Journal of Radioanalytical and Nuclear Chemistry
https://doi.org/10.1007/s10967-026-10832-0

A comparative study of the gross alpha and beta sample preparation method with a liquid scintillation counter

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Received: 1 October 2025 / Accepted: 7 March 2026

Abstract
Gross alpha and beta (GAB) measurements provide a rapid screening tool for assessing radionuclide contamination in water. This study aimed to establish a sensitive, simple method for low-level GAB detection using a liquid scintillation counter (LSC). Different sample preparation approaches (direct, co-precipitation with $Fe(OH)_3$, $Ca_3(PO_4)_2$, MnO_2, and evaporation) were tested on four water samples containing natural and anthropogenic radionuclides from the IAEA 2022 proficiency test. Results, evaluated by recoveries and Zeta-scores, showed preparation methods influence recovery and quenching. Co-precipitation with $Ca_3(PO_4)_2$ and evaporation performed best, though GAB remains a complementary rather than absolute analytical method, as not all radionuclides can be detected simultaneously.

Keywords Gross alpha and beta · Pre-concentration methods · Liquid scintillation counting · Recovery · Zeta-score

Introduction

Gross alpha and beta (GAB) measurements are one of the fastest, cheapest and simplest radioanalytical procedures, which are widely applied in the field of radioecology, environmental monitoring and industrial applications. The GAB has been developed as a fast, reliable screening tool for environmental and drinking-water monitoring programmes, providing an initial indication of whether radionuclide-specific analysis is required for more detailed sample characterization.

In the last few decades, increasing attention has been paid to restrict the population`s exposure to any kind of radiation [1–4]. To minimize health hazards, the quality of drinking water should be continuously monitored and analysed to obtain reliable information on the level and trends of any kind of pollution. In World Health Organization (WHO) guidelines, the screening levels in drinking water are 0.5 Bq L^{-1} for gross alpha and 1 Bq L^{-1} for gross beta activities [5]. Whereas the European Union has set the screening levels of 0.1 Bq L^{-1} for gross alpha and 1 Bq L^{-1} for gross beta [6]. If the measured values are below the screening levels, the drinking water is acceptable for consumption without any further measures regarding radioactivity. If the screening levels are exceeded, radionuclides must be identified and their individual activity concentrations need to be measured.

In many laboratories around the world, the GAB activity in water is investigated in order to determine potential health hazards from natural radionuclides. Radionuclides in water originate from several naturally occurring and man-made sources. The total alpha activity contribution comes primarily from the naturally occurring decay series of U and Th, where ^{238}U, ^{234}U, ^{232}Th, ^{230}Th, ^{226}Ra, and ^{222}Rn with their progenies have the biggest inputs. In natural beta radioactivity, ^{40}K, ^{14}C, ^{234}Th, and $^{210}Pb/^{210}Bi$ are the largest natural radioactivity contributors to the total beta activity [7]. GAB method also has applications in measurements of anthropogenic radioactivity, where gross alpha may relate to screening for transuranic wastes, while gross beta may be useful in screening for fission products in accidental nuclear exposures (^{3}H, ^{90}Sr, ^{137}Cs) [8].

Many of the standard procedures for determining GAB measurements apply gas-flow proportional counting or ZnS scintillator counting [9–12]. Another method utilises a combination of alpha-particle and gamma-ray spectrometry [13]. Nowadays, to overcome the drawbacks of standard

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Published online: 25 March 2026

methods, especially in the case of counting efficiency and chemical composition of the sample, liquid scintillation counting (LSC) has become a popular method of choice [3, 4, 14–16]. The performance of the GAB method is significantly improved when using LSC instead of gas-flow proportional counting, offering higher sensitivity, reduced sample preparation time and operator intervention, as well as lower counting times and overall analytical costs.

The main advantages of the GAB method measured by LSC include its low cost and quick, simple measurements, made possible by low-maintenance hardware, inexpensive sample preparation, and the ability to achieve statistically reliable counts rapidly. However, the determination of accurate GAB activities remains challenging because mixed radionuclide compositions must often be measured simultaneously, and LSC may exhibit reduced sensitivity for regulatory environmental monitoring. Samples may contain a variety of natural alpha and beta emitters, as well as artificial radionuclides at different concentrations. Low-energy beta emitters such as ^{3}H, ^{14}C, and ^{63}Ni, along with weak beta emitters like ^{99}Tc, can limit LSC sensitivity. Long-lived environmental alpha emitters, including ^{226}Ra and ^{238}U, often require extended counting times due to low activity, while alpha emitters such as ^{241}Am and ^{239}Pu show low LSC efficiency. Many of these radionuclides are part of complex decay chains, and the ingrowth of daughter products can further affect measurement accuracy through overlapping signals in mixed radionuclide samples [17]. Therefore, laboratories around the world struggle to provide a comparable result for GAB measurements. An example from two of the proficiency tests (PT) in 2012 and 2019 showed that at least half of participating laboratories reported results with deviations exceeding ± 30% of the stated value [14, 18]. Similar problems emerged from the 2021 IAEA TEL PT, where also many participants had problems with reporting on accurate GAB results [19]. PT samples used for intercomparison were typically water samples without interferences affecting measurement results, generally exhibiting elevated target gross activity concentrations and minimal mineral content. Although GAB methods have been well studied and applied, more work should be done to ensure the results are fit-for-purpose and can be comparable between different laboratories and methods used. Therefore, it is essential to establish corrections based on the method used that will allow comparison of results, especially in routine monitoring of water.

The validation of GAB analyses by LSC is an important step, especially the optimization of the alpha/beta discrimination performance and the determination of alpha and beta counting efficiencies, as well as spillover in the selected alpha and beta windows. Calibration can become more complicated due to difference in quenching between standards, and because real samples may contain several alpha and beta emitters with particle energies that differ substantially from those used for calibrations. Therefore, calibrations need to be performed precisely and appropriate quench corrections are necessary to obtain the best possible results for GAB activity. Overall, method validation is essential for confirming that the analytical procedure is fit-for-purpose and produces accurate and defensible results.

This study is divided into two parts. In the first part, the validation of the GAB method by LSC was carried out to ensure the best possible precision and accuracy before applying the method to real samples. The detector calibration was first verified, including the determination of counting efficiency and the establishment of a quench curve. Subsequently, accuracy and precision tests were performed, and the detection limit was determined by measuring a large number of blank samples. To complete the method validation, a linearity curve was established, and additional tests of selectivity and robustness were conducted. The second part of the study focused on evaluating different sample preparation approaches to assess their influence on the precision and accuracy of the GAB method. The aim was to identify an analytical procedure that would minimize quenching and provide the most accurate results, with the smallest deviation from the theoretical activity. This is particularly important when establishing a reliable and preferred method for GAB determination in water samples. Overall, the results of the method validation and the comparison of sample preparation procedures support the development of a sensitive, rapid, and simple methodology for measuring GAB activity, particularly in low-level concentration samples.

Materials and method

Materials

To achieve the lowest possible detection limit, all acids and reagents used were of analytical grade and obtained from commercial suppliers. Deionized water (≥ 18 MΩ·cm) was used throughout the experiments.

^{241}Am and ^{90}Sr/^{90}Y standard solutions were used for LSC calibration, which were diluted gravimetrically. ^{241}Am standard (diluted activity: 109.74 Bq g^{-1}) was received from CERCA-LEA FRAMATOME: AM241-ELSB30; NO 5104 [20], ^{90}Sr/^{90}Y standard (diluted activity: 143.70 Bq g^{-1}) was procured from NIST Standard Reference Material 4234A. Standards were diluted with dilute HNO_3 (2M) and HCl (1M) carrier solutions, respectively.

Samples analysed in this study were from IAEA TERC PT 2022. The Quality control (QC) sample and Sample 1 were water spiked with known activities of anthropogenic and natural radionuclides. Sample 2 was spiked with anthropogenic and natural radionuclides, at lower activity concentration levels. Sample 3 was water spiked with gamma

emitters and transuranic radionuclides. The radionuclides included in the IAEA 2022 PT samples were selected for their relevance to environmental monitoring and nuclear-emergency response, representing those commonly measured in real water samples as well as radionuclides of importance during accidental releases. The radionuclides spiked in the IAEA TERC PT 2022 samples, which are presented in Table 1, are referred to throughout the text as Theoretical GAB activities.

Instrumentation

The measurement of GAB activities was performed using a Wallac Quantulus 1220™ (PerkinElmer) liquid scintillation counter. The LSC is equipped with a pulse shape discrimination adjustable parameter and pulse shape analyser (PSA) to perform simultaneous alpha/beta gross counting, allowing distinction between alpha and beta pulses. The Quantulus 1220 has a ^{152}Eu external standard, which enables measurement of the external spectral quench parameter (SQP(E)). The technique uses 20 mL polyethylene counting vials to hold samples and the scintillation cocktail (Ultima Gold AB). To analyse spectra, the EASY View spectrum analysis software was used. The counting windows were set between the channels 600–1000 (alpha window of both MCA) and between the channels 20–1000 (beta window of both MCA) ensuring most of the alpha and beta pulses are within the respective windows. All samples and cocktail volumes were volumetrically measured at 8 mL and 12 mL, respectively, by pipette or dispenser. All vials were placed inside the counter for at least one hour prior to counting for dark and temperature adaptation.

Method validation of the counting procedure

Calibration

The optimal PSA setting was established with ^{241}Am and ^{90}Sr/^{90}Y standard solutions. The calibration samples included 20 µg of each spiked standard solution, corresponding to activities of 2.4 Bq for ^{241}Am and 1.7 Bq for ^{90}Sr/^{90}Y, with 8 mL Milli-Q water as a matrix, and 12 mL of scintillation cocktail Ultima Gold AB. The samples were measured at different PSA levels. The percentage spillovers obtained by ^{241}Am (alpha spillover) and ^{90}Sr/^{90}Y (beta spillover) were plotted against the PSA to obtain the optimum PSA. The misclassification of alpha as beta (α_S) and beta as alpha (β_S) was calculated using Eqs. (1) and (2):

$$\alpha_S = \frac{alpha\ counts\ in\ beta\ windows}{total\ alpha\ counts} \times 100\% \quad (1)$$

$$\beta_S = \frac{beta\ counts\ in\ alpha\ windows}{total\ beta\ counts} \times 100\% \quad (2)$$

The optimal PSA setting for alpha and beta discrimination is normally affected by the degree of quenching in the sample [21]. The effect of quenching on the PSA settings was studied by analysing a pure alpha standard solution and a pure beta standard solution containing an increasing amount of nitromethane as a quenching agent. Each sample was counted at different PSA levels and the alpha and beta spillovers were plotted against the discrimination factor to find the optimal PSA setting for each quench level.

Alpha and beta detection efficiencies were evaluated by measuring ^{241}Am and ^{90}Sr/^{90}Y standard solutions, respectively. The counting efficiencies for alpha and beta emitters were determined using Eqs. (3) and (4) and were calculated separately for ^{241}Am and ^{90}Sr/^{90}Y:

$$\varepsilon_\alpha = \frac{R_{Sample,\alpha}}{R_{Standard,\alpha}} \times 100\% \quad (3)$$

$$\varepsilon_\beta = \frac{R_{Sample,\beta}}{R_{Standard,\beta}} \times 100\% \quad (4)$$

where $R_{\mathrm{Sample},\alpha}$ and $R_{Standard,\alpha}$ [cps] are the sample and standard count rates from ^{241}Am, respectively. $R_{\mathrm{Sample},\beta}$ and $R_{Standard,\beta}$ [cps] are the sample and standard count rates from ^{90}Sr/^{90}Y, respectively.

Quality parameters

Blank samples were prepared by adding 8 mL of Milli-Q water to 12 mL of scintillation cocktail Ultima Gold AB in a polyethylene counting vial to achieve the lowest possible minimum detection activity (MDA). The MDA was calculated using the International Organization for Standardization (ISO) standard method [16]. Additionally, other parameters such as standard uncertainty, decision threshold, detection limit, and confidence limits were calculated using equations in the ISO standard method for GAB, with the help of a Kragten spreadsheet [16]. Blank samples were

Table 1 Radionuclides present in the IAEA TERC PT 2022 samples with their progeny shown in parentheses

Sample QC	Sample 1	Sample 2	Sample 3
^{210}Pb (^{210}Bi, ^{210}Po)	^{210}Pb (^{210}Bi, ^{210}Po)	^{210}Pb (^{210}Bi, ^{210}Po)	^{134}Cs
^{134}Cs	^{134}Cs	^{137}Cs	^{137}Cs
^{137}Cs	^{137}Cs	^{90}Sr (^{90}Y)	^{239}Pu
^{90}Sr (^{90}Y)	^{90}Sr (^{90}Y)	^{3}H	^{244}Cm
^{3}H	^{60}Co	^{241}Am	
^{241}Am			

always counted along with each test sample to observe the behaviour of the instrument over time. Additionally, QC samples spiked ^{241}Am and ^{90}Sr/^{90}Y standard solutions were measured each time with test samples and control charts were developed to monitor instrument quality performance. To verify the range of good precision and accuracy of the instrument, a linearity curve was analysed with different concentrations of spiked standard solutions of ^{241}Am and ^{90}Sr/^{90}Y.

The GAB activity calculations [in Bq L^{-1}] are determined by Eqs. (5) and (6):

$$A_\alpha = \frac{R_{sample,\alpha} - R_{blank,\alpha}}{\varepsilon_\alpha \times V_{sample} \times t_{measurement}} \quad (5)$$

$$A_\beta = \frac{R_{sample,\beta} - R_{blank,\beta}}{\varepsilon_\beta \times V_{sample} \times t_{measurement}} \quad (6)$$

where $R_{\text{sample},\alpha}$, $R_{\text{sample},\beta}$, $R_{\text{blank},\alpha}$, and $R_{\text{blank},\beta}$ [cps] are the sample count rates from alphas or betas and the blank count rates from alphas and beta, respectively, ε_α and ε_β are counting efficiencies for standard solution of alpha and beta, V_{sample} is volume of the test sample [L] and $t_{\text{measurement}}$ is sample counting time [s]. Gross alpha and gross beta activities were calculated separately for each test sample.

All measurements were performed on the IAEA PT 2022 samples within their certification validity period. The PT instructions indicate a three-month window for analysis, and all measurements in this study were conducted within this timeframe. For comparison with measured results, the theoretical GAB activities were decay-corrected from the sample reference date to the measurement date. This correction accounts for the decay of each radionuclide and its progeny over time, ensuring that the theoretical activities accurately reflect the sample composition at the time of measurement.

Sample preparation

Some of the most commonly used radionuclide pre-concentration techniques were evaluated to find the best GAB method with the smallest variance from the theoretical values of PT 2022 samples, for QC sample, Sample 1, Sample 2, and Sample 3.

Four different pre-concentration techniques for water samples were tested: co-precipitation with either $Fe(OH)_3$, $Ca_3(PO_4)_2$, or MnO_2, and evaporation. Pre-concentration methods were checked with the direct method, where 8 mL of PT 2022 sample was added directly into a polyethylene vial with 12 mL of scintillation cocktail Ultima Gold AB. For co-precipitation with $Fe(OH)_3$, 1 mL of $FeCl_3$ solution (5 mg mL^{-1}) was added to PT 2022 water sample (~30 mL) and the pH was increased to 9 with concentrated ammonia solution to initiate co-precipitation of radionuclides with $Fe(OH)_3$. For co-precipitation with $Ca_3(PO_4)_2$, 0.5 mL of 1.25M $Ca(NO_3)_2$ was added to the sample and heated until the water solution was boiling. $Ca_3(PO_4)_2$ precipitate was formed by adding 0.2 mL of 3.2M $(NH_4)_2HPO_4$ into a boiling solution with enough concentrated ammonia solution to form a precipitate. Co-precipitation with MnO_2 was achieved by adding 0.2M $KMnO_4$ solution (1 mL per 1 L) to a sample acidified with HCl and the pH was adjusted to 9 using concentrated ammonia solution, then adding 0.3M $MnCl_2$ solution (2 mL per 1 L). For the pre-concentration of GAB using evaporation, the PT 2022 water sample was evaporated on a hot plate to dryness. All four residues (from precipitates and evaporation) were dissolved with 8 mL of 2M H_3PO_4, stirred until everything was dissolved, transferred to a polyethylene counting vial, and then 12 mL of scintillation cocktail Ultima Gold AB was added and mixed thoroughly.

All samples were counted for 60 min on the Quantulus 1220 ™ with a blank and quality control sample (spiked standard solutions of ^{241}Am and ^{90}Sr/^{90}Y).

All results of PT samples measured in this study were evaluated using recoveries and Zeta-scores. Recoveries were calculated separately as the relative difference between the measured and theoretical values of gross beta or gross alpha activity, using Eqs. (7) and (8). Theoretical values of gross beta or gross alpha activity were calculated as the sum of known activity concentrations of each radionuclide added to the spiked PT samples and contributions from progeny radionuclides.

$$\eta_\alpha = \frac{measured_\alpha activity}{theoretical_\alpha activity} \times 100\% \quad (7)$$

$$\eta_\beta = \frac{measured_\beta activity}{theoretical_\beta activity} \times 100\% \quad (8)$$

Zeta-score (ζ), was calculated to quantitatively compare the measured activity value ($A_{\text{measured},\alpha}$ and $A_{\text{measured},\beta}$) with a standard uncertainty ($u_{\text{measured},\alpha}$ and $u_{\text{measured},\beta}$) with the theoretical activity value ($A_{\text{theoretical},\alpha}$ and $A_{\text{theoretical},\beta}$) and its associated standard uncertainty ($u_{\text{theoretical},\alpha}$ and $u_{\text{theoretical},\beta}$) (Eqs. (9) and (10)).

$$\zeta_\alpha = \left| \frac{A_{measured\alpha} - A_{theoretical\alpha}}{\sqrt{u^2_{measured\alpha} + u^2_{theoretical\alpha}}} \right| \quad (9)$$

$$\zeta_\beta = \left| \frac{R_{measured\beta} - R_{theoretical\beta}}{\sqrt{u^2_{measured\beta} + u^2_{theoretical\beta}}} \right| \quad (10)$$

Alpha and beta activities were calculated separately. Results are comparable with the theoretical value if absolute Zeta-score is ≤ 2.0 (95% confidence).

Results and discussion

Method validation

PSA setting

In order to find the optimal PSA setting, two vials of Milli-Q water, spiked with ^{241}Am and ^{90}Sr/^{90}Y standard solutions were measured at different PSA levels. In the case of GAB, optimal PSA is difficult to achieve, as the radionuclides present in the sample are unknown. In the standardized method, artificial sources with a similar emission type and energy range are normally selected [16]. ^{241}Am and ^{90}Sr/^{90}Y standard solutions were chosen because they are considered as suitable representatives for the measurement of the entire energy window and are often used for calibrations in GAB measurements using LSC.

The percentage spillover obtained by ^{241}Am (alpha spillover into beta window) and ^{90}Sr/^{90}Y (beta spillover into alpha window) were plotted against the PSA levels as shown in Fig. 1a. The optimum PSA was found to be 65, where the alpha and beta spillover curves cross each other and both spillovers are minimal. Here, the misclassification of the beta emitter decreases, with increased PSA values. Alpha emitter misclassification remains almost the same throughout different PSA values but begins to slowly increase after PSA level 70. Although the misclassification of beta emitters decreases further with a PSA higher than 65, the focus of this work was to find the optimal spillover for both alpha and beta emitters and going to higher PSA levels would lose a significant number of alpha emitters when real-life sample measurements will be made. Additionally, the counting efficiency at different PSA levels was also calculated. At optimum PSA level 65, the counting efficiency for alpha and beta emitters reached its highest value, approximately 90% (Fig. 1b). This shows that the best performance of our Quantulus 1220 ™ for GAB determination will be at PSA 65, which was used for all further measurements in this study.

Quench curve

The optimal PSA setting for alpha and beta discrimination is normally affected by the degree of quenching in the sample [21]. To evaluate this effect, alpha and beta spillover were compared across different PSA levels and discrimination factors to determine the optimal PSA setting for each quench level. The count rates in the alpha and beta channels varied at different PSA levels, depending on the amount of alpha/beta spillover. Different quench levels varied in the SQP(E) range between 470 and 720. It was also observed that low PSA settings are more suitable for higher quench values, while for lower quench values higher PSA settings are acceptable to minimize the spillover.

Figure 2 presents the dependence of the level of quenching on the optimum PSA value (65) evaluated with ^{241}Am and ^{90}Sr/^{90}Y standard solutions quenched at different degrees and measured counting efficiency for alpha and beta emitters. The sample spiked with standard solutions exhibited an SQP(E) range between 470 and 720, while the tested PT samples with different pre-concentration procedures varied between 620 and 700. In tested PT samples, the maximum counting efficiency for alpha and beta emitters was estimated at 96%. Given this high counting efficiency, the quench curve equation was not included in the counting efficiency calculation. Instead, for each measurement, a sample of the spiked standard solution was prepared and counted in the same way as the tested samples and corrections were made based on these measurements.

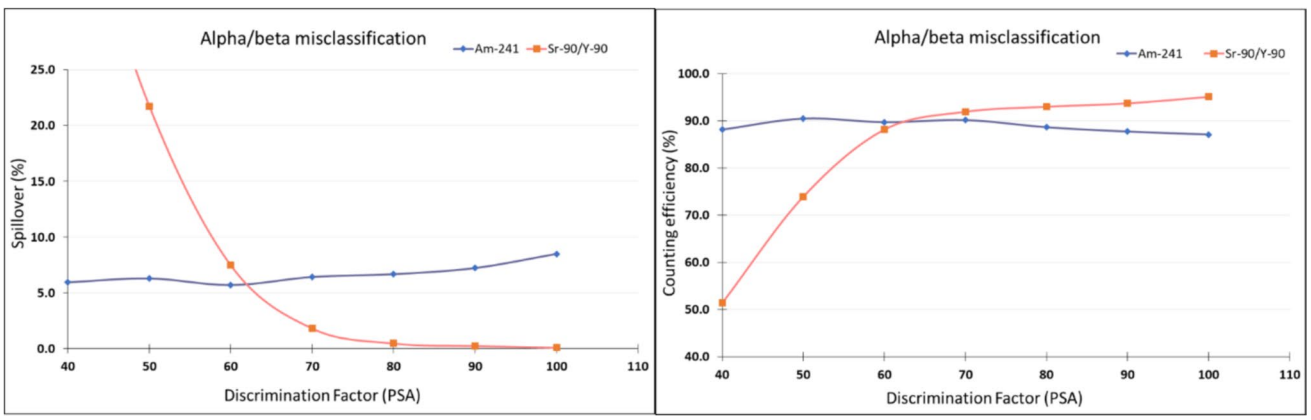

Fig. 1 The Alpha/Beta spillover curve (**a**) and counting efficiency (**b**) for ^{241}Am and ^{90}Sr/^{90}Y over 60 min at different PSA levels

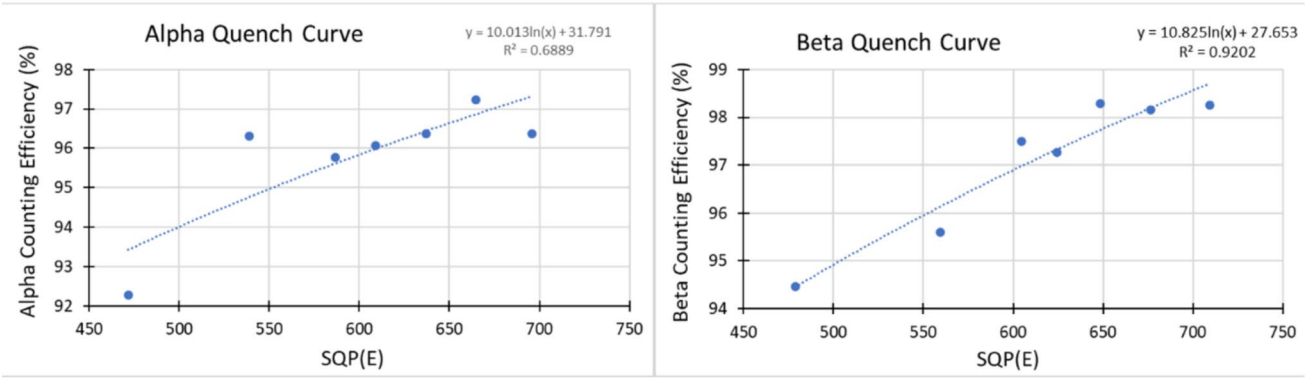

Fig. 2 Alpha and beta quench curves at a PSA value of 65, prepared by adding increasing amounts of nitromethane (up to 0.25 g) to the ^{241}Am and ^{90}Sr/^{90}Y standards. The resulting SQP(E) values and measured efficiencies are presented together with a logarithmic fit, illustrating the expected increase in efficiency with increasing SQP(E)

Linearity

Linearity is where the signals are directly proportional to the concentration of the analyte in the sample over a range of concentrations. It should be confirmed for the expected working range of a method, including the chosen matrix [16]. The GAB linearity was checked in the range between the detection limit and 100 Bq L^{-1}. The detection limit for direct counting on an 8 mL sample was 0.48 Bq L^{-1} and 2.07 Bq L^{-1} for gross alpha and gross beta, respectively. However, the detection limit would be significantly lower in the case of higher sample volumes. The maximum activity concentration was chosen to be fit-for-purpose as it was assumed that environmental water samples would not have an activity concentration higher than 100 Bq L^{-1}. For the linear relationship to be acceptable there should be no outliers. Figure 3 shows, that the LSC measurements for GAB method is assumed to be linear in the tested range and therefore suitable for measuring real-life samples.

Source preparation

Several approaches can be used to prepare sample sources for GAB measurements using LSC. The most common are a combination of 2M H_3PO_4 and Milli-Q water, 2M H_3PO_4, or only Milli-Q water. In this study, the potential influence of different source preparation solution on the precision and accuracy of LSC measurements was evaluated. Spiked solutions with known activity of ^{241}Am and ^{90}Sr/^{90}Y standard solution were added to each type of source solution and measured by LSC for 60 min. The sample-to-cocktail ratio was 8:12. Results of ^{241}Am and ^{90}Sr/^{90}Y standard solution activities are presented in Table 2, with the recoveries and Zeta-scores.

The results show that spiked solution preparations using Milli-Q water and/or 2M H_3PO_4 measured by LSC have no significant deviation from the reference activities of the ^{241}Am and ^{90}Sr/^{90}Y standards, with recoveries around 100%. This indicates that Milli-Q water and 2M H_3PO_4 results were

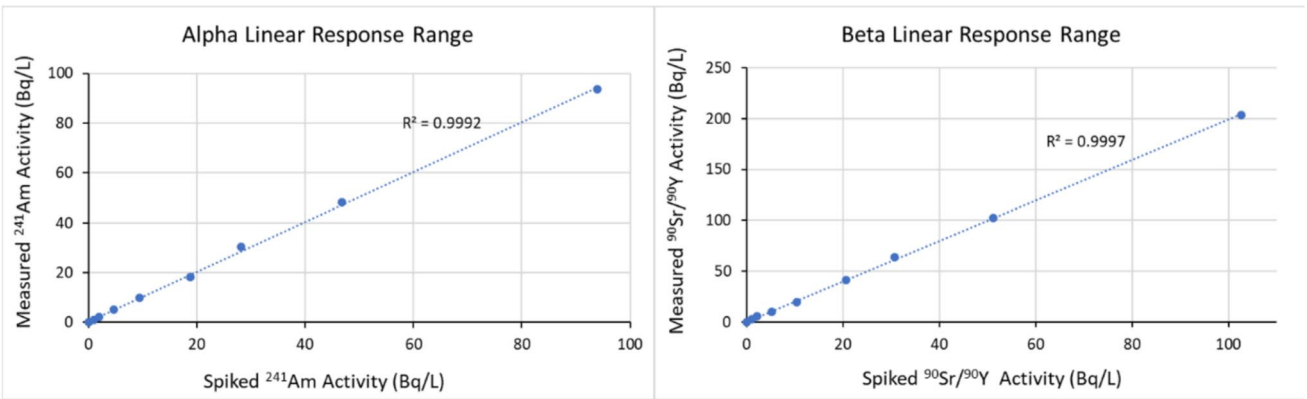

Fig. 3 Alpha and beta linearity curves at a PSA value of 65, verified using ^{241}Am and ^{90}Sr/^{90}Y standards over the activity range from the detection limit up to 100 Bq L^{-1}

not affected by quenching. Furthermore, the SQP(E) values for these samples were high, providing additional confirmation that quenching did not influence the results. Zeta-score values are 2 or less, which means that the measured ^{241}Am and ^{90}Sr/^{90}Y standard solution activities in these three source preparations are in good agreement with theoretical values. When source preparation contained nitric acid, larger deviations were observed. The recoveries were 134% for gross beta and 42% for gross alpha, and Zeta-score values also deviate considerably from theoretical values. Nitric acid caused pronounced peak shifting and strong colour quenching, leading to misclassification of alpha emitters as beta counts. The colour quenching occurs when nitric acid forms yellow–brown oxidation products that absorb scintillation light. To overcome this issue would require re-optimization of PSA settings, or the use of an efficiency correction curve, when measuring HNO_3 prepared samples. Similar effects have been reported in previous studies [21]. Additional tests using 1M, 3M, and 6M HNO_3 confirmed that increasing acidity significantly worsens alpha–beta discrimination. Gross-alpha recoveries declined from 88% (1M) to 42% (3M) and 9% (6M). Another study reported that SQP(E) values below 550 produce the largest spillover [22]. These findings highlight the necessity of re-validating the method when HNO_3 is used for residue dissolution to prepare samples that are pre-concentrated.

GAB during different sample preparation

GAB measurements with direct counting

GAB activity was measured using the average of three replicates of all four PT 2022 samples (QC sample, Sample 1, Sample 2, and Sample 3), by direct counting with LSC, presented in Table 3. There was no need for any corrections for alpha and beta spillover due to good optimization of the PSA settings. A quality control sample and a blank were measured alongside each set of samples, and efficiency corrections for gross alpha and gross beta activities were applied based on these measurements. The efficiency calculations remain valid for the mixed-nuclide samples, provided that the quench remains within the verified range, PSA is optimized for alpha–beta discrimination, and the regions of interest are correctly defined. This ensures accurate and reliable determination of the gross alpha and beta activities. Measured GAB results were compared with theoretically calculated GAB activities by evaluating the recovery and Zeta-scores. Theoretical GAB activities were calculated as the sum of known activity concentrations of each radionuclide added to the spiked PT samples including contributions from progeny radionuclides. Some radionuclides present in PT samples had short half-lives and for a closer comparison of results between theoretical and measured GAB activities, theoretical GAB activities were corrected to the day of measurement. For comparison of samples prepared with different co-precipitation techniques, the same calculations were made.

To compare theoretical GAB activities with measured GAB activities, it was necessary first to determine whether the spiked radionuclides have alpha or beta progenies and whether they are in equilibrium. Since all alpha or beta progeny radionuclides can be detected with GAB measurements, these contributions must be added to the activity concentration budget. In this study, the radionuclide solutions used to spike the PT samples were characterized, and ^{210}Pb was known to be in equilibrium with ^{210}Bi and ^{210}Po, and ^{90}Sr was in equilibrium with ^{90}Y. The counting efficiency of the LSC instrument for each radionuclide also effects measured

Table 2 ^{241}Am and ^{90}Sr/^{90}Y measured activities with expanded combined uncertainties, recoveries and Zeta-scores for source preparation testing

GAB direct counting	Theoretical activity, Bq kg^{-1}		Measured activity, Bq kg^{-1}		Recovery %	ζ-score
		Unc. (k = 2)		Unc. (k = 2)		
2 mL 2M H_3PO_4 + 6 mL MQ water						
Gross beta	146740	420	147100	2800	100	−0.12
Gross alpha	106000	2200	104400	2400	99	0.49
8 mL 2M H_3PO_4						
Gross beta	146740	420	150200	2900	102	−1.2
Gross alpha	106000	2200	107500	2300	101	−0.49
8 mL MQ water						
Gross beta	146740	420	141200	2700	96	2.0
Gross alpha	106000	2200	101000	2300	95	1.6
8 mL 3M HNO_3						
Gross beta	146740	420	196300	3200	134	−15
Gross alpha	106000	2200	44500	1500	42	23

Table 3 PT 2022 samples GAB activities (average of three replicates) with expanded combined uncertainties, recoveries, and Zeta-scores measured by direct counting

GAB direct counting	Theoretical activity, Bq kg^{-1}		Measured activity, Bq kg^{-1}		Recovery %	ζ-score
		Unc. (k = 2)		Unc. (k = 2)		
QC Sample						
Gross beta	297.6	5.3	284.3	5.1	96	1.8
Gross alpha	96.6	1.5	97.6	2.2	101	− 0.39
Sample 1						
Gross beta	158.3	2.6	152.9	1.9	97	1.6
Gross alpha	30.95	0.55	36.58	0.71	118	− 6.3
Sample 2						
Gross beta	35.74	0.60	37.8	1.4	106	− 1.4
Gross alpha	15.29	0.21	16.6	1.2	108	− 1.1
Sample 3						
Gross beta	30.33	0.36	30.33	0.77	100	− 0.0012
Gross alpha	10.72	0.18	11.76	0.43	110	− 2.2

activity. Due to the low penetrative power of beta radiation, the counting efficiency of the low energy beta emitters (^{3}H, ^{14}C, ^{41}Ca, ^{55}Fe, ^{60}Co, ^{63}Ni…) can be much lower than 100% [7]. For alpha emitters, counting efficiency is generally not an issue due to their high energies, and their detection efficiencies are typically assumed to be 100%. The theoretical activity for each radionuclide in the PT samples was corrected using the experimentally determined counting efficiencies. Efficiency corrections were determined by preparing source samples spiked with a known activity for each alpha and beta emitter individually. The measured activities were then compared with the theoretical values—corrected to the date of measurement—to derive the corresponding correction factors for the counting efficiency. The counting efficiencies for beta radionuclides were calculated using Eqs. 3 and 4, and are presented in Table 4.

Table 4 Counting efficiencies for beta emitters present in PT 2022 samples

Radionuclide	Counting efficiency %
Pb-210	99
Bi-210	99
Sr-90	98
Y-90	98
H-3	31
Co-60	59
Cs-134	94
Cs-137	94

Due to low beta energies, corrections were needed for ^{3}H and ^{60}Co, whose counting efficiencies were measured as 31% and 59%, respectively. The other beta emitting radionuclides present in tested samples have higher beta energies and counting efficiencies closer to 100%. Measured counting efficiencies were used to calculate theoretical GAB activity, presented in Table 3. After counting efficiency corrections, recoveries and Zeta-scores for each PT 2022 sample were calculated and the results show very good agreement between measured and theoretical GAB activities. The recovery for QC sample were 96% for gross beta and 101% for gross alpha; for Sample 1, 97% for gross beta and 118% for gross alpha; for Sample 2, 106% for gross beta and 108% for gross alpha and for Sample 3, 100% and 110% for gross beta and gross alpha. Recoveries higher than 100% for gross alpha activities are possible due to the uncertainty budget, and beta spillover into alphas. There is also a possibility that the counting efficiency for alpha emitters present in tested samples is less than 100% for LSC measurements, resulting in the theoretical gross alpha values being slightly higher than the actual values. The counting efficiency for alpha emitters were subsequently assessed, revealing that the measured counting efficiency for ^{241}Am was 97% and 100% for ^{210}Po. This indicates that the detection efficiency of alpha emitters did not significantly contribute to the higher recovery of the measured gross alpha activities. Zeta-scores for measured GAB activities by direct counting show good agreement with the corresponding theoretical GAB values, indicating good optimization of PSA settings and other validation parameters. This indicates that the higher recovery for gross alpha was mostly due to uncertainty and variability of LSC sample preparation and measurements. The biggest contributors to the direct counting uncertainty budget were the sample count rate (78% for alpha; 73% for beta), the standard solution count rate (12% for alpha; 24% for beta), and the initial calculated activity of the standard solution spike (10% for alpha; 2% for beta). Another small additional contribution from the half-life of the gross beta standard solution (1%) was included.

The spectrum of the spiked ^{241}Am and ^{90}Sr/^{90}Y standard solutions was compared with the QC Sample from direct

counting. Figure 4 shows good agreement between the two spectrums, with no clear deviations of alpha and beta peaks caused by different quenching or poor PSA settings. This means that ^{241}Am and ^{90}Sr/^{90}Y standard solutions were good representatives for the measurement of the entire GAB energy window.

GAB measurements with different pre-concentration techniques

Direct counting is usually an acceptable choice for measuring GAB activities in different types of samples, especially for screening water samples. However, in environmental samples where activity concentrations of different radionuclides are usually very low, direct counting can make it difficult to distinguish between different radionuclides. In surface water, gross-alpha activities usually range from 0.01 to 0.05 Bq L^{-1} and gross-beta from 0.01 to 0.1 Bq L^{-1}, while in drinking water, gross-alpha can reach up to 0.1 Bq L^{-1} and gross-beta up to 0.5 Bq L^{-1}. At these low activity levels, the limit of detection for direct counting may be too high to achieve the required results, making a pre-concentration step necessary. Several EU directives on drinking water and environmental monitoring also set activity limits so low that pre-concentration is generally required to achieve them (e.g., Council Directive 2013/51/Euratom; Drinking Water Directive 98/83/EC; Environmental Directive 2011/92/Euratom). For these reasons, different pre-concentration procedures commonly used for radionuclides in water samples were tested. Four different pre-concentration techniques for water samples were tested: co-precipitation with $Fe(OH)_3$, $Ca_3(PO_4)_2$, or MnO_2 and evaporation in three replicates. The average measured GAB results for each pre-concentration technique were compared to the theoretically calculated GAB activity in four PT 2022 samples (QC sample, Sample 1, Sample 2, and Sample 3) and results were evaluated using recoveries and Zeta-scores. Results are shown in Table 5.

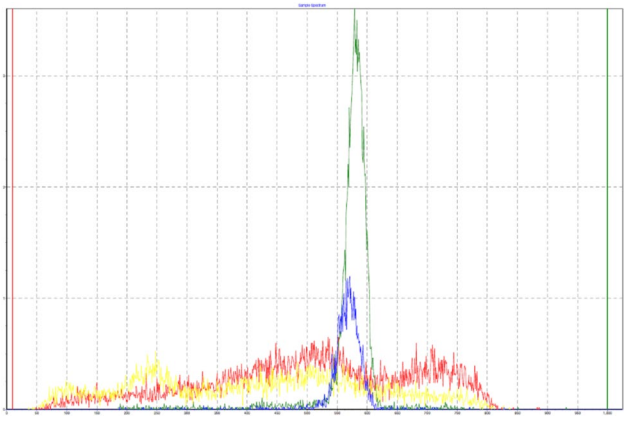

Fig. 4 Spectrum of GAB peaks of spiked ^{241}Am and ^{90}Sr/^{90}Y standard solution (red and green) and QC sample (yellow and blue), measured at PSA 65 for 60 min

The sum of the theoretical GAB activity in each PT 2022 sample was corrected for radionuclide progeny activities and counting efficiencies for low beta emitters. In order to make some possible comparisons with recovery and Zeta-score, the theoretical GAB activities were also corrected to the day of sample measurement. For Samples 1, 2, and QC sample comparison of three different co-precipitation procedures, $Fe(OH)_3$, $Ca_3(PO_4)_2$, or MnO_2 was performed. For three PT 2022 samples, co-precipitation with $Ca_3(PO_4)_2$ had the best GAB recovery, and co-precipitation with $Fe(OH)_3$ had the lowest recovery. Recoveries for co-precipitation with $Ca_3(PO_4)_2$ for gross beta were 95–100% and for gross alpha 88–97%, compared to co-precipitation with $Fe(OH)_3$, where the recoveries were 73–77% and 95–104% for gross beta and gross alpha, respectively. This variation for gross beta is likely due to selective adsorption and solubility differences. Alpha-emitting actinides readily hydrolyze and strongly adsorb onto the $Fe(OH)_3$ matrix, ensuring efficient co-precipitation. In contrast, beta-emitting radionuclides such as ^{90}Sr largely remain as soluble cations under the same conditions, with weaker surface interactions and competition from other matrix ions, further limiting their incorporation into the precipitate [23]. This selective behaviour explains the alpha/beta imbalance and indicates that beta recovery may require modified precipitation conditions or other co-precipitation strategies. For gross alpha co-precipitation with $Ca_3(PO_4)_2$, recoveries were not as high as expected. This may be because Samples 1, 2, and QC sample have ^{210}Po present in the sample and ^{210}Po is easily co-precipitated with MnO_2 [24]. For example, gross alpha recoveries for co-precipitation with MnO_2 are in the range of 94 and 105%. Recoveries higher than 100% again indicates uncertainty contributions. The biggest contributors to the uncertainty budget for all four different pre-concentration techniques were the sample count rate (48% for alpha; 41% for beta), the standard solution count rate (29% for alpha; 53% for beta), and the initial activity of the standard solution spike (23% for alpha; 4% for beta). A minor contribution from the half-life of the gross beta standard solution (2%) was included.

$Ca_3(PO_4)_2$ co-precipitation resulted in the highest GAB recoveries and Zeta-scores for the QC sample out of the three co-precipitation techniques, therefore co-precipitation with $Ca_3(PO_4)_2$ using QC sample was selected for further analyses.

Recovery of gross alpha activity using $Ca_3(PO_4)_2$ co-precipitation was found to improve significantly with increasing sample volume. Initial tests performed with a smaller volume (~ 30 mL) yielded recoveries of 88%, whereas analyses conducted with a larger sample volume (~ 100 mL) achieved recoveries up to 98%. This increase can be attributed to both chemical and physical mechanisms. Chemically,

Table 5 PT 2022 samples GAB activities (average of three replicates) with expanded combined uncertainties, recoveries, and Zeta-scores, prepared with different pre-concentration techniques

GAB pre-concentration	Theoretical activity, Bq kg^{-1}		Measured activity, Bq kg^{-1}		Recovery %	ζ-score
		Unc. (k = 2)		Unc. (k = 2)		
QC Sample						
Co-precipitation with $Fe(OH)_3$						
Gross beta	223.1	3.9	161.9	4.2	73	11
Gross alpha	96.5	1.5	91.8	3.4	95	1.3
Co-precipitate with MnO_2						
Gross beta	223.1	3.9	167.6	4.6	75	9.2
Gross alpha	96.5	1.5	91.0	3.4	94	1.5
Co-precipitation with $Ca_3(PO_4)_2$						
Gross beta	223.1	3.9	218.5	5.3	98	0.70
Gross alpha	96.5	1.5	85.4	3.3	88	3.1
Evaporation						
Gross beta	281.2	4.6	280.4	6.4	100	0.11
Gross alpha	96.2	1.5	88.9	3.0	92	2.2
Sample 1						
Co-precipitation with $Fe(OH)_3$						
Gross beta	122.4	2.2	93.8	2.8	77	8.0
Gross alpha	30.93	0.55	31.9	1.5	103	−0.62
Co-precipitate with MnO_2						
Gross beta	122.4	2.2	93.2	2.8	76	8.1
Gross alpha	30.93	0.55	32.1	1.6	104	−0.70
Co-precipitation with $Ca_3(PO_4)_2$						
Gross beta	122.4	2.2	116.5	3.2	95	1.5
Gross alpha	30.93	0.55	27.6	1.5	89	2.1
Sample 2						
Co-precipitation with $Fe(OH)_3$						
Gross beta	24.59	0.34	18.43	0.19	75	16
Gross alpha	15.29	0.21	15.89	0.35	104	−1.5
Co-precipitate with MnO_2						
Gross beta	24.59	0.34	19.3	1.1	78	4.8
Gross alpha	15.29	0.21	16.1	1.0	105	−0.77
Co-precipitation with $Ca_3(PO_4)_2$						
Gross beta	24.59	0.34	24.7	1.2	100	−0.060
Gross alpha	15.29	0.21	14.89	0.96	97	0.40
Sample 3						
Co-precipitation with $Ca_3(PO_4)_2$						
Gross beta	30.33	0.36	Below the detection limit			
Gross alpha	10.81	0.18	12.76	0.96	118	−2.0

larger sample volumes modify the solubility–precipitation equilibrium by reducing the relative concentration of radionuclides to the co-precipitating ions (Ca^{2+} and PO_4^{3-}), which promotes the formation of larger and more stable $Ca_3(PO_4)_2$ precipitates. Under these conditions, radionuclides are more efficiently incorporated into the growing solid phase through lattice substitution and surface adsorption. Moreover, reduced supersaturation minimizes partial redissolution of the precipitate, further limiting analyte loss [25]. Physically, larger sample volumes generate a greater mass of $Ca_3(PO_4)_2$ precipitate, which improves sedimentation efficiency and reduces losses during centrifugation and washing. In contrast, the smaller precipitate mass formed in 30 mL samples is more prone to resuspension and mechanical loss, explaining the lower recovery observed. Taken together, these results demonstrate that sample volume plays

a critical role in co-precipitation efficiency, and based on the recovery behaviour observed, a minimum sample volume of approximately 100 mL is recommended to ensure consistent gross alpha recoveries of ≥ 98% while maintaining practicality for routine analysis.

Sample 2, which represents an environmental-level matrix with theoretical gross alpha activity of 15.3 Bq L^{-1}, has a better recovery (97%) for co-precipitation with $Ca_3(PO_4)_2$. This performance was higher than that observed for both the QC sample (96.6 Bq L^{-1}; 88% recovery) and Sample 1 (30.9 Bq L^{-1}; 89% recovery), indicating that lower-activity environmental samples may favour more efficient radionuclide incorporation during co-precipitation. The superior recovery of Sample 2 can be attributed to its low activity and simpler matrix. Fewer radionuclide atoms relative to available $Ca_3(PO_4)_2$ lattice sites enhance incorporation via lattice substitution and surface adsorption. Reduced concentrations of competing ions minimize matrix interferences, allowing more efficient co-precipitation. Lower activity also favours the formation of stable, well-crystallized precipitate, reducing losses during centrifugation and washing. These observations are consistent with established studies on Ca-phosphate co-precipitation, which indicate that lower competing ion concentrations and trace-level radionuclides improve recovery efficiency [26].

Initially, recoveries for gross beta were much lower for co-precipitation methods compared to direct addition. Upon further investigation, it was noted that ^3H and Cs radionuclides were not co-precipitated by any methods. In Sample 3, the only beta emitters were Cs isotopes, and results of co-precipitation with $Ca_3(PO_4)_2$ show that the gross beta activity was below the detection limit, therefore only alpha radionuclides were precipitated in Sample 3. It can be concluded, that Cs radionuclides do not co-precipitate with $Ca_3(PO_4)_2$. Usually, the standard method for Cs pre-concentration is with the ammonium phosphomolybdate (AMP) procedure [27]. An alternative method for determining Cs radionuclides for GAB is evaporation. When the GAB spectrum obtained using the evaporation method was evaluated, Cs radioisotopes were detected in the sample, but no ^3H was observed. This is expected, as the evaporation procedure cannot retain ^3H, which is lost with the water. Consistent with ISO 11704:2018, ^3H is generally excluded from standard gross alpha/beta methods and is measured separately when required [16].

There are three main options for ^3H determination by LSC, to measure ^3H separately with the distillation method, to use Tritium columns, or if the concentrations are high enough, direct counting is also possible. Tritium columns (e.g., from Triskem International) are particularly useful when ^3H needs to be measured in the same sample as other radionuclides. These columns separate ^3H from all other radionuclides and only tritiated water passes through tritium columns, other radionuclides are stuck to the resin [28]. This method for ^3H determination is rapid, cost-effective, and faster than the usual distillation method. However, it can be challenging to elute all other radionuclides retained on the tritium resins. Results from the QC sample testing with Tritium columns and determination of GAB using LSC are presented in Table 6.

An investigation into the elution of all radionuclides from the tritium columns was performed. Elution with 15 mL of 9M HNO_3 stripped most of the beta emitters from the resins, but only half of all alpha emitters contained in the QC sample. Therefore, elution with three times 15 mL of 9M HNO_3 was required to elute almost all alpha emitters, achieving approximately 80% recovery. It appears that some alpha emitters could not be fully stripped from the columns, whereas beta emitters were efficiently eluted. This indicates that further investigation is needed to optimize the removal of all alpha radionuclides from the resin. A higher-than-100% recovery was again observed for gross

Table 6 GAB and ^3H activities with extended combined uncertainty, recoveries, and Zeta-scores in QC sample, analysed by Tritium columns

QC sample	Theoretical activity, Bq kg^{-1}		Measured activity, Bq kg^{-1}		Recovery %	ζ-score
		Unc. (k = 2)		Unc. (k = 2)		
GAB, 1 × elution with 9M HNO_3						
Gross beta*	281.7	4.6	257.1	5.7	91	3.3
Gross alpha	96.4	1.5	46.6	3.5	48	13
GAB, 3 × elution with 9M HNO_3						
Gross beta*	281.7	4.6	311.3	8.5	111	−3.1
Gross alpha	96.4	1.5	77.5	3.5	80	5.0
^3H direct counting, 1 × elution with 9M HNO_3						
^3H	41.16	0.67	41.4	4.3	101	−0.059
^3H direct counting, 3 × elution with 9M HNO_3						
^3H	41.16	0.67	41.2	3.9	100	−0.043

*Excluding ^3H activities

beta activity after three elution with 9M HNO_3, likely due to the uncertainty inherent from the counting statistics. ^3H was determined in each tested elution by direct counting and in both cases, the recovery was 100%. This alternative method for ^3H determination, which has not previously been applied in GAB analyses, offers an option for measuring both ^3H and GAB activity in the same sample, if sample volume is limited. However, caution is required when proceeding with this approach to ensure accurate determination of the GAB activity.

In the end, an overall comparison of the GAB spectrums of individual pre-concentration methods with the direct counting of PT samples was evaluated. The comparison was made for the QC sample and is presented in Fig. 5.

The GAB spectrums in Fig. 5 show a larger shift of both alpha and beta peaks for co-precipitation with $Fe(OH)_3$ and with MnO_2, while for $Ca_3(PO_4)_2$ co-precipitation and evaporation, these shifts are almost unnoticeable. Quenching in MnO_2 and $Fe(OH)_3$ co-precipitated samples arises from a combination of residual colour in the sample, chemical interactions, and physical light scattering. In this case, colour quenching contributes the most to peak shifting, since some colour was still visible in the source preparation using co-precipitation with $Fe(OH)_3$ and with MnO_2. In contrast, it was observed that co-precipitation with $Ca_3(PO_4)_2$ and evaporation resulted in the smallest deviations from direct counting peaks, where residual source colour and quenching was minimal. Overall, the results show that co-precipitation with $Ca_3(PO_4)_2$ is the most effective among the tested co-precipitation techniques, while evaporation remains a reliable pre-concentration method for determining GAB activities using LSC.

Advantages and disadvantages of GAB measurements by LSC

Direct counting is usually the method of choice for water sample GAB measurements by LSC. The direct counting method is quick and easy, and no additional preparation steps are required for the measurements. However, this

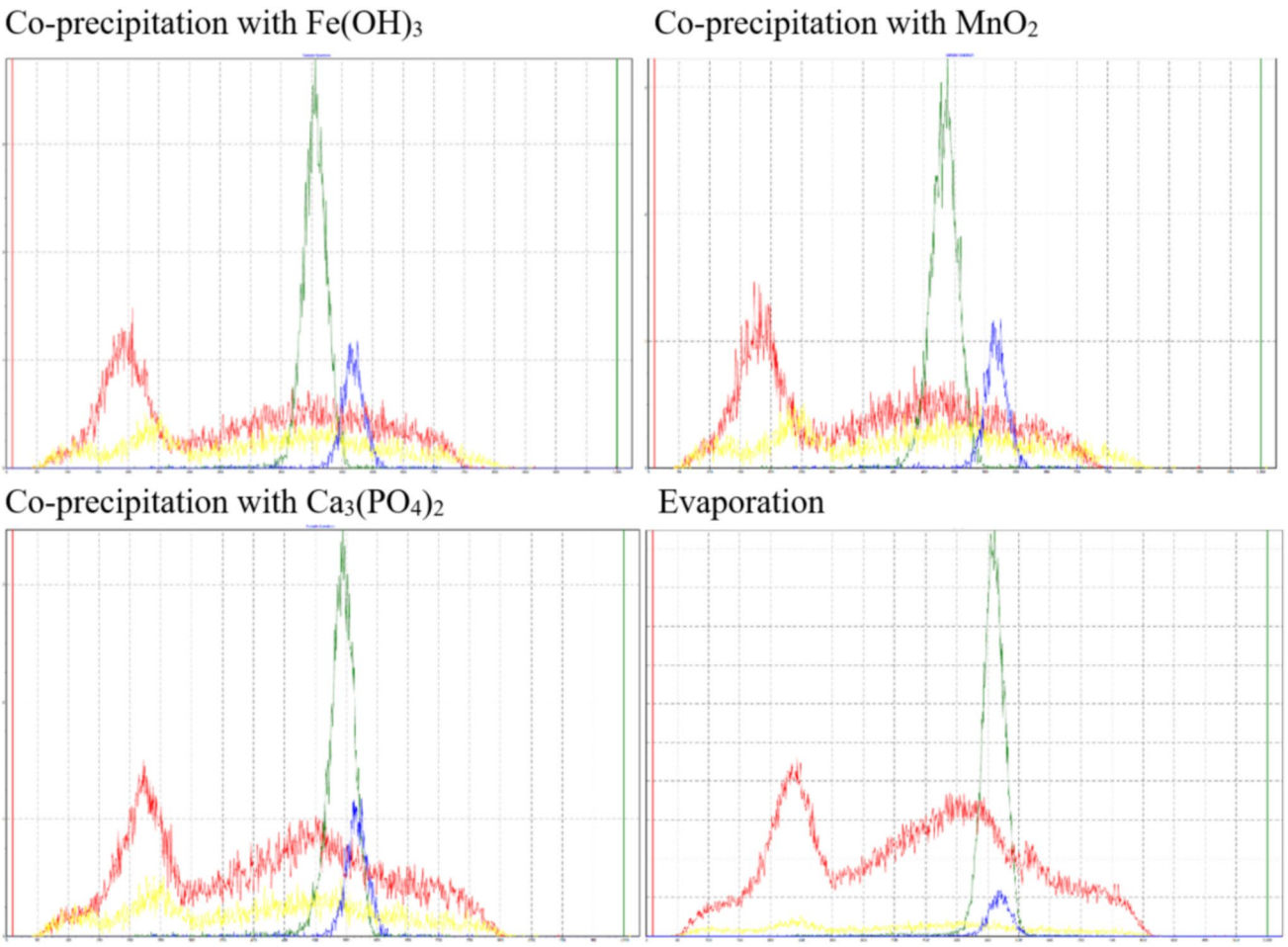

Fig. 5 Spectrum of GAB peaks for QC sample of different pre-concentration techniques (red and green) and direct counting (yellow and blue), measured at PSA 65 for 60 min

method is not suitable for environmental samples, where the activity concentrations are very low, or for analysis requiring low MDLs. Identification of individual radionuclides in the spectrum is very difficult or even impossible. A pre-concentration step is then needed to achieve sufficient resolution in the GAB spectrum, to accurately measure activity concentration with a lower MDL, and to distinguish radionuclides in unknown samples. Consequently, the precision and accuracy of analysed results will be higher with the pre-concentration step.

In this study, four different pre-concentration techniques for water samples were tested: co-precipitation with $Fe(OH)_3$, $Ca_3(PO_4)_2$, or MnO_2 and evaporation. Most other studies use evaporation as a method of choice for a pre-concentration step [16, 29]. The evaporation method is a reliable, easy technique, where most of the radionuclides are pre-concentrated. This method is not suitable for volatile radionuclides, such as ^{3}H, ^{210}Po, and ^{137}Cs. Another problem of the evaporation method is the time required to complete the analysis; as higher temperature or extended evaporation time are needed for large sample volumes. To get appropriate precision and accuracy in the GAB result, a suitable sample volume is required. Sometimes, the activity concentration in an unknown sample is very low, a larger sample volume (greater than 1 L) is required and such volumes take considerable time to evaporate to dryness. Additionally, after evaporation, some sample residue may remain, which can be difficult to dissolve for the source preparation. This is especially true for water samples with higher salt concentrations (e.g. mineral waters). In those cases, the co-precipitation method can be used instead.

Co-precipitation methods are generally faster than evaporation, particularly when processing small numbers of samples. However, not every co-precipitation method is suitable for every radionuclide. In this study, co-precipitation with $Ca_3(PO_4)_2$ showed the best outcome in terms of recovery and low quenching, but it was still not possible to co-precipitate all investigated radionuclides in tested samples. Some radionuclides simply cannot be co-precipitated with others. Limitations are common in GAB methods, e.g. ^{40}K cannot be co-precipitated in the gross beta source because it always stays in the supernatant [30]. The ^{40}K content has to be separately determined either with a low background gamma-ray spectrometry or with emission flame photometry [30]. The same problem was also observed with the other two co-precipitation methods. For this reason, in an unknown sample, the gross beta results may always be lower than the true gross beta value. The selection of the method should always consider the expected or targeted radionuclides in the samples.

Limitations of GAB measurements

When GAB activities are measured in unknown environmental samples, radon ingrowth must be taken into consideration, as it cannot be quantified using any pre-concentration technique. Many natural waters contain ^{226}Ra in different concentrations, and the progenies of ^{226}Ra play a significant role in GAB measurements since they are produced from ^{226}Ra continuously after the source preparation. The progenies contribute to the gross alpha and beta count rates, and vary as a function of time until equilibrium is reached. Careful control of timing, such as the elapsed time between source preparation and the start of measurement and measurement duration is required [30]. One option is to wait approximately 30 days for secular equilibrium between ^{226}Ra and ^{222}Rn and its progenies before measurement. However, this is still difficult to assess because ^{222}Rn is a gaseous radionuclide and may escape from the sample, even when teflon vials are used. Additionally, while waiting for secular equilibrium in the sample, some of the original GAB activity in the water may be lost before measurement.

However, the question remains how GAB methods are best used for quantifying unknown water samples. It is important to predict the relevant radionuclides expected to be present in the sample. It has been shown that almost all actual samples such as drinking water, environmental, and effluent samples in routine monitoring programmes show high beta and low alpha activity concentrations due to the radionuclides present in the sample [1, 3, 13, 31]. Therefore, when analysing the samples for GAB activities, it is helpful to know the approximate activity level, source, and chemical nature of the sample. These factors would lead to a much easier estimation of the alpha and beta energy ranges, sample volume and method, needed for LSC window calibration and for optimal final results.

GAB methods are intended to be a screening tool, metrological levels of accuracy, repeatability, and uncertainty budget should not be expected. GAB measurement results should generally fall within acceptable deviations from the true value (~30%) [18]. Influencing factors between sample preparation and the measurement procedure can sometimes be unpredictable, leading to a wide range of outcomes and uncertainty. The GAB method should therefore be used with caution, considering certain limitations; for example, temporary changes in the composition of radionuclides should be minimised, avoid complex decay chains, and measurement parameters must be consistently evaluated and adjusted throughout the analysis. Laboratories working with the GAB method must be aware of all decay and chemical processes that may affect the measurements. Within these limitations, GAB results are well suited as a complementary or alternative approach for qualitative radionuclide-specific analysis and for monitoring trends in the same sample source over

time. Nevertheless, it remains important to develop a method that is sensitive, rapid, and simple, and in which correction for potential quenching in the samples can be applied. Establishing a correction-based protocol would enable comparison of results across different GAB methods, and could lead to an approach can be reliably applied in laboratories worldwide.

Conclusions

In this study, various analytical methods were evaluated for determining GAB activities in water samples using LSC. The pre-concentration method exhibiting the smallest deviation from theoretical GAB values and minimal quenching was considered the optimal choice for application to real samples. The study results indicate that co-precipitation with $Ca_3(PO_4)_2$ and evaporation are the most suitable pre-concentration procedures. However, not all radionuclides in the tested samples were effectively recovered by these methods. Therefore, a cautious approach is necessary when assessing GAB activities in unknown samples. Accurate and precise GAB determination was achieved through verification and validation of LSC measurements, including careful control of quenching, source geometry, calibration radionuclides, chemical composition, and time delays between sampling and counting. Because numerous parameters influence GAB results, these conditions must be strictly standardized to ensure comparability and reliability.

Method validation remains essential for quality-assurance. Performance characteristics—repeatability, accuracy, reproducibility, linearity, and a realistic uncertainty budget—should be thoroughly assessed before routine application. When selecting a GAB procedure, considerations of cost, time efficiency, and analytical performance and limitations, must be balanced to determine whether a method is truly fit-for-purpose. Given that the original radiochemical composition of environmental samples is typically unknown and cannot be reconstructed from GAB measurements, GAB methodologies should continue to be used only as screening tools. The primary role is to identify further radionuclide-specific analyses and to provide long-term trend monitoring, rather than to serve as definitive indicators of total radiological content.

Acknowledgements The authors wish to thank other staff of IAEA TERC laboratory for the organisation and preparation of the PT 2022 samples.

Author contribution LRS: investigation, methodology, writing—original draft, writing—review and editing. SP: visualization, writing—review and editing, supervision.

Data availability No datasets were generated or analysed during the current study.

Declarations

Conflict of interest The authors declare no competing interests.

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