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Measurement of Content of ^{226}Ra in Drinking Water From Some States of Mexican Republic by Liquid Scintillation Method

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ABSTRACT

To assess the quality of drinking water in respect to the content of radioactivity, usually is carried out an screening program in the locations of interest, that program consist in pick representative samples of drinking water from the wells in that locations, water samples are analyzed to measuring the gross alpha/beta radioactivity by a low background proportional counter or a liquid scintillation system. When some sample exceeds the normative limit then it must be known which radionuclides are in that sample. Expected radionuclides in water are the NORM (normal occurring radioactive material) from the natural radioactive chains. ^{226}Ra is frequently present in drinking water and is one of most important radionuclide because its "radiotoxicity", the WHO [World Health Organization, Guidelines for drinking-water Quality, (2016)] recommends a reference level for ^{226}Ra of 1 Bq/L (the dose coefficient for ^{226}Ra is 2.8 x 10^{-7} Sv/Bq). From a national program of drinking water screening in the Mexican Republic, the samples that exceeded the national normative limits were picked again in the same well and analyzed by LS (liquid Scintillation), using the method of two phases with a not water miscible scintillator cocktail. Results of concentrations of ^{226}Ra from drinking water are presented. In general the content of ^{226}Ra in drinking water samples was lower that the guide values recommended for the WHO.

1. Introduction

1.1 Overview

Mexican water authorities (National Water Commission, CONAGUA), knowing that there could be a risk in the population due to the intake of water with radioactive content, had the initiative to undertake a study with the support of the National Science Council and Technology (CONACYT) to know the radioactivity content in water for human consumption from wells in the Mexican Republic. The National Institute of Nuclear Research (ININ) in collaboration with the ABC Analitic ® Laboratory carried out this study.

Sources of drinking water may contain radionuclides of natural and/or artificial origin. Natural radionuclides include ^{40}K, and those corresponding to the radioactive chains of Thorium and Uranium, in particular ^{226}Ra, ^{228}Ra, ^{238}U and ^{210}Pb may be present in the water as a result of natural processes of absorption from the ground or technological processes that involve radionuclides of natural origin (NORM), such as mining.

In case of the radionuclides of artificial origin, these may come from nuclear, radioactive or industrial facilities. Radium (Z = 88) is an alkaline earth metal and behaves chemically similar to Barium and Calcium [1]. In nature, we can find four radio isotopes: ^{226}Ra (half-life = 1600 years), ^{228}Ra (half-life = 5.8 years), ^{223}Ra (half-life = 11.4 days) and ^{224}Ra (half-life = 3.6 days). In drinking water, the two most important isotopes of Ra from the point of view of radiological risk are ^{226}Ra and ^{228}Ra [2-4].

Radium content of surface water is low compared to that of most groundwater [5]. Th is insoluble and strongly adsorbed on negatively charged mineral surfaces [6-8]. However, the Th that decays in surface rocks can introduce a significant amount of Ra directly to the water reservoirs [9-10]. Although there are more ^{232}Th in nature than ^{238}U in nature, there are geochemical factors that cause higher local concentrations of uranium, which often causes the water to have higher concentrations of ^{226}Ra in relation to the concentration of ^{228}Ra.

Studies conducted on samples of drinking water and groundwater in India, indicate ranges of radio concentrations (^{226}Ra) in water from 3.5 mBq/L to 208 mBq/L [11]. In the United States, the Environmental Protection Agency (USEPA) [21] conducted radioactivity measures at 1000 drinking water supply sites from

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groundwater. The average activity concentration of all samples was 15 mBq/L of ^{226}Ra [12]. The results of the study carried out in Egypt [13], indicate that the Nubian deep aquifer has activities of ^{226}Ra and ^{228}Ra ranging from 0.168 to 0.802 and from 0.056 to 1,032 Bq/L, respectively. The surface aquifer has activities of ^{226}Ra and ^{228}Ra ranging from 0.033 to 0.191 and from 0.029 to 0.312 Bq/L, respectively. Shallow alluvial aquifers have activities of ^{226}Ra and ^{228}Ra from 0.014 to 0.038 and from 0.007 to 0.051 Bq/L, respectively.

1.2 Radiological risk

Radiation protection is based on the fact that exposure to any amount of radiation involves a risk. In case of prolonged exposures such as ingestion of water with radioactive content, the risk of cancer is not observed in less than 100 mSv [15]. Considering a linear risk model without threshold, an individual dose criterion (IDC) of 0.1 mSv/year is considered, which represents an imperceptible level of risk in human health. The methodology recommended by WHO [15] for risk assessment and limitation due to water intake consists of 4 steps:

- An IDC = 0.1 mSv/year is adopted for water consumption.
- An initial screening is performed which considers levels of 0.5 Bq/L for total alpha activity and 1 Bq/L for total beta activity.
- If the screening level is exceeded, the values of individual radionuclide concentrations should be determined and compared with guide values (Table 1).
- The result of this evaluation indicates the actions to be taken based on these guide values.

Table 1. Guide levels for some natural Radionuclides, WHO [14]

Radionuclide	Dose Coefficient (Sv/Bq)	Guide Level (Bq/L)
^{238}U	4.5 x10^{-8}	10
^{234}U	4.9 x10^{-8}	1
^{230}Th	2.1 x10^{-7}	1
^{226}Ra	2.8 x10^{-7}	1

1.3 Mexican legislation

Particularly in Mexico, radiological aspects of water consumption are regulated by the Ministry of Health through NOM-127-SSA-1994 [16] for water for human use and consumption and NOM 201-SSA1-2015 [17] for bottled waters and ice for human consumption indicating as *maximum permissible limits* 0.56 Bq/L for Gross alpha activity and 1.85 Bq/L for Gross beta activity.

1.4 Geographical Location of Mexican Republic

Mexican Republic (Figure 1) is located in the northern hemisphere, bordering the north with the US, to the south with Belize and Guatemala, West with the Pacific Ocean and east with the Atlantic Ocean In the northern part of Mexico, the territory reaches 32° 43' 06", North latitude and 114° 45' West Longitude, in the state of Baja California, which constitutes its northernmost tip and in the southern part of Mexico, its territory reaches 14° 32' 27" North latitude and 92° 13' 0" Longitude West, in the state of Chiapas, which constitutes its southernmost tip. Mexico is divided into 31 states and Mexico City is its capital, its area is 1,964,375 km^2 with a population of 127,000,000 million inhabitants, [18] Instituto Nacional de Estadística y Geografía (INEGI).

Figure 1:.Geographical location of Mexican Republic

2. Methodology

2.1 Sampling

A screening plan was carried out in which 1,100 drinking water wells were selected in 27 states of the Mexican Republic (Table 2), from which water samples were taken. The Liquid Scintillation Counter (LSC) measured gross alpha-beta radioactivity from the well water samples. For the samples that exceeded the limit values contained in the Mexican legislation, the content of ^{226}Ra was determined.

2.2 Measurement of Samples Overview

Measurement of ^{226}Ra was made with the two-phase method by liquid scintillation [19]. This method is applicable for non-saline waters. ^{226}Ra is indirectly determined by measuring ^{222}Rn by extraction, and liquid scintillation counting. ^{222}Rn is extracted from aqueous solution by means of a scintillation cocktail not miscible with water inside the

scintillation vial and counted as the equilibrium with its short lived decay products is reached.

Precondition is that the content of ^{222}Rn in the bottle from which the aliquot to be measure is extracted, only contains Rn due to decay from ^{226}Ra, that is, the content of Rn dissolved in the sample by other different sources has already decayed, this is achieved by letting the sample stand for approximately 7 radioactive half-lives of ^{222}Rn (22.5 d) and then ^{226}Ra and ^{222}Rn reach secular equilibrium.

Table 2: Number of water samples by State.

Mexican State	Number of Wells
Aguascalientes	23
Baja California	54
Chiapas	5
Chihuahua	65
Coahuila	82
Colima	33
CDMex	2
Durango	135
Estado de Mexico	14
Guanajuato	176
Hidalgo	19
Jalisco	39
Michoacan	24
Morelos	14
Nayarit	19
Nuevo Leon	17
Oaxaca	19
Puebla	6
Querétaro	13
San Luis Potosi	63
Sinaloa	57
Sonora	72
Tabasco	9
Tamaulipas	47
Tlaxcala	20
Veracruz	9
Zacatecas	67

2.3 Materials and Equipment

- Water, grade 3 (ISO 3696)
- Scintillation cocktail, not water miscible UltimaGold F®
- Ethanol, 95 %.
- Radium Certified standard solution (611Bq/g ± 3 %)
- Wide-mouth glass sample bottles, volumen 500 ml
- Wide-mouth Erlenmeyer flask, volumen 500 ml
- Gas-tight syringe.
- Polyethylene scintillation vials, PTFE coated, volume 20 ml.
- Calibrated Balance (Resolution:0.001 mg)
- Hidex ® Liquid Scintillation Counter, model 300 SL.

2.4 Measurement Method Description

The aqueous sample is drawn by the mean of a gas-tight syringe from inside the water volume, below of surface to avoid radon losses during sampling and transferred into a scintillation vial containing 10 mL of scintillation cocktail. The water sample is injected below the cocktail surface. The vial is tightly capped, shaken and kept for 3 h in the dark and at controlled temperature. The sample is then counted by a liquid scintillation counter. In this case alpha only counts are considered. In these conditions ^{222}Rn and its short-lived progeny ^{218}Po, and ^{214}Po are measured.

2.5 Calibration

Two calibration sources of 42.3 ± 3% and 71.7 ± 3% Bq respectively, were prepared in one polyethilene vial each using the certified ^{226}Ra solution. Each one with 10 mL of water grade 3 including the ^{226}Ra and 10 mL of scintillation cocktail. 30 days were allowed for the ^{226}Ra and ^{222}Rn to reach equilibrium. Finally, sources were measured after 3 hours of extracting the Rn to the organic phase by agitation. Values of 2.24 ± 3% and 2.22 ± 3% of efficiency were obtained (alpha region) respectively giving an efficiency average of 2.23 ± 3%. Alpha spectrum is showed in Figure 2.

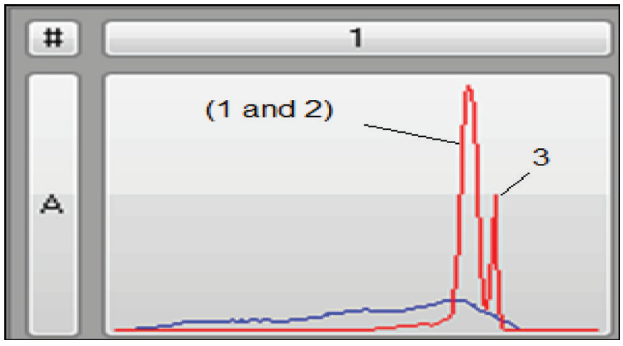

Figure 2. Alpha spectrum with LSC, 1) ^{222}Rn (5.489 MeV); 2)^{218}Po (6.002 MeV); 3) ^{214}Po (7.687 MeV).

Two blank samples were prepared, keeping the proportion of 10 ml of scintillation cocktail and 10 mL from a 3 grade water. Sample Preparation and counting Samples from screening that exceeded the regulatory limits were prepared after more than 30 days those were chosen in time according

to the measuring method agreement. They were counted as well, in LSC counter after Rn was extracted to the organic phase by agitation after elapsed 3 hours so the ^{218}Po and ^{214}Po reached the secular equilibrium with ^{222}Ra. Samples were counted for 4 hours to get a minimal detectable concentration (MDC) of 0.32 Bq/L for 2.1 counts per minute (CPM) of average blank sample.

3. Results

From the 1,100 drinking-water wells selected in the screening program, 25 exceeded the Mexican normative limits for Gross alpha beta (0.56 Bq/L and 1.85 Bq/L respectively).

According to WHO recommendations, the content of ^{226}Ra in the water samples from such wells was measured using the methodology described above. Geographical location by State of each well as the measured values of ^{226}Ra of each sample is showed in Table 3.

Table 3: location of wells which samples exceeded the limit values of Gross alpha-beta radioactivity and its corresponding content of ^{226}Ra measured with LSC.

No	State	latitude	Longitude	Ra-226 (Bq/L)
1	DURANGO	24.18502	−103.63499	<0.32
2	DURANGO	24.84292	−104.48885	<0.32
3	SAN LUIS POTOSI	22.16275	−101.86761	<0.32
4	SAN LUIS POTOSI	22.16275	−101.86761	<0.32
5	SAN LUIS POTOSI	22.62326	−101.70246	<0.32
6	SAN LUIS POTOSÍ	22.19879	−100.88663	<0.32
7	GUANAJUATO	20.73339	−101.91014	<0.32
8	ZACATECAS	22.72228	−102.49688	<0.32
9	CHIHUAHUA	28.58921	−105.54731	0.33 ± 6%
10	EDOMEX	20.02586	−100.10232	<0.32
11	EDOMEX	20.02552	−100.10368	<0.32
12	CHIHUAHUA	28.87427	−106.23605	<0.32
13	CHIHUAHUA	27.46720	−105.28491	<0.32
14	CHIHUAHUA	28.09053	−105.52504	<0.32
15	CHIHUAHUA	28.72672	−105.95289	<0.32
16	GUANAJUATO	20.55670	−101.16149	<0.32
17	TAMAULIPAS	25.00335	−98.316658	<0.32
18	DURANGO	24.87026	−104.77324	<0.32
19	HIDALGO	20.73600	−99.35800	<0.32
20	DURANGO	24.75929	−104.53577	<0.32
21	GUANAJUATO	20.53763	−101.16084	<0.32
22	GUANAJUATO	20.55368	−101.16972	<0.32
23	GUANAJUATO	20.54177	−101.17010	<0.32
24	SONORA	29.40136	−110.43803	0.59 ± 5%
25	AGUASCA–LIENTES	22.21557	−102.16878	0.34 ± 6%

4. Discussion

Only 25 of the 1,100 wells exceeded the Mexican regulatory value in terms of Gross alpha-beta radioactivity values, that constitutes 2.5% of the wells sampled and analyzed.

According to WHO recommendations, it is necessary to find out which radionuclides are they contained within the samples that exceed the limit values, in this case the ^{226}Ra was measured since this is the most important radionuclide from the radiological point of view. The guideline recommended by WHO for ^{226}Ra is 1 Bq/L. From the samples measured, only 3 were higher than the established CMD value that was 0.32 Bq/L.

The three samples that exceeded the CMD value for ^{226}Ra did not exceed the guide value that is 1 Bq/L. This means that as for the ^{226}Ra it is not necessary to take any action, however it is necessary to evaluate the other radionuclides of natural origin found in the water samples, that is, those corresponding to the natural chains of ^{232}Th, ^{235}U and ^{238}U.

Regarding the radiological risk associated, with the values obtained, in 97.5% of the samples and the wells considered, the doses would be less than 0.1 mSv/year, since that is the basic for IDC, that is an important result, due that, from the radiological point of view, drinking water does not constitute any risk in almost all sampled and measured wells.

Regarding the measurement it is necessary to establish that the method allows to have an adequate detection limit of 0.32% of the guide value for ^{226}Ra (1 Bq/L) in counting times of 4 hours, without requiring any additional preparation in the sample, which allows measuring of the order of 5 samples daily, due that the system can be programmed to measure the samples automatically, the evaluation is very simple.

The sample counting time can be reduced by evaporating them in a manner similar to those concentrated to be measured by gamma spectrometry, in which 20 L is concentrated to 0.5 L and even the detection limits reached with the scintillation method are not achieved. The main

advantage of the method by LSC is due to the measurement efficiency of 2.23, when values of efficiency about 0.01 are typical for gamma spectrometry.

Other disadvantage in gamma spectroscopy is the fact of the marinelli beaker must be sealed to measure ^{226}Ra to avoid release of radon and ^{226}Ra and his descendants are in secular equilibrium.

Conclusions

From the measured samples it is inferred that the great generality of them does not exceed the limit values established in Mexican legislation and that means that the dose to the population due to the ingestion of water from those wells would be less than 0.1 mSv/year so which the radiological risk [20] is imperceptible. As for the content of ^{226}Ra, only 3 exceeded the CMD of 0.32 Bq/L and none exceeded the guideline value recommended by the WHO and therefore no action should be taken. The 1,100 wells constitute approximately one sixth of all water wells in the country, representing a significant amount reflecting all of them.

All sampled and analyzed wells will be re-sampled and analyzed to have a second set of data, taking into account that the radionuclides dissolved in the water are due to the physico-chemical phenomena of the underground wells. The importance of making a more thorough study is that these phenomena is seasonal and, it is advisable to systematically follow the study of the largest number of wells. Drink-water from sampled and analyzed wells does not constitute an appreciable risk from the radiological point of view.

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