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Abstract

The conventional methods for the ^{226}Ra determination by liquid scintillation counting require to attain secular equilibrium between ^{226}Ra and ^{222}Rn prior to the counting. This study describes a method that allows the immediate counting of a sample after the dissolution of Ba(Ra)SO_4 in EDTA. This results from a detailed modelling of the activity of the parent ^{226}Ra and its daughters in both the aqueous and organic scintillator phases. This methodology was tested on standard solutions of ^{226}Ra showing promising results.

Key words: radium; scintillation counting; hydrology;

1 Introduction

Radioactive isotopes are naturally present in the environment, as well as in food and water bodies, and their consequent intake by humans is part of the normal exposure to natural radioactivity. Among the natural radioactive isotopes, ^{226}Ra is very significant from a radioprotection point of view. In fact, it is a radionuclide with long half–life and a high dose coefficient [1].
Moreover, radium is absorbed into the blood from the gastrointestinal tract or lungs and, due to its chemical and biological behavior which is similar to other elements of Group II (particularly calcium), it can be easily accumulated in the bones, where it decays in short–living radionuclides of high specific activity. Belonging to the decay chain of ^{238}U, radium is naturally present in soils, sediments, rocks, with varying concentrations depending on local geological features.

Moreover, radium can be released from human activities involving naturally occurring radioactive materials, as mining, coal production [2], extraction of natural gas through hydraulic fracturing, [3], [4] or the production and use of phosphate fertilizers [5]–[8] and, due to its moderate rate

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of decay, it can accumulate in soil and, through the soil–to–plant transfer, can be introduced in the food chain [9], [10] to a larger extent with respect to uranium, thorium, polonium or lead [11]. On the other hand, radium is a relatively mobile ion, being readily soluble in water thus, due to natural phenomena as run–off of the soil by rainwater, it can be found in ground and spring water and, hence, also in drinking and bottled water [12], [13]. Normally, the radium activity in water is not harmful, but it may happen that its contribution to natural radioactivity is significantly higher than average (for example in radon prone areas), may be a health risk, and thus the problem of its presence in drinking water cannot be overlooked.

In fact, the consumption of water and food containing radium can lead to its accumulation, increasing the dose from internal radiation [14]. This accumulation may, over time, result in an increased risk of bone cancer, leukemia, and lymphoma [15], [16].
In the guidelines of the World Health Organization the guidance level set for ^{226}Ra is 1 Bq/L [17], but, due to its radiotoxicity, many countries require very low ^{226}Ra concentration limits in drinking water. The Council of the European Union in the Directive 2013/51/EURATOM [18] regarding the radioactive substances in water intended for human consumption, limits the ^{226}Ra to 0.5 Bq/L. The same limit is set in Italy (Dlgs 28/2016) [19].
The potential continuous intake of radium with food or/and water prompted great interest about ^{226}Ra determination in a wide variety of food, beverages, and environmental samples [7], [20]–[25]. On the other hand, the determination of Ra isotopes in water also gives useful information on biological, hydrological [26], [27] and geochemical processes [28].

To detect ^{226}Ra many different analytical methods are being used, based on different chemical or physical principles. Several reviews about analytical methods for the determination of Ra isotopes in environmental samples appear in the literature, reporting details not only about measurement techniques but also preconcentration, separation, and purification procedures for sample preparation [29], [30]–[34].
However, even if methods based on mass spectrometry, as inductively coupled plasma mass spectrometry (ICP–MS), accelerator mass spectrometry (AMS), thermal ionization mass spectrometry (TIMS), resonance ionization mass spectrometry (RIMS) are reported [7], [29], [35]–[38] radiometric techniques are routinely employed for radium analysis.
They include both direct methods as alpha [39]–[42] and gamma spectrometry, [43]–[47] using α particles and γ–rays from ^{226}Ra, and indirect methods in which radium is determined by emission of its daughter nuclides after the secular equilibrium between ^{226}Ra and ^{222}Rn has been established.
Alpha spectrometry has the advantage to have high sensibility, but the sample preparation is cumbersome and there are problems of self–absorption by the sample itself that can occur affecting the final result.
Gamma spectrometry is a non–destructive technique allowing ^{226}Ra analysis in water samples directly from its own γ peaks, even if the γ–emission probability is relatively low (186 KeV, 3.51%), and the possible interference of 185.7 KeV γ–rays from ^{235}U can be difficult to eliminate. Indirect measures are also possible using γ peaks of descendant nuclides as ^{214}Bi (609.3 keV, 46.1%) and ^{214}Pb (351.9 KeV, 37.6%) but radon leakage from the sample must be effectively prevented to allow secular equilibrium between ^{226}Ra and ^{222}Rn. Moreover, considering the efficiency of gamma spectrometry and the very low detection limit required (0.04 Bq/L [18], [19]) large volumes of water may be needed, particularly because of the low radium concentration usually present in the

samples.

Among the radiometric techniques, liquid scintillation counting (LSC) is one of the most effective methods for radionuclide determination; therefore it is often used for the determination of radium radioisotopes in environmental samples, particularly in liquids [12], [23], [24], [36], [48]–[54].
Some of the LSC advantages are a high and rather constant detection efficiency for α (close to 100%) and high–energy β emitters, a relatively simple and fast sample preparation and the ability to obtain the spectral energy response of the sample.
The ^{226}Ra activity can be directly obtained by α discrimination in the emission spectrum. ^{226}Ra can be also determined measuring its progenies. In fact, after the secular equilibrium has been reached, α–particles (from ^{222}Rn, ^{218}Po, ^{214}Po) and β–particles (from ^{214}Pb, ^{214}Bi) allow indirect determination.
For radium analysis, LSC is generally used after a preconcentration/separation step. Chemical separation by forming the Ba(Ra)SO_4 precipitate is largely used to this purpose [49], [50]. The indirect methods allow to minimize pretreatment in that, using a water organic immiscible cocktail, only the ^{222}Rn produced by ^{226}Ra is transferred in the organic phase and counted after equilibrium is attained. However, this method requires a long time, since the Ba(Ra)SO_4 precipitate dissolved in ethylenediaminotetraacetic acid (EDTA) solution is stored for the ingrowth of ^{222}Rn (1 month) before being counted.

2 Results and Discussion

In this paper we report a novel approach to the LSC indirect method, that allows to obtain the radium concentration in a much shorter time with respect to the time required to attain equilibrium. The method is based on a detailed calculation of the activity of all radionuclides generated by the decay of ^{226}Ra, including the partition of ^{222}Rn between the acqueous phase containing the dissolved Ba(Ra)SO_4 and the immiscible organic scintillator phase. The total counts detected by the scintillator is proportional to the initial activity of ^{226}Ra, the only radionuclide at time zero. A known initial concentration in the sample allows the evaluation of the efficiency for the alpha signals of ^{226}Ra from the aqueous phase and the mass transfer coefficient between water and scintillator for radon. Once these parameters are known, an unconstrained optimization of the observed number of counts versus time with respect to the initial ^{226}Ra activity affords the latter.

We begin by considering a volume of water with a number density x_0 of ^{226}Ra nuclei (decay constant $\lambda_1 = 1.3728 \times 10^{-11}$ s^{-1}) put into contact with an equal volume of an organic phase containing a scintillator. At $t = 0$ the ^{222}Rn (decay constant $\lambda_2 = 2.0982 \times 10^{-6}$ s^{-1}) starts diffusing into the organic phase with a mass transfer coefficient k_1, and diffusing back from the organic phase into the water with a mass transfer coefficient k_2. At the same time, the ^{222}Rn in both phases decays to its daughter products in the sequence $^{222}\mathrm{Rn} \to\ ^{218}\mathrm{Po} \to\ ^{214}\mathrm{Pb} \to\ ^{214}\mathrm{Bi} \to\ ^{214}\mathrm{Po} \to\ ^{210}\mathrm{Pb}$. Since the decays $^{218}\mathrm{Po} \to\ ^{214}\mathrm{Pb}$ and $^{214}\mathrm{Po} \to\ ^{210}\mathrm{Pb}$ are fast compared to the other time scales of the system, we consider these processes as instantaneous according to the scheme

$$\begin{tikzcd}
{}^{226}\mathrm{Ra}_{aq}\ (x) \arrow[r, "\lambda_1"] & {}^{222}\mathrm{Rn}_{aq}\ (y) \arrow[r, shift left, "k_1"] \arrow[d, "\lambda_2"] & {}^{222}\mathrm{Rn}_{org}\ (z) \arrow[l, shift left, "k_2"] \arrow[d, "\lambda_2"] \\
 & {}^{214}\mathrm{Pb}_{aq} \arrow[d, "\lambda_3"] & {}^{214}\mathrm{Pb}_{org}\,(u) \arrow[d, "\lambda_3"] \\
 & {}^{214}\mathrm{Bi}_{aq} \arrow[d, "\lambda_4"] & {}^{214}\mathrm{Bi}_{org}\,(v) \arrow[d, "\lambda_4"] \\
 & {}^{210}\mathrm{Pb}_{aq} & {}^{210}\mathrm{Pb}_{org}
\end{tikzcd} \tag{1}$$

where the rate $\lambda_2 z$ represents the two decays ${}^{222}\mathrm{Rn} \rightarrow {}^{218}\mathrm{Po} \rightarrow {}^{214}\mathrm{Pb}$, the rate $\lambda_3 u$ the single decay ${}^{214}\mathrm{Pb} \rightarrow {}^{214}\mathrm{Bi}$, and the rate $\lambda_4 v$ the two decays ${}^{214}\mathrm{Bi} \rightarrow {}^{214}\mathrm{Po} \rightarrow {}^{210}\mathrm{Pb}$. We define the reduced number densities of each species (x, y, z, u, v) in the scheme as the ratio of the number density of the species at time t to the equilibrium value of the number density of ${}^{222}\mathrm{Rn}$ nuclei in the aqueous phase in the absence of any organic phase, $(\lambda_1/\lambda_2)\, x_0 = \Lambda_1 x_0 = 6.54 \times 10^{-6}\, x_0$.

In the non–dimensional time unit $\lambda_2 t$, the reduced density of the radon in the water and organic phases follows the system of equations

$$\dot{y} \;=\; -\left(\omega_1 + 1\right) y + \omega_2 z + e^{-\Lambda_1 t} \tag{2}$$

$$\dot{z} \;=\; \omega_1 y - \left(\omega_2 + 1\right) z \tag{3}$$

with the parameters $\omega_1 = k_1/\lambda_2$ and $\omega_2 = k_2/\lambda_2$. The system of equations (2–3) has a stationary state for $\Lambda_1 t \gg 1$ with

$$y_{\mathrm{SS}} \;=\; \frac{\omega_2 + 1}{\omega_1 + \omega_2 + 1} \tag{4}$$

$$z_{\mathrm{SS}} \;=\; \frac{\omega_1}{\omega_1 + \omega_2 + 1}. \tag{5}$$

The actual count due to the sample in secular equilibrium is

$$\begin{aligned} q_{\mathrm{SS}} &= \hat{\epsilon}_\alpha \hat{q}_{\text{Ra-226}} + 2\hat{\epsilon}_\alpha \hat{q}_{\text{Rn-222}} + 2\epsilon_\alpha q_{\text{Rn-222}} + \epsilon_\beta q_{\text{Pb-214}} + \left(\epsilon_\alpha + \epsilon_\beta\right) q_{\text{Bi-214}} \\ &= \lambda_2 t\ \Lambda_1 x_0 \left[\hat{\epsilon}_\alpha + 2\hat{\epsilon}_\alpha \frac{\omega_2 + 1}{\omega_1 + \omega_2 + 1} + \left(3\epsilon_\alpha + 2\epsilon_\beta\right) \frac{\omega_1}{\omega_1 + \omega_2 + 1}\right], \end{aligned} \tag{6}$$

where the coefficient $\hat{\epsilon}$ represents the efficiency in water and ϵ the corresponding efficiency in the organic phase. Many methods are based on the measure of counts given by eq. (6) and suffer the drawback of the long time required to attain equilibrium, of the order of a few times $\lambda_2^{-1} \approx 5.4$ d. By modeling the time dependence of the total counts before equilibrium, we aim to complete the analysis in about one unit of λ_2^{-1}.

To this purpose, we solve the system of equations (2–3) to obtain the total count from the decays in water and in the organic phase. Defining $-\alpha_n$ $(n = 1, 2)$ as the eigenvalues of the system matrix of eqs. (2–3), i.e. the solutions of the equation

$$(\omega_1 + 1 + \alpha)(\omega_2 + 1 + \alpha) - \omega_1\omega_2 = 0 \tag{7}$$

($-\alpha_1 = \omega_1 + \omega_2 + 1$, $-\alpha_2 = 1$), we have the two eigenvectors of the matrix $[1 \quad \zeta_n]$, with $\zeta_n = (\omega_1 + 1 - \alpha_n)/\omega_2$, $\zeta_1 = -1$, and $\zeta_2 = \omega_1/\omega_2$. The initial conditions y_0 and z_0 are included in the constants

$$A_1 = y_0 - z_0/\zeta_2 + (\Lambda_1 - \alpha_1)^{-1} \tag{8}$$
$$A_2 = y_0 - z_0/\zeta_1 + (\Lambda_1 - \alpha_2)^{-1} \tag{9}$$
$$A_3 = (\Lambda_1 - \alpha_2)^{-1} - (\Lambda_1 - \alpha_1)^{-1} \tag{10}$$
$$B_1 = A_1/\zeta_1 \tag{11}$$
$$B_2 = \left[y_0 - z_0/\zeta_1 - (\Lambda_1 - \alpha_2)^{-1}\right]/\zeta_2 \tag{12}$$
$$B_3 = \left[\zeta_2(\Lambda_1 - \alpha_2)\right]^{-1} + \left[\zeta_1(\Lambda_1 - \alpha_1)\right]^{-1}. \tag{13}$$

The solution of the system of equations (2–3) gives the count from the decay of ^{226}Ra and ^{222}Rn in water (indicated by $\hat{q}$) as

$$\hat{q}_{\text{Ra-226}} = x_0\left(1 - e^{-\Lambda_1 t}\right), \tag{14}$$

$$\hat{q}_{\text{Rn-222}} = x_0\Lambda_1 \int_0^t y \, \mathrm{d}s, \tag{15}$$

$$\int_0^t y \, \mathrm{d}s = \zeta\left(B_1 g_{\alpha_1} - B_2 g_{\alpha_2} - B_3 g_{\Lambda_1}\right), \tag{16}$$

and in the organic phase (indicated by q), as

$$q_{\text{Rn-222}} = x_0\Lambda_1 \int_0^t z \, \mathrm{d}s \tag{17}$$

with

$$\int_0^t z \, \mathrm{d}s = \zeta\left(A_1 g_{\alpha_1} - A_2 g_{\alpha_2} + A_3 g_{\Lambda_1}\right), \tag{18}$$

and

$$\zeta = \frac{\zeta_1\zeta_2}{\zeta_2 - \zeta_1} = -\frac{\omega_1}{\omega_1 + \omega_2}, \quad g_\mu = \frac{1 - e^{-\mu t}}{\mu}. \tag{19}$$

The count from the ^{214}Pb decay in the organic phase is given by

$$q_{\text{Pb-214}} = x_0\Lambda_1\Lambda_2 \int_0^t u \, \mathrm{d}s, \tag{20}$$

with $\Lambda_2 = \lambda_3/\lambda_2 = 2.05 \times 10^2$,

$$\int_0^t u \, \mathrm{d}s = \zeta\left(-A_1 G_{\Lambda_2\alpha_1} + A_2 G_{\Lambda_2\alpha_2} - A_3 G_{\Lambda_2\Lambda_1}\right), \tag{21}$$

and

$$G_{\mu\nu} = \frac{g_\mu - g_\nu}{\mu - \nu}. \tag{22}$$

The count from the ^{214}Bi decay in the organic phase is given by

$$q_{\text{Bi-214}} = x_0 \Lambda_1 \Lambda_3 \int_0^t v \, \mathrm{d}s, \tag{23}$$

with $\Lambda_3 = \lambda_4/\lambda_2 = 2.77 \times 10^2$,

$$\int_0^t v \, \mathrm{d}s = \Lambda_2 \zeta \left(A_1 \hat{G}_{\Lambda_3 \Lambda_2 \alpha_1} - A_2 \hat{G}_{\Lambda_3 \Lambda_2 \alpha_2} + A_3 \hat{G}_{\Lambda_3 \Lambda_2 \Lambda_1} \right), \tag{24}$$

and

$$\hat{G}_{\mu\nu\rho} = \frac{G_{\mu\nu} - G_{\mu\rho}}{\nu - \rho}. \tag{25}$$

Considering all the decays from ^{226}Ra to ^{214}Po, the actual count due to the sample is

$$q_{\mathrm{S}} = \hat{\epsilon}_\alpha \left(\hat{q}_{\text{Ra-226}} + \hat{q}_{\text{Rn-222}} \right) + 2\epsilon_\alpha q_{\text{Rn-222}} + \epsilon_\beta q_{\text{Pb-214}} + (\epsilon_\alpha + \epsilon_\beta) q_{\text{Bi-214}}, \tag{26}$$

while the experimental total count is

$$q = q_{\mathrm{S}} + a_{\mathrm{B}} \frac{t}{\lambda_2}. \tag{27}$$

Taking into account equations (14), (15), (17), (20), and (23) we have

$$\begin{aligned} \frac{q_{\mathrm{S}}}{x_0} &= \hat{\epsilon}_\alpha \Lambda_1 g_{\Lambda_1} + 2\hat{\epsilon}_\alpha \zeta \Lambda_1 \left(B_1 g_{\alpha_1} - B_2 g_{\alpha_2} - B_3 g_{\Lambda_1} \right) \\ &+ 2\epsilon_\alpha \zeta \Lambda_1 \left(A_1 g_{\alpha_1} - A_2 g_{\alpha_2} + A_3 g_{\Lambda_1} \right) \\ &- \epsilon_\beta \zeta \Lambda_1 \Lambda_2 \left(-A_1 G_{\Lambda_2 \alpha_1} + A_2 G_{\Lambda_2 \alpha_2} - A_3 G_{\Lambda_2 \Lambda_1} \right) \\ &+ (\epsilon_\alpha + \epsilon_\beta) \zeta \Lambda_1 \Lambda_2 \Lambda_3 \left(A_1 \hat{G}_{\Lambda_3 \Lambda_2 \alpha_1} - A_2 \hat{G}_{\Lambda_3 \Lambda_2 \alpha_2} + A_3 \hat{G}_{\Lambda_3 \Lambda_2 \Lambda_1} \right). \end{aligned} \tag{28}$$

In principle, the value of ζ depends on both k_1 and k_2, but, since the value of the equilibrium constant k_1/k_2 for the distribution of radon between water and the organic phase (in this work Opti–Fluor, dodecylbenzene) is known (35.3 ± 1.6) [55], only k_1 need to be determined. Its value was obtained by counting solutions of ^{226}Ra with known activity, optimizing the values of $\hat{\epsilon}_\alpha$ and k_1 for each run obtaining the average values $\langle \hat{\epsilon}_\alpha \rangle = 0.82 \pm 0.10$, $\langle k_1 \rangle = 6.67 \pm 2.01 \times 10^{-6}$ s^{-1}, and, consequently, $\omega_1 = 3.18$, $\omega_2 = 0.090$, and $\zeta = -0.97$. From the value of k_1 and the thickness of the water layer in the vial ($h = 2.04 \times 10^{-2}$ m), we may also estimate the mass transfer coefficient as $k_1' = k_1 h = 4.04 \times 10^{-5}$ m s^{-1}, that turns out to be greater than the experimental value for radon in the air-water system (1.16×10^{-5} m s^{-1}). The ratio between the diffusion coefficient of radon in water ($D = 9.641 \times 10^{-10}$ m^2 s^{-1}) and k_1' also gives 2.39×10^{-5} m as the thickness of the boundary layer between water and the scintillator.

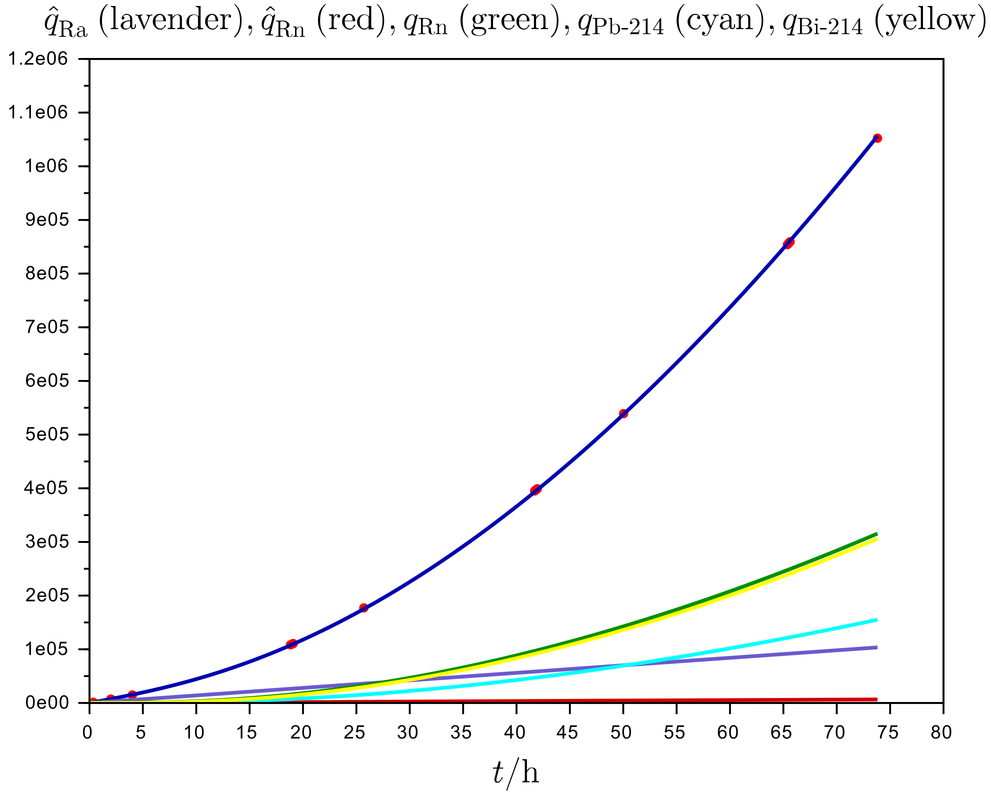

Figure 1: Plot of counts given by eq. (28) with $a_{\text{Ra-226}} = 3.1371$ Bq (blue). The individual contributions to the total count are also shown: ^{226}Ra (eq. (14), lavender), ^{222}Rn in water (eq. (15), red), ^{222}Rn in the scintillator (eq. (17) green), ^{214}Pb (eq. (20) cyan), and ^{214}Bi (eq. (23) yellow).

Given the relative deviation $q_i/\bar{q}_i - 1$ of the total count q_i, computed with eqs. (27–28), with respect to the n experimental determinations $\bar{q}_i$ in each run, we indicate with σ_{fit} the root mean square

$$\sigma_{fit} = \sqrt{\frac{1}{n}\sum_{1}^{n}\left(\frac{q_i}{\bar{q}_i} - 1\right)^2}. \tag{29}$$

The activity $\lambda_1 x_0$ of an unknown sample is obtained by the unconstrained minimization of σ_{fit} with respect to the radium concentration x_0. The standard deviation of the results is evaluated as

$$\sigma_{\lambda_1 x_0} = \sqrt{\left(\partial_{a_{\rm B}}\lambda_1 x_0\right)^2 \sigma_{a_{\rm B}}^2 + \left(\partial_{\epsilon_\alpha}\lambda_1 x_0\right)^2 \sigma_{\epsilon_\alpha}^2 + \left(\partial_{k_1}\lambda_1 x_0\right)^2 \sigma_{k_1}^2}, \tag{30}$$

where each term under the square root is computed numerically. The results in Table 1 show the values of the individual contributions to the total standard deviation of samples with radium activity $a_{\text{Ra-226}}$.

Table 1: Values of the terms in eq. (30) for solutions of ^{226}Ra with known activity $a_{\text{Ra-226}}$ measured in OPTI unmixable scintillator, standard deviation for the activity, and the corresponding coefficients of variation $c_v = \sigma_{\lambda_1 x_0}/a_{\text{Ra-226}}$. These measures were used to compute the averages $\langle \hat{\epsilon}_\alpha \rangle = 0.82 \pm 0.10$ and $\langle k_1 \rangle = 6.67 \pm 2.01 \times 10^{-6}$ s^{-1}

$a_{\text{Ra-226}}$/mBq	$(\partial_{a_\text{B}} \lambda_1 x_0)^2 \sigma^2_{a_\text{B}}$	$(\partial_{k_1} \lambda_1 x_0)^2 \sigma^2_{k_1}$	$(\partial_{\epsilon_\alpha} \lambda_1 x_0)^2 \sigma^2_{\epsilon_\alpha}$	$\sigma_{\lambda_1 x_0}$/mBq	c_v
3137.1	7.54×10^{-5}	3.21×10^{-2}	9.19×10^{-4}	182	5.80×10^{-2}
2091.4	5.60×10^{-5}	1.61×10^{-2}	4.05×10^{-4}	129	6.16×10^{-2}
3137.1	7.82×10^{-5}	4.36×10^{-2}	1.25×10^{-3}	212	6.76×10^{-2}
1880.8	4.97×10^{-5}	1.32×10^{-2}	3.13×10^{-4}	116	6.19×10^{-2}

In Figure 1 the individual contribution to the total activity (blue curve) are shown along with the experimental results in red. The plot of q_S versus time for a sample with total activity $a_{\text{Ra-226}} = 3.1371$ Bq exhibits a remarkable good agreement between the computed and measured count.

The lower limit of quantitation (LLQ) of a sample is given (for a signal described by the Poisson distribution) as the count given by eq. (28) with q_S equal to the q_LLQ given by Currie [56]

$$\begin{aligned} q_\text{LLQ} &= 50\left(1 + \sqrt{1 + q_\text{B}/12.5}\right) \\ &\simeq 50\sqrt{\frac{q_\text{B}}{12.5}} \\ &\simeq 14.14\sqrt{q_\text{B}}, \end{aligned} \tag{31}$$

where q_B represents the background count, measured after each run. For our instrument, the observed average background count is 0.61 cps, with a standard deviation of 7.12×10^{-3} cps, while the theoretical standard deviation $\sigma_{a_\text{B}} = \sqrt{a_\text{B}/t_s}$ can be as low as 1.22×10^{-3} cps for $t_s = 120$ h. Although it is common to consider the standard deviation of the background activity as given by $\sigma_{a_\text{B}} = \sqrt{a_\text{B}/t_s}$, we will keep these two cases distinct. We can estimate the background count during a measure as $q_\text{B} = a_\text{B} t/\lambda_2$ and use eq. (31) or, more conservatively, interpret the expression $\sqrt{q_\text{B}}$ as σ_B and write

$$\begin{aligned} q_\text{LLQ} &\simeq 14.14\,\sigma_\text{B} \\ &= 14.14 \frac{\partial\left(a_\text{B} t\right)}{\lambda_2 \partial a_\text{B}} \sigma_{a_\text{B}} \\ &= 14.14\,\sigma_{a_\text{B}} \frac{t}{\lambda_2}. \end{aligned} \tag{32}$$

We thus achieve the limit of quantitation if the counting time satisfies the inequality

$$q_\text{S} - q_\text{LLQ} \geq 0 \tag{33}$$

with q_{LLQ} given by either eq. (31) or the more stringent eq. (32). For the lower limit of detection (LLD), the numerical factor 14.14 in eqs. (31–32) is replaced by 2.33 [56]. Plots of eq. (33) for $a_{\text{Ra-226}} = 0.17$ Bq and q_{LLQ} given by eq. (31) and (32) are shown in Figure 2. Table 2 shows the required counting times for specified LLQ and LLD values in the samples processed with the analytical procedure described in this work.

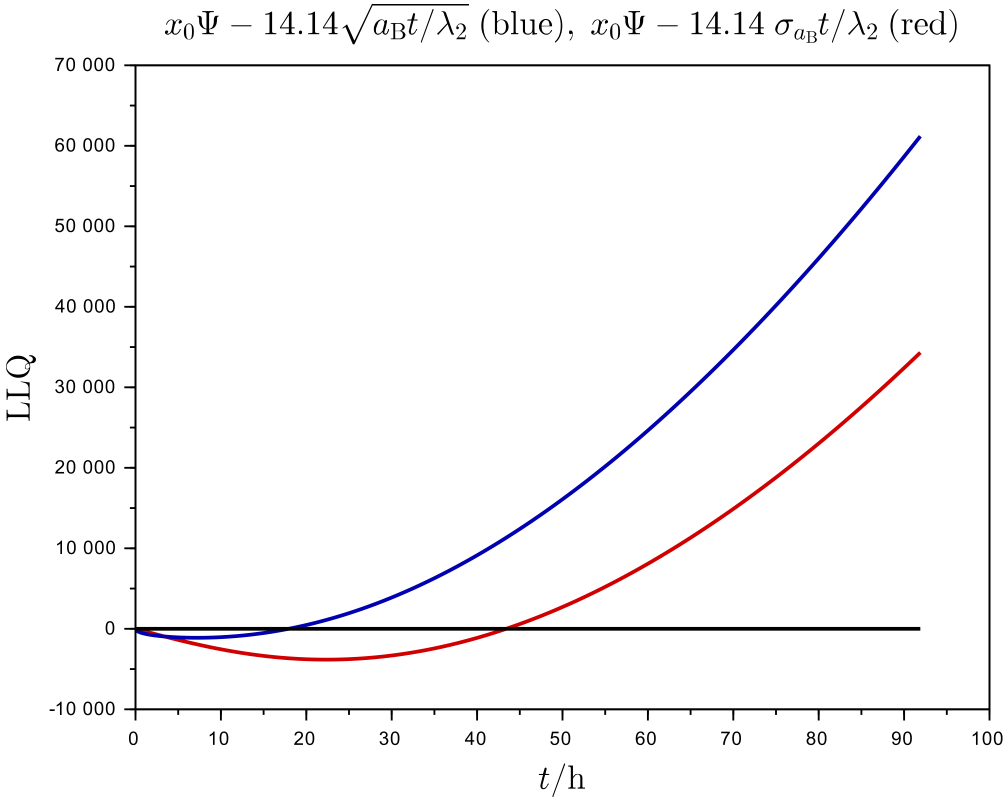

Figure 2: Plot of eq. (33) with q_{LLQ} given by eq. (31) (blue) and (32) (red) with $a_{\text{Ra-226}} = 0.17$ Bq.

Table 2: Required sampling times (in hours) for detection (t_{D}) and quantitation (t_{Q}) for different activities, given by eq. (33) making use of eqs. (31) and (32), respectively.

$\lambda_2 x_0$/mBq	t_{D} (eq. 31)	t_{Q} (eq. 31)	t_{D} (eq. 32)	t_{Q} (eq. 32)
500	0.033	1.19	t^*_{min}	t_{min}
250	0.13	4.45	t_{min}	13.63
100	0.81	17.89	t_{min}	71.18
75	1.43	24.59	t_{min}	102.34
50	3.12	36.14	t_{min}	177.70
25	10.24	63.80	40.71	1039.44
10	30.29	130.35	135.07	-

* t_{min} indicates a sampling time of the order of one minute or less

We see that, for our equipment, the LLQ of ^{226}Ra is about 50 mBq. This limit could be lowered by using a scintillator with a lower background count.

3 Experimental

Table 3 reports the experimentally determined ^{226}Ra activity of standard samples, considered as samples of unknown activity and subjected to analysis. The corresponding standard deviation and coefficient of variation $c_v = \sigma_a / (\lambda_1 x_0)$ are reported for each entry. As an indication of the validity of the model, the root mean square in eq. (29) is also given. The relative errors do not exceed 6% and are often below 1%.

Table 3: Experimental determinations of the ^{226}Ra activity ($\lambda_1 x_0$/mBq) of water samples with known activity $a_{\text{Ra-226}}$/mBq in OPTI unmixable scintillator, its experimentally determined coefficient of variation $c_v = \sigma_{\lambda_1 x_0} / (\lambda_1 x_0)$, and the relative error ($\varepsilon = \lambda_1 x_0 / a_{\text{Ra-226}} - 1$).

t_c/h	a_{B}/cpm	$a_{\text{Ra-226}}$	$\lambda_1 x_0$	c_v	ε	σ_{fit}
91.90	37.35	155.78	158.1	1.13×10^{-2}	1.49×10^{-2}	5.27×10^{-2}
88.72	38.01	2081.0	2068	6.12×10^{-2}	6.50×10^{-3}	1.78×10^{-2}
73.82	38.28	3138.1	3140	6.76×10^{-2}	-6.69×10^{-4}	1.47×10^{-2}
93.35	35.90	2091.4	1972	5.93×10^{-2}	-5.71×10^{-2}	4.54×10^{-2}
91.02	36.56	1871.3	1963	5.90×10^{-2}	4.90×10^{-2}	1.80×10^{-2}

The root mean square of c_v is 0.056 and the corresponding RMS for the relative error ε is 0.034.

The ^{226}Ra source was supplied by EUROSTANDARD CZ. All the other reagents were ACS grade or higher and obtained from Sigma Aldrich. All reagents were tested and found to be free of radium. Teflon–coated polyethylene vials and Opti–Fluor O water immiscible liquid scintillation counting (LSC) cocktail (PerkinElmer) were used for the liquid scintillation counting. ^{226}Ra activity was analysed using Packard 2200 CA liquid scintillation instrument. The solution used to prepare the radium spiked samples is obtained by dissolution of 200 mg of barium sulphate in 100 mL of EDTA 0.25 M adjusting pH to 10 with ammonium hydroxide 13 M, to have a sample with composition similar to that obtained with the coprecipitation method [49], [50]. The measured samples were prepared introducing in the scintillation vial 10 mL of the liquid sample, above described. After the addition of accurately weighed amounts of ^{226}Ra standard solution (to have the desired activity) helium was bubbled through it to remove the ingrown radon, 10 mL of Opti–Fluor O cocktail were added and, finally, the samples were counted by LSC for 73 hours in all the energy range of the instrument. The counting was started without mixing and immediately after sample preparation.

4 Conclusions

The proposed computational model for the total liquid scintillation counts of a system containing an unknown initial concentration of ^{226}Ra in water solution allows the determination of the radium activity trough unconstrained minimization of the residues of the calculated with respect to the experimental number of counts. The detailed modelling allows immediate counting after the preparation of the sample, thus avoiding the requirement to be at secular equilibrium. Testing of the methods with standard radium solutions shows promising results.

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