

URANIUM DETERMINATION IN TAP WATER BY INAA

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ABSTRACT

Uranium can exist in the water as a result of soil leaching or technological processes (mining and processing of phosphate minerals to fertilizer production). The INAA (instrumental neutron activation analysis) usually is used to determination of trace elements through the conversion of stable nuclei to another via nuclear reactions. The present work used INAA method for determination of U in water samples. The goals are validate a methodology to determine U in water samples, apply this methodology and determinate the physical chemical parameters pH, total solids and alkalinity in tap waters samples. The validation was established based on varying the irradiation and counting times. A-one-liter sample with 87 μg of U was prepared from the standard solution of U 1000 mg L^{-1} (SPEX CERTIPREP). From this prepared solution was taken ten samples of 100 mL each. After complete evaporation at 100°C in hot plate and at 60°C in infrared lamp, the ten samples were irradiated in the IEA-R1 nuclear research reactor. Two samples from different regions were collected for determination of pH, total solids, alkalinity and U concentration.

1. INTRODUCTION

Uranium can be found in the water through different processes, such as soil leaching and technological activities. This element can appear in significant concentrations in superficial and groundwater due to the interaction with the local rocks, influenced by the type of aquifers rock, redox conditions, acidity, alkalinity, concentrations of CO_2 and O_2 in gas phase, temperature, presence of the inorganic and organic compounds [1]. Most of the uranium is in the dissolved phase in natural waters, mainly in oxidant environments [2].

The determination of uranium in water have been widely studied for different purposes, such as: weathering and transport processes [3], hydrogeo-chemistry [4], environmental [5] and radiological studies [6].

Due to the fact that ^{238}U activity concentrations are expected to be low (10 Bq L^{-1}) [7], and the recommendation of the WHO about a maximum value of 30 $\mu\text{g L}^{-1}$, it's necessary the use of an analytical method capable of determinations in ppm or ppb order of magnitude.

In the present study, neutron activation analysis method was used for the determination of U concentrations in water samples. Although there are many articles about this issue, a very few papers use this technique as an analytical method for this purpose [8].

The NAA method consists in measuring the gamma radiation released by the element decay after irradiation of a target nuclei by a neutrons flux, or measuring the gamma radiation instantly released by the neutron interaction with the target nuclei, as can be seen in figure 1 [9].

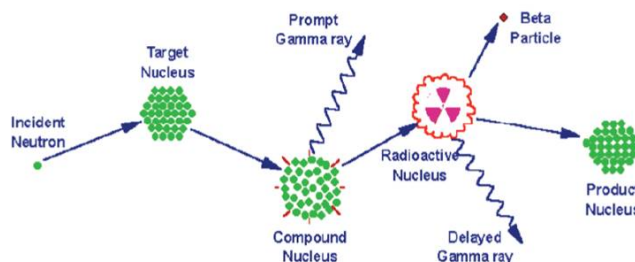


Figure 1: Sequence of events for a (n,γ) reaction.

In this study it was measured the gamma radiation after the element decay (gamma delayed). The technique applied was instrumental neutron activation analysis (INAA). In this technique, the elements of interest are determined through the decay rate of each radioisotope formed during the irradiations and its activity is compared with the activity obtained for a standard irradiated and counted in the same conditions of the samples [10].

2. OBJECTIVES

The objective of this study was to establish a methodology to determine ultra-trace levels of U in water samples. Apply this methodology to determine U concentrations in water samples collected from tap water and, additionally, also to determine the physical-chemical parameters pH, total solids and alkalinity.

3. METHODOLOGY

The tap water samples were collected from two different regions of São Paulo State: LA1 (Campestre in the city of Santo André in São Paulo State) and GA2 (Palmas do Tremembé in the Northern zone of São Paulo city).

3.1. Physical-chemical parameters determination

All physical chemical parameters were determined in triplicate.

3.1.1. pH

The pH was measured immediately after the samples were collected, through a potentiometer with electrodes for determining hydrogen potential.

3.1.2. Total solids

A porcelain capsule previously cleaned and decontaminated with HNO_3 0.1 mol L^{-1} was dried in a furnace at 105°C for one day. Later, the capsule was allowed to cool to room temperature in a desiccator. An aliquot of 100 mL of the water sample was added to the capsule, weighed and put in a furnace at 100°C up to total liquid evaporation. The obtained residue was then dried in a furnace at 180°C for one hour [11], allowed to cool to room temperature in a desiccator and weighed again. The total solids content was determined as the difference in the mass between the beginning (mass of the 100 mL water) and the end of the procedure (mass of the residue).

3.1.3. Alkalinity

Alkalinity was measured by titration of approximately 150 mL of the sample with standard solutions of H_2SO_4 0.01 mol L^{-1} [12].

For this analysis, the first step is to measure the pH of the sample. If the initial pH is higher than 8.3, sulfuric acid is added up to $\text{pH} = 8.3$. In cases in which $4.5 < \text{pH} < 8.3$, sulfuric acid should be added up to $\text{pH} = 4.5$. The volume of acid used in the titration and its concentration are necessary to calculate the total alkalinity from the equation 1, as follows:

$$\frac{V_a \cdot C_a \cdot 100}{V_s} = \text{Alk} \quad (1)$$

Where, Alk is alkalinity, V_a (acid volume), V_s (sample volume) and C_a is acid concentration in mol L^{-1} [13].

The alkalinity is expressed in mg L^{-1} of CaCO_3 .

3.1.4. Instrumental Neutron Activation Analysis

For the validation of the methodology for the determination of U concentration in water samples by INAA, synthetic samples were prepared to present uranium concentrations in the order of few $\mu\text{g L}^{-1}$. Diluted solutions of uranium were prepared from standard solutions (SPEX CERTIPREP 1000 mg L^{-1}) in ultra-pure water to give concentrations of $87 \mu\text{g L}^{-1}$ of uranium. As ultra-pure water is almost free of ions, those solutions basically contain uranium in their composition and the physical chemical parameters were not determined for them.

The diluted solutions were used to simulate water samples and they will be called from now on synthetic samples. Aliquots of 100 mL of the synthetic samples were weighted and dried in a hot plate at 100°C up to approximately 1 mL, that was then transferred to a polyethylene capsule with 1.5 mL of volume. The beaker containing the sample was washed with a small portion of HNO₃ 0.1 mol L⁻¹, that was also dried and transferred to the polyethylene capsules in order to guarantee the quantitative transfer of the sample. The volume transferred to capsule was evaporated under an UV lamp at approximately 60°C, up to the obtainment of solid residue.

The capsules with synthetic samples were irradiated together with standard material consisting of a SPEX CERTIPREP 1000 mg L⁻¹ solution from which 20 µL were pipetted in the same type of polyethylene capsule and let to dry under UV lamp in the same temperature of the samples. It was tested the irradiation time, irradiating the synthetic samples for 2, 4, 6 and 8 hours that were counted after two, three, four and seven days of cooling times, respectively. Each synthetic sample was counting for three hours and the standard solutions, for two hours. The gamma activity measurements were performed using two hyper pure Ge detector from ORTEC, model GEM 20190-P with the same efficiency of 20%, being the detector 1 with resolution of 0.79 keV and 2.03 keV, and detector 2, a resolution of 0.96 keV and 1.88 keV for the photo-peaks of 122 keV from ⁵⁷Co and 1332 keV from ⁶⁰Co, respectively.

4. RESULTS AND DISCUSSIONS

4.1. Instrumental Neutron Activation Analysis

In Tables 1, 2, 3, and 4 are demonstrated the concentrations detected of uranium obtained for different times of irradiation and 1, 2, 3 hours of counting time. It can be observed that the counting time do not exerted significant influence on the obtained results, the same sample counted for different time period presents just a small variation. Nevertheless, all the obtained results were below the expected value, indicating a trend of systematic error in the analysis, that must be still verified.

Table 1: Uranium Concentration at 2h of irradiation

Detectors	Sample (2h)	Counting (s)	[U] (µg L ⁻¹)	[Uexp] (µg L ⁻¹)
Detector1	U5	3600	62.9 ±0.5	87
Detector1	U5	7200	63.2 ±0.4	87
Detector1	U5	10800	63.7 ±0.3	87
Detector2	U10	3600	63.2 ±0.3	87
Detector2	U10	7200	64.1 ±0.3	87
Detector2	U10	10800	64.7 ±0.3	87

Table 2: Uranium Concentration at 4h irradiation

Detectors	Sample (4h)	Counting (s)	[U] ($\mu\text{g L}^{-1}$)	[Uexp] ($\mu\text{g L}^{-1}$)
Detector1	U7	3600	68.3 \pm 0.3	87
Detector1	U7	7200	68.9 \pm 0.3	87
Detector1	U7	10800	69.3 \pm 0.3	87
Detector2	U9	3600	75.3 \pm 0.3	87
Detector2	U9	7200	75.6 \pm 0.3	87
Detector2	U9	10800	76.5 \pm 0.3	87

Table 3: Uranium Concentration at 6h irradiation

Detectors	Sample (6h)	Counting (s)	[U] ($\mu\text{g L}^{-1}$)	[Uexp] ($\mu\text{g L}^{-1}$)
Detector1	U8	3600	64.3 \pm 0.3	87
Detector1	U8	7200	64.8 \pm 0.3	87
Detector1	U8	10800	65.4 \pm 0.3	87
Detector2	U6	3600	78.6 \pm 0.3	87
Detector2	U6	7200	79.4 \pm 0.3	87
Detector2	U6	10800	79.9 \pm 0.3	87

Table 4: Uranium Concentration at 8h irradiation

Detectors	Sample (8h)	Counting (s)	[U] ($\mu\text{g L}^{-1}$)	[Uexp] ($\mu\text{g L}^{-1}$)
Detector1	U3	3600	77.2 \pm 0.5	87
Detector1	U3	7200	79.3 \pm 0.4	87
Detector1	U3	10800	80.5 \pm 0.4	87
Detector1	U4	3600	66.8 \pm 0.4	87
Detector1	U4	7200	66.7 \pm 0.3	87
Detector1	U4	10800	67.2 \pm 0.3	87
Detector2	U1	3600	72.2 \pm 0.5	87
Detector2	U1	7200	73.4 \pm 0.3	87
Detector2	U1	10800	74.1 \pm 0.3	87
Detector2	U2	3600	67.4 \pm 0.5	87
Detector2	U2	7200	67.4 \pm 0.4	87
Detector2	U2	10800	68.2 \pm 0.4	87

Table 5: Detectors Comparison

Detectors	Samples	IT* (h)	[U _{mean}] ($\mu\text{g L}^{-1}$)	[U _{exp}] ($\mu\text{g L}^{-1}$)	σ	Relative error
detector 1	U5	2	63,3	87	0,4	-27,2
detector 2	U10	2	64,0	87	0,8	-26,4
detector 1	U7	4	68,8	87	0,5	-20,9
detector 2	U9	4	75,8	87	0,6	-12,9
detector 1	U8	6	64,8	87	0,6	-25,5
detector 2	U6	6	79,3	87	0,7	-8,9
detector 1	U3	8	79,0	87	1,7	-9,2
detector 1	U4	8	66,9	87	0,3	-23,1
detector 2	U1	8	73,2	87	1,0	-15,9
detector 2	U2	8	67,7	87	0,5	-22,2

*IT: irradiation time.

Although the only clear difference between the detectors is the resolution, it is also clear a difference in the concentration measured when samples are counted in detector 1 or detector 2. For samples irradiated for 1, 4, and 6 hours the results obtained in detector 2 were more accurate than the ones obtained with detector 1. For the samples irradiated for 8 hours, this tendency is not so clear. Table 5 shows the relative errors for some measurements made in both detectors for the different time of irradiation and time of counting. The relative error varied from 8.9 to 27.2%. According to Prichard and Barwick [14] the expected relative standard error for concentration in the range of 10 to 100 L^{-1} should be in the range of 23 to 32%. Considering these values, even though with the results showing a systematic error they can be considered sufficiently accurate for the order of magnitude of the concentrations being measured in this study.

4.2. Physical Chemical Parameters and U analysis in tap water samples

Table 6: Physical Chemical Parameters and U analysis

Samples	pH _i	alkalinity (mg L^{-1})	total solids (mg)	U ($\mu\text{g L}^{-1}$)
Campestre	7.4	48.3 \pm 1.3	4.0 \pm 1.5	0.14 \pm 0.04
Palmas do Tremembé	7.5	64.8 \pm 1.1	4.0 \pm 1.5	0.2 \pm 0.1

Table 6 shows the results for the physical chemical parameters and U concentrations obtained for the 2 samples analyzed up to now. The pH measured was neutral ranging from 7.4 to 7.5 in conformity with the resolutions of Ministério da Saúde, (between 6.0 and 9.5) [15].

The alkalinity for the water samples from Campestre and Palmas do Tremembé presented values of 48.3 and 64.8 mg L^{-1} of CaCO_3 , respectively.

Generally the values of total alkalinity shall not exceed 500 mg L^{-1} of CaCO_3 [16].

The values for total solids were in the order of mg. The values were low, 4.0 mg for an aliquot of 100 mL of sample. There is no recommendation for a maximum amount for total solids in potable waters [17].

The values for U presented in table 6 are very low and in conformity with the guidelines [7].

These values represent an activity concentration of 3.5 and 5.0 mBq L⁻¹ for natural uranium present in the samples.

5. CONCLUSIONS

The paper presented the INAA validation methodology for the determination of U in water samples together the determinations of the physical chemical parameters pH, alkalinity and total solids for tap water samples collected in two different regions of São Paulo State. The results obtained with synthetic samples showed that there is no significant difference in the irradiation and counting times. Although a trend in the results had been observed, with all values lower than the expected, the result can be considered accurate for the order of magnitude tested in this study. The samples of tap water measured showed pH and alkalinity in conformity with the regulations and U concentration in the order of tenths of $\mu\text{g L}^{-1}$.

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