Simultaneous determination of gross alpha, gross beta and ^{226}Ra in natural water by liquid scintillation counting

J. Fons [a],[*], D. Zapata-García [b], J. Tent [a], M. Llauradó [a]

[a] Laboratory of Environmental Radiology, Analytical Chemistry Department, Universitat de Barcelona, Martí i Franquès 1-11, 3ª Planta, Catalunya, Barcelona 08028, Spain
[b] Ionizing Radiation Division, Physikalisch-Technische Bundesanstalt, Bundesanstalt, Germany

ABSTRACT

The determination of gross alpha, gross beta and ^{226}Ra activity in natural waters is useful in a wide range of environmental studies. Furthermore, gross alpha and gross beta parameters are included in international legislation on the quality of drinking water [Council Directive 98/83/EC].[1] In this work, a low-background liquid scintillation counter (Wallac, Quantulus 1220) was used to simultaneously determine gross alpha, gross beta and ^{226}Ra activity in natural water samples. Sample preparation involved evaporation to remove ^{222}Rn and its short-lived decay daughters. The evaporation process concentrated the sample ten-fold. Afterwards, a sample aliquot of 8 mL was mixed with 12 mL of Ultima Gold AB scintillation cocktail in low-diffusion vials.

In this study, a theoretical mathematical model based on secular equilibrium conditions between ^{226}Ra and its short-lived decay daughters is presented. The proposed model makes it possible to determine ^{226}Ra activity from two measurements. These measurements also allow determining gross alpha and gross beta simultaneously. To validate the proposed model, spiked samples with different activity levels for each parameter were analysed. Additionally, to evaluate the model's applicability in natural water, eight natural water samples from different parts of Spain were analysed. The eight natural water samples were also characterised by alpha spectrometry for the naturally occurring isotopes of uranium (^{234}U, ^{235}U and ^{238}U), radium (^{224}Ra and ^{226}Ra), ^{210}Po and ^{232}Th. The results for gross alpha and ^{226}Ra activity were compared with alpha spectrometry characterization, and an acceptable concordance was obtained.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

To determine ^{226}Ra activity concentration is an important task due its high radio-toxicity as review Guogang and Jing (2012). Gross alpha, gross beta and ^{226}Ra activity can be used to establish the TID (Total Indicative Dose). There are various methods of measuring ^{226}Ra, including γ-spectrometry (Kahn et al., 1990; Cazala et al., 2003; Dulaiova and Burnett, 2004), α-spectrometry (Purkl and Eisenhauer 2003; Bojanowski et al., 2005), radon emanometric methods (Lucas et al., 1990; Maharana et al., 2010) and liquid scintillation techniques with radiochemical separation (Salonen, 1993; Repine and Benedik, 2002) or without separation (Salonen, 2006).

When liquid scintillation spectrometry without radiochemical separation is applied, the point is to eliminate radon and its short-lived daughters of the sample and to evaluate the increase of the alpha activity between the sample treatment and 21 days after this

treatment. The variation was attributed to the increase of ^{222}Rn and its short-lived daughters into the sample vial. This method was tested by several authors and useful results were obtained (Sanchez-Cabeza and Pujol, 1998; Fernandes et al., 2011). However to measure after 21 days of the sample treatment is an important drawback for this method. In this work a mathematical model was developed in order to determinate ^{226}Ra activity measuring the first time just after sample treatment and the second one before 21 days after that treatment.

The advantages of this mathematical model application are, on one hand joint the determination of gross alpha, gross beta and ^{226}Ra in one technique and on the other hand avoid radiochemical separation which entails a reduction in sample manipulation and in the reactive consumption.
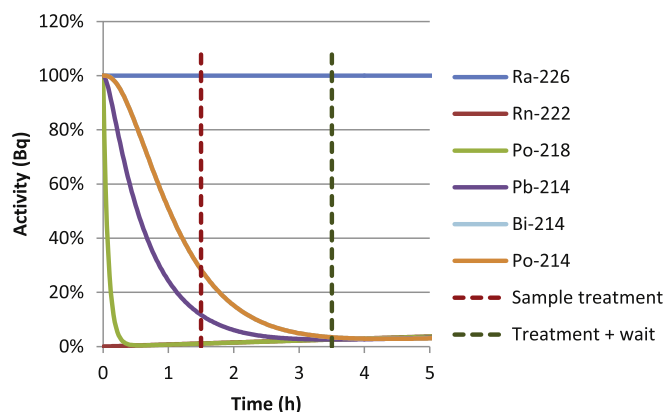
2. Methods and materials

2.1. Detector

A low background liquid scintillation counter (1220 QUANTULUS, Wallac (Turku, Finland)) was used. The *Pulse Shape Analyser*

Fig. 1. Activity evolution for ^{226}Ra and its short-lived daughters in a sample which ^{222}Rn was completely removed.

(PSA) of the 1220 QUANTULUS discriminates between alpha and beta pulses and separates the pulses into different multi-channels. The optimal PSA value for the alpha–beta discrimination was established by a misclassification study using ^{236}U and ^{40}K as standards. Please see the report CSN (2011).

This detector also has a quench control parameter. The Spectral Quench Parameter of the External Standard (SQP[E]) is the lowest channel below which 99.75% of the counts generated when the sample is irradiated with a ^{152}Eu source, included in the counter, are registered. The SQP[E] was evaluated in all samples. In this study, we used constant quench conditions.

This detector is under the quality control (internal and external) of the Laboratory of Environmental Radiology. (ISO/IEC 17025, ENAC accreditation n° 520/LE1117).

2.2. Reagents

High capacity and specially designed for the alpha beta discrimination cocktail Ultima Gold AB (Perkin Elmer, Turku, Finland) was used throughout the work.

The radioactive solutions were prepared by weight from the following radioactive standards: ^{230}Th 40.83 ± 0.16 Bq g^{-1} standard supplied by NIST *National Institute of Standards and Technology* (Gaithersburg, Maryland); ^{226}Ra 176.0 ± 2.4 Bq g^{-1} standard supplied by CIEMAT *Centro de Investigaciones Energéticas Medioambientales y Tecnológicas* (Madrid, Spain); ^{210}Pb 35,500 ± 700 Bq g^{-1} standard supplied by DAMRI *Département des applications et de la métrologie des rayonnements ionitzants* France; ^{nat}U 957.2 ± 19.1 Bq g standard and ^{236}U 761.1 ± 15.7 Bq g^{-1} standard both supplied by Eckert and Ziegler (Valencia, California). The ^{40}K solutions were prepared from dry KCl salt supplied by Merck (Berlin, Germany). The activity was calculated by applying the natural abundance of ^{40}K.

2.3. Material

Twenty-millilitre polyethylene liquid scintillation vials were supplied by Perkin Elmer.

General purpose materials in the laboratory were used.

2.4. Analytical procedure

A 100 mL aliquot of a water sample was evaporated at what temperature to dryness. When the precipitate obtained was cooled to room temperature, it was dissolved in 10 mL of deionised water acidified by HCl to pH = 1.5 as describe Zapata-García et al. (2009). It was necessary to stir the solution for 5 min to ensure that all the precipitated material was dissolved. With this treatment, ^{222}Rn is completely eliminated from the sample. The elimination of their short-lived daughters occurs by means of radioactive decay. Fig. 1 show the activity evolution in a ^{226}Ra sample with their decay daughters when ^{222}Rn is removed. To perform this simulation we have used the Laplace transform solution of the equations of radioactive decay. About 3 h and a half are required for a quantitative removal of the short-lived daughters (Catchen, 1984).

An 8 mL aliquot of the evaporated sample was mixed with 12 mL of the scintillator cocktail in a low diffusion scintillator vial. Under these conditions, the sample remained homogenous and was stable for several months. The vial was counted in a liquid scintillation counter that was able to discriminate between alpha and beta pulses. It is recommended that the vial should remain in the counter for 2 h before counting to avoid photoluminescence phenomena. The 2 h time period is also necessary to allow the decay of the short-lived daughters of ^{222}Rn. To find the appropriate calibration standard, many alpha emitters (^{230}Th, ^{236}U and ^{241}Am) and beta emitters (^{40}K, ^{137}Cs, ^{90}Sr/Y) were used to conduct a misclassification study (Zapata-García et al., 2012). Both ^{236}U and ^{40}K were selected as calibration standards because they are the emitters with the worst misclassification. Please see the report CSN (2011) for more details.

2.5. Samples

2.5.1. Synthetic samples

A synthetic water sample containing 95 mg L^{-1} Ca^{2+}, 51 mg L^{-1} Mg^{2+}, 38 mg L^{-1} Na$^+$, 2 mg L^{-1} K$^+$, 227 mg L^{-1} SO$_4^{2-}$, 149 mg L^{-1} Cl$^-$ and 138 mg L^{-1} HCO$_3^-$ was prepared. It was acidified by HNO$_3$ to pH = 1. Several aliquots of this synthetic water sample were spiked with natural isotopes. The composition of these solutions is shown in Table 1.

2.5.2. Natural samples

Eight natural water samples from different parts of Spain were analysed. As shown in Table 2, the selected water samples have different radioactivity contents and a wide range of dry residue. A 100 L volume of water was taken at each sampling point. The water samples were acidified with HNO$_3$ (1.25 mL L^{-1}) for preservation.

Table 1
^{nat}U, ^{226}Ra, ^{210}Po and gross alpha activity for the spiked samples.

Code	U-nat (Bq kg^{-1})	Ra-226 (Bq kg^{-1})	Po-210 (Bq kg^{-1})	Gross alpha (Bq kg^{-1})
URa 100:0	0.201 ± 0.004	–	–	0.201 ± 0.004
URa 75:25	0.169 ± 0.003	0.108 ± 0.002	0.076 ± 0.002	0.353 ± 0.006
URa 50:50	0.118 ± 0.002	0.128 ± 0.002	0.090 ± 0.002	0.336 ± 0.005
URa 25:75	0.072 ± 0.002	0.181 ± 0.003	0.127 ± 0.002	380 ± 0.006
URa 0:100	–	0.208 ± 0.002	0.146 ± 0.002	0.354 ± 0.004
URa	0.214 ± 0.004	0.198 ± 0.003	0.138 ± 0.006	0.550 ± 0.008
URaPo	0.196 ± 0.004	0.202 ± 0.003	0.418 ± 0.010	0.816 ± 0.015

Table 2
Chemical and radiochemical characteristics of the natural water samples.

CODE	Characteristics
SUBT-A	Dry residue: 1 g L^{-1}. Activity ^{226}Ra $\sim$ 0.40 Bq L^{-1}, ^{234,238}U $\sim$ 1.0 Bq L^{-1}, Po $\sim$ 0.02 Bq L^{-1}
POT-A	Dry residue: 5 g L^{-1}. Activity ^{226}Ra $\sim$ 0.40 Bq L^{-1}, ^{210}Po $\sim$ 0.06 Bq L^{-1}, ^{234,238}U $\sim$ 0.60 Bq L^{-1}
SUP-A	Dry residue: 1.5 g L^{-1}. Activity ^{234,238}U $\sim$ 0.10 Bq L^{-1}
POT-B	Dry residue: 0.4 g L^{-1}. Activity ^{226}Ra $\sim$ 0.002 Bq L^{-1}
POT-C	Dry residue: 0.9 g L^{-1}. Activity: ^{234,238}U $\sim$ 0.08 Bq L^{-1}, ^{226}Ra $\sim$ 0.002 Bq L^{-1}
POT-D	Dry residue: 4.7 g L^{-1}. Activity: ^{226}Ra $\sim$ 1.0 Bq L^{-1}, ^{228}Ra $\sim$ 0.03 Bq L^{-1}, ^{234,238}U $\sim$ 0.03 Bq L^{-1}
SUP-B	Dry residue: 0.6 g L^{-1}. Activity: ^{226}Ra $\sim$ 0.01 Bq L^{-1}, ^{234,238}U $\sim$ 0.06 Bq L^{-1}
SUBT-B	Dry residue: 0.9 g L^{-1}. Activity: ^{226}Ra $\sim$ 0.10 Bq L^{-1}, ^{234,238}U $\sim$ 1.0 Bq L^{-1}

2.6. Calibration

2.6.1. Alpha–beta discrimination

The *Pulse Shape Analyser* is used to discriminate between alpha and beta pulses. With the aim of establishing the optimal PSA value, the misclassification phenomenon was studied using ^{236}U and ^{40}K as standards. In this study one vial for each one of the standards was prepared and measured at different PSA values. The optimal PSA is found as the value in which the total misclassification, alpha plus beta, is lower. Fig. 2 shows the graphical representation of this misclassification study. We can see that the optimal PSA value is around 100. In this PSA value the misclassification is lower than 10% for both alpha and beta emitters.

3. Results and discussion

3.1. Mathematical model

The aim of this study was to establish a mathematical function that describes the alpha evolution in a closed system with ^{226}Ra and without ^{222}Rn and its short-lived daughters. A simple case is considered in which the parent nuclide A decays to a daughter nuclide B, which in turn decays to a stable nuclide C. In such decay chains, the number of atoms of B as a function of time is described by Equation (1):

$$N_B(t) = \frac{\lambda_A}{\lambda_B - \lambda_A} * N_A^0 * \left(e^{-\lambda_A t} - e^{-\lambda_B t}\right) + N_B^0 * e^{-\lambda_B t}$$ (1)

where

$N_B(t)$ is the number of atoms of B at time (t); λ_A and λ_B are the decay constants of A and B, respectively; N_A^0 and N_B^0 are the numbers of atoms of A and B, respectively, at time zero and t is the elapsed time.
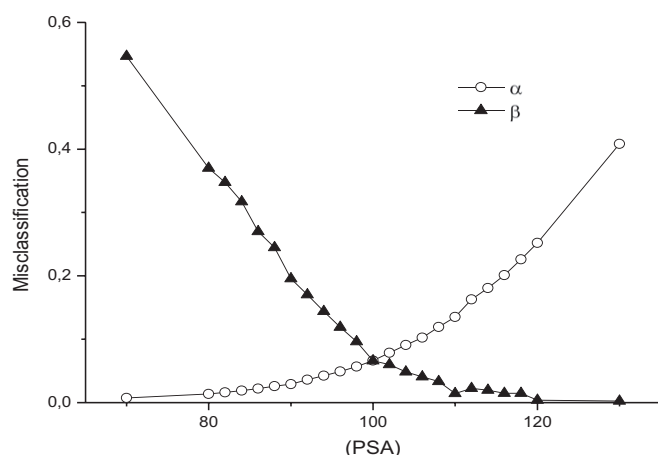
Secular equilibrium conditions and an absence of B atoms at time zero are considered in Equation (2):

$$A_B(t) = A_A^0 * \left(1 - e^{-\lambda_B t}\right)$$ (2)

where

$A_B(t)$ is the activity of B at time (t) in Bq; λ_B is the decay constant of B in s^{-1}; A_A^0 is the activity of A at time zero in Bq and t is the elapsed time in s.

In Equation (2), a null B activity at time zero is shown. At later time points, the B activity is equal to the A activity when secular equilibrium is reached (Annunziata, 1998). *A priori*, this equation cannot describe our problem because ^{226}Ra is a parent radionuclide with a numerous daughters. However, it is possible to apply the philosophy of Equation (3) because ^{222}Rn, the first of the daughter of ^{226}Ra, has the longest half-life within the decay series and all the other short-lived daughters remain in secular equilibrium with ^{222}Rn while it is still being generated.

^{226}Ra has three alpha emitter short-lived daughters: ^{222}Rn, ^{218}Po and ^{214}Po. Considering the secular equilibrium between ^{222}Rn and all the short-lived daughters, the alpha activity in a closed system with only ^{226}Ra at time zero is described by Equation (3):

$$\text{Act}_\alpha^{226}\text{Ra}(t) = 3\text{Act}(^{226}\text{Ra})^0 * \left(1 - e^{-\lambda_{Rn} t}\right) + \text{Act}(^{226}\text{Ra})^0$$ (3)

where

Act^{226}Ra(t) is the alpha activity in a closed system (which only contains ^{226}Ra at time zero) elapsed at t time in Bq; Act$(^{226}$Ra$)^0$ is the ^{226}Ra activity at time zero in Bq and λ_{Rn} is the ^{222}Rn decay constant in s^{-1}.

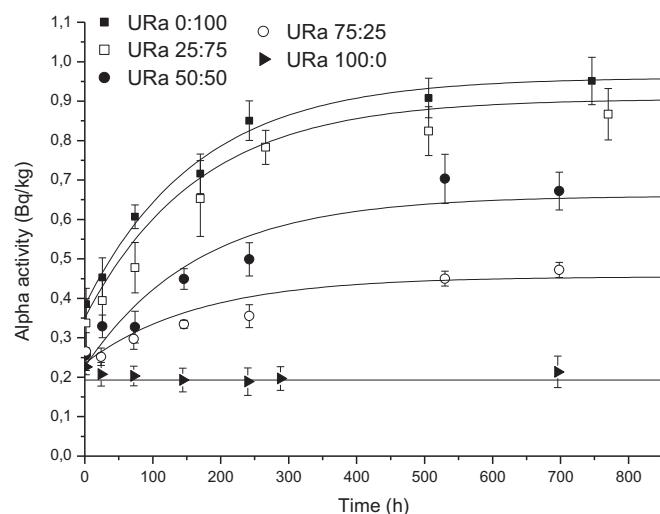**Fig. 2.** Alpha and beta misclassification versus PSA value.

Fig. 3. Evolution of the alpha activity over time for samples with similar gross alpha values and increasing ^{226}Ra activity. The solid lines represent the model evolution.

Table 3
Fitted model parameters and bias in the gross alpha and ^{226}Ra activities for samples with similar gross alpha activities and increasing ^{226}Ra activities.

Samples	Fitted parameters			Bias	
	A (Bq kg^{-1})	b (h^{-1})	C gross alpha at t_0 (Bq kg^{-1})	Gross alpha	^{226}Ra activity
URa 0:100	0.578 ± 0.051	0.006 ± 0.002	0.382 ± 0.022	7.9%	7.4%
URa 25:75	0.556 ± 0.026	0.006 ± 0.001	0.350 ± 0.060	−7.9%	2.4%
URa 50:50	0.434 ± 0.006	0.006 ± 0.003	0.226 ± 0.018	−32.7%	16.7%
URa 75:25	0.220 ± 0.029	0.006 ± 0.003	0.235 ± 0.033	−33.4%	−32.1%
URa 100:0	0.000	−	0.193 ± 0.024	−4.0%	−

Table 4
Fitted model parameters and bias in the gross alpha and ^{226}Ra activities for samples with similar ^{226}Ra activities and increasing gross alpha activities.

Samples	Fitted parameters			Bias	
	A (Bq kg^{-1})	b (h^{-1})	C gross alpha at t_0 (Bq kg^{-1})	Gross alpha	^{226}Ra activity
Ra 0:100	0.578 ± 0.051	0.006 ± 0.002	0.382 ± 0.022	7.9%	−7.4%
URa	0.628 ± 0.057	0.007 ± 0.001	0.512 ± 0.041	−7.5%	5.7%
URaPo	0.632 ± 0.049	0.005 ± 0.002	0.717 ± 0.024	−12.1%	4.3%

Considering that our closed system may contain nuclides other than ^{226}Ra and considering that their activities do not decay significantly in the considered time, the alpha activity in the system is described by Equation (4):

$$\text{Act}_\alpha(t) = A^* \left(1 - e^{-b^*t} \right) + C \tag{4}$$

where

Act (t) is the alpha activity in the closed system elapsed at t time in Bq; A is a parameter corresponding to the maximum increase in the alpha activity and is equal to $3^*\text{Act}(^{226}\text{Ra})^0$ in Bq; b is the ^{222}Rn decay constant in s^{-1} and C is the parameter corresponding to the gross alpha at time zero in Bq.

It should be noted that the current model (Equation (4)) is indicative of the real alpha activity in closed systems where only short-lived daughters of ^{226}Ra are generated.

3.2. Model's verification using synthetic samples

To validate the proposed theoretical model, several synthetic samples (shown in Table 1) were analysed. Each sample was measured at several time points (2, 24, 72, 144, 240, 504 and 720 h) after the sample treatment.

3.2.1. ^{226}Ra proportion effect
To evaluate the ^{226}Ra proportion effect in the evolution profiles, synthetic samples with similar gross alpha values, but increasing ^{226}Ra contributions, were prepared. Fig. 3 shows the mean and standard deviation of replicate measurements of alpha activity evolution over time. Error bars represent the standard deviation of each replicate. The modelled activity evolution for each sample is also shown (solid line).

As shown in Fig. 3, the alpha activity of the URa 100:0 sample with no ^{226}Ra content remains constant. Furthermore, the alpha activity of all the samples containing ^{226}Ra increases over time. Fig. 3 also demonstrates that the experimental data match the proposed model.

The fitted model parameters are shown in Table 3. This table also shows the bias between the calculated and spiked gross alpha and ^{226}Ra activities. (Table 4).

3.2.2. Gross alpha effect
To evaluate the gross alpha effect in the evolution profiles, synthetic samples with similar ^{226}Ra activities (approximately 0.200 Bq L^{-1}) but increasing gross alpha activities (adding ^{nat}U or ^{nat}U and ^{210}Po) were prepared.

Fig. 4 shows the mean and standard deviation of replicate measurements of alpha activity evolution over time. Error bars represent the standard deviation of each replicate. The modelled activity evolution for each sample is also shown (solid line).

As demonstrated in Fig. 4, the three samples with the same ^{226}Ra activity have profiles that remain equidistant. The only difference between the profiles is the addition of a constant component. Fig. 3 also shows that the experimental data match the proposed model.

The fitted model parameters are shown in Table 3. This table also presents the bias between the calculated and spiked gross alpha and ^{226}Ra activities.

3.3. Model's application to natural samples

The proposed model, Equation (4), permits the calculation of gross alpha activity at time zero and the ^{226}Ra activity. For this purpose, two gross alpha determinations at two different times are required. To test the proposed model in natural samples, several analyses were performed. Two measurements of gross alpha at two different times were made for each of the eight natural samples. The first measurement was performed two hours after sample treatment. The second measurement was conducted six days after
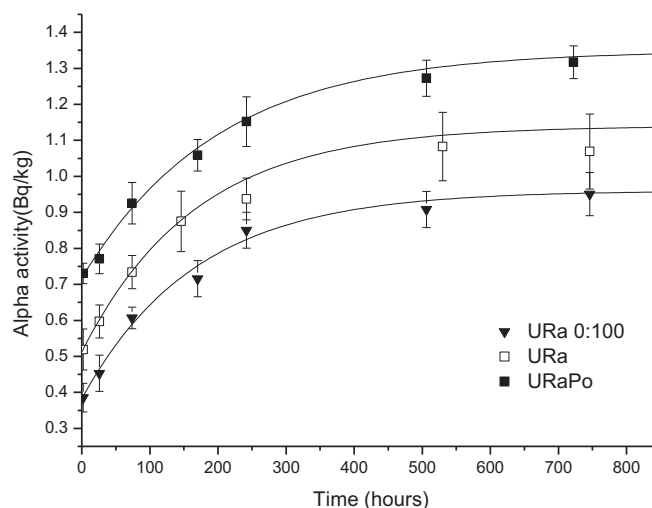
Fig. 4. Evolution of the alpha activity over time for samples with similar ^{226}Ra activities and increasing gross alpha activities. The solid lines represent the model evolution.

Table 5
Alpha activities, fitted model parameter, reference values and bias calculation for gross alpha and ^{226}Ra activity for each natural sample.

Sample	Measure		Fitted parameters			Reference values[c]		Bias	
	Activity 1[a] (Bq kg^{-1})	Activity 2[b] (Bq kg^{-1})	A (Bq kg^{-1})	C (Act α) (Bq kg^{-1})	Act ^{226}Ra (Bq kg^{-1})	Act α (Bq kg^{-1})	Act ^{226}Ra (Bq kg^{-1})	Act α %	Act ^{226}Ra %
SUBT-A	1.974 ± 0.176	2.703 ± 0.155	1.129 ± 0.313	1.957 ± 0.640	0.376 ± 0.104	2.170 ± 0.206	0.467 ± 0.114	−9.8%	−19.5%
SUBT-B	6.283 ± 0.152	6.507 ± 0.164	0.347 ± 0.303	6.278 ± 0.624	0.116 ± 0.101	6.225 ± 0.583	0.134 ± 0.018	0.9%	−13.4%
POT-A	1.315 ± 0.078	2.330 ± 0.088	1.572 ± 0.162	1.292 ± 0.453	0.524 ± 0.054	1.385 ± 0.175	0.552 ± 0.064	−6.7%	−5.1%
POT-D	0.315 ± 0.010	0.697 ± 0.037	0.593 ± 0.056	0.306 ± 0.241	0.198 ± 0.019	0.280 ± 0.038	0.214 ± 0.033	9.3%	−7.7%
POT-B	<0.025	<0.025	–	–	–	0.038 ± 0.013	0.002 ± 0.001	–	–
POT-C	0.031 ± 0.017	0.047 ± 0.013	0.025 ± 0.028	0.031 ± 0.192	0.008 ± 0.009	0.060 ± 0.015	0.004 ± 0.001	−48.7%	100.0%
SUP-A	0.182 ± 0.010	0.173 ± 0.034	−0.014 ± 0.052	0.182 ± 0.055	−0.005 ± 0.017	0.186 ± 0.029	0.005 ± 0.003	−2.1%	−209.5%
SUP-B	0.098 ± 0.023	0.105 ± 0.028	0.011 ± 0.050	0.098 ± 0.081	0.004 ± 0.017	0.099 ± 0.024	0.004 ± 0.001	−1.1%	−7.0%

[a] Activity 1: Alpha activity measured 2 h after sample treatment.
[b] Activity 2: Alpha activity measured 144 h after sample treatment.
[c] Reference values: Act α sum of current alpha emitters determined by alpha spectrometry. Act ^{226}Ra determined by alpha spectrometry.

the sample treatment. During the six-day measurement period, the increase of alpha activity was significant, which permitted the estimation of ^{226}Ra activity.

Equations (5) and (6) show the values of the model parameters A (maximum growth) and C (gross alpha at time zero):

$$A = \frac{\text{Act}_2 - \text{Act}_1}{e^{-bt_1} - e^{-bt_2}} \tag{5}$$

$$C = \frac{\text{Act}_2\left(1 - e^{-bt_1}\right) - \text{Act}_1\left(1 - e^{-bt_2}\right)}{e^{-bt_2} - e^{-bt_1}} \tag{6}$$

Table 5 contains both activities measured at two hours and six days after the sample treatment, the fitted model parameters and the bias in the gross alpha and ^{226}Ra determination. Table 5 also contains the reference values used to calculate bias. The reference value for ^{226}Ra is the mean of three replicates, as evaluated by alpha spectrometry after a radiochemical separation. For gross alpha, the reference value is the sum of the isotopes found in natural water: ^{234,235,238}U, ^{226,228}Ra, ^{210}Po and ^{232}Th.

For ^{226}Ra determination, samples containing on the order of 10^{-1} Bq kg^{-1} ^{226}Ra have a bias less than 20%. However, when the sample contains on the order of 10^{-3} Bq kg^{-1} of ^{226}Ra, the bias obtained is unacceptable.

The results obtained from applying the model to gross alpha determination generally have a bias below 10%, which is as low as the bias obtained from single determination. However, a large bias was obtained for the POT-C sample. A very low alpha activity (near the Minimum Detectable Activity) is the cause of this unacceptable bias.

4. Conclusions

The proposed model makes it possible to quantify ^{226}Ra activity in a closed system using two measurements of alpha activity. To make this measurement possible, it is necessary for all the ^{226}Ra short-lived daughters to be removed during the treatment of the sample. The model permits the second measurement to be conducted within the first 21 days after sample treatment instead of waiting until secular equilibrium is reached.

A liquid scintillation vial containing the cocktail and the treated sample approximates the described closed system. The proposed model can be applied for two gross alpha measurements to estimate ^{226}Ra activity. Biases lower than 20% were obtained for samples with ^{226}Ra activities on the order of 10^{-1} Bq kg^{-1}.

Acknowledgements

References

Annunziata, M.F., 1998. Nuclear radiation. Its interaction with matter and radioisotope decay. In: "Handbook of Radioactivity Analysis" (Chapter 1–5). Academic Press, San Diego, California, pp. 53–67.

Bojanowski, R., Radecki, Z., Burns, K., 2005. Determination of radium and uranium isotopes in natural waters by sorption on hydrous manganese dioxide followed by alpha-spectrometry. Journal of Radioanalytical and Nuclear Chemistry 264 (2), 437–443.

Catchen, J.G., 1984. Application of the equation of radioactive growth and decay to geochronological models and explicit solution of the equations by Laplace transform. Isotope Geosciences 1984 (2), 181–185.

Cazala, C., Reyss, J.L., Decossas, J.L., Royer, A., 2003. Improvement in the determination of ^{238}U, ^{228,234}Th, ^{226,228}Ra, ^{210}Pb, and ^{7}Be by g spectrometry on evaporated fresh water samples. Environmental Science and Technology 37 (21), 4990–4993.

Council Directive 98/83/EC of 3 November 1998 on the Quality of Water Intended for Human Consumption.

Dulaiova, H., Burnett, W.C., 2004. An efficient method for γ-spectrometric determination of radium-226, 228 via manganese fibers. Limnology and Oceanography. Methods 2, 256–261.

Fernandes, P., Sousa, O., Juliao, Q.C., Dantas, M., 2011. Development and validation of a technique for the determination of 226Ra and 228Ra by liquid scintillation in liquid samples. Radiation Protection Dosimetry 144, 335–338.

Guogang, J., Jing, J., 2012. Determination of radium isotopes in environmental samples by gamma spectrometry, liquid scintillation counting and alpha spectrometry: a review of analytical methodology. Journal of Environmental Radioactivity 106, 98–119.

Kahn, B., Rosson, R., Cantrell, J., 1990. Analysis of ^{228}Ra and ^{226}Ra in public water supply by a γ-ray spectrometry. Health Physics 59, 125–131.

Lucas, H.F., Markun, F., Boulenger, R., 1990. Methods for measuring radium isotopes: emanometry. In: The Environmental Behaviour of Radium (Chapter 3–2). Technical Reports Series No. 310, vol. 1. International Atomic Energy Agency, Vienna, pp. 149–172.

Maharana, M., Eappen, K.P., Sengupta, D.J., 2010. Radon emanometric technique for 226Ra estimation. Journal of Radioanalytical and Nuclear Chemistry 285, 469–474.

Purkl, S., Eisenhauer, A., 2003. A rapid method for α-spectrometric analysis of radium isotopes in natural waters using ion-selective membrane technology. Applied Radiation and Isotopes 59 (4), 245–254.

Repine, U., Benedik, L., 2002. Development of a method for the determination of ^{226}Ra by liquid scintillation counting. Journal of Radioanalytical and Nuclear Chemistry 254, 181–185.

Salonen, L., 2006. Alpha/Beta liquid scintillation spectrometry in surveying Finnish groundwater samples. Radiochemistry 48, 606–612.

Salonen, L., 1993. A rapid method for monitoring of uranium and radium in drinking water. Science of the Total Environment 130/131, 23–35.

Sanchez-Cabeza, J.A., Pujol, L., 1998. Simultaneous determination of radium and uranium activities in natural water samples using liquid scintillation counting. Analyst 123, 399–403.

Zapata-García, D., Llauradó, M., Rauret, G., 2009. Establishment of a method for the rapid measurement of gross alpha and gross beta activities in sea water. Applied Radiation and Isotopes 67, 978–981.

Zapata-García, D., Llauradó, M., Rauret, G., 2012. The implications of the particle energy an acidic media on gross alpha and gross beta determination using liquid scintillation. Applied Radiation and Isotopes 70, 705–711.