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Rapid evaluation of gross alpha and gross beta in water samples for emergency response

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Abstract

This paper presents a three-stage protocol for gross alpha and gross beta evaluation in water samples in emergencies. The novelty of this approach is the great level of detail for its application in this type of sample, following the criteria proposed in well-established safety guidelines. This protocol makes use of a rapid method adapted from different proposals found in the scientific literature. The method is based on a simple preparation of the sample and a rapid measurement by liquid scintillation counting on Quantulus 1220, which permits the evaluation of waters with different salt content (from 5 g l^{-1} of continental and drinking water, to 35 g l^{-1} of seawater) and pH (from 1 to 8) in emergency situations. The protocol and the method allow to prioritize the most active samples and to assess contamination is less than 2 hours. Both were tested and validated with spiked water samples with different ratios of alpha and beta emitters (1:1, 1:10 and 10:1) and with intercomparison water samples. Relative bias are below 10 %, except in the samples with activities close to the limits of detection and relative standard deviation are below 10 % in most of the samples, which give a clear idea of the robustness of the method.

Keywords
Environmental radioactivity; gross alpha; gross beta; water samples; emergency response; rapid method

1. Introduction

In emergencies, because of nuclear and radiological accidents or malevolent acts, numerous radionuclides could be released into the environment, and a rapid response is necessary to evaluate the possible contamination of the environment and population.

The Laboratorio de Radiactividad Ambiental of the Universitat Politècnica de València (LRA-UPV) is a support laboratory within the emergency response plan of the Valencian Community (Spain) in case of radiological emergency. LRA-UPV is developing rapid methods for determining alpha, beta and gamma emitters in different environmental matrices, such as water, aerosol filters, vegetation, food, etc. (Ordóñez et al., 2019; Sáez-Muñoz et al., 2018).

Gross alpha and gross beta determination in a radiological emergency is a useful and rapid screening method to detect alpha and beta emitters' contamination. In particular, the evaluation of the radiological quality of water is necessary to protect population. The Spanish and European regulation limit gross alpha and gross beta activities in drinking water to 0.1 Bq l^{-1} and 1 Bq l^{-1} in normal situations (RD 314/2016; Council Directive 2013/51/EURATOM). However, these limits can be exceeded in a radiological emergency. The International Atomic Energy Agency proposes operational intervention levels (OILs) in their safety guides, which must be taken into account in decision making during an emergency. The OILs are 5 Bq kg^{-1} and 100 Bq kg^{-1} for gross alpha and gross beta respectively, to ensure that total effective dose of 10 mSv $year^{-1}$ will not be exceeded (IAEA, 2011). Moreover, the United States Environmental Protection Agency establishes analytical action levels (AALs), analytical decision levels (ADLs) and requirements in the activity uncertainties (u_{MR}) in water samples corresponding to a dose of 5 and 1 mSv for both gross alpha and gross beta (EPA, 2008).

The main procedures found in the scientific literature for gross alpha and gross beta determination are both based on evaporation or co-precipitation in a thin source deposit prior to measurement by gas-flow proportional counting or liquid scintillation counting (Fons et al., 2013; ISO 10704, 2019; ISO 11704, 2018; Todorović et al., 2012; Zapata et al., 2009). However, these methods may not be appropriated in case of an emergency because of the time necessary for the preparation of the sample, the extra laboratory material needed in case of analysing several samples at the same time, and the possible cross contamination of the samples. For these reasons, some research studies proposed the direct measurement of the water sample in case of a nuclear or radiological emergency (Rusconi, et al., 2004; Sanchez-Cabeza and Pujol, 1995; Stojković et al., 2017).

In a similar line of research, the LRA-UPV proposes a three-stage protocol for emergency response. It enables to assess gross alpha and gross beta contamination in water samples in less than 2 hours and prioritize the analysis of the most active samples according to decision levels from safety guides. The rapid method proposed is based on the direct counting of the sample by liquid scintillation in Quantulus 1220. The procedure is applicable to waters with different salt content (from 5 g l^{-1} of continental and drinking water, to 35 g l^{-1} of sea water) and pH (from 1 to 8), since different corrections must be applied in the measurement and calculation according to the characteristics of the sample. This paper describes the protocol and method proposed, the calibration and the optimization of the parameters necessary to carry out the measurement and its validation with intercomparison and spiked water samples.

2. Materials and methods

2.1 Spiked and intercomparison water samples

Different standards were prepared for the development of the method and the calibration of the system. Moreover, spiked samples and intercomparison water samples were used to test and validate both the method and the response plan.

Among alpha emitters, standard solutions of different activities of ^{209}Po (7.65(0.02) Bq g^{-1}, supplied by NIST), ^{226}Ra (10.01(0.11) Bq g^{-1}, supplied by CIEMAT), ^{241}Am (437.7(2.3) Bq g^{-1}, supplied by Amersham plc) and uranyl nitrate (>98 % purity, supplied by Panreac) were used for spiking water samples. In case of beta emitters, standard solutions of different activities of ^{90}Sr/^{90}Y (810(6) Bq g^{-1}), ^{89}Sr (55.3(0.4) Bq g^{-1}), ^{3}H (973(13) Bq g^{-1}), ^{14}C (954 Bq g^{-1}) in carbonate form, ^{63}Ni (912 Bq g^{-1}) supplied by Amersham plc and potassium standard solution (1000(2) mg l^{-1}) supplied by Panreac were employed.

Intercomparison water samples used for validation were a natural sea water supplied by the Spanish Nuclear Safety Council (CSN, in Spanish) in the intercomparison CSN/CIEMAT 2015 (Water 7); and two spiked water samples containing organic and inorganic compounds from the Mixed Analyte Performance Evaluation Program (MAPEP-14-GrW31, MAPEP-16-GrW34) supplied by the Department of Energy of the United States.

2.2 Sample preparation and measurement

The methodology for gross alpha and gross beta determination in water samples consists of a simple and fast preparation of the sample and the measurement by scintillation counting.

The water sample is homogenized and filtered (0.45 µm pore size) in case of a non-potable water. In addition, samples are heated (80 ºC) and stirred for 30 minutes if they contain dissolved ^{222}Rn and its descendants (ISO 11704, 2018), controlling the weight loss of the sample by gravimetry. Then, 8 ml of the sample are added to a 20 mL polyethylene vial (supplied by PerkinElmer) and mixed with 12 mL of scintillation cocktail UltimaGold LLT (PerkinElmer). For blank samples, HPLC grade water was used following the same methodology.

After the preparation of the samples, vials are immediately measured by scintillation counting in a low background scintillation spectrometer Quantulus 1220 (PerkinElmer). One of the main parameters that must be taken into account is the sample quench level. Quenching includes all mechanisms that reduce the light produced in the scintillation process and it implies a decrease in detection efficiency. In addition, the emission spectrum shifts to lower energy channels. The detector was configured with the low coincidence bias and the multichannel analyser (MCA) in the Alpha/Beta configuration. Pulse Shape Analyzer (PSA) parameter was selected depending on the Standard External Quenching Parameter (SQP(E)). Counting times for the samples and blanks were variable and the external standard gamma source was measured for 2 minutes to determine the SQP(E). Counting windows for alpha and beta emitters were appropriately selected also to avoid chemiluminescence and photoluminescence extra counting.

WinQ was the windows software for controlling Quantulus 1220 and acquiring measurement spectra. EASY View was the spectrum analysis program used and the spectra shown in this paper were obtained using Matlab code.

2.3 Calibration of Quantulus 1220

Calibration sources of an alpha emitter certified reference solution and a beta emitter certified reference solution without other interferents were prepared. ^{241}Am and ^{90}Sr/^{90}Y standards were selected for identification of emergencies due to an artificial radionuclide contamination by alpha and beta emitters, respectively.

The same standards were used in the selection of the optimal PSA, which permits the discrimination between alpha and beta pulses. The optimal PSA is obtained minimizing the total interference (τ), sum of alpha interference (τ_α) and beta interference (τ_β) given by Eqs. (1) and (2) that are shown below:

$$\tau_\alpha = \frac{cpm_{\alpha\to\beta}}{cpm_{\alpha\to\beta}+cpm_{\alpha\to\alpha}} \qquad 0 \le \tau_\alpha \le 1 \qquad (1)$$

Where $cpm_{\alpha\to\beta}$ are the counts per minute produced by alpha pulses but misclassified as beta pulses in beta spectrum and beta window; and $cpm_{\alpha\to\alpha}$ are the counts per minute produced by alpha pulses and detected correctly in the alpha spectrum and alpha window.

$$\tau_\beta = \frac{cpm_{\beta\to\alpha}}{cpm_{\beta\to\alpha}+cpm_{\beta\to\beta}} \qquad 0 \le \tau_\beta \le 1 \qquad (2)$$

Where $cpm_{\beta\to\alpha}$ are the counts per minute produced by beta pulses but misclassified as alpha pulses in alpha spectrum and alpha window; and $cpm_{\beta\to\beta}$ are the counts per minute produced by beta pulses and detected correctly in the beta spectrum and beta window.

Three replicates of ^{241}Am calibration standard (43 Bq) and three replicates of ^{90}Sr/^{90}Y calibration standard (58 Bq) were prepared in the same geometry than water samples. The standards were measured with different PSA values from 10 to 250 to obtain the minimal interference. Moreover, optimal PSA depends on the energy of the calibration standards selected (^{241}Am and ^{90}Sr/^{90}Y) and the sample quench level (SQP(E)). In normal water samples it usually depends on their acidification or pH. For this reason, chemical quench was studied and several drops of carbon tetrachloride were added to the standards to obtain five different values of SQP(E), from 740 to 680 approximately.

Detection efficiencies for gross alpha (E_α) and gross beta (E_β) were obtained measuring ^{241}Am and ^{90}Sr/^{90}Y calibration standards respectively, for each optimal PSA depending on the sample quench level. E_α and E_β and their uncertainty $u\ (E)$ for k=1 were calculated following Eq. (3) and (4), respectively.

$$E = \frac{(cpm_{CS} - cpm_B)}{60 \cdot A_{CS} \cdot M_{CS}} \qquad (3)$$

$$u\ (E) = E \cdot \sqrt{\frac{u^2\ (cpm_{CS}) + u^2\ (cpm_B)}{(cpm_{CS} - cpm_B\ )^2} + \frac{u^2(A_{CS})}{{A_{CS}}^2} + \frac{u^2(M_{CS})}{{M_{CS}}^2}} \qquad (4)$$

Where cpm_{CS} are the counts per minute of the calibration standard (^{241}Am for gross alpha and ^{90}Sr/^{90}Y for gross beta) and cpm_B are the counts per minute of the blank, both counts in the alpha spectrum and alpha window for gross alpha, and in the beta spectrum and beta window for gross beta. A_{CS} (Bq g^{-1}) is the activity of the calibration standard and M_{CS} (g) is the mass of the calibration standard. Moreover, $u\ (cpm_{CS})$ and $u\ (cpm_B)$ are the uncertainties of the counts per minute that are calculated as $\sqrt{cpm/t}$, being t the time of measurement of the calibration standard or the blank; $u(A_{CS})$ and $u(M_{AS})$ are the uncertainties of the activity of the calibration standard and the mass.

2.4 Calculation of activity and limit of detection

Gross alpha and gross beta activity (A_α, A_β) and their uncertainties were calculated by Eq. (5) and (6), respectively.

$$A\ (Bq\ l^{-1}\ ) = \frac{(cpm_S - cpm_B)}{60 \cdot E \cdot V} \qquad (5)$$

$$u\ (A) = A \cdot \sqrt{\frac{u^2\ (cpm_S) + u^2\ (cpm_B)}{(cpm_S - cpm_B\ )^2} + \frac{u^2(E)}{E^2} + \frac{u^2(V)}{V^2}} \qquad (6)$$

Where cpm_S and cpm_B are the counts per minute of the sample and the blank respectively, both counts in the alpha spectrum and alpha window for gross alpha, and in the beta spectrum and beta window for gross beta. E is the efficiency for gross alpha or gross beta calculated by Eq. (3) and V is the volume (l) of the water sample (8 ml). Moreover, $u\ (cpm_S)$ $u\ (cpm_B)$ are the uncertainties of the counts per minute that are calculated as $\sqrt{cpm/t}$, being t the time of measurement of the sample or the blank; $u(E)$ and $u(V)$ are the uncertainties of the activity of the efficiency (by Eq. (4)) and the mass.

The limit of detection for gross alpha and gross beta (LD_α, LD_β) in Bq l^{-1} was calculated with the blank samples following the equation proposed by Currie, 1968:

$$LD = \frac{2.71 + 4.65 \cdot \sqrt{c_{blank}}}{E \cdot V \cdot t} \qquad (7)$$

where c_{blank} is the number of counts for the blank, V is the volume of sample (l), t is the counting time (s) and E is the detection efficiency of the standard solution.

3. Results and discussion

3.1 Windows selection

Alpha and beta windows were selected in alpha and beta spectrum respectively, for efficiency and activity calculation. The windows were selected after studying the spectra obtained in Quantulus 1220 by different alpha and beta emitters. As it can be seen in Fig. 1, the spectra of alpha emitters with energies that range from 4.2 to 7.7 MeV appear in channels higher than 400. In case of beta emitters, Fig. 2 shows the spectra of radionuclides with different maximum energy of emission from 18.6 keV (^{3}H) to 2280 keV (^{90}Y). By definition, gross beta activity excludes radionuclides with maximum energies below 100 keV, in particular tritium. Therefore, a beta window higher than 250 removes ^{3}H spectrum and also part of ^{14}C, which is suitable for gross beta determination. In addition, the efficiencies for high energy beta emitters, such as ^{90}Sr (546 keV), ^{89}Sr (1500 keV) and ^{90}Y (2280 keV), are still high. For these reasons, the counting alpha window comprises channels 400 – 1024, and the counting beta window channels 250 – 1024. Moreover, chemiluminescence and photoluminescence counting will not affect alpha and beta activities because it appears in channels below 120.

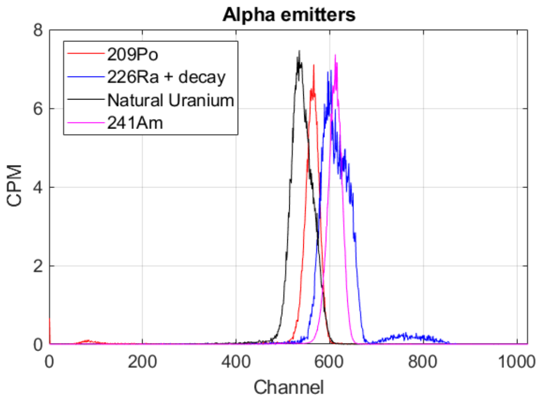

Fig. 1. Spectrum of different alpha emitters: ^{238}U (4.2 MeV), ^{209}Po (4.9 MeV), ^{241}Am (5.5 MeV), ^{226}Ra (4.8 MeV) and its decay, ^{218}Po (6 MeV) and ^{214}Po (7.7 MeV).

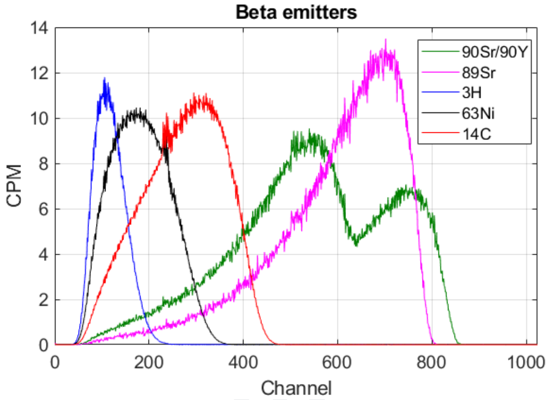

Fig. 2. Spectrum of different beta emitters: ^{3}H (18.6 keV of E max.), ^{63}Ni (67 keV of E max.), ^{14}C (156.5 keV of E max.), ^{90}Sr (546 keV of E max.), ^{89}Sr (1500 keV of E max.) and ^{90}Y (2280 keV of E max.).

3.2 PSA selection and efficiency calibration

For the correct discrimination of alpha and beta emissions, the PSA was optimized depending on the sample quench level (SQP(E)). Different calibration standards were measured modifying the PSA and the total interferences were calculated. Fig. 3. shows the variation between τ and PSA for different chemical quench levels of the sample (SQP (E)). There is a minimum interference for each quenching value, but the more quenched sample, the greater the minimum interference.

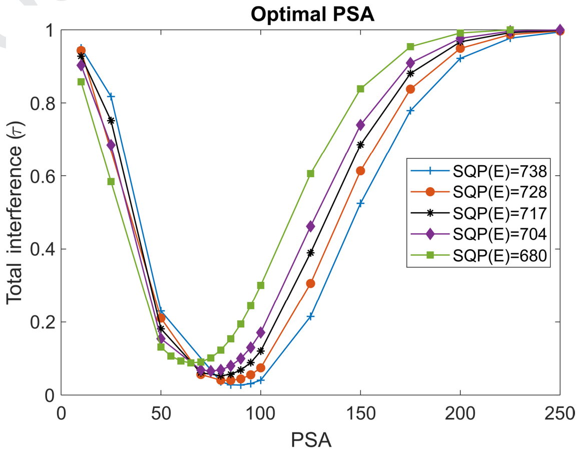

Fig. 3. Total interference (τ) as a function of the PSA, for different levels of sample quenching (SQP (E)).

Table 1 shows the minimum interference for each optimal PSA depending on the quenching parameter with their experimental standard deviation between three replicates. The minimum τ is 2.8 % for a PSA of 90 when the calibration standards were not quenched with CCl_4 (SQP(E) of 738), and the interference is 5 % or lower for quenching values between 738(3) to 717(3) and PSA between 90 to 80. The highest interference studied is 8.8 % for PSA of 65 and SQP(E) of 680. Alpha and beta efficiencies and their uncertainties (k = 1) for gross alpha and gross beta activity calculation were also obtained. E_α is close to 100 % and E_β approximately 90 %, but they also decrease with more quenched samples (lower SQP (E) values).

Table 1
Optimal PSA, total interference, alpha interference, beta interference and alpha and beta efficiencies according to the sample quench level (SQP(E)). Efficiency uncertainties calculated for k =1.

SQP(E)	Optimal PSA	τ	τ_α	τ_β	E_α (%) ± u	E_β (%) ± u
738(3)	90	0.027	0.006	0.021	116.1 ± 0.7	90.5 ± 0.4
728(3)	85	0.040	0.008	0.032	115.7 ± 0.7	89.0 ± 0.4
717(3)	80	0.053	0.010	0.043	115.9 ± 0.7	87.2 ± 0.4
704(3)	75	0.066	0.011	0.055	115.8 ± 0.7	85.5 ± 0.4
680(3)	65	0.088	0.013	0.075	114.9 ± 0.7	82.1 ± 0.4

Moreover, the relationship between the optimal PSA and the quenching parameter SQP(E) is linear and can be adjusted to a line defined by Eq. (8) with a 99.7 % of adjustment.

$$PSA_{optimal} = 0.422 \cdot SQP(E) - 222.12 \qquad (8)$$

3.3 Measurement protocol for emergency response

In case of an emergency, a fast evaluation of gross alpha and gross beta activities in water samples is necessary to protect population. For this reason, an emergency response plan was developed with the establishment of measurement protocols that permit a rapid evaluation of the contamination and prioritize most active samples. Measurement protocols were selected taking into account the sample quench level to optimize the PSA, and the limit of detection and the uncertainty obtained for the activity to reduce the time of measurement. In addition, emergency decision levels found in the literature were taken into account in the development of the plan (EPA, 2008; IAEA, 2011).

Regarding the sample quench level, different continental waters (drinking water, surface water, groundwater and rainwater) with and without being acidified for preservation were evaluated to establish an optimal PSA based on the normal SQP(E) of the samples. According to the results, the average quenching value for non-acidified samples (pH = 7-8) was 738, ranging from 736 to 742; while the effect of the acidity (pH = 2) causes a slight decrease in the quenching parameter, with an average of 734, ranging from 731 to 738. Therefore, due to the SQP(E) values of the studied waters an optimal PSA of 90 was selected for gross alpha and gross beta measurement.

The time of measurement was selected after an evaluation of the limit of detection and the uncertainty of the activity. Three blank replicates were measured for different times with PSA of 90 (SQP(E) = 738), and the average counts per minute obtained were 2.63 for beta and 0.14 for alpha. The LD_α obtained with the proper alpha efficiency were 6.31, 1.05 and 0.13 Bq l^{-1} for 10, 60 and 500 minutes of measurement, respectively; and LD_β of 30.3, 5.05 and 0.61 Bq l^{-1}. Table 2 shows different effective dose levels proposed in emergency international safety guides (IAEA, 2011; EPA, 2008) and routine drinking water regulations (RD 314/2016; Council Directive 2013/51/EURATOM), from 0.01 to 10 mSv. To avoid discrepancies between the dose factors used by the different organizations, the activities related to these doses were calculated using the water consumption of 2 l day^{-1} and ingestion dose coefficients of ^{241}Am and ^{90}Sr for an adult included in ICRP (1991). Gross alpha ranges from 0.1 to 70 Bq l^{-1}, while gross beta ranges from 1 to 500 Bq l^{-1}. Table 2 also shows the gross counts per minute that the detector would measure for these activities and the uncertainties of gross alpha and gross beta activities for 10, 60 and 500 minutes of measurement. These results are useful to evaluate the emergency and establish the measurement protocol for emergency response. Moreover, the national authorities may establish dose limits and demand requirements in the uncertainty of the activity that mainly depend on the time of measurement.

Table 2
Gross alpha and gross beta activities, gross counts per minute and activity uncertainties for k = 2 with 10, 60 and 500 minutes of measurement calculated for different dose levels.

	Alpha						Beta					
Dose (mSv)	0.01	0.07	0.9	1	5	10	0.02	0.1	0.6	1	5	10
A (Bq l^{-1})	0.1	0.5	6	7	35	70	1	5	30	50	250	500
Gross cpm	0.22	0.45	3.5	4.1	20	40	3.05	4.8	16.0	24.5	111	220
u (Bq l^{-1})-10 min	0.5	0.8	2	2.3	5.1	7.2	2.6	3.22	6	7.24	15.52	22.1
u (Bq l^{-1})-60 min	0.2	0.3	0.9	1	2.1	3	1.1	1.4	2.4	3	6.7	10
u (Bq l^{-1})-500 min	0.1	0.1	0.3	0.3	0.8	1.3	0.6	0.6	1	1.2	3.2	5.5

Fig. 4 shows the measurement steps of the emergency response plan selected after studying the influential parameters in the evaluation of the emergency and taking into account the decision levels proposed by the safety guides. They consist of a screening step, a fixed measurement step and a variable measurement step.

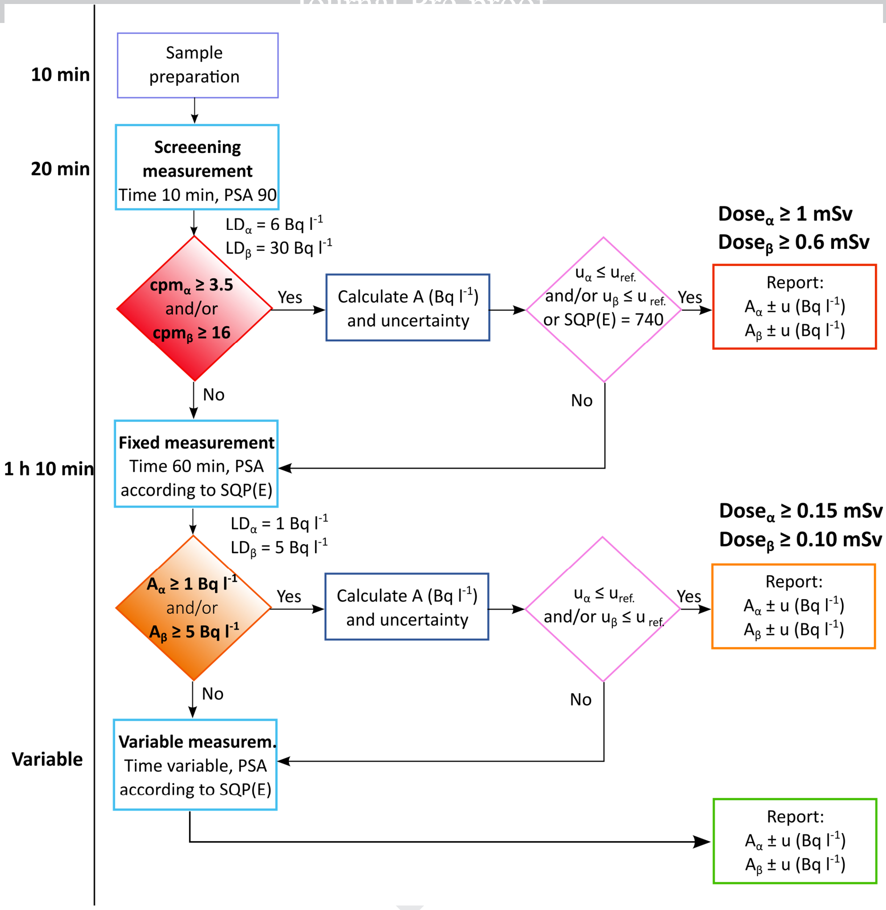

Fig. 4. Diagram of the response plan to evaluate gross alpha and gross beta activities in an emergency.

In the screening step, the samples are measured for 10 minutes with an initial PSA of 90 and the SQP(E) is evaluated to know the sample quench level. This step allows quickly to assess gross alpha and gross beta contamination and prioritize the analysis of most active samples. The gross counts per minute (cpm) measured by Quantulus 1220 are used to evaluate the emergency. Table 2 shows the equivalence between the cpm and the approximate gross alpha and gross beta activity and the effective doses by ingestion. Samples with gross alpha and gross beta activities above the limit of detection for 10 minutes of measurement, that are 6 Bq l^{-1} (3.5 cpm$_{\alpha}$) and 30 Bq l^{-1} (16 cpm$_{\beta}$), respectively, correspond to doses close to 1 mSv. These samples are high contaminated, and they may not need a longer measurement step if the uncertainties of gross alpha or gross beta activity are below the values required by the emergency stakeholders. Relative uncertainties of these activities for 10-minute measurement are less than 30 % for gross alpha and less than 20 % for gross beta. In addition, a following measurement step will be necessary if the quenching parameter is far from 738, the corresponding to optimal PSA of 90.

After identifying the most active samples, a fixed measurement step of 60 minutes is performed and the PSA is adapted to the SQP(E) measured in the screening step. The optimal PSA used for the measurement of the samples is obtained from Eq. (8). Gross alpha and gross beta activities were calculated with detection efficiencies shown in Table 1 and according to the sample quench level (SQP(E)). In this case, LD_{α} and LD_{β} are 1.05 and 5.05 Bq l^{-1}, which correspond to committed effective doses of 0.15 and 0.10 mSv, respectively. The relative uncertainties of the activities, A_{α} of 6 Bq l^{-1} and A_{β} of 30 Bq l^{-1}, improved considerably to 8 % and 15 %, respectively. Samples with an intermediate activity (A_{α} between 1 – 6 Bq l^{-1} and A_{β} between 5 – 30 Bq l^{-1}) have a relative uncertainty below 40 % for gross alpha and below 30 % for gross beta.

For low activity samples (A_{α} < 1 Bq l^{-1} or A_{β} < 5 Bq l^{-1}) or strict uncertainty requirements, a variable measurement step is performed. In this case, the protocol is the same, but the measurement time is adapted according to the estimated activities, the limits of detection or uncertainty requirements.

3.4 Testing and validation of the method and the measurement protocol

The proposed method was applied to distilled water samples spiked with different ratios of ^{241}Am and ^{90}Sr/^{90}Y (1:1, 10:1 and 1:10) to test the robustness of the method. The average SQP(E) of the samples was 736 and an optimal PSA of 90 was selected for the 60-minute measurement. Table 3 shows the average gross alpha and gross beta activities obtained for the three replicates performed for each ratio. Average relative bias between the spiked and the experimental activity were below 10 % for all the ratios and relative standard deviation between replicates below 20 %.

These good results confirm the applicability of the method for different gross alpha and gross beta activity contamination.

Table 3

Average gross alpha and gross beta activities with uncertainties for k =2, relative bias and relative standard deviation between the replicates of spiked samples with different ratios of ^{241}Am and ^{90}Sr/^{90}Y.

Ratio α:β	SQP(E)	Spectrum	Reference A (Bq) ± u	Experimental A (Bq) ± u	Relative bias (%)	RSD (%)
1:1	737 ± 2	α	43.8 ± 0.5	44.6 ± 0.5	1.9	15.4
		β	37.3 ± 0.4	38.0 ± 0.4	2.0	12.4
10:1	733 ± 4	α	438.4 ± 4.6	444.0 ± 5.3	1.3	1.5
		β	37.3 ± 0.4	38.5 ± 0.4	3.2	5.9
1:10	739 ± 2	α	43.8 ± 0.5	47.0 ± 0.6	7.2	9.9
		β	374.4 ± 2.8	378.8 ± 3.5	1.2	14.4

The measurement protocol for emergency response was tested with the analysis of spiked samples and intercomparison water samples. The same samples were used for the validation of the method. Five spiked water samples, three of them with low activity (S1 to S3) and two with high activity (S4 and S5), and three intercomparison water samples (I1 to I3) were analysed. I1 is a natural seawater sample from intercomparison CSN/CIEMAT 2015, and I2 (MAPEP-14-GrW31) and I3 (MAPEP-16-GrW34) were supplied by the Mixed Analyte Performance Evaluation Program from the Department of Energy of the United States. Table 4 shows the radionuclides present in the samples and gross alpha and gross beta reference activities. Gross alpha activities range from the water potability limit, approximately 0.1 Bq l^{-1}, to 35 Bq l^{-1}. Gross beta activity range from approximately 1 Bq l^{-1} (beta potability limit) to 337 Bq l^{-1}. Three replicates of each sample were analysed, and the potential use of the method for emergencies and for low activity samples was studied.

Table 4

Spiked and intercomparison water samples contaminated with different alpha and beta emitters. Gross alpha and gross beta reference activities (in Bq l^{-1}) and their uncertainties (k =2).

Ref.	Isotopes	A_α ± u	A_β ± u	Ratio α:β
S1	^{241}Am + ^{90}Sr/^{90}Y	0.511 ± 0.031	0.727 ± 0.015	1:1
S2	^{241}Am + ^{90}Sr/^{90}Y + ^{40}K	0.511 ± 0.031	16.98 ± 0.43	1:30
S3	^{40}K	-	16.25 ± 0.43	0:1
S4	^{241}Am + ^{90}Sr/^{90}Y	34.6 ± 0.4	34.1 ± 1.2	1:1
S5	^{241}Am + ^{90}Sr/^{90}Y	11.64 ± 0.2	337 ± 10	1:30
I1	Not spiked	0.15 ± 0.02	14.9 ± 1.8	1:100
I2	^{230}Th + ^{90}Sr	-	6.5*	0:1
I3	^{230}Th + ^{90}Sr	0.67	2.15*	1:3

*Uncertainty not available

The samples were measured and analysed following the measurement protocol for emergency response proposed. Table 5 shows the results for the different measurement steps (screening, fixed and variable). In the screening step, the cpm_α, cpm_β and the quenching parameter SQP(E) of the samples were obtained. The most active samples were S4 and S5 with values for gross alpha and gross beta above 16 cpm_β and 3.5 cpm_α, corresponding to doses higher than 1 mSv. Intermediate values of 0.3 - 0.5 cpm were obtained for S1, S2 and I2 in gross alpha, and values of 6 – 10 cpm for S2, S3, I1 and I2 in gross beta. The rest, S3, I2 and I3 in alpha and S1 and I3 in beta, presented values close to background (0.14 cpm_α, 2.63 cpm_β). The quenching parameter in most of the samples range from 733 to 742, except the intercomparison samples I2 and I3 with an average SQP(E) of 709 due to their higher acidification. Activities for samples S4 and S5 were calculated applying Eq. (5) and Eq. (6). Average values of S4 were 32.1 ± 4.8 Bq l^{-1} for gross alpha and 35.3 ± 6.2 Bq l^{-1} for gross beta; and S5 obtained 12 ± 3 Bq l^{-1} and 348.3 ± 18.5 Bq l^{-1} for gross alpha and gross beta respectively.

After the screening step, a fixed measurement step of 60 minutes was performed to evaluate the activity of the intermediate samples and reduce the uncertainty in the activity of most active samples. Gross alpha and gross beta activities of the samples were calculated, and they are shown in Table 5. However, some activities were below the limits of detection (LD_α = 1 Bq l^{-1}, LD_β = 5 Bq l^{-1}) and a longer measurement step is necessary to quantify the alpha and beta activity of S1 and I3, and the alpha activity of S2. Samples I2 and I3 were also measured with an optimal PSA.

Finally, samples S1, S2, I2 and I3 were measured in a variable measurement step to calculate gross alpha and gross beta activities. All the samples were measured for 500 minutes, S1 and S2 with PSA of 90, and I2 and I3 with an optimal PSA of 75 obtained from Eq. (8). Results in Table 5 show that all the activities are above limits of detection (0.13 and 0.61 Bq l^{-1} for gross alpha and gross beta, respectively).

Table 5
Results obtained for different spiked and intercomparison water samples analysed following the emergency protocol (screening step, fixed measurement step and variable step). Activities and limits of detection calculated in Bq l^{-1} and expanded uncertainties for k = 2.

		Screening step		Fixed measurement step				Variable measurement step				
Ref.	SQP(E)	cpm_α ± u	cpm_β ± u	A_α ± u	A_β ± u	LD_α	LD_β	PSA	A_α ± u	A_β ± u	LD_α	LD_β
S1	735 ± 1	0.41 ± 0.20	3.12 ± 0.56	< LD	< LD	0.97	5.1	90	0.47 ± 0.15	1.1 ± 0.6	0.12	0.6
S2	735 ± 1	0.44 ± 0.21	10.6 ± 1.0	< LD	18.4 ± 2.1	0.98	5.1	90	0.54 ± 0.16	18.4 ± 1.2	0.12	0.6
S3	734 ± 1	0.18 ± 0.13	10.3 ± 1.0	< LD	17.4 ± 1.9	0.97	5.0	-	-	-	-	-
S4	733 ± 1	18.1 ± 1.3	17.9 ± 1.3	32.1 ± 2.0	35.3 ± 2.6	1.05	5.0	-	-	-	-	-
S5	733 ± 1	6.9 ± 0.8	153.4 ± 3.9	12.0 ± 1.2	348.3 ± 8.4	1.05	5.0	-	-	-	-	-
I1	732 ± 2	0.27 ± 0.16	8.9 ± 0.9	< LD	14.1 ± 1.8	1.01	4.8	-	-	-	-	-
I2	706 ± 3	0.18 ± 0.13	6.0 ± 0.8	< LD	8.2 ± 1.6	1.06	5.1	75	< LD	6.9 ± 0.7	0.13	0.6
I3	703 ± 1	0.15 ± 0.12	3.8 ± 0.6	< LD	< LD	1.03	5.0	75	0.42 ± 0.14	2.5 ± 0.6	0.13	0.6

Once the measurement protocol was tested, the same spiked and intercomparison water samples were used for validation of the method, taking into account its repeatability and accuracy. The repeatability of the method was evaluated with the standard deviation (SD) and the relative standard deviation (RSD) between the three replicates analysed of each sample. The assessment of the accuracy was performed through the calculation of the relative bias between the average experimental activity and the reference activity.

Table 6 show the results obtained for the samples studied. The method obtained a RSD of the replicates lower than 7 % for beta activities (between 1 to 350 Bq l^{-1}), lower than 3 % for high alpha activities (between 12 to 32 Bq l^{-1}) and 17 % for low alpha activities (between 0.4 to 0.6 Bq l^{-1}). Results of repeatability are good enough because the deviation is lower or similar to the individual uncertainties of the samples. For this reason, only one sample is going to be analysed in the emergency protocol. Relative bias obtained for gross alpha and gross beta are below 10 % in case of activities far from LD_α and LD_β respectively. Relative bias close to the limits of detection increased to values between 30 – 50 %. However, the scope of the method proposed focuses on emergency situations, where the activities are expected to be high.

Table 6
Average activity, standard deviation (SD), relative standard deviation (RSD) and relative bias for gross alpha and gross beta activity of the spiked and intercomparison water samples.

Ref.	Gross alpha				Gross beta			
	A_α (Bq l^{-1})	SD (Bq l^{-1})	RSD (%)	Relative bias (%)	A_β (Bq l^{-1})	SD (Bq l^{-1})	RSD (%)	Relative bias (%)
S1	0.47	0.01	2.6	-6.8	1.08	0.07	6.8	48.2
S2	0.54	0.09	16.8	5.5	18.5	0.2	0.9	8.9
S3	-	-	-	-	17.5	0.4	2.2	7.7
S4	32.1	0.6	1.9	-7.3	35.3	1.0	2.8	3.6
S5	12.0	1.2	0.2	3.4	348.3	2.6	0.7	3.5
I1	-	-	-	-	14.1	0.2	1.3	-5.6
I2	-	-	-	-	6.9	0.3	3.8	6.3
I3	0.42	0.07	16.3	-37.0	2.45	0.14	5.8	13.8

4. Conclusions

The proposed method and the measurement protocol for emergency response developed permit a rapid evaluation of gross alpha and gross beta activities in water samples. Samples with different salt content (from 5 g l^{-1} of continental and drinking water, to 35 g l^{-1} of seawater) and pH (from 1 to 8) can be analysed prioritising the most active samples in case of radiological emergencies.

Water samples were mixed with scintillation cocktail in a polyethylene vial and measured on Quantulus 1220. The measurement conditions were optimized and the equipment was calibrated. Counting windows selected were between channels 400 – 1024 for gross α, and 250 - 1024 for gross β; and calibration standards were ^{241}Am and ^{90}Sr/^{90}Y for gross α and gross β, respectively. Pulse Shape Analyzer (PSA) parameter was optimized to achieve the best alpha and beta discrimination as a function of the quenching parameter SQP(E) of each sample. Gross alpha and gross beta activities were calculated with the corresponding efficiencies for each PSA. Moreover, the emergency response plan proposed consists of three-stage protocol: screening (10 min.), fixed measurement (60 min.) and variable measurement (variable time). In case of a radiological emergency, depending on the activity of the samples, one or two measurement protocols are performed and the active samples are evaluated in less than 2 hours.

Testing and validation of the method and the response procedure were presented. Spiked water samples with different ratios of α(^{241}Am):β(^{90}Sr/^{90}Y), 1:1, 1:10 y 10:1, other spiked samples with alpha and beta emitters and intercomparison water samples were analysed. Relative bias were below 10 %, except in samples with activities close to the limits of detection, and repeatability of the method was also evaluated with relative standard deviations below 7 % in highly contaminated samples. For these reasons, the laboratory is prepared to give a fast and accurate response in case of an emergency.

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