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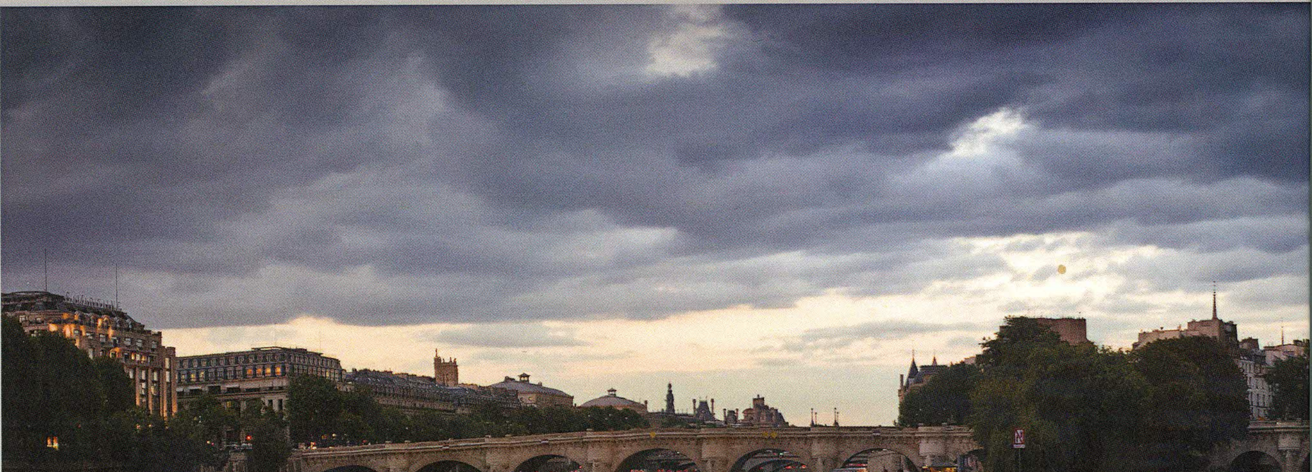

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QUALITY ASSURANCE ON GROSS-ALPHA AND GROSS-BETA MEASUREMENTS IN WATER SAMPLES BY LSC

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ABSTRACT. A method for the determination of gross-alpha and gross-beta activity concentrations in nonsaline waters by liquid scintillation counting (LSC) was validated with spiked water samples in terms of accuracy, precision, detection limits, and uncertainty budget. An internal quality control was implemented by performing replicate analysis of the quality control (QC) sample on a monthly basis. Participation in intercomparison exercises was also performed as an external evaluation of the performance of the method.

INTRODUCTION

The establishment of systematic quality assurance (QA) and quality control (QC) programs allows analytical laboratories to improve their methods, to identify problems, to implement preventive and corrective actions, to maintain a higher level of accuracy and precision of their results, and to achieve a stable level of high-quality output (IAEA 2004). All analytical methods should be validated for their intended use (Chałupnik and Mielnikow 2009a). The equipment should be calibrated, tested, and maintained operational (Pates et al. 1998; Jaubert et al. 2006; Chałupnik and Mielnikow 2009b). Participation in proficiency tests and intercomparison exercises should be performed regularly to ensure that the QA system is operating satisfactorily (Betti and de las Heras 2004).

The QA program involves systematic actions to guarantee the system is performing according to specific requirements and to ensure that standards of quality are being met (including laboratory handling operations, selection and validation of the methodologies, resources used for the analyses, and the quality control). Two key principles characterize the QA program: "fit for purpose" (method should be suitable for the intended purpose) and "right first time" (mistakes should be eliminated). The QC program (external and internal) comprises all necessary actions to verify the specified requirements, such as accuracy, precision, and performance of the instrumentation.

The QA/QC programs should be implemented in accordance with national and international demands. General requirements for the competence of testing laboratories are specified by the ISO/IEC 17025 international standard (ISO 2005). This international standard defines management and technical requirements that analytical laboratories shall fulfill to perform their tests on a well-defined quality (Chung et al. 2006).

A QA system based on this standard has been implemented at the Radiological Protection and Safety Unit (UPSR). All activities were carried out in accordance with the Quality Manual's written and approved procedures and instructions. Concerning the liquid scintillation counting (LSC) determination of gross-alpha and gross-beta activity concentrations in nonsaline waters, the technical procedure has been improved (Lopes et al. 2005; Lopes and Madruga 2006) regarding the sample preparation and the measurements. The biggest changes concern the strict control of the dry residue and the pH of the sample (ISO 2010). New calibration of the liquid scintillation counter was performed and the method was validated under the new counting conditions. The assessment of uncertainty and the characteristic limits were improved. Thus, this paper presents the applied QA/QC program on gross-alpha and gross-beta measurements in waters by LSC.

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LSC 2010, Advances in Liquid Scintillation Spectrometry
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MATERIALS AND METHODS

Experimental Procedure

All reagents used were of recognized analytical grade. The water sample was acidified with nitric acid at a pH value not lower than 2.5 ± 0.5. An aliquot of 50 mL was used for determination of the dry residue. An evaporation method was applied to water samples that include dry residue of less than 500 mg L^{-1} to avoid difficulty in the source preparation for LSC. The sample (250 g) was slowly evaporated on a hot plate until a quantity of ~25 g and weighed at room temperature. The evaporation of water samples that include a lot of dry residue may lead to salt precipitation or to a problem in source preparation using the scintillation cocktail. In these cases, the sample volume was reduced or the sample was directly measured without the evaporation treatment. For direct measurement of the sample, an aliquot of the water sample was transferred to a beaker and the pH value was adjusted to 1.5 ± 0.5 with nitric acid and an ammonium hydroxide solution. In both cases, the sample amount (8 g) was mixed with the scintillation cocktail (Ultima Gold™ LLT, PerkinElmer) into a scintillation glass vial (with urea screw caps). An 8:12 ratio of sample to cocktail was always kept to maintain the same quenching level in the sample solution before measurement (Sanchez-Cabeza and Pujol 1995). The background samples were prepared in the same way as the routine samples using a nitric acid solution (0.03 mol L^{-1}).

Measurements were performed using a liquid scintillation spectrometer (Tri-Carb® 3170 TR/SL, PerkinElmer) equipped with a pulse-decay analysis (PDA) option. The counter was previously optimized and calibrated using a set of ^{241}Am and ^{90}Sr/^{90}Y standards prepared with the same activity (~10 Bq) from certified standard solutions (^{241}Am from Eckert & Ziegler Analytics and ^{90}Sr/^{90}Y from Amersham) with different volumes of CCl_4 (0–50 μL) and consequently with different quenching levels. The quenching effect was quantified by the tSIE parameter (transformed spectral index of the external standard). The curves of the counting efficiency versus the tSIE parameter obtained for alpha and beta standards are illustrated in Figure 1 and Figure 2, respectively. The measurements were performed in normal counting mode, in the channel region 76–215 keV for gross alpha and 26–905 keV for gross beta, using an optimum pulse-decay discriminator (PDD) setting at 123. As the quench level influences the PDD setting and the alpha/beta misclassification (DeVol et al. 1996; Sanchez-Cabeza and Pujol 1997), the optimum PDD value was determined using the alpha and beta standards with tSIE values identical to the routine samples. Figure 3 illustrates the percentage of alpha and beta misclassification for that PDD value. Counting times of 30 min and 240 min were used for standards and samples, respectively. The gross-alpha and gross-beta activity concentrations were determined using the following equation (Cook et al. 2003):

$$c_{Ai} = \frac{\eta_i(1-\chi_{ji}) - \eta_j\chi_{ji}}{\varepsilon_i V(1-\chi_{ij}-\chi_{ji})}$$

where c_{Ai} is the activity concentration for the i emitter, n_i and n_j the net count rates on windows i and j, ε_i the detection efficiency for i particles, V the volume, and χ_{ij} and χ_{ji} the spillover corrections. The combined uncertainty ($u(c_{Ai})$) is calculated using the following expression, where u is the standard uncertainty and u_r is the relative standard uncertainty:

$$u(c_{Ai}) = \frac{\sqrt{(1-\chi_{ji})^2u^2(n_i) + \chi_{ji}^2u^2(n_j) + (c_{Ai}\varepsilon_i V)^2\{(1-\chi_{ij}-\chi_{ji})^2[u_r^2(\varepsilon_i)+u_r^2(V)] + u^2(\chi_{ij}) + u^2(\chi_{ji})\} + [(n_i+n_j)^2 - 2c_{Ai}\varepsilon_i V(n_i+n_j)]u^2(\chi_{ji})}}{\varepsilon_i V(1-\chi_{ij}-\chi_{ji})}$$

The result is presented as $c_{Ai} \pm U(c_{Ai})$ where $U(c_{Ai})$ is the expanded uncertainty, using a coverage factor (k) of 2.

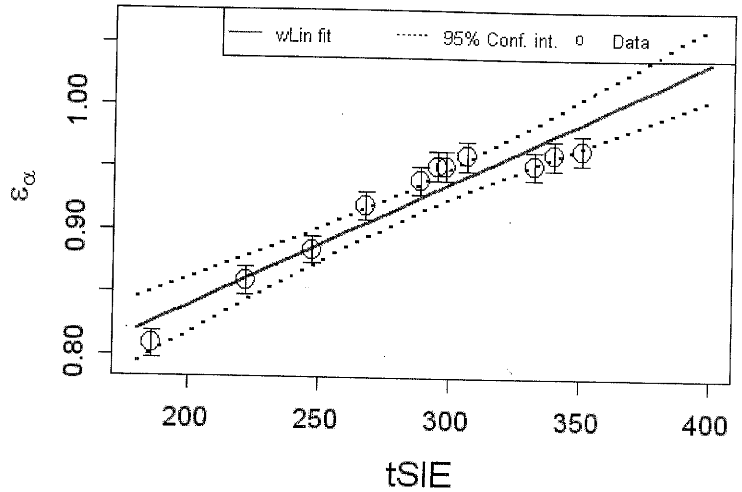

Figure 1 Alpha counting efficiency versus tSIE quenching parameter

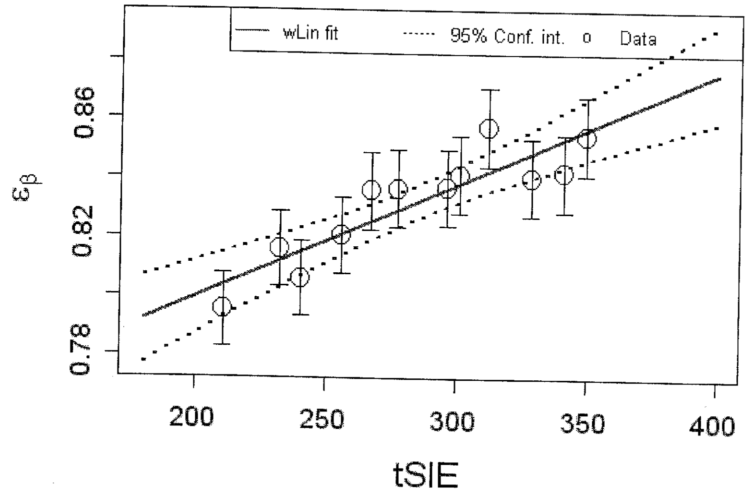

Figure 2 Beta counting efficiency versus tSIE quenching parameter

Identification and quantification of uncertainty components were performed, and verified that the main sources of standard uncertainty are the count rates, counting efficiencies, and the percentage of interferences ("spillover"). Counting time and weight relative uncertainties were neglected.

The characteristic limits, such as the decision threshold (c^*_{Ai}) and the detection limit ($c^\#_{Ai}$) were calculated according to the international standard (ISO 2009) using the following equations:

$$c^*_{Ai} = \frac{k}{\varepsilon_i V(1-\chi_{ij}-\chi_{ji})}\sqrt{(1-\chi_{ji})^2\left[\frac{b_i}{t}+u^2(b_i)\right]+\chi_{ji}^2\left[\frac{b_j}{t}+u^2(b_j)\right]+\frac{(1-\chi_{ji})\chi_{ji}}{t}c_{Aj}\varepsilon_j V+(c_{Aj}\varepsilon_j V)^2u^2(\chi_{ji})}$$

$$c_{Ai}^{\#} = \frac{\dfrac{2c_{Ai}^{*}}{k^2} + \dfrac{1}{t\varepsilon_i V(1-\chi_{ij}-\chi_{ji})^2}[(1-\chi_{ij}-\chi_{ji}) + \chi_{ji}(2\chi_{ij}+\chi_{ji}-1)]}{\dfrac{1}{k^2} - (\varepsilon_i V)^2\{(1-\chi_{ij}-\chi_{ji})^2[u_r^2(\varepsilon_i) + u_r^2(V)] + u^2(\chi_{ij})\}}$$

where b is the background count rate and t the acquisition time. For 8.0 g of sample and a concentration factor of 10, the detection limits for 4 hr of counting time, were 0.09 Bq L^{-1} for gross-alpha and 0.19 Bq L^{-1} for gross-beta measurements, respectively. The Portuguese law (Decree-Law 306, 2007) for drinking water quality recommends values of 0.5 and 1.0 Bq L^{-1} for gross-alpha and gross-beta activity concentrations, respectively.

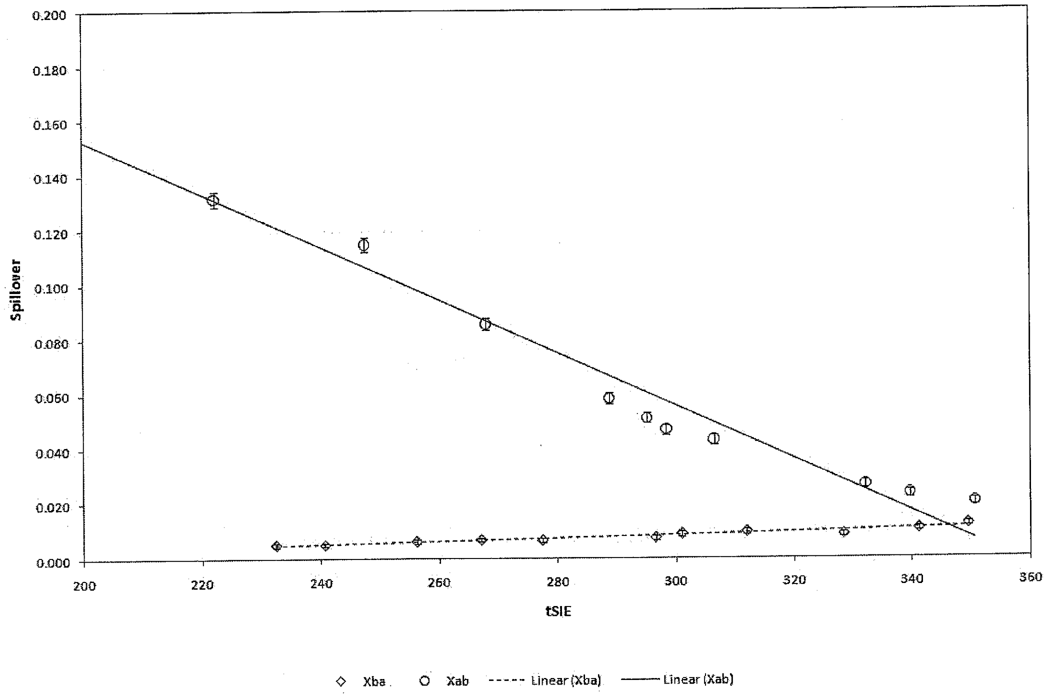

Figure 3 Percentage of alpha and beta spillover versus tSIE quenching parameter

METHOD VALIDATION

For method validation, water samples spiked with ^{241}Am (0.152–1.014 Bq L^{-1}) and ^{90}Sr (0.620–2.208 Bq L^{-1}) were prepared and measured, according to the experimental procedure, in order to determine the recovery percentages (Table 1). The mean recovery values for gross alpha and gross beta were, respectively, 87 ± 10% (n = 7) and 88.8 ± 1.5% (n = 6). These values are within the acceptable range of 80–120% (criterion defined based on previous trials). A good relationship between the added and the measured activities was obtained for both gross-alpha and gross-beta measurements with correlation coefficients (R^2) of 0.98 and 0.99, respectively, which proves the linearity of the method. The precision was also evaluated with 10 aliquots of the quality control (QC) sample. The relative standard deviation (%RSD) was 7% for gross-alpha and 18% for gross-beta measurements.

Table 1 Comparison of theoretical and measured values of ^{241}Am and ^{90}Sr in spiked water samples.

	^{241}Am (Bq L^{-1} ± U; $k = 2$)			^{90}Sr (Bq L^{-1} ± U; $k = 2$)		
Spiked sample	Theoretical value	Measured value	^{241}Am recovery (%)	Theoretical value	Measured value	^{90}Sr recovery (%)
1	0.15 ± 0.01	0.12 ± 0.04	80.17	—	—	—
2	0.20 ± 0.01	0.17 ± 0.04	84.56	—	—	—
3	0.50 ± 0.01	0.44 ± 0.07	88.33	—	—	—
4	1.01 ± 0.02	1.08 ± 0.14	106.95	—	—	—
5	—	—	—	0.63 ± 0.01	0.56 ± 0.10	88.57
6	—	—	—	1.18 ± 0.01	1.01 ± 0.12	86.08
7	—	—	—	2.23 ± 0.02	1.99 ± 0.17	88.94
8	0.15 ± 0.01	0.11 ± 0.03	75.15	0.62 ± 0.01	0.55 ± 0.09	88.85
9	0.49 ± 0.01	0.40 ± 0.06	80.80	1.17 ± 0.01	1.06 ± 0.12	90.05
10	0.98 ± 0.02	0.88 ± 0.12	90.25	2.21 ± 0.02	2.00 ± 0.18	90.34

QUALITY CONTROL

Internal Quality Control

An internal quality control (QC) program was put in practice performing periodic analysis of the QC sample. This water contains relatively higher levels of natural radioactivity and a matrix similar to the routine samples. A batch of 10 aliquots of the QC water was prepared and measured. The mean value ($\bar{X}$) was calculated and the standard deviation was used to set the warning ($\bar{X} \pm 2\sigma$) and actions limits ($\bar{X} \pm 3\sigma$). After setting up the control charts, replicate analyses of the QC water were performed on a monthly basis and the individual values obtained were plotted (Figures 4 and 5). Those values were compared with the established limits to decide the acceptability of the batch's data. The precision was simultaneously evaluated with triplicate samples and the results were considered acceptable if the %RSD ≤ 20% and %RSD ≤ 30% for gross-alpha and gross-beta measurements, respectively. A background sample was always measured with each set of 10 samples. The performance of the equipment was checked through background samples and sealed standards (^{241}Am and ^{36}Cl). Specific control charts for the equipment were also used to help in the identification of possible systematic deviation from regular performance in time, for inspection of trends, and to verify the stability of the counter. The equipment was operated under controlled room temperature and humidity conditions and all the necessary adjustments or repairs are registered.

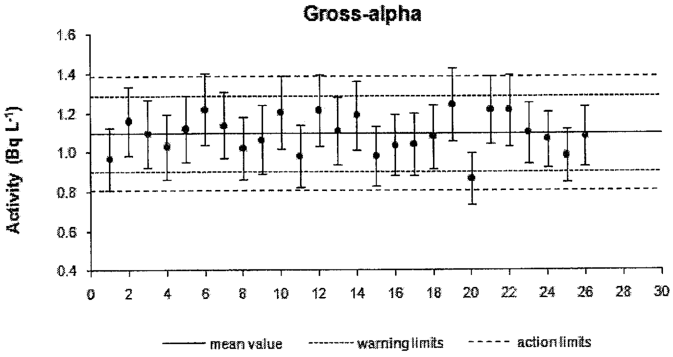

Figure 4 Control chart for gross-alpha activity in quality control sample

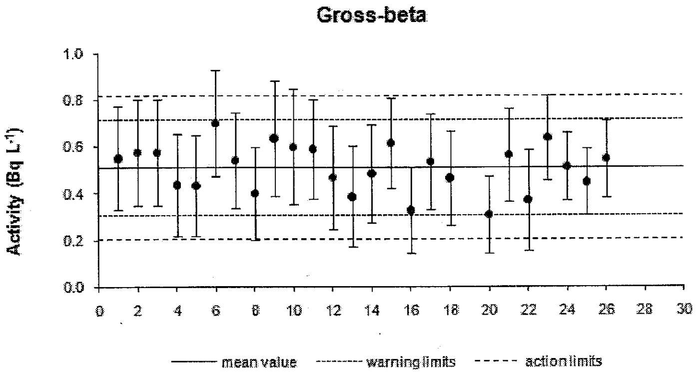

Figure 5 Control chart for gross-beta activity in quality control sample

External Quality Control

The accuracy of the results was assessed through the participation in an intercomparison exercise (LMR 2010). The results for the determination of gross-alpha and gross-beta activity concentrations in drinking water showed acceptable *Z* score values for both gross-alpha (*Z* score = 0.76) and gross-beta measurements (*Z* score = 0.87). This means that the accuracy of the analysis was verified, providing confidence on the measurement results. Better results were obtained (Table 2) performing the analysis of the same water sample after a new calibration of the equipment. The values of the relative bias (*D*%) and the precision estimator (*P*%) were also acceptable, according to the criteria established for the respective exercise.

Table 2 Interlaboratory comparison results for gross alpha and gross beta in water samples.

Analyte	Reference value (Bq $L^{-1} \pm U$; $k = 1$)	Measured value (Bq $L^{-1} \pm U$; $k = 1$)	*Z* score	Relative bias (*D*%)	Precision (*P*%)
Gross alpha	18.83 ± 0.81	20.37 ± 1.21	0.41	–8.18	7.33
		20.02 ± 1.19	0.31	–6.32	7.34
Gross beta	51.05 ± 2.03	51.50 ± 1.96	0.06	7.66	5.50
		50.81 ± 1.93	–0.03	7.66	5.50

CONCLUSIONS

Some important requirements of the QA/QC program were implemented and improved for gross-alpha and gross-beta measurements. The relative uncertainties and the characteristic limits are better evaluated and characterized now. The linearity of the method was checked and the precision and accuracy were also determined and verified. An internal quality control program was put in practice and the evaluation of the external control was acceptable. The greater confidence of the results produced now will allow the method to be accredited in the near future, as expected.

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