Gross alpha and gross beta activities measurements in groundwaters using liquid scintillation counting (LSC)

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Abstract. In this work Authors describe the methodology of gross alpha and gross beta activities determination in water samples. The chosen method is dedicated to LSC and is based on ISO 11704:2018 and it is suitable for ground waters with low and medium salinity, especially drinking or tap waters as well as medicinal waters (with healing properties, using in health resorts). Authors describe the proper sampling, laboratory preparation including radon removal and measurements conditions. The local and European law regulations showing the limits of radioactivity of drinking waters and medicinal waters are presented. This work presents also selected data of gross alpha and gross beta activities from selected research: the highest levels is measured in Jordanian (gross alpha) and in Brazil (gross beta) and it is respectively 3.58 Bq/L and 5.22 Bq/L.

1. Introduction

Groundwaters have different origins, chemical compositions, and their use by human can be different. They are used as utility waters, tap waters (intended for human consumption), or they could be basic minerals (brines, thermal waters, healing waters). Due to the fact that they occur in different places, and therefore come from different reservoir rocks, their qualitative and quantitative composition is different. Waters used in the industry or water supply networks are subject to detailed monitoring - their quality must be controlled. Not only microbiological and chemical safety, but also radiological safety is subject to control. The latter, due to the potential risk of consuming increased effective doses by consumers, is a particularly significant problem. The simplest screening test of waters in terms of the risk associated with ionizing radiation is the measurement of gross alpha and beta activity [1]. Although the basis for introducing these tests was the desire to quickly detect possible radioactive contamination caused by tests of nuclear weapons or nuclear reactor failures, they have retained their popularity to this day, providing a quick screening even for environmental samples. It is worth emphasizing, however, that in order to detect possible contamination of the environment with artificial isotopes, the determination of tritium can also be performed, and for low concentrations, the method requires high sensitivity and precise calibration - and such levels are expected in environmental samples.

2. Natural radioactivity of groundwaters

The composition of groundwater is determined by the composition of reservoir rocks and rocks with which these waters come into contact on their flow path. Depending on the origin, depth of occurrence, and time of flow through aquifers, groundwater has a different chemical and isotopic...
composition. Basically, the ingredients dissolved in groundwater can be divided into those that are beneficial to future users or consumers, and those ingredients whose presence prevents their use. Such ingredients include, among others, radioactive ones that affect the effective dose of potential consumers or patients of health resorts [2]. Groundwaters with increased concentrations of natural radioactive isotopes occur in many places around the world. Sometimes these are natural outflows, including mineral waters or outflows of thermal waters, e.g. in Iran, sometimes their getting to the surface is related to the exploitation of minerals (e.g. in Poland) [3]. The increased radioactivity of groundwaters is influenced in particular by isotopes of radium, uranium and, above all, radon [2,4]. They are both alpha emitters (\(^{238}\text{U}, \, {^{234}\text{U}}, \, {^{232}\text{Th}}, \, {^{226}\text{Ra}}, \, {^{222}\text{Rn}}, \, {^{210}\text{Po}}\)) and beta emitters (\(^{40}\text{K}, \, {^{228}\text{Ra}}, \, {^{210}\text{Pb}}\)). The energies released during the emission of the alpha and the beta particles are different - this should be an important part of interpreting the gross alpha and gross beta activities.

2.1. Law regulations

One of the natural sources of ionizing radiation in the human environment are radioisotopes present in groundwaters. When the waters are used as drinking water or tap water, their quality is controlled in accordance with local regulations. These are based on European directives or guidelines of the World Health Organization [5-7].

In addition to quality control and chemical or microbiological purity, it is recommended - depending on the use - radiation monitoring of these waters. The content of the individual isotopes as well as the total alpha and beta radioactivity are measured. The reason and the basis for performing radiochemical tests in environmental samples are not only the requirements for water producers, but also scientific geochemical research - radioactive isotopes are used in geochemistry as environmental tracers that allow the analysis of geochemical processes occurring in the groundwater environment [8]. However, gross activity determination is required only by current legislation. It does not yield any usable results from a scientific point of view because of different decays’ energies of different isotopes.

In each country, a number of legal regulations provide the quality of water intended for consumption or used for other purposes, e.g. for therapeutic and recreation purposes.

In Poland, depending on the future use of these waters, the parameters of its quality (radioactive substances levels) are described in the following legal acts:

2.1.1. Waters intended for human consumption.

Regulation of the Minister of Health on the quality of water intended for human consumption [9] implements Council Directive 98/83/EC [5] and Council Directive 2013/51/EURATOM [6]. The requirements for radioactive substances refer to: radon for which the parametric value is 100 Bq/L, tritium, the parametric value of 100 Bq /L, and the effective dose of 0.10 mSv/year. The limits for other isotopes activities concentrations in waters are also determined, e.g. permissible concentration of \(^{226}\text{Ra}, \, {^{228}\text{Ra}}\) and uranium isotopes.

According to the assessment methodology, recommended by WHO [7], initial screening should be performed for both high \(\alpha\) and \(\beta\) activity. If the measured activities concentrations for gross \(\alpha\) and \(\beta\) are below 0.5 Bq/L and 1 Bq/L respectively, then no further action is required.

2.1.2. Medicinal (healing) waters.

Polish Act of 9 June 2011 – Geological and Mining Law [10] determines the parameters that should be met by water to be considered as therapeutic product – medicinal water. This water should be groundwater (but not mine drainage) which is neither microbiologically nor chemically contaminated. In addition, it must meet one of the criteria describing the appropriate content of variable physical and chemical characteristics and properties, which may include, e.g. the proper concentration of radon (medicinal, radon water). In Poland such water, with radon activity concentration exceeding 74 Bq/L is medicinal, radon water [10].
Also, according to the Regulation of the Minister of Health of April 13, 2016 [11] in the scope of research necessary to determine the therapeutic properties of waters and gases, it is necessary to examine the physical and physicochemical properties, including gross $\alpha$ and $\beta$ activity $\alpha$, $\beta$ as well as $^{226}$Ra and $^{222}$Rn concentration.

2.2. Gross alpha and gross beta activities in groundwaters

Research on gross alpha and beta radioactivity is carried out by many research centers around the world. They are often the first screening analyzes aimed at recognizing whether a given area of water occurrence may be characterized by increased concentrations of radioactive isotopes. Knowing the properties of waters and soils is often the basis for learning about the properties of food that is produced in a given area with the use of these soils and waters [12].

Table 1 summarizes the archival results of measurements of gross alpha and beta radioactivity in water samples from various countries. The minimum and maximum values are presented, while the values marked with (*) are average values. Various types of water were tested - spa waters, spring waters, bottled water, thermal water, tap waters, but the test method was common - the liquid scintillation counting.

| Location/Country [ref.] | Gross alpha activity $Bq/L$ | MDA$^c$ $Bq/L$ | Gross beta activity $Bq/L$ | MDA$^c$ $Bq/L$ | Type of water | Number of measurements |
|-------------------------|----------------------------|----------------|---------------------------|----------------|----------------|------------------------|
| Andalusia – Spain [13]  | 0.07-2.42 (0.54$^a$)       | 0.02           | 0.10-5.80 (0.22$^a$)      | 0.05           | spa water     | 31                     |
| Balaton Upland Region-  | 0.032-1.749 (0.189$^a$)    | 0.0008         | 0.033-2.015 (0.209$^a$)   | 0.003          | spring water  | 31                     |
| Hungary [14]            | <1-0.428                   | 0.8            | 0.08-5.22                 | 0.8            | spa groundwater | 75                   |
| Dhaka – Bangladesh [16] | 0.0007-0.0010 (0.0008$^a$) | not given      | 0.0655-0.0773 (0.0715$^a$) | not given      | bottled water | 16                     |
| Ireland [17]            | <0.008-0.2508 (0.0545$^a$) | 0.005$^b$      | 0.0483-0.5536 (0.1117$^a$) | 0.005$^b$      | groundwater   | 203                    |
| Jordan [18]             | 0.26-3.58 (1.57$^a$)       | 0.11           | 0.51-3.43 (1.62$^a$)      | 0.28           | groundwater   | 87                     |
| Katsina (Rafin Dadi) –  | 0.080-2.300                | not given      | 0.120-4.970               | not given      | groundwater   | 40                     |
| Nigeria [19]            |                           |                |                           |                |                |                        |
| Ankara Province –       | 0.09-2.58 (1.67$^a$)       | 0.05-0.41      | 0.25-2.61 (1.32$^a$)      | 0.04-0.29      | thermal water | 5                      |
| Turkey [20]             |                           |                |                           |                |                |                        |
| Kumasi – Ghana [21]     | 0.0157-0.1427 (0.0423$^a$) | not given      | 0.1220-0.2800 (0.1732$^a$) | not given      | underground water | 8                     |
| Los Angeles – USA [22]  | (0.05$^a$)                 | not given      | (1.85$^a$)                | not given      | well water    | unspecified            |
| Northern Vietnam [23]   | 0.0046-0.1190 (0.0373$^a$) | 0.0018         | 0.001-0.189 (0.0554$^a$)  | 0.0016         | spa and mineral waters | 8                     |
| Nevesehir – Turkey [24] | 0.008-0.380 (0.192$^a$)    | 0.007          | 0.120-3.470 (0.579$^a$)   | 0.008          | groundwater   | 21                     |
| Mandya – India [25]     | 0.0585-0.0645 (0.0276$^a$) | not given      | not measured              |               | groundwater   | 10                     |
| Upper Silesia – Poland  | 0.04-0.14                 | not given      | 0.16-0.33                 | not given      | tap water     | 1                      |
| [26]                    |                           |                |                           |                |                |                        |

$^a$ Average  
$^b$ Typical Minimum Detectable Activities  
$^c$ Minimum Detectable Activities

Among the presented data, the highest values of the measured alpha radioactivity were recorded in Jordan, where it reached the maximum value of 3.58 Bq/L (with the average of 87 measurements
being 1.57 Bq/L) [18]. The highest value of gross beta radioactivity was recorded in the spa water sample from Andalusia - 5.80 Bq/L. The average of 31 measurements of spa waters samples from Andalusia is only 0.22 Bq/L, so the occurrence of water with such high beta activity was probably rare or single [13]. Additionally, the mean results of alpha and beta activity concentrations were the highest for the waters examined in Jordan [18]. The occurrence of high activities may result from the fact that the reservoir rocks of these waters are rocks such as sandstones, shales, which contain increased thorium concentrations [18]. Also in other places, occurrences of groundwaters and spring waters with relatively high alpha and beta activities were recorded in water samples taken from Brazil, Hungary, and Turkey [14, 15, 20, 24].

When analyzing the results presented in Table 1, it can be noticed that increased concentrations of gross alpha and beta activity were obtained for groundwater and thermal waters, which can be explained by the presence of uranium and thorium isotopes in reservoir rocks, as well as possibly increased mineralization of these waters. It is known that with the increase of TDS (total dissolved solids), the probability of the presence of radioactive isotopes in water also increases [2, 27].

3. Method of measurement

The total alpha and beta radioactivity consists of all alpha and beta decays from the different isotopes present in the sample. Although it seems more reasonable to determine individual isotopes, the method for determining the sum of alpha and beta activities is still in use. Each radioactive isotope decays by emitting an alpha or beta particle with a different recoil energy, so quantitatively the sums of alpha or beta decays cannot be compared to each other. It is extremely important to bear this fact in mind when interpreting the results. Another aspect that makes the interpretation of the results more difficult is the removal of gaseous radon from the sample before the measurement - it is part of any gross alpha and gross beta determination method. Radon often has the greatest influence on the radioactive properties of water [4, 28]. An important fact is also the inability to convert the final result to the time of water outflow from the aquifer or its collection. Each radioactive isotope decays at a different rate (with a different half-life), and the conducted study does not give any knowledge about which isotope affects the sum of alpha and beta activities in a given sample.

Among different methods useful to determine the gross alpha and beta water activity (e.g. evaporation or co-precipitation followed by measurement with gas proportional counter), the liquid scintillator technique is the simplest. The following describes, based on the European standard [29], the method of sampling natural waters, laboratory preparation of measuring samples and determination of total alpha and beta activity using a liquid scintillation counter.

3.1. Sampling

European Standard ISO 11704:2018 [29] recommends that 0,1L to 1L of water should be collected into a plastic bottle for testing the gross alpha and beta activity of groundwaters. Water sampling can be performed in accordance with the ISO 5667-3:2018 [30]. It is recommended that immediately after taking the water sample, it should be filtered (if necessary - assess whether the sample contains solid impurities, such as sand or leaves) and nitric acid (HNO3) added to the bottle with water to obtain a pH not lower than 1.7 ± 0.2 or 2.7 ± 0.2 depending on the further handling of the sample. It should be noted that adding nitric acid to the collected water sample allows minimizing the loss of radioactive isotopes as a result of adsorption. Adding nitric acid is especially important when acidification of the sample takes place before the filtration process because it allows desorption of isotopes previously.

3.2. Laboratory procedure

After the water sample is transported to the laboratory, the estimation of TDS (total dissolved solids) is needed and one of the two sample preparations methods described below has to be chosen. The salinity of the tested water also determines the pH to which the sample should be brought. Handling procedures of waters with salinity levels greater than 500 mg/L: 50g (m1) is sampled into a beaker and acidified with nitric acid if the sample has not been acidified immediately after sampling in the field or
laboratory directly after transportation. The pH required for waters with this salinity is $1.7 \pm 0.2$. Removal of the gaseous isotope $^{222}\text{Rn}$ dissolved in water requires heating of the water sample to $80^\circ\text{C}$ and its continuous stirring for 30 minutes. The sample is reweighted ($m_2$) after it cools down, considering the evaporation of the sample during heating.

In the case of water sample with a TDS lower than 500 mg/L the handling process differs. Thermal preconcentration of such sample is required to increase the sensitivity of the method. 200g ($m_1$) of the collected sample is transferred into a beaker and, if the sample has not been previously acidified, nitric acid is added to obtain a pH of $2.7 \pm 0.2$. Evaporation of the sample to 20g is then required and weighting it ($m_2$) after the sample has reached room temperature.

Hard waters (dry residue more than 500 mg/L) may give the salt precipitations or to may affect difficulties homogenization with the scintillation cocktail.

The test sample (taken from prepared, evaporated, or concentrated water, to a mass of $m_3$) with a mass of about 8 g ($m_3$) should be transferred to a scintillation vial (preferably PET or Teflon-coating vial). The scintillation vial requires purification with ethanol or methanol before use. Then 12 ml of scintillation cocktail (e.g. Ultima Gold A B) is added to the sample and the mixture is shaken to mix the scintillator with the water sample, and then place to the counter (LSC). Measuring conditions could be different. The authors recommend at least 9 measuring cycles of 60 minutes for each vial.

Finally, it is possible to calculate the exact weight of the test sample according to the formula (1):

$$m = \frac{m_1m_3}{m_2}$$

where:

$m$ – mass of the test sample, g
$m_1$ – mass of initial sample subject to heating or concentration, g
$m_2$ – mass of heated or concentrated sample, g
$m_3$ – mass of heated or concentrated sample transferred to the vial, g

### 3.3. Set-up parameters and calibration recommendations

Before performing this type of measurement, it is important to standardize and calibrate the method. The method using liquid scintillation counters allows for quick measurements, but requires certain set-up parameters. One of them is PSA (pulse shape analysis) - a parameter that guarantees the proper separation of alpha counts from beta counts. In order to find the optimal PSA, the standard [29] recommends performing a test with standard solutions and preparing a spillover diagram. The test consists in making a measurement series of calibration sources - alpha emitter, as $^{241}\text{Am}$, or $^{238}\text{U}$, and beta emitter, e.g. $^{40}\text{K}$ or $^{90}\text{Sr}$ with the use of different discrimination parameter PSA.

The diagram below shows the result of such a test performed by the authors, based on the calibration sources test: $^{241}\text{Am}$ and $^{90}\text{Sr}$ (in equilibrium with $^{90}\text{Y}$). Thanks to these measurements, it can be concluded that the optimal PSA is 80, and the misclassification of the counts is 4%.
Figure 1. The diagram of the optimum PSA level determination for plastic vial in UltimaGold AB scintillation cocktail.

The method, in addition to determining the proper discrimination parameter, also requires a standard calibration, e.g. a series of tests leading to the difference between the number of counts measured by the spectrometer and the theoretical amount, which is actually counting efficiency. Measurements of blank samples will allow to estimate the influence of the background, and allow to determine the lower limit of detection of a given method.

The method should be well standardized, because it is more effective for high concentrations and for artificial isotopes, and its use today is no longer associated with the rapid detection of possible contamination after nuclear weapons tests - for such tests it is helpful to determine the concentration of tritium in an environmental sample. Moreover, LSC is burdened with interferences and quenching [31].

4. Summary
Gross alpha and gross beta activity determination is a kind of screening method. Every researchers always start the investigations with screening but in this case it is more worth to determine single isotopes which may have an impact of radioactive properties of groundwaters. The values of total alpha or beta radioactivity gives no information about the energy that this activity carries - it is not known what isotope decays affect it. Each radioisotope decays with its half-life. However, radioactive decays (alpha, beta, gamma) have different energies. It is also impossible to convert the obtained results into the actual water activity at the time of outflow from the aquifer or the time of its collecting (from the intake, well or tap). This is the main reason for such measurements to be relatively widely criticized by the scientific community.

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