Present Status of Radon and Radium Activity Measurements in Well and Bottled Water at the Federal University of Technology (UTFPR, Brazil)

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Abstract

This work describes the present status and obtained results concerning ^{222}Rn activity in drinking water from artesian bores at Curitiba (Brazil). The measurements were performed using the Professional Radon Monitor (ALPHA GUARD). The ^{222}Rn concentration levels were analyzed using the software DataEXPERT by GENITRON Instruments. The collected data were processed taking into account the volume of water sample and its temperature, atmospheric pressure and the total volume of air in the system. Studied samples of water presented an average ^{222}Rn activity of 60 Bq/L approximately, which is almost 6 times bigger than the maximum level of 11.1 Bq/L recommended by the USEPA. A few artesian drillings presented the radon activity of almost 200 Bq/. Further measurements are planned to be performed in other regions of Parana State including mineral water sources, artesian drillings and soil samples as well. Another subject of this work is the preliminary results concerning ^{226}Ra activity measurements in bottled mineral water available in the market of Curitiba (Brazil). In these measurements the experimental setup was based on the Professional Radon Monitor RAD7 (Durridge Company, Inc.). The background of RAD7 detector together with Radon In Water Accessory (RAD H_20) was evaluated using the samples of distilled water. The measurements of radium activity were performed when ^{222}Rn in water samples reached the secular equilibrium. For this purpose, collected water samples were stored in hermetic bottles of 250 mL during 45 - 50 days before the measurements. The minimum and maximum ^{226}Ra concentrations were found of 0.03 and 2.95 Bq/L, respectively. Eight samples of bottled mineral water presented values of ^{226}Ra concentration range above the maximum activity level for alpha global radioactivity of 0.1 Bq/L established by the Norms and Regulation of Brazilian Ministry of Health. Further measurements are planned with other brands of bottled mineral water.

Key-words: radium, radon, activity concentration, water

1. Introduction and Objectives

Among naturally occurring heavy radioactive elements, the most common are ^{238}U and ^{232}Th, which produce other radioactive isotopes of radium and radon.. ^{226}Ra is the most common of radium isotopes found in water, which is a radioactive element from the decay-series of ^{238}U, and has the half-life of approximately 1622 years. Undergoing alpha decay, ^{226}Ra produces ^{222}Rn. These radioactive isotopes (^{226}Ra and ^{222}Rn) have different chemical properties, but both after intake with water can cause potentially health problems such as cancer [1]. The ^{226}Ra concentration in water depends on its content in rocks and soil, soil permeability and solubility of uranium and radium compounds in water. Commonly, the surface waters have lower concentrations of ^{226}Ra then groundwater [2].

The ^{222}Rn soluble in water is a source of human exposure, mainly because this gas is released from tap water and incorporated into the indoor atmosphere [3]. Higher levels of ^{222}Rn are found in groundwater and are correlated with the occurrence of high levels of ^{226}Ra in the rocks. Crystalline rocks, especially granite, could be a source of high levels of radon comparing with sedimentary rocks that usually are associated with lower levels of exhaled radon.

The soil of Paraná, more specifically at the metropolitan area, contains rocks, which are mostly classified as metamorphic. At this region could be found a great variety of igneous intrusive rocks, including granites and granitoids [4]. This fact leads to the conclusion that the soil of Paraná has considerable contribution to the concentration of radon in ground water of this region since granites usually contain significant amount of the precursor (parent) radioisotopes as uranium and thorium.

The results of research concluded by EPA's [3] on the concentration of ^{222}Rn in ground water samples of sedimentary rocks show low concentrations in general. On the other hand, the same document presented the results of studies of waters in small communities with rather high levels.

According to The United States Environmental Protection Agency (EPA), the main health effects associated with intake of ^{226}Ra are the bone cancer and different kinds of soft tissues cancers. The radium has a behavior similar to calcium, therefore it is mainly distributed at the bones of human skeleton and its quantity is bigger when the individual is in the process of growth. In this way it contributes significantly to the dose absorbed by the tissue of children [5].

Since ^{226}Ra is considered the second largest source of radiation in water [1, 5], several agencies set limits for the concentration of its total activity in water used by human beings. The World Health Organization (WHO) in 2011 set a limit of 0.5Bq/L for gross alpha radiation for safe consumption of water when no decision concerning mitigation or dose reduction should be taken [1].

The upper limit of radioactivity for ^{222}Rn in drinking water proposed by EPA [5] is of 11.1Bq/L. This limit was estimated considering the probable contribution of radon released from water to the indoor environment. The USA and International limits recommended for indoor radon concentration in the air are of 148Bq/m^3 [5] and 200Bq/m^3 [6], respectively. The Brazilian Committee on Nuclear Energy (CNEN) established the upper limit for indoor radon within dwellings of 300Bq/m^3 that corresponds to the maximum annual dose of 10mSv [7, 8].

This article describes the present status and preliminary results concerning ^{226}Ra activity measurements in bottled mineral water available in the market of Curitiba, Brazil. Since the consumption of bottled mineral water in Brazil is increasing, present study was performed with an aim to characterize the quality of bottled mineral waters mainly with respect to the concentration of soluble radionuclides.

Brazil is the seventh largest producer of mineral water in the world. The country produced approximately 10 billion liters in 2007, with annual consumption estimated at 45 liters per person [9]. Previously performed studies [5, 6] estimated the dose received by Brazilian population due to radionuclides found in mineral waters. The values of ^{226}Ra concentration in mineral waters in Brazil have a minimum of 0.002 Bq/L and a maximum of 0.22 Bq/L [9, 10, 11].

During the decades of studies International regulatory organizations validated and approved several methods for radium concentration measurements in water such as, for example, liquid scintillation counting, gamma spectroscopy, emanation technique (the Lucas Cell method), alpha spectroscopy, Cherenkov counting, solvent extraction, etc. [12, 13, 14]. One of the most modern methods of the radon activity measurement is alpha spectroscopy that is realized in the RAD7 radon detector. This equipment allows separating ^{222}Rn from ^{220}Rn. But as it is mentioned in the User Manual, its lower limit of detection is less than 370 Bq/m^3. The aim of present work was to develop the methodology that permits to perform the measurements of radon concentration in mineral water samples lower than 100 Bq/m^3 [12].

2. Methods

In order to measure the ^{222}Rn activity in drinking water collected from artesian bores within the urban area of Curitiba, it was used the experimental setup based on AlphaGUARD detector connected through the air pump to a specific kit of glass vessels Aqua KIT, shown in Figure 1. Following the recommendations of the manufacturer [15] and previously performed methodological studies was adjusted to continuous flow of 0.5 L/min. The measurements were performed immediately after the water sample was collected and when the radon in water sample reached secular equilibrium.

The radon detector AlphaGUARD is based on the optimized design of pulse-ionization chamber. In regular operation this detector measures the radioactivity of the air using the diffusion of gas through the large surface of the glass fiber filter installed inside the ionization chamber. This filter permits that only the ^{222}Rn gas can pass through and prevents the products of the radon decay from entering to the ionizing chamber. It also protects the ionizing chamber from contamination by dust particles.

Water samples were taken from the depth of about 1.5 m below the level of water surface of water in the well using 1000 mL PET bottles. Completely filed PET bottles were tightly closed to prevent the entry of air into the bottle as well as to prevent the release of radon from it. The sealed samples were transported to the Laboratory of Applied Nuclear Physics of the Federal University of Technology – Paraná (UTFPR, Curitiba, Brazil) to be submitted with minimum delay to the radon concentration measurements. When the time delay between the sample collection and its measurements was significant, the correction was introduced taking into account the time interval between the water sampling and the activity measurements and the decay constant for ^{222}Rn.

Each water sample was submitted to measurement during the time interval of about 60 minutes. Such measurements were repeated after time intervals of a few days. The final measurement was performed after approximately two months since the water samples were collected. Detected ^{222}Rn activity levels were analyzed by the computer using the software DataEXPERT by GENITRON Instruments [15]. Obtained data were processed taking into account the volume of water sample and its temperature, atmospheric pressure and the total volume of the air in the vessels.

Figure 1. General view of ALPHA GUARD SETTED to measure ^{222}Rn in well water.

In the case of ^{226}Ra activity measurements in bottled mineral water available in the market of Curitiba – Brazil, the experimental setup was based on the Professional Radon Monitor RAD7. The measurements were performed when ^{222}Rn in water samples reached the secular equilibrium. For this purpose, collected water samples were stored in hermetic bottles of 250 mL during 45 - 50 days before the measurements.

The RAD7 Manual suggests two specific protocols for the measurements of radon activity in water: the Wat-40 and Wat250 for the sample volume of 40 and 250 mL, respectively. Initially these protocols consist of a water sample's aeration stage, which takes place for five minutes (Figure. 2). After that, the equipment uses 4 cycles of 5 minutes each one to measure the ^{218}Po activity within sampling cavity and to recalculate in ^{222}Rn activity concentration [13].

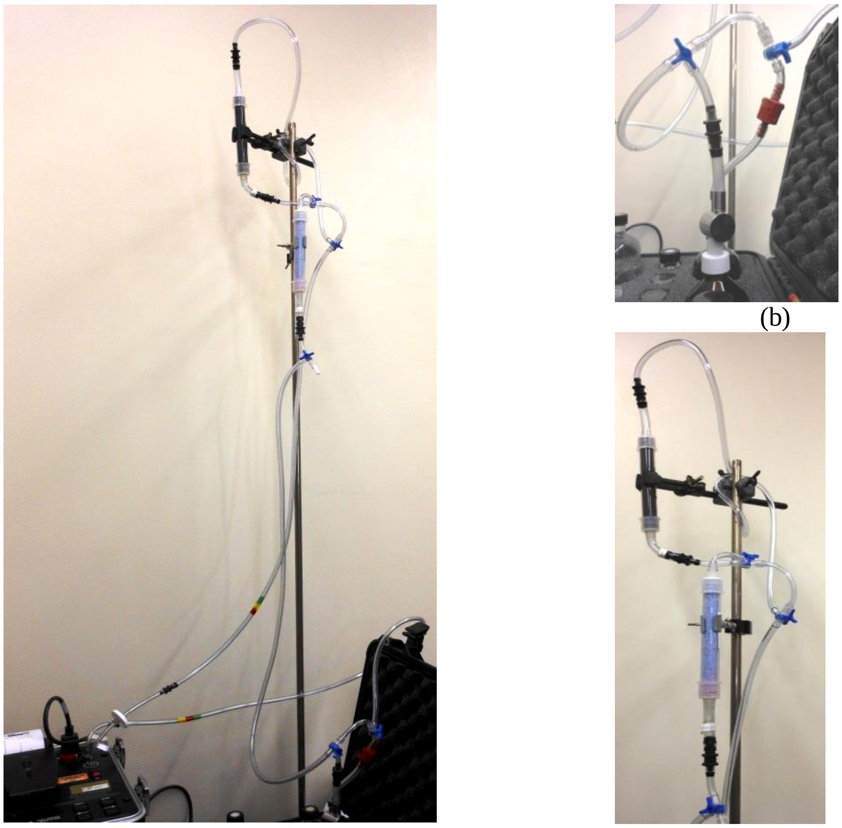
Therefore, for measurements of low activity samples, one of the most important questions is the radon concentration in the system air before aeration (background). One of the suggestions given in the RAD7 RAD H_2O [13] manual is to use the external laboratory air to fill the system before measurements. As the number of measurements of the laboratory air was performed and the results show that the value of the background reaches hundreds of Bq/m^3 and the error of its determination with Wat250 protocol, proposed in the manual as the basic protocol for low activity measurements, also reaches hundreds of Bq/m^3.

With such a level of background and associated errors it is not possible to perform the measurements of low activity of water samples. To decrease the background value the activated charcoal filter was used to clean the laboratory air before the measurement. All of measurements were performed with an enclosed volume of air. To avoid the contact of the system with the laboratory air, 5 tap connectors were installed at each point of interest as it is shown in Figure 2. These changes allowed a decrease of the background level up to tens of Bq/m^3 with Wat250 protocol.

Another important question in the measurement of low activity samples is the measurement time. To decrease the measurement error it is necessary to increase the measurement time. The principal protocol Wat250 has 4 cycles of 5 min. To increase the measurement time three other protocols were tested:

- 4 cycles of 1h 30min using small drying tube;
- 6 cycles of 1h using drying tube;

- 24 cycles of 15min using small drying tube.



(a) (b) (c)

Figure 2. (a) Picture of the system adapted to enable the exchange of the silica and sample keeping the air inside the system. It also enables the use of activated carbon through the selection of the route using the tap connectors, (b) Picture in details of the taps that allow the sample replacement, (c) Picture in details of the part of the system that allows exchange of silica and selection of the route passing through activated carbon to clean up the air inside the system with minimal contact with the outside air.

Each of them presents the same problem. They decrease the measurement error but the humidity overcomes 10% during the measurement. The system's humidity should not exceed 10%, according to the manufacturer's information because for higher humidity one can only say that the activity concentration is higher than that of presented in the outcome. Usually 30-40 min of the measurement is sufficient for the humidity to become higher than the upper limit. Therefore, the conclusion was not to change the measurement protocol but to repeat the principal Wat250 protocol and to dry the system between the measurements.

Preliminary investigation of the process of measurement of low activity water samples with RAD7 shows the importance of minimization of the ambient air access to the system. This means that after the background measurement the introduction of a water sample to the system should be done with smallest possible addition of the ambient air.

Another important result is that before the background measurement the system should always be cleaned with Granular Activated Carbon.

Fulfilling the above requirements we could reach the error of 50-100 Bq/m^3 measuring the ^{226}Ra activity in the distilled water with protocol WAT250. This result is not satisfactory for concentration measurement of about 100 Bq/m^3. The main source of this error is the uncertainty in the background determination. Repeating the protocol WAT250 four times we succeeded to achieve the background error of the order of 50 Bq/m^3. To reduce more the error value it is necessary to change the protocol and to increase the measurement time significantly.

3. Results and Conclusions

The frequency of ^{222}Rn and ^{226}Ra activity concentration in drinking water collected from artesian bores is shown in Figure 3 and 4, respectively.

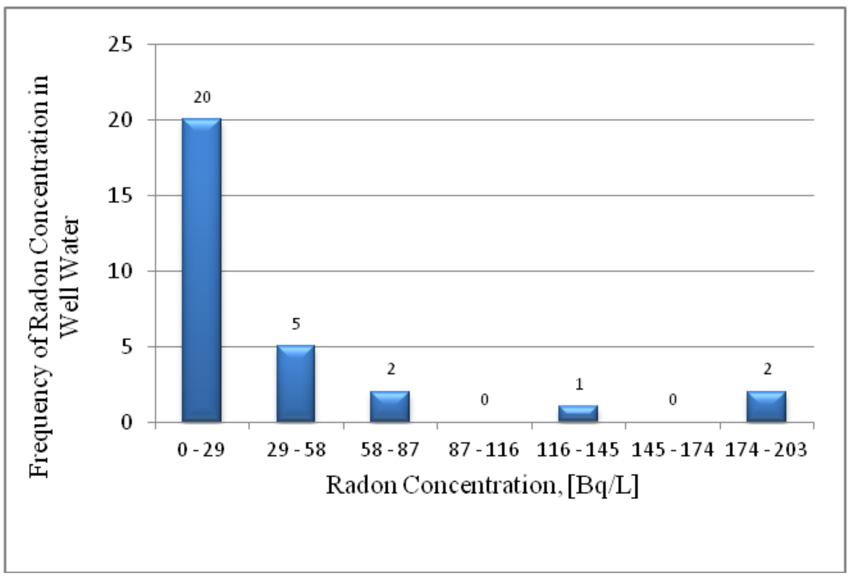


Figure 3. Frequency Distribution of ^{222}Rn activity concentration in well water of Curitiba –Brazil.

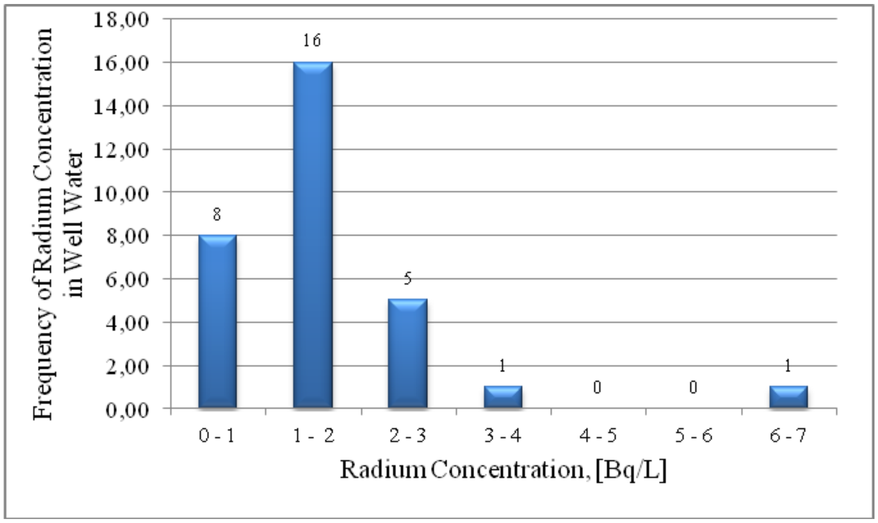


Figure 4. Frequency Distribution of ^{226}Ra activity concentration in well water of Curitiba –Brazil.

Comparing obtained experimental results (Figure 3 and 4) with similar studies from other Brazilin states (mainly at São Paulo, Minas Gerais and Rio de Janeiro States) [16 - 20] it could be concluded that obtained values of measured radon concentrations are similar.

Present study shows rather high concentration levels of ^{222}Rn in well water from the region of Curitiba. Moreover, about 70% of investigated water samples presented radioactivity of radon bigger than 11.1 Bq/L, recommended by the United States Environmental Protection Agency (EPA) [5], which requires the implementation of mitigation measures for radon reduction in drinking water.

It should be noted that the main source of ^{222}Rn in water is soil and not soluble ^{226}Ra compounds. The only one sample of water where obtained ^{226}Ra activity was found of 6.76 Bq/L is an isolated case and requires further investigation.

Table 1 shows the ^{226}Ra concentration in samples of bottled mineral waters using RAD7 and developed method. The minimum and maximum ^{226}Ra concentration in bottled mineral water were found of -4.24±92.65 and 239.25±69.55Bq/L, respectively. It can be concluded that in the case of ^{226}Ra low concentration measurements in bottled mineral water, modifying the system with an enclosed volume of air that includes tap connectors, drying tube and the activated charcoal filter, it is possible to measure the radon activity lower than 100 Bq/m^3 with the accuracy of at least tens of Bq/m^3. Further measurements are planned with other brands of bottled mineral water present in the market of Parana State, Brazil.

Table 1. Radioactivity concentration (Bq/m^3) in bottled mineral water available in the market of Curitiba-Brazil.

Sample	^{226}Ra Concentration (Bq/m^3)	Errors (Bq/m^3)
1	-4,24*	±92,651
2	104,79	±42,00
3	166,35	±49,43
4	67,72	±28,07
5	192,45	±46,03
6	130,59	±96,69
7	22,69	±59,35
8	58,89	±38,34
9	116,26	±43,65
10	23,89	±47,87
11	66,22	±27,07
12	40,52	±53,07
13	164,73	±46,18
14	116,20	±51,22
15	75,93	±29,56
16	239,25	±69,55
17	128,94	±54,90
18	64,21	±59,65
19	199,46	±40,27
20	56,66	±54,57
21	124,66	±44,63
22	73,41	±56,61
23	215,59	±56,77
24	149,14	±41,74

* The negative mean value was obtained due to statistical subtraction of background.

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