of the Cretaceous period[1,10], located about 270 km north of the city of São Paulo. At present, the remnant of the intrusion takes the form of a circular caldera, about 35 km in diameter, covering an area of approximately 800 $km^2$. On this plateau many health resorts are found, based on sources of thermal and mineral waters. The Águas da Prata and Poços de Caldas spring waters are among the most visited by tourists and patients from Brazil[7,8].

The Águas da Prata spring waters chosen for the present study are: Vilela, São Bento, Prata Antiga, Prata Nova, Prata Radioativa, Vitória, Balneário, Paiol, Platina. Regarding the aquifer lithology, these springs can be classified in two main groups: the first one which includes the springs Vilela, São Bento and Prata Radioativa, is fed by aquifers composed of sandstone rocks; the second one, in which are included the remnant sources, is fed by water passing through alkaline rocks of volcanic origin. The waters of the second group, which rise through alkaline rocks of volcanic origin aquifers, have deep origin and are highly mineralized. These waters present high concentrations of bicarbonate and sulfate salts in their composition. On the other hand, waters rising from sandstone rock aquifers are poorly mineralized and have no deep origin[7,8].

The spring waters analyzed in Poços de Caldas were Santana, Macacos, Boca do Leão and Amores. The waters from the springs Santana and Amores show low levels of soluble salts, whereas the remaining ones can be classified as sulfureous waters[7,8].

The present investigation was undertaken in order to supplement previous studies concerning the determination of $^{226}Ra$, $^{228}Ra$ and $^{210}Pb$ in such waters, which have already been published elsewhere[9], and to estimate the risk due to the ingestion of these radionuclides.

The methodology adopted can be divided into the following steps:

- U and Th isotopes separation and purification by anion-exchange chromatography,
- electrodeposition and
- α-spectrometric determination.

## EXPERIMENTAL

The water samples were collected in 14 spring sites scattered over the Poços de Caldas plateau over a period of one year. For U and Th isotopes determination, 10 to 20 litres of water were collected whenever possible quarterly at each spring site. The pH was adjusted by addition of nitric acid to prevent losses by sorption in the vessels during storage.

The water samples were evaporated to dryness and the residue was redissolved in 8M hydrochloric acid. After dissolution, an aliquots of $^{232}U$ and $^{234}Th$ tracer solutions were added in order to determine the chemical yield. This solution was passed through a

pyrex glass column filled with Dowex 1x8 (100-200 mesh) resin. Uranium is adsorbed in the column, whereas, thorium is found in the eluate. The uranium adsorbed on the column was eluted by passing 0.5M hydrochloric acid through the column[2,6].

The solution containing uranium was evaporated to dryness, the residue was redissolved with 2N sulfuric acid. This solution was then passed through a pyrex glass column filled with Dowex 1x8 (50-100 mesh) resin and the uranium eluted by washing the resin with 0.5M hydrochloric acid.

The solution containing thorium was evaporated to dryness and the residue was redissolved with 8M nitric acid. This solution was passed through a pyrex glass column filled with Dowex 1x8 (100-200 mesh). Thorium was then eluted from the resin with 1M hydrochloric acid.

Uranium and thorium were then plated on stainless steel planchets by electrodeposition, using a saturated solution of $NH_4Cl$ and applying a current of 1.2 A. The $\alpha$-spectrum was obtained by using a surface barrier detector. The resolution of the detector is 54.6 keV full width at half maximum at the peak of 5.157 MeV of $^{239}Pu$. The counting efficiency was 30% and the lower limits of detection for this methodology were 1.1 $mBq.l^{-1}$ for $^{238}U$, 1.6 $mBq.l^{-1}$ for $^{234}U$, 0.2 $mBq.l^{-1}$ for $^{232}Th$, 0.3 $mBq.l^{-1}$ for $^{230}Th$ and 0.8 $mBq.l^{-1}$ for $^{228}Th$.

The methodology was checked experimentally by measuring uranium and thorium standard solutions. The reproducibility was characterized by variation coefficient values of 14% and 9%, with an accuracy of 5% and 6% for uranium and thorium, respectively[3].

## RESULTS AND DISCUSSION

The radionuclide concentration data are presented in Table 1.

The concentration varied from <1.1 to 28.4 $mBq.l^{-1}$ and from <1.6 to 141 $mBq.l^{-1}$ for $^{238}U$ and $^{234}U$, respectively. Thorium isotope measurements varied from <0.2 to 1.8 $mBq.l^{-1}$, from <0.3 to 4.9 $mBq.l^{-1}$ and from <0.8 to 19.9 $mBq.l^{-1}$ for $^{232}Th$, $^{230}Th$ and $^{228}Th$, respectively.

Measurable concentrations of uranium were observed in 13 springs, whereas for thorium isotopes most of them showed activities close to the detection limits of the counting system. The reason uranium isotopes are more abundant in the groundwater than thorium isotopes is mainly due to their relative solubility.

In a survey carried out in public water supplies of USA by Hess et al.[5], the uranium concentration levels varied from 0.74 to 85.47 $mBq.l^{-1}$. The results obtained in this paper are within this range. According to Oliveira et al.[9], the springs of Águas da Prata which presented higher concentrations of $^{226}Ra$ and $^{210}Pb$ were Vilela and São Bento. The same behavior was not observed for $^{238}U$ and $^{234}U$ activity measurements, which were higher in other springs: Prata Nova and Balneário.

Calculations of thorium and uranium isotopic activity ratios were carried out giving values ranging from 1.9 to 7.2, from 1.2 to 3.0 and from 7.7 to 15.3 for $^{234}U/^{238}U$, $^{230}Th/^{232}Th$ and $^{228}Th/^{232}Th$, respectively.

Based upon measured concentrations, doses were evaluated for $^{238}U$ and $^{234}U$ in the spring water which presented higher levels of such isotopes: Prata Nova. The individual dose was evaluated by considering a daily consumption of 2 litres and dose factors from ICRP

TABLE 1

Uranium and thorium concentration in mineral spring waters of Águas da Prata (AP) and Poços de Caldas (PC)

| Spring | Radionuclide concentration, $mBq.l^{-1}$ | | | | |
|---|---|---|---|---|---|
| | $^{238}U$ | $^{234}U$ | $^{232}Th$ | $^{230}Th$ | $^{228}Th$ |
| Vilela Captação (AP) | 6.5±1.1 | 16.1±1.0 | 1.8±0.2 | 4.9±0.3 | 19.9±2.4 |
| Vilela Bosque (AP) | 5.1±0.2 | 13.2±0.8 | 0.6±0.3 | 1.8±0.9 | 4.6±1.8 |
| São Bento (AP) | 3.8±1.4 | 8.7±3.7 | <0.2 | 0.9±0.2 | 5.5±1.8 |
| Prata Antiga (AP) | 6.5±1.8 | 46.7±12.2 | nd | nd | nd |
| Prata Nova (AP) | 28.4±8,6 | 141±42 | 0.3±0.1 | <0.3 | <0.8 |
| Vitória (AP) | 4.8±1.1 | 24.4±6.2 | nd | nd | nd |
| Prata Radioativa (AP) | 13.0±0.9 | 50.1±5.1 | nd | nd | nd |
| Balneário (AP) | 25.5±9.3 | 119±27 | nd | nd | nd |
| Paiol (AP) | 2.0±0.7 | 4.8±1.1 | nd | nd | nd |
| Platina (AP) | 3.7±1.7 | 16.6±2.2 | nd | nd | nd |
| Santana (PC) | 1.8±0.9 | 3.4±1.8 | 0.4±0.1 | 0.7±0.1 | 6.1±0.8 |
| Macacos (PC) | <1.1 | <1.6 | 0.9* | 1.1* | 8.3* |
| Boca do Leão (PC) | 1.3±0.8 | 4.5±2.2 | 0.5* | 1.1* | 6.0* |
| Amores (PC) | 1.2* | <1.6 | <0.2 | 0.6±0.0 | 6.2±0.1 |

*Only one determination.
nd - Not determined.

67[4]. The results obtained for the committed effective dose due to the ingestion of water from Prata Nova spring were $1.4 \times 10^{-3}$ mSv $y^{-1}$ and $8.0 \times 10^{-3}$ mSv $y^{-1}$ for $^{238}U$ and $^{234}U$, respectively. Doses in the bone due to the ingestion of such water were expected to

reach $2.1 \times 10^{-2}$ mSv $y^{-1}$ and $1.2 \times 10^{-1}$ mSv $y^{-1}$ for $^{238}U$ and $^{234}U$, respectively.

The expected doses due to the ingestion of $^{238}U$ and $^{234}U$ present in such waters are not relevant when compared with those related with $^{226}Ra$ and $^{210}Pb$[9]. Therefore, $^{226}Ra$ and $^{210}Pb$ are still the most significant radionuclides as far as the consumption of such waters is considered.

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