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Current status of gross alpha/beta activity analysis in water samples: a short overview of methods

Viktor Jobbágy · Uwe Wätjen · Jana Meresova

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Abstract Gross alpha/beta measurement is one of the simplest radioanalytical procedures which are applied widely as a screening technique in the field of radioecology, environmental monitoring and industrial applications as well. Due to the uncertainties of gross alpha/beta measurements this method is often the subject of discussions and debates. The aim of this work is to collect information about recently used standard and routine methods concerning gross alpha/beta activity determination in drinking waters in order to get an overview about the current situation and evaluate their possibilities. Sample preparation methods—e.g. evaporation, co-precipitation—and detection systems—e.g. gas flow proportional counting, liquid scintillation counting and scintillation counting—are compared on the ground of literature data. In the course of our work, the following parameters were analyzed and discussed: background, counting efficiency, interferences, sample capacity, minimal detectable activity, typical counting time, time demand of sample preparation.

Keywords Gross alpha/beta activity · Gas flow proportional counter · Liquid scintillation counting · Water quality

Abbreviations

WHO	World Health Organization
EC	European Commission
ISO	International Organization for Standardization
EPA	United States Environmental Protection Agency
MDA	Minimum detectable activity
LSC	Liquid scintillation counting
cpm	counts per minute
TDS	Total dissolved solids
PSA	Pulse shape analyzer

Introduction

Surface and underground water may contain some natural pollutants such as radionuclides which can be transported by them. Radionuclides in water originate from a number of naturally occurring and man-made sources, but in general, natural origin is more of a concern than artificial. As water is essential for human life, it must be consumed daily in various volumes. Nowadays there is an increased demand for reliable and fast screening methods which provide immediate information about the chemical and radiochemical composition of drinking water. It has an outstanding importance in the field of food safety and quality control with an aim to strengthen consumers' security.

In the last few decades, increasing attention is paid to restrict exposure of the public to the naturally occurring radiation. The WHO [1] and the EU Council [2, 3] have determined the reference level of the effective dose received from drinking water consumption at 100 μSv year^{-1}. This value excludes the dose received from ^{3}H, ^{40}K, ^{222}Rn, and radon decay products, but it includes the other alpha- and beta-emitting radionuclides.

In general, gross alpha/beta analysis—which is one of the simplest radioanalytical procedures—is used as the first step of the radiological characterization of drinking waters as a screening method in the field of radioecology,

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V. Jobbágy (✉) · U. Wätjen · J. Meresova
European Commission, Joint Research Centre, Institute for Reference Materials and Measurements (IRMM), Retieseweg 111, 2440 Geel, Belgium
e-mail: viktor.jobbagy@ec.europa.eu
URL: http://irmm.jrc.ec.europa.eu/

environmental monitoring and industrial applications as well. Its main advantages are the relatively low costs and simplicity. Nevertheless, the determination of gross alpha and beta activities faces some specific problems because a mixed radionuclide composition has to be simultaneously measured. Drinking water samples may contain different natural alpha (^{238}U, ^{234}U, ^{232}Th, ^{226}Ra and ^{210}Po) and beta emitters (^{40}K, ^{228}Ra and ^{210}Pb), and artificial radionuclides (^{241}Am, ^{90}Sr) in various concentrations [4]. Most of them are members of a complex decay chain.

In the third edition of WHO guidelines for drinking water quality the recommended levels are 0.5 Bq L^{-1} for gross alpha and 1 Bq L^{-1} for gross beta activities, respectively [1]. If the measured values are below the reference levels of gross activity, the drinking water examined is acceptable for human consumption without any further action with respect to its radioactivity. Otherwise, nuclide specific analysis is required to determine the radionuclide content using more sophisticated, more expensive and time-consuming procedures.

Most of the standards concerning gross alpha/beta measurement [5–10] apply a proportional counter as detector and are mainly based on ISO methods [7–9] for the determination of gross alpha/beta activity in drinking water. The method consists of two steps, the evaporation of the water to dryness and the measurement of the residue deposited on a planchet in a proportional detector.

The counting efficiency of these methods is strongly affected by the total dissolved solids in water and the chemical composition of the sample as well. Besides these standards, some alternative techniques—either based on liquid scintillation counting (LSC) [11–15] or the combination of alpha-particle and gamma-ray spectrometry [16]—have been developed in order to overcome the drawbacks of the standard methods.

On one hand, the paper gives an overview of the recently used techniques; on the other hand, it tries to help finding a suitable gross alpha/beta radioanalytical tool adapted to the laboratory's demands. This work is part of our effort to develop a reliable method to determine reference values for gross alpha/beta activity in water samples to be used for an interlaboratory comparison between EU monitoring laboratories in the near future.

Sample preparation and determination of gross alpha/beta activity

Gas flow proportional counter and scintillation counting

A known amount of water sample is evaporated slowly to complete dryness. The initial volume of the sample varies usually from 0.1 to 2 L as a function of total dissolved solids. It is well known that the sample presentation to the detector plays a significant role in producing reliable results, requiring a uniform thickness, a homogeneous layer of residue material on the planchet.

Attention must be paid to the surface density of the source which influences the self absorption of alpha and beta particles within the final precipitate.

The surface density should be controlled very carefully as written in different standards and protocols [7–10]. It varies from 0.5 to 25 mg cm^{-2} [7–9, 17, 18] in order to achieve satisfying counting statistics.

If the precipitate is hygroscopic and nitrates are present, then the planchet should be heated on an asbestos pad with a gas burner for 1 min to destroy the nitrates in order to reduce water uptake [19].

It is not sufficient to get the appropriate amount of residue, but the surface must be very thin and uniform as well avoiding rough surfaces with encrustations. The final result is significantly affected by technical proficiency as well.

For instance, the standard EPA method—which consists of sample acidification and evaporation steps—results in a nonuniform residue. As is described in more detail elsewhere [18], three main modifications were done to the EPA method in order to improve the homogeneity and the quality of the dried water residues: roughening of surfaces of the planchettes, temperature-controlled heating, and two-step evaporation.

Time is also an important influential factor. For instance, it was discovered by Parsa [20] that short-lived ^{224}Ra ($T_{1/2} = 3.66$ days) can remain undetected because of the time delays between sampling and routine gross alpha analysis. It is certainly possible that high alpha activity from ^{224}Ra could be missed by routine monitoring protocols, because of the lack of a guiding regulation concerning the holding time of water samples collected for routine radioactivity measurements. On one hand, in order to assess the ^{224}Ra contribution the gross alpha activity should be performed as short as possible after the time of sampling (within 48 h), on the other hand, it is recommended that the alpha counting should be delayed by 24 h to reduce anomalies from radon progeny for gross alpha activity [21]. Then the samples can be counted by a low background gas flow proportional counter. In general, counting time may vary from some hours to some days as well.

Here we have to note that, since the sample is evaporated and later treated by heat, this method does not allow determining volatile radionuclides (e.g. ^{3}H, ^{210}Po, ^{137}Cs). These nuclides escape from the sample and from the residue as well during heat treatment, therefore the gross alpha and beta activity concentration might be underestimated. For instance, it was reported that ^{210}Po losses begin to occur above 100 °C and the amount of loss could vary with the chemical form of the element [22, 23].

Some of these drawbacks can be avoided by using co-precipitation for the water sample treatment [24]. The pH of the filtered water sample is set and is heated in order to purge radon and CO_2. Then the radium isotopes are co-precipitated with barium as $Ba(Ra)SO_4$, whereas uranium, thorium and polonium isotopes can be co-precipitated with $Fe(OH)_3$ by adding Fe^{3+} carrier while NH_4OH is used to adjust the pH (~ 6.8). The gross alpha and beta activity of the filtered and dried precipitate is counted by a ZnS(Ag) scintillation detector.

On one hand, this method needs more chemical treatment than the evaporation methods and the precipitate might be hygroscopic, on the other hand, more uniform and homogeneous residues can be obtained especially for highly saline waters (e.g. ocean and mineral waters).

Liquid scintillation counting

Several authors have recently proposed different methods for measuring gross alpha and beta activities in water samples by LSC [11–14].

Ultra low-level α/β-discrimination LSC, due to its high detection efficiency (up to 100%) and low background count rate, is a useful tool for the determination of gross alpha–beta activities [25].

The basic steps of the sample preparation for liquid scintillation counting are very simple. In general, an aliquot of water (50–200 mL) is acidified to $pH = 1.5–2.5$ and then it is slightly evaporated to 10 mL on a hot plate. Sometimes the water should be stirred in order to eliminate radon and its short-lived daughters and to avoid salt precipitation [14]. Then the treated water sample is mixed with scintillation cocktail in a 20 mL low diffusion polyethylene vial. The choice of vial is important. In general, glass vials have higher background than polyethylene vials due to the ^{40}K content, but the organic solvents may diffuse into the wall of polyethylene vials. In order to achieve low background, good efficiency and to avoid diffusion of scintillation cocktail into the walls of the counting vial, the use of Teflon coated low-diffusion polyethylene or low potassium bearing glass vials with copper caps may be necessary [26].

Quenching—which can be chemical, colour or physical—may also be present in real samples. It can reduce the counting efficiency, therefore, a quench correction should be made. For example, higher levels of Fe^{3+} can be found in waters of natural origin. If iron is not removed from them (e.g. in case of spring and mineral waters) it will affect the measurement (colour quench).

It is presented that [11, 12], the separation of beta energies from all alpha energies can be complete. This is not really true, because the alpha/beta energy separation in LSC depends on many factors as is demonstrated [13].

For this reason the correct setting of the different parameters (type of the vial, cocktail, α/β pulse discrimination, the determination of counting efficiency) is essential for gross alpha/beta measurements by LSC. Many other factors, like the physical–chemical behaviour of the radionuclides, dissolved anions and the energies of the emitted particles may influence the detection. The same parameters should be used during the measurement as is set for the calibration for the corresponding radionuclides. As it is mentioned by Rusconi et al. [13], purchasing suitable certified reference materials is difficult.

For the gross α activity measurement an LSC procedure was applied in a recent study [27] and demonstrated that it is a reliable screening assay for non-volatile natural α-emitting radionuclides in drinking waters. It suggests that drinking water samples of total α activities >0.05 Bq L^{-1} could be well identified using the proposed LSC procedure.

An alternative procedure has been developed for gross alpha measurements using LSC and highly specific resin [11]. After the water sample is passed through the chromatographic resin, the resin is removed from the column and dried. Finally, the resin is mixed with an appropriate amount of scintillation cocktail and counted by LSC.

Combination of alpha-particle and gamma-ray spectrometry

An alternative method was developed for the determination of gross alpha and beta radioactivity in water by using alpha-particle and gamma-ray spectrometry [16].

It consists of a two steps evaporation of the water samples. It uses a relatively inexpensive well type NaI(Tl) scintillation detector for counting the gamma-rays and a surface barrier detector for the alpha-particles. This combined method is relatively new, thus not widespread yet and has some limitations as well. Laboratories must have both types of detectors, and the analyst should have experience in the data analysis and system calibration. The determination of pure beta-emitters (^{90}Sr/^{90}Y, ^{228}Ra) can not be done with this method, or in case of ^{228}Ra it is complicated via its daughters.

Compared to the other routine gross alpha and beta measurement techniques, it looks more complicated and time consuming. But it has some important advantages. One of the most important is that a low MDA (minimum detectable activity) can be achieved—0.001 and 0.03 Bq L^{-1} for gross alpha and beta activity, respectively. This method does not require special reagents and lab ware. It allows direct identification of certain radionuclides after the calibration of the system. We have to emphasise, that it can not give accurate quantitative information about alpha emitter radionuclides in the sample. For the nuclide specific analysis more sophisticated and reliable methods should be used (e.g. isotope separation step then alpha spectrometry or LSC).

Discussion

Comparison of detectors and methods

A comparison of the different detectors and methods and a summary of the parameters are shown in Tables 1 and 2.

Gas flow proportional counter

In general gas flow proportional counting has been used for performing gross alpha and beta measurements in drinking water samples. Some of the properties of the detector are influenced by the sample preparation when water is evaporated obtaining the final source in dry residue or precipitate form. Due to energy loss and self absorption of the alpha and beta particles in the sample matrix, their counting efficiency is far less than 100%. It should also be mentioned that no energy resolution is possible with the proportional counters and it is not suitable to determine volatile radionuclides (^{3}H, ^{210}Po).

In spite of the disadvantages, proportional counters are very useful for high throughput screening when fast quantitative analyses are required. Alpha and beta activity can be determined simultaneously which reduces the time of the analysis.

Low background can be obtained, which makes proportional counters effective for measuring environmental level radioactivity. The spillover between alpha and beta signals is low, even below statistical significance can be achieved. Several detectors (4–16) can be installed into one detector housing such that more samples can be measured simultaneously. Automatic sample changers with up to 250 places are also available in order to attain high capacity measurements.

Scintillation counter

Counters with solid scintillation detector materials like ZnS(Ag), can be used for water analysis. The main features are similar and comparable to gas flow proportional counters, but some of its properties are worse. Solid type scintillation counters have higher spillover between alpha and beta signals and have higher background as well. Detectors should be kept in a dark, light-tight lead shielding. Counting efficiency is lower than in case of proportional counters, but it can be increased significantly by applying vacuum. Detection of volatile nuclides is also not possible and also self absorption might be significant due to the sample preparation. It is possible to collect alpha and beta counts at the same time using a "sandwich type" scintillation detector, which contains ZnS(Ag) and a plastic detector. Its advantages are simplicity to handle and maintain, it has relatively low operation and maintenance costs.

Liquid scintillation counting

Liquid scintillation counting is an excellent tool for simultaneous measurement of gross alpha–beta activity and in certain cases for isotope specific analysis as well, when rapid information is necessary [25, 28]. The misclassification of alpha and beta signals due to spillover is below 0.5%. To some extent the alpha-particle energies can be discriminated from each other, but the resolution is not as good as it can be attained by alpha spectrometry. Thus, the identification of alpha emitting radionuclides is very

Table 1 Main features of the different detector systems

	Gas flow proportional counter	Scintillation counter	Ultra low-level liquid scintillation counting	Alpha spectrometry
Background (cpm)	α: 0.5–0.05; β: < 1	α: 0.02–1; β: < 5	α: < 0.1; β: < 2	α: 0.003–0.01
Energy discrimination	No	No	Yes (Resolution: 300–500 keV)	Yes (Resolution: 15–35 keV)
Simultaneous α/β counting	Yes	Yes	Yes	No
Counting efficiency (%)	α:19–42; β:24–47	α: 1–30; β: 10–35	α: > 99; β: > 99	α: 20–35
α/β spillover (%)	0–3	1–5	<0.5	0
Self absorption	Yes	Yes	No	Yes[a]
Detection of ^{222}Rn and ^{3}H	No	No	Yes	No
Automatic sample changer	Yes	No	Yes	No
Relative time demand	++	++	+; ++	+++
Relative cost	++	+	+++	+++

[a] Less or no self absorption can be obtained

Table 2 Comparison of gross alpha beta activity determination methods

Radioanalytical method	Sample preparation	Sample volume (L)	Detector system	MDA (Bq/L)	Counting efficiency (%)	Detector[a]: samples/ day	Interference	Counting time (min)	Form of the source	References
ISO 9696/9697	Evaporation, heat treatment	Depends on TDS	ZnS(Ag); proportional counter	α: 0.004 β: 0.025	n.d.	1	Hygroscopic precipitate; Self absorption; LV	750	Dry residue	[33]
EPA	Evaporation	1.5	Proportional counter	α: 0.003 β: 0.006	α: 19–21 β:71–73	10–20	Hygroscopic precipitate; Self absorption; LV	500	Dry residue	[34]
Modified EPA	Two steps evaporation	0.3	Proportional counter	α: 0.012 β: 0.018	n.d.	5	Hygroscopic precipitate; Self absorption; LV	500	Dry residue	[35]
Coprecipitation	$Fe(OH)_3$ and $BaSO_4$ coprecipitation	0.5	ZnS(Ag) detector	α: 0.0019–0.0023 β: n.d.	α: 23.1–26.8 β: n.d.	~4	Hygroscopic precipitate; Self absorption	300	Dry precipitate	[24]
LSC	Evaporation and mixing sample with cocktail	0.1	Ultra low-level LSC with PSA	α: 0.13 β: 1.3	α: 99 β: 95	3	Quenching	400	Liquid	[14]
LSC + Actinide resin	Sample passing through the resin; Dried resin mixed with cocktail	0.1	Ultra low-level LSC with PSA	α: 0.04 β: 0.04	~100	6	Fe(III) on extraction, quenching; Ca^{2+}	240	Slurry	[11]
Alpha + gamma spectroscopy	Evaporation	1	α: surface barrier; Si(Au) β: NaI(Tl); well type	α: 0.001 β:0.030	n.d.	~1	Salinity; Spectral interferences	α: 1167–1883 β: 583–1250	Dry residue	[16]

n.d. not described, *LV* loss of volatile isotopes

[a] Depends on the configuration of the system as well

complicated. It has the highest counting efficiency of almost 100%, due to the fact that the sample is completely dissolved and mixed homogenously in the scintillating cocktail and no self absorption is disturbing. Procedures designed for LSC are usually simple, efficient and involve minimal laboratory work, such that sample preparation does not require too much experience. A large number of samples can be measured applying an automatic sample changer system which is an important point of view in environmental monitoring laboratories, when high throughput screening is performed. There is a limitation of the LSC, namely it can be counted just one sample at a time because only one detector is installed in a device, but on the other hand in most cases lower counting times (100–400 min) are sufficient. Sample volume is at least one order of magnitude lower than in case of evaporation methods which makes sample preparation faster. But it has to be considered that radioactive organic cocktail waste has to be collected and handled very carefully.

Methods using LSC can be adapted to monitor low-energy beta emitters such as ^{14}C and ^{3}H [12, 25, 26, 29]. Radon in water may be determined separately using alternative liquid scintillation methods [5, 30].

LSC is proposed as a standard method for gross alpha–beta activity determination in water samples in some countries (e.g. in Italy) [31] and in a new ISO standard 11704 [32].

Alpha-particle spectrometry

Alpha-particle spectrometry has relatively low counting efficiency and it requires sophisticated chemical separation steps and experience in the source preparation. Due to its complexity and time demand, alpha spectrometry is seldom used as rapid screening method. Besides its drawbacks, the main advantage of alpha spectrometry is that it provides the best alpha-particle energy resolution and the lowest background among the introduced measurement methods. It can also be the best choice if isotope specific measurements must be done. If the alpha source is prepared in a proper way, there is no significant self absorption in the alpha source itself. Volatile compounds can be measured (e.g. ^{210}Po), if sample and source preparation are chosen very carefully.

Conclusions

In practice, two basic types of methods—evaporation with proportional counter and LSC—can be used for gross alpha and beta activity measurement in water. Whichever technique is chosen according to the laboratory's demands, it must be repeatable and the WHO recommendation should also be kept in mind: "Where possible, standardized methods should be used to determine concentrations of gross alpha and beta activities" [1].

As shown, the evaporation method in combination with a proportional counter is still a suitable tool for gross alpha and beta activity measurements. It is a simple method ensuring prompt information about samples. The obstacles associated with the evaporation methods may be overcome using LSC, thus LSC provides an alternative way to the commonly used evaporation procedures. Therefore, a new ISO standard for gross alpha and beta measurement with LSC [32] is being developed and evaluated.

As a conclusion, it can be stated that proportional counting and LSC can be applied for low-level radioactivity measurements of environmental water in high-throughput screening analysis. Both techniques meet the requirements for routine analysis and for research as well, but their applicability and limitations should be carefully taken into account.

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