



Critical remarks on gross alpha/beta activity analysis in drinking waters: Conclusions from a European interlaboratory comparison

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HIGHLIGHTS

- Gross alpha/beta standard methods for drinking water analysis are discussed.
- Large spread of results (up to 2 orders of magnitude) observed in comparisons.
- Sources of interferences are reviewed.
- We propose to use true standardized methods to obtain better measurement results.

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ABSTRACT

The most common gross alpha/beta standard methods used for drinking water analysis are discussed, and sources of interferences are reviewed from a metrological point of view. Our study reveals serious drawbacks of gross methods on the basis of an interlaboratory comparison analyzing commercial mineral water samples with the participation of 71 laboratories. A proposal is made to obtain comparable measurement results using true standardized methods.

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1. Introduction

Gross alpha/beta activity measurement is applied widely as a screening technique in the field of radioecology, environmental monitoring and industrial applications. Water intended for drinking purposes has to be analyzed first for gross alpha/beta activity content according to many different national and international standards and recommendations. Anticipating the new European Union (EU) Drinking Water Directive (EC, 2012) which incorporates gross alpha/beta activity screening levels, the Institute for Reference Materials and Measurements (IRMM) organized an interlaboratory comparison (ILC) to check the fitness for purpose of this method and the performance of European monitoring laboratories. On the basis of the reported values from the 71 participating laboratories, we review some of the most influential parameters on gross measurements.

The claimed main advantages of the gross alpha/beta methods are the relatively low costs, rapidity and simplicity. Although it is one of the simplest, it is also one of the most disputed radioanalytical methods because the determination of gross alpha and beta activities

faces some specific problems that may refute the afore-mentioned claims. There are many sources of interferences in gross alpha/beta measurement that may corrupt the comparability of the measurement results (Arndt and West, 2004; Rusconi et al., 2006; Semkow et al., 2004; Montaña et al., 2012). First one is related to the radionuclide composition of the sample. During gross alpha/beta activity measurement, a mixed radionuclide composition must be simultaneously measured. Drinking water samples may contain different naturally occurring alpha (^{238}U , ^{234}U , ^{232}Th , ^{226}Ra and ^{210}Po) and beta (^{40}K , ^{228}Ra and ^{210}Pb) emitters, and artificial radionuclides (^{241}Am , ^{90}Sr) in various concentrations (UNSCEAR, 2000). Moreover, most of these are members of a complex decay chain, therefore the ingrowths of the daughter products influence the measurement result.

The second important source of interference is due to the final source thickness that causes self absorption of the emitted particles already in the source itself. In this respect, it is crucial to use standardized methods (Jobbágy et al., 2010). The WHO recommends that, "Where possible, standardized methods should be used to determine concentrations of gross alpha and beta activities" (WHO, 2011). For this reason, the most common standard methods – based on direct evaporation, co-precipitation and liquid scintillation counting – are discussed in this paper with respect to the sample preparation and counting techniques. Regarding the measurement methods, the influence of the following parameters must be considered: counting efficiency, self absorption, moisture absorption,

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chemical recovery and the interferences due to the isotopic composition of the water sample. Experimental comparisons of the gross alpha/beta standard methods were done using real drinking water samples with different salinity and radionuclide activity concentration.

Besides the pitfalls of the gross measurements, the paper also tries to give examples where gross measurements can be used as a rapid alternative technique to the radionuclide-specific analysis.

2. Materials and methods

2.1. Reagents

All the chemicals (conc. H_2SO_4 , FeCl_3 , BaCl_2) were analytical grade and all the stock solutions were prepared using de-ionized water. Three water samples, with different salinity and radionuclide activity concentrations, were used for the described experiments and in the interlaboratory comparison. Two water samples (Water A and B) were commercially available natural mineral waters. The third one (Water C) was prepared by spiking de-ionized water with a known activity of ^{241}Am and $^{90}\text{Sr}/^{90}\text{Y}$ solutions standardized at IRMM by liquid scintillation counting using the CIEMAT/NIST method. The total dissolved solid was set to a final total concentration of about 10 mg/L by adding the following inactive inorganic salts: NaCl , CaCl_2 and $\text{Sr}(\text{NO}_3)_2$. The major sources of gross alpha activity for Water A are ^{234}U and ^{238}U (~ 40 mBq/L each), for Water B this is ^{226}Ra (~ 330 mBq/L) and for Water C ^{241}Am (~ 950 mBq/L).

2.2. Sample preparation

Sources were prepared in accordance with ISO 9696/9697 (“thick source method”) or ISO 10704 (“thin source method”). The surface density of a source prepared under ISO 9696/9697 must exceed 10 mg/cm². An aliquot of sample was evaporated to dryness, and the dried residue converted to sulfate form by sulfuric acid and ignited at 350 °C for an hour (ISO 9696, 2007; ISO 9697, 2008). The surface density of the source in the thin source method must be below 5 mg/cm², and has been described previously (ISO 10704, 2009; Montaña et al, 2012; Suarez-Navarro et al., 2002). The pH of the filtered water sample was adjusted with sulfuric acid and heated to purge radon and CO_2 . Then the radium isotopes were co-precipitated as $\text{Ba}(\text{Ra})\text{SO}_4$, whereas uranium, thorium and polonium isotopes are co-precipitated with $\text{Fe}(\text{OH})_3$ after pH adjustment (pH ≈ 7 –8) (ISO 10704, 2009; Suarez-Navarro et al., 2002).

2.3. Gross counting system and activity calculation

For the gross alpha/beta measurement, a 10-detector, low-background gas-flow proportional counting system was used. The high voltage was set to 1450 V and the counting gas (Ar/CH_4 , 90/10) flow was kept stable with a flow rate of ~ 25 mL/min. The gross alpha/beta count of the filtered/dried precipitate was measured in 5 h cycles repeating it several times (from three to twelve cycles).

For the counting efficiency and self absorption experiments, ^{241}Am and ^{90}Sr standard solutions were used, since these are the most frequently used radionuclides for this purpose. Gross alpha/beta activity concentrations were calculated from count rates by following the formulae of the corresponding ISO standard (ISO 9696, 2007; ISO 9697, 2008; ISO 10704, 2009; ISO 11704, 2010).

3. Results and discussion

3.1. Summary of the interlaboratory exercise

After radiochemical characterization of the three water samples at IRMM, they were sent to the European monitoring laboratories for gross alpha/beta analysis. The gross alpha/beta reference values were determined independently from the laboratory comparison from the results determined by the three laboratories involved in the reference value determination (Table 1).

Water C is, in principle, the easiest sample to measure since its gross alpha/beta activity concentration is the highest among the ILC samples. However, from a measurement point of view, the gross alpha activity is not the only key factor, but the alpha/beta emitting radionuclides and the total dissolved solid content have to be considered as well. Taking into account all three factors one can make an order of difficulty in terms of measurement as follows: Water C < Water A \leq Water B.

As is evident from the reported results (Fig. 1 and 2), the outcome of the laboratory comparison exercise is far from satisfactory. The measurement results span a wide range, e.g. for Water C the maximum reported gross beta activity was more than 3000 times higher than the minimum reported gross beta activity.

Furthermore, several laboratories (no. 49, 50 etc.) present for one type of sample a measurement result several times higher than the reference, whilst for another type of sample the same laboratory has a result several times lower. The gross alpha activity results for Water C (spiked sample, i.e. the best case scenario) are sorted according to the applied counting techniques in Fig. 2.

For Water A and B (natural waters) we could observe a similar data spread but with a higher degree of variation for each technique. Possible reasons for the diversity of results are given in the next sections, but a detailed evaluation of the laboratory comparison itself will be published later in a separate report.

3.2. Method comparison

It is well-known that the sample form or geometry play a significant role in producing reliable results from thicker sources, requiring a uniform thickness and a homogeneous layer of residue material on a planchet (60 mm in diameter). The surface density, influencing the self absorption of alpha and beta particles, should be controlled and determined very carefully (ISO 9696/9697; ISO 10704; Montaña et al., 2012; Suarez-Navarro et al., 2002; Semkow et al., 2004; Parsa, 1998). A surface density higher than 10 mg/cm² (ISO 9696/9697) achieves satisfying counting statistics and constant self absorption. The self absorption of the alpha and beta particles limits their counting efficiency to usually less than 50%. It should be mentioned that no energy resolution is possible with proportional counters.

Since the sample is evaporated and later heat-treated, ISO 9696/9697 does not allow determination of the volatile radionuclides (e.g. ^3H , ^{210}Po , ^{137}Cs), which escape from the sample and

Table 1

The reference activity concentration values (A_{ref}) in the ILC water samples with their expanded uncertainties (U_{ref}) with a coverage factor $k=2$. Reference values determined by three laboratories external to the laboratory comparison.

Parameter	Reference value with expanded uncertainty $A_{\text{ref}} \pm U_{\text{ref}}$ (mBq/L)		
	Water A	Water B	Water C
Gross alpha activity	47.5 ± 22.8	434.7 ± 56.6	954.5 ± 77.3
Gross beta activity	309.8 ± 57.4	190.4 ± 32.6	1037.3 ± 83.0
Total dissolved solids (mg/L)	955 ± 44	364 ± 27	10.2 ± 0.1

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