MONITORING OF GROSS ALPHA, GROSS BETA AND TRITIUM ACTIVITIES IN PORTUGUESE DRINKING WATERS

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1. INTRODUCTION

Natural waters contain a number of alpha (^{238}U, ^{230}Th, ^{226}Ra, ^{210}Po) and beta emitters from the natural decay series of uranium, thorium and actinium, the primordial isotope, ^{40}K and artificial isotopes, such as ^{90}Sr and ^{137}Cs. The tritium (^{3}H) a radioactive hydrogen isotope is also present in natural waters not only due to natural processes but mainly as a product of discharges from nuclear fuel cycle facilities and nuclear tests. The long lived α emitters and the high-energy β emitters have significant radiotoxicity. Drinking waters containing high concentrations of these radionuclides may originate a serious radiological health problem to the population.

The Portuguese Decree Law nº243/2001, transposed from the Drinking Water Directive (98/83/CE), approves the guidelines to drinking water quality. The guidance levels defined on the Decree Law for gross alpha, gross beta and ^{3}H concentrations in drinking waters are 0.1 Bq L^{-1}, 1.0 Bq L^{-1}, and 50 Bq L^{-1}, respectively. The gross alpha activity includes all the alpha emitters, excluding radon and the gross beta activity includes all beta emitters, excluding ^{3}H. The approach taken in the guidelines for controlling the radiological hazards consists in an initial screening where the total radioactivity presents in the form of alpha and beta radiation is first determined, without regard to the identity of specific radionuclides. However, if the guidance levels values are exceeded the determination of the individual activity concentration of specific radionuclides is recommended (Guidelines for Drinking Water Quality).

In Portugal, the standard procedures used for gross alpha and gross beta drinking water analyses are based on ISO standard methods (Portuguese guidelines NP 4332/ 1996 and NP 4330/ 1996). The water samples are evaporated to dryness, calcined and the activity of the residue measured with gas proportional counters. However, some authors (Semkow et al., 2004) recognize difficulties and interferences in gross alpha and gross beta detection using gas-proportional counting.

The availability of low background liquid scintillation counter equipped with alpha and beta discrimination provides an alternative for gross alpha and beta determinations and offers several advantages over the traditional procedure. The liquid scintillation (LSC) technique requires a minimal sample preparation time. There is no self-absorption problem like the one observed in the conventional analytical method where the sample is evaporated to dryness

on a planchet. In the liquid scintillation technique the sample is homogeneously mixed with the scintillation cocktail, the counting geometry is essentially 4π, providing high efficiencies (closer to 100%) and eliminating matrix effects (Sanchez-Cabeza et al. 1993; Sanchez-Cabeza and Pujol 1995; Burnett et al. 1999; Kleinschmidt 2004; Wong et al. 2005).

A methodology based on LSC technique for the determination of gross alpha and gross beta activities in drinking waters was developed. Counting parameters have been optimized for the best possible separation of alpha and beta emitters and validation tests have also been performed in order to assure the accuracy of the method (Lopes et al., 2004; Lopes and Madruga, 2006)

A set of drinking water samples was analyzed and the gross alpha and gross beta measurements performed using the two methodologies. The LSC technique was tested by comparing its outcomes with ISO procedure. The tritium determination has also been carried out by liquid scintillation following the Portuguese guidelines (NP 4362/1997) with isotopic enrichment.

This study has been developed in the framework of a collaborative protocol between the Nuclear and Technological Institute (ITN) and the Portuguese Association for the Consumer Defence (DECO PROTESTE).

2. MATERIAL AND METHODS

The drinking water samples were collected in cities and villages from the tap (public water supply systems) from wells, artesian bore holes and springs, located in the Centre and North regions of Portugal. The water samples for alpha and beta determinations were acidified at the collection.

Gross Alpha/ Gross Beta Measurements Using NP 4332/1996 and NP 4330/1996 Guidelines

Acidified water samples were evaporated until almost 50 ml then precipitate with 1 ml of concentrated sulfuric acid. The sulfates were calcinated at 350ºC, during one hour. The residue was transferred to steel planchets of 50 mm diameter and the measurement of alpha and beta activity was performed simultaneously with a gas proportional counter (TENNELEC, Canberra) calibrated with alpha (^{241}Am) and beta (^{40}K) standards.

Gross Alpha/ Gross Beta Measurements by Liquid Scintillation Counting

Acidified water samples (1000 ml) were pre-concentrated to volumes ranging from 80 to 120 ml by slow evaporation on a hot plate. One aliquot of 10 ml of the aqueous concentrate was withdrawn and added to 10 ml of Ultima Gold LLT (Packard) in 22 ml glass scintillation vial (Packard). LSC was performed by a Tri-Carb (Packard) equipped with alpha and beta discrimination. The counting time used for each sample and background samples was 240 minutes with an open window of 0-1000 keV for alpha and of 0-2000 keV for beta energy range. Detection efficiency was evaluated with internal standards (^{241}Am and ^{90}Sr/ ^{90}Y) at a optimum PDD level of 127. This value was obtained using alpha (^{241}Am; 24 Bq L^{-1}) and beta (^{90}Sr/ ^{90}Y; 23 Bq L^{-1}) standards, as described elsewhere (Lopes and Madruga, 2006).

Tritium (^{3}H) Measurements Using NP 4362/1997 Guidelines with Isotopic Enrichment

Determination of ^{3}H concentration in drinking waters was performed by liquid scintillation counting. The water samples were purified by distillation, followed by isotopic enrichment procedure using electrolysis through direct current. After the neutralization procedure by addition of $PbCl_2$, a new distillation was performed in order to separate the PbO from the water. Afterwards, one aliquot of 8 ml was withdrawn to a glass scintillation vial with 12 ml of Ultima Gold LLT scintillation cocktail (Packard) at a sample pH value ranging from 5 to 7. The samples were measured in a Liquid Scintillation Counter (Beckman LS6500). The counting efficiency was evaluated with tritiated water standards (Amersham). The background samples were prepared using 12 ml of liquid scintillation cocktail, mixed with 8 ml of the reference water (with very low tritium concentration). All measurements were performed using 300 minutes of counting time.

3. RESULTS AND DISCUSSION

The results of gross alpha and gross beta activities using the Portuguese Guidelines are presented in Table 1. It can be observed that the values of gross beta activity range of one order of magnitude, from 0.018 ± 0.003 to 0.457 ± 0.015 Bq L^{-1}. However, these values are below 1 Bq L^{-1}, the guidance level recommended. For gross alpha the activities range from values lower than 0.015 Bq L^{-1} (minimum detectable activity) to 0.330 ± 0.026 Bq L^{-1}. In general, the alpha activity are lower than recommended level (0.1 Bq L^{-1}) with the exception for the samples referenced as #22, #29, #30, #36, #39, #40 e #49, which exceeded this value. These higher values are related with the geologic characteristics of the soils. The water samples are originated from the Centre and North regions where the bedrock is mainly granite, and enriched in natural radioactivity. These results do not imply that these waters are unsuitable for consumption but should be regarded as indication for radionuclide specific analyses. However, the concentrations of uranium, radium, polonium and dissolved radon in tap waters collected in these regions are generally low (Carvalho et al. 2005) and below the guidance levels recommended by WHO.

The tritium activity values, determined using the Portuguese Guideline with isotopic enrichment (Table 1) are, in general, lower than the minimum detectable activity (0.8 Bq L^{-1}). The quantified values range from 0.81 ± 0.63 to 2.44 ± 0.63 Bq L^{-1}. These values are positioned very below the recommended level (50 Bq L^{-1}).

These results are in agreement with others studies already performed concerning the radiological quality of the Portuguese drinking waters (Lopes et al. 2004; Carvalho et al. 2004; Madruga et al. 2005). In general, the drinking waters radioactivity levels are low and the waters are suitable for human consumption.

Some of these drinking water samples were analyzed for gross alpha and gross beta by Liquid Scintillation Counting (LSC). The sample preparation method provides quenching level (tSIE - transformed Spectra Index of the External standard) ranging from 192 to 240. In order to determine the counting efficiencies for that quenching level, ^{241}Am and ^{90}Sr/ ^{90}Y were added, as internal standards, to the drinking water samples. Counting efficiencies of 94.6% and 92.1% were the higher values found for the alpha and beta emitters, respectively, using a PDD setting at 127. The mean value of background counts in the 0-1000 keV region was 2.49 cpm for alpha and 14.67 cpm for beta emitters. The minimum detectable activity values of 0.096 Bq L^{-1} and 0.235 Bq L^{-1} were achievable for alpha and beta measurements, respectively, for a confidence level of 95% with a total counting time of 240 minutes and for a sample concentration factor of 0.09. Comparing the results, the gross beta values obtained by LSC technique are higher than the beta activities determined by ISO standard methodology. It can be explained by an unsuitable alpha/ beta discrimination which is under investigation. The gross alpha values for the samples analyzed by LSC technique are below the minimum detectable activity value (0.096 Bq L^{-1}) with the exception for the water sample referenced as #49 which presents a activity value of 0.24 ± 0.16 Bq L^{-1}. This water sample presents also the highest value (0.33 ± 0.03 Bq L^{-1}) for alpha activity of all the samples analyzed using the ISO standard *methodology (Table 1). In order to decrease the detection limits and to allow the detection of lower alpha activities the samples counting time was increased to 360 minutes. In the same way, only the alpha activity corresponding to the water sample referenced as #49 was quantified. It is justified to improve the technique by increasing the concentration factor of the sample. In further analyses the samples may be pre-concentrated to a volume of approximately 50 ml in order to achieve lower minimum detectable activities for gross alpha and gross beta measurements.*

Table 1 – Gross alpha, gross beta and tritium activities (Bq L^{-1} ± 2σ) in drinking water samples.

Sample Reference	Gross Alpha	Gross Beta	Tritium
#A	< MDA	0.024 ± 0.004	< MDA
#B	0.017 ± 0.005	0.057 ± 0.004	< MDA
#1	< MDA	0.069 ± 0.005	1.27 ± 0.62
#4	< MDA	0.037 ± 0.004	< MDA
#6	0.056 ± 0.008	0.119 ± 0.005	< MDA
#8	< MDA	0.026 ± 0.003	< MDA
#9	0.019 ± 0.005	0.042 ± 0.004	< MDA
#10	0.075 ± 0.008	0.064 ± 0.004	< MDA
#11	0.017 ± 0.006	0.080 ± 0.005	< MDA
#13	< MDA	0.018 ± 0.003	< MDA
#14	0.060 ± 0.007	0.049 ± 0.004	< MDA
#15	0.017 ± 0.005	0.024 ± 0.003	< MDA
#17	0.073 ± 0.009	0.106 ± 0.005	< MDA
#18	0.020 ± 0.006	0.061 ± 0.004	0.81 ± 0.63
#19	0.022 ± 0.006	0.053 ± 0.004	< MDA
#20	0.021 ± 0.009	0.055 ± 0.006	2.44 ± 0.63
#21	0.057 ± 0.008	0.074 ± 0.004	< MDA
#22	0.161 ± 0.016	0.196 ± 0.008	< MDA
#23	0.018 ± 0.005	0.028 ± 0.003	< MDA
#24	< MDA	0.027 ± 0.003	< MDA
#25	< MDA	0.027 ± 0.003	1.65 ± 0.59
#29	0.179 ± 0.012	0.169 ± 0.006	< MDA
#30	0.161 ± 0.025	0.238 ± 0.014	< MDA
#31	0.038 ± 0.006	0.070 ± 0.004	< MDA
#32	< MDA	0.039 ± 0.004	< MDA
#34	0.037 ± 0.006	0.055 ± 0.004	< MDA
#36	0.124 ± 0.010	0.128 ± 0.005	1.19 ± 0.63
#37	0.018 ± 0.005	0.044 ± 0.004	< MDA
#39	0.162 ± 0.011	0.158 ± 0.006	< MDA
#40	0.115 ± 0.014	0.162 ± 0.008	< MDA
#41	0.019 ± 0.009	0.044 ± 0.005	< MDA
#42	0.025 ± 0.005	0.054 ± 0.004	1.77 ± 0.63
#43	0.032 ± 0.005	0.038 ± 0.003	< MDA
#45	0.020 ± 0.004	0.031 ± 0.003	< MDA
#46	0.039 ± 0.008	0.072 ± 0.005	< MDA
#47	0.073 ± 0.008	0.083 ± 0.004	< MDA
#49	0.330 ± 0.026	0.457 ± 0.015	< MDA
#51	0.032 ± 0.006	0.047 ± 0.004	1.75 ± 0.62
#52	0.023 ± 0.005	0.031 ± 0.003	< MDA
#53	< MDA	0.031 ± 0.003	< MDA

MDA- Minimum detectable activity for gross alpha = 0.015 Bq L^{-1}; Minimum detectable activity for tritium = 0.8 Bq L^{-1};

4 CONCLUSIONS

The gross beta and tritium activities in the forty Portuguese drinking waters analyzed using the ISO standard methods (Portuguese Guidelines) are below the guidance levels proposed in the Portuguese Drinking Water Quality Guidelines. In what concerns the gross alpha activity only 18% exceeded the recommended level. In general, it can be concluded that the ingestion of these drinking waters does not create a radiological hazard to the human consumption, however, more detailed analyses will be necessary mainly the determinations of the individual alpha emitters radionuclide concentrations.
The minimum gross alpha and gross beta detectable activities by LSC methodology are higher than for the proportional counting technique (ISO method). Higher concentration factors will be needed to reach lower required detection limits.

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