

# An Easy Method for the Determination of Ra Isotopes and Actinide Alpha Emitters from the Same Water Sample\*

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Radium isotopes and actinide  $\alpha$  emitters are easily determined from the same water sample. The Ra fraction is obtained by coprecipitation with Ba, while a Fe coprecipitation is used for the actinides. Both fractions are measured with a gas-flow proportional counter. Additionally the isotopic Ra composition is obtained by measuring at two or three different times the  $\alpha$  activity from the Ra-fraction. The method is applied to rain water and drinking water samples.

## 1. Introduction

Collection of the dry residue upon evaporation, and subsequent reading of the low and high amplitude pulses with a proportional counter and a two channel analyser, provide a fast and low cost simultaneous estimation of the total  $\alpha$  and  $\beta$  activities in water.<sup>(1,2)</sup> This may be sufficient for a quick general knowledge of the activity levels in the aqueous environment. However the method has serious limitations: (a) First the indiscriminate collection of all the solid matter present in the water produces thick samples with weak and poorly known  $\alpha$ -efficiency (because of the absorption) unless small volumes of water are treated and consequently small absolute activity collected. In either case the effect is a relatively high inaccuracy of the result. (b) Moreover, as the potential danger assigned to different radionuclides is different and the method distinguishes only  $\alpha$  from  $\beta$ -activity, not different elements, the information gained is often insufficient.

On both grounds these shortcomings are particularly important for  $\alpha$  emitters because their contamination hazard is dangerous to human beings even at low concentration levels. In this paper an easy method to separate  $\alpha$  activity from water samples is given. From the same measurement we can obtain the  $\alpha$  activity associated with actinides and the  $\alpha$  activity associated with Ra. Moreover, a careful study of the temporal evolution of the Ra fraction activity can give the isotopic contribution, mostly due to  $^{226}\text{Ra}$  and  $^{224}\text{Ra}$ .

With this technique for counting the total  $\alpha$  activity, more detailed information is obtained which includes:  $\alpha$  activity due to actinides, which are related to U and Th present in the sample, plus  $^{226}\text{Ra}$  and  $^{224}\text{Ra}$  activities separately. Hence, an increase in the quality of the obtained data is reached and an easier handling of the data is possible.

A description of the radiochemical method is given in Section 2. The calibration of our proportional detector for  $\alpha$ -activity is presented in Section 3. In Section 4, we describe the technique used to evaluate the contribution of each radium isotope. Some results on different water samples are given in Section 5, with a summary and conclusions in Section 6.

## 2. Radiochemical Method

Essentially the method is one of coprecipitation of radium with Ba and of the actinides with Fe, either jointly [as described by Lieberman in Ref.(5)] or successively. Figure 1 outlines the steps followed: A 500 mL water sample, preserved with  $\text{HNO}_3$ , is first neutralized with  $\text{NH}_4\text{OH}$ , then 20 mL of 1 M  $\text{H}_2\text{SO}_4$  are added and the sample is heated at about 50 °C. Five mg  $\text{Ba}^{2+}$  are dissolved in the sample while being stirred. The Ba-Ra sulphate formed precipitates and is filtered out through a Millipore membrane. The precipitate is dried first in a hot plate and later in a silicagel desiccator to prepare it for counting.

The remaining aqueous phase is boiled to eliminate Rn and  $\text{CO}_2$  (the latter can otherwise induce the formation of complex compounds of U with carbonate and bicarbonate ions that are very soluble). The water is then brought to room temperature and heated again at about 50 °C to start the process of

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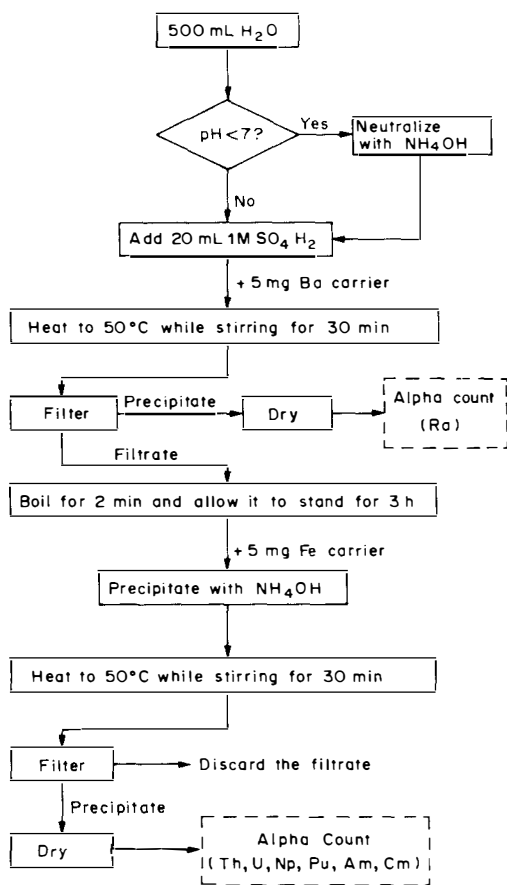


Fig. 1. Scheme of the process.

precipitation of actinides. To achieve this, 5 mg of  $\text{Fe}^{3+}$  are dissolved in the solution and  $\text{NH}_4\text{OH}$  is added dropwise until the precipitation is produced. This precipitate contains the actinides,  $\alpha$  emitters included, and is likewise filtered and dried, as before. The final aqueous phase is discarded.

In principle all the actinides are contained in the second fraction, but in most cases natural  $\alpha$  emitters, i.e. U and Th, will dominate the  $\alpha$  activity of the sample.

Both fractions, radium and actinides, are separately counted with a conventional gas flow proportional detector which has been described elsewhere.<sup>(3)</sup>

### 3. Calibration of the Counting System

The  $\alpha$  efficiency of the detector is essentially energy independent in the typical region of interest (4–7 MeV), but it varies strongly with the sample thickness as shown in Fig. 2. The calibration was made with a 500 mL water sample to which a known activity of  $^{239}\text{Pu}$  was added. It was acidified with 20 mL of 1 M  $\text{H}_2\text{SO}_4$  and  $\text{Ba}^{2+}$  and  $\text{Fe}^{3+}$  added. The resulting specific activity was  $(53.2 \pm 1.2)$  dpm/mL. Several aliquots of this sample were taken, between 10 and 115 mL, and completed, when necessary, with distilled water up to 100 mL each. Thus we obtained

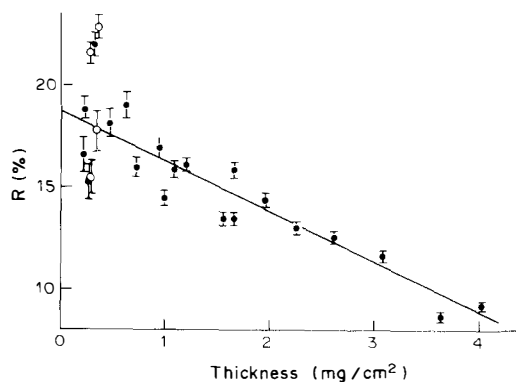


Fig. 2. Calibration curve of the counting system by a straight line.

precipitates with different thicknesses by the procedure outlined in the previous section, only modified in that both Ba and Fe were jointly precipitated.

The total efficiency,  $R_T$ , was obtained as the ratio between the net  $\alpha$  counts and the known activity of the aliquot.  $R_T$  is dependent on: geometry (which is the same for all the samples), self absorption of alphas (which is negatively correlated with the thickness, as expected) and the radiochemical yield of the process described in Section 2. The error bars take into account the counting statistics and the uncertainty of the pipetting, not the fluctuation of the chemical yield. It is clear that they underestimate the fluctuation of real values of  $R_T$  about the smooth analytical calibration  $R(x)$  of Fig. 2. The latter has been taken, for convenience, without any theoretical prejudice and in view of the large actual fluctuation, as the least squares linear expression

$$R(x) = 18.75 - 2.486x \quad (1)$$

with Pearson correlation coefficient  $r = -0.89$ , where  $R$  is given in % and the thickness  $x$  in  $\text{g}/\text{cm}^2$ .

To this calibration formula we assign the experimental relative error of 7% for  $x > 0.48 \text{ mg}/\text{cm}^2$  and 20% for  $x < 0.48 \text{ mg}/\text{cm}^2$ . This "error" is accumulated quadratically to the statistical errors of the problem samples considered in Section 5. A smaller set of  $^{241}\text{Am}$  samples of known activity has confirmed the validity of calibration (1) for this radionuclide.

Larger volumes (500 mL) will be treated for the problem samples than those used for calibration (100 mL). To confirm the irrelevance of the volume and to explore an eventual dependence on the radionuclide, eight large (0.5 L) samples with known activity of  $^{239}\text{Pu}$  or  $^{241}\text{Am}$  were prepared and counted. The average ratio of their efficiency to that predicted by equation (1) is  $(100 \pm 7)\%$ . A similar experience with  $^{226}\text{Ra}$  activity gave an average ratio of  $(106 \pm 7)\%$  which is compatible with equation (1) but suggests a few % higher yield in the Ra precipitate. Consequently, when applying calibration (1) to Ra samples we renormalize it with a factor 1.06.

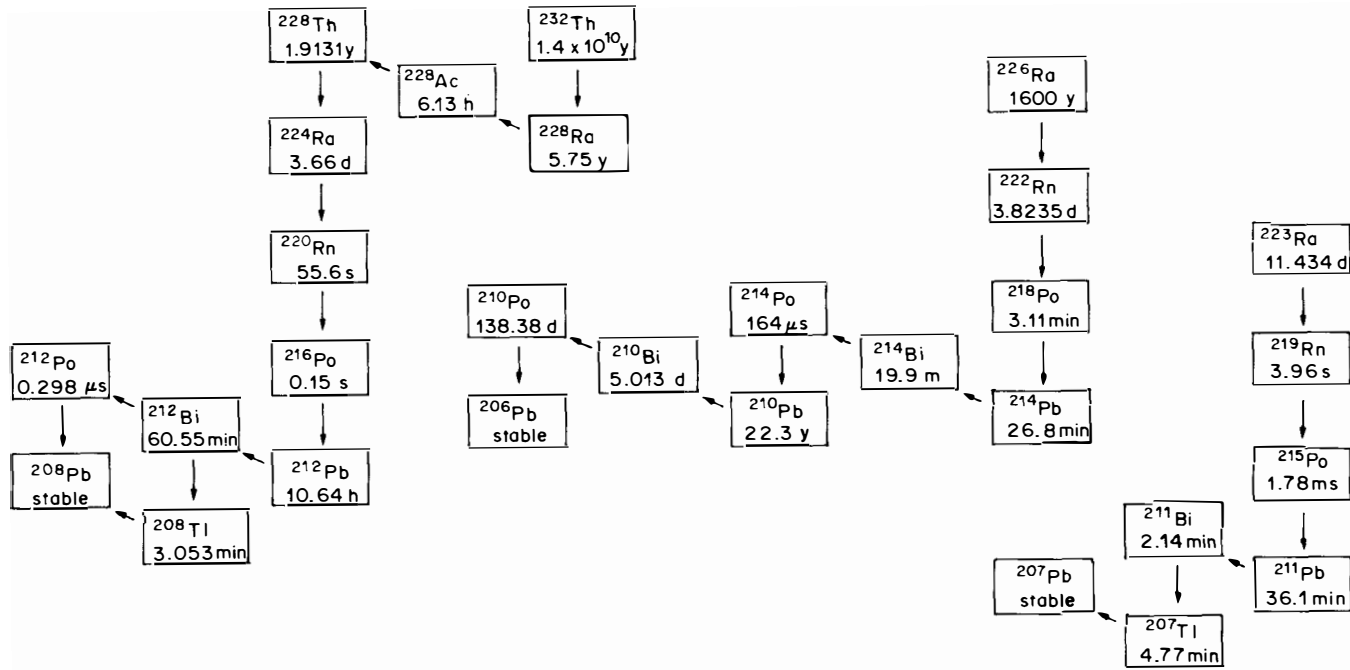


Fig. 3. Part of three radioactive series showing natural radium isotopes with their descendants and half-lives. Alpha decay goes downwards and beta decay goes up left.

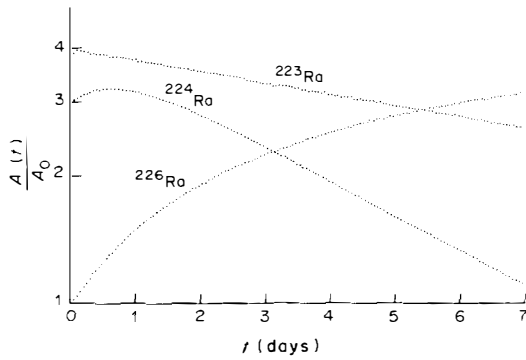


Fig. 4. Time evolution of the total activity of  $^{223}\text{Ra}$ ,  $^{224}\text{Ra}$  and  $^{226}\text{Ra}$ , with their descendants, starting with unit activity of the parent at  $t = 0$ .

#### 4. Measurement of the Isotopic Composition of the Ra Fraction

Four Ra isotopes are found in Nature, associated with their ancestors and descendants. Their place in the radioactive series is shown in Fig. 3. Three of them are  $\alpha$  emitters and (particularly  $^{224}\text{Ra}$  and  $^{223}\text{Ra}$ ) have, among their descendants, other very short lived  $\alpha$  emitters. Immediately after coprecipitation with Ba, the sole activity due to radium isotopes remains. Of course, this will soon receive the contribution of their daughters. Figure 4 shows the time evolution of the total activity of each,  $^{223}\text{Ra}$ ,  $^{224}\text{Ra}$  and  $^{226}\text{Ra}$  with their descendants, starting with unit activity of the parent at  $t = 0$ .  $^{223}\text{Ra}$  and  $^{224}\text{Ra}$  grow in a few seconds to about three times the original activity and after two or three days the whole family will decay in secular equilibrium with the parent's period (11.4 d and 3.66 d respectively). It is possible that, since  $^{228}\text{Ra}$  is also collected in the precipitate, it can regenerate  $^{224}\text{Ra}$ . There is, however, a link, which has not been collected in the precipitate ( $^{228}\text{Ac}$  and  $^{228}\text{Th}$ , the second having an almost 2 year half-life). Thus 1 month (2 months) after the hypothetical separation of sole  $^{228}\text{Ra}$ , the total  $\alpha$  activity of its descendants will reach 12% (26%) of the initial  $\beta$  activity of the parent  $^{228}\text{Ra}$ . The activity of the  $^{226}\text{Ra}$  family is characterized mostly by the half-life of the daughter

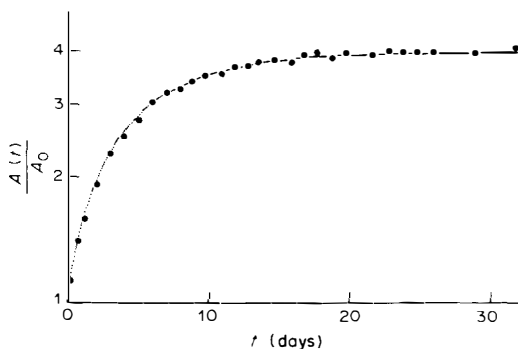


Fig. 5. Experimental values of the activity in different times compared with the theoretical predictions for  $A_0 = 97.4$  cpm and  $t_0 = 140$  min.

$^{222}\text{Rn}$  (3.8 d) which is followed by two more  $\alpha$  emitters with short lives. Thus in a few weeks the family reaches four times the initial  $\alpha$  activity: 380% in 15 days and 398.7% in 30 days. The contribution of the  $^{210}\text{Po}$  is strongly delayed by the interposed long-lived (22.3 y)  $\beta$  emitter  $^{210}\text{Pb}$ .

For a given isotopic composition of the radium precipitate the expected activity and number of counts at a later time can be computed with the equations given in the Appendix, by adding the contributions of the four families ( $^{224}\text{Ra}$  is now an independent family initially disconnected from  $^{226}\text{Ra}$ ). Reciprocally it should be possible to deduce the isotopic composition of the precipitate from the time evolution of the  $\alpha$  activity.

There is, however, a previous question to be resolved: Is there a  $t = 0$ ? In the process described in Section 2, is there an instant when all the radium to be collected is already in the precipitate without any members of the radioactive family other than Ra, and after this instant neither the developing daughters nor any Ra is dissolved? And, if so, when after the addition of the Ba carrier does that happen? We have looked for an experimental answer to this double question by preparing a standard water sample with a known amount of  $^{226}\text{Ra}$ , then performing a series of readings of the activity during a few weeks and comparing them with predictions of equation (A3) from the Appendix.

(i) As a first approximation for the initial counting rate,  $R_0$ , we take  $\frac{1}{4}$  of the experimental counting rate found in the last reading, 3 or 4 weeks after the preparation of the sample. This seems reasonable in view of the considerations given above.

(ii) Several values for the origin of time,  $t_0$ , after the addition of the Ba carrier, are tried in the fit, i.e.  $t - t_0$  is substituted instead of  $t$  in equation (A3).

(iii) The quality of the several fits thus obtained is measured through the quantity

$$\Delta \equiv \sqrt{\chi^2/N}$$

with

$$\chi^2 = \sum_{i=1}^N (R_{\text{th}} - R_{\text{exp}})_i / (R_{\text{exp}})_i$$

where  $N$  is the number of readings,  $R_{\text{exp}}$  the experimental values and  $R_{\text{th}}$  the predictions of equation (A3).  $\Delta$  depends on  $R_0$ , which for the moment is not changed, and from  $t_0$ . The best fit corresponds to minimum value of  $\Delta$ . For  $N$  large enough a good theory and good values of  $R_0$  and  $t_0$  imply  $\Delta \sim 1$ .

(iv) For the chosen value  $R_0$ ,  $\Delta$  is expected to depend quadratically on  $t_0$  in the vicinity of  $\Delta_{\text{min}}$ . Thus it takes just a few trials to find the best  $t_0$  for a given  $R_0$ , if we fit the values  $\Delta(t_0)$  found by a parabola.

(v) Now other values of  $R_0$  are investigated through steps (ii)–(iv). Thus the  $\Delta_{\text{min}}$  (with respect to  $t_0$ ) depends on the chosen value  $R_0$ . Again the dependence  $\Delta_{\text{min}}(R_0)$  is expected to be quadratic near

the minimum (with respect to  $R_0$ ), and a few trials suffice to find the best values  $R_0$ ,  $t_0$  which yield the real minimum of  $\Delta$  with respect to both of them.

This sequence has been followed with two 500 mL water samples, each with an initial  $^{226}\text{Ra}$  added activity of  $(531 \pm 10)$  dpm. The number of readings was  $N = 29$  in 32 days and  $N = 26$  in 31 days respectively. The minimum  $\Delta$  obtained was 1.86 with  $t_0 = 140$  min and  $R_0 = 97.4 \pm 0.3$  cpm for the first sample (see Fig. 5) and  $\Delta = 1.78$  with  $t_0 = 167$  min and  $R_0 = 98.7 \pm 0.3$  cpm for the other. The deduced efficiencies of  $(18.3 \pm 0.4)$  and  $(18.6 \pm 0.4)\%$  compared with the calibration of equation (1) for the experimental thicknesses ( $0.56$  and  $0.52$  mg/cm<sup>2</sup>) yielded the average efficiency of the chemical process for Ra as compared with Am and Pu which was quoted in the previous Section as  $(106 \pm 7)\%$ .

The values of  $\Delta$  near the minimum, and of the corresponding  $R_0$ , are not very sensitive to changes of a few tens of min in  $t_0$ . So we will assume a  $t_0 = 150$  min after the addition of the Ba carrier as the origin of time for equations (A1) and (A3) of the Appendix. The values  $\Delta$  are close enough to 1 to give confidence to the method. But the procedure is too long for a routine-like determination of the isotopic composition of a radium sample.

However a much shorter number of measurements is sufficient, especially if one makes the following reasonable assumptions: (i)  $^{223}\text{Ra}$ , being a descendant from the relatively scanty  $^{235}\text{U}$ , is expected to be in negligible proportion compared to the other Ra isotopes, unless the sample comes from places contaminated by the nuclear industry. Consequently, its presence can be discarded at a guess. (ii)  $^{228}\text{Ra}$  contributes almost nothing in the first two months.

Therefore two readings should be enough for a determination of the initial activity of  $^{224}\text{Ra}$  and  $^{226}\text{Ra}$ : one in the first or second day, when the  $^{224}\text{Ra}$  family is relatively more active, and the other one after 2 or 3 weeks when almost only the  $^{226}\text{Ra}$  family is active. Thus if  $C_1$  and  $C_2$  are the total activities obtained from the number of counts collected in the readings started at  $t_1$  and  $t_2$ ,  $F_4(t)$  and  $F_6(t)$  the predictions of equation (A3) for unit initial activity of  $^{224}\text{Ra}$  and  $^{226}\text{Ra}$  respectively, then the corresponding experimental initial activities  $A_4$  and  $A_6$  are obtained from the system:

$$\begin{aligned} C_1 &= A_4 F_4(t_1) + A_6 F_6(t_1) \\ C_2 &= A_4 F_4(t_2) + A_6 F_6(t_2) \end{aligned} \quad (2)$$

(iii)  $^{224}\text{Ra}$  and  $^{228}\text{Ra}$  can be in secular equilibrium if the sample has not undergone chemical actions in the previous few years. This implies equal activity at time  $t_0$  ( $A_8 = A_4$ , following the notation of the previous paragraph). A new measurement made some months later (say  $t_3$ ) may confirm the hypothesis of secular equilibrium if the reading  $C_3$  fulfills

$$C_3 = A_6 F_6(t_3) + A_4 F_8(t_3)$$

with obvious notation as in the previous equations. Once the presumption of secular equilibrium ( $A_8 = A_4$ ) has been confirmed for a type of environmental source, it can be systematically assumed in the future with only occasional confirming tests.

## 5. Application of the Method

The method is currently being applied to different environmental water samples. We present some of the results here.

Table 1. The  $\alpha$  activity of rainwater collected in three different periods of time (column 2) has been measured by the different methods described in this work. Columns 3 and 4 are the initial activities of  $^{226}\text{Ra}$  and  $^{224}\text{Ra}$  obtained through equation (2) from the measurements of the Ba precipitate. Column 5 gives the activity of the matter precipitated with Fe and is attributed to actinides. Columns 6-9 give the total  $\alpha$  activity measured at two different times from the joint Fe + Ba precipitate, according to the method of Ref. (5). The compatibility of these results with those of columns 3-5 is explained in the text. (Time is given in days in columns 7 and 9)

Sample	Sampling date	Activity (mBq/L)						
		$^{226}\text{Ra}$	$^{224}\text{Ra}$	Actinides	Total $\alpha$ activity			
					$A_1$	$t_1$	$A_2$	$t_2$
R1	Feb.-Apr. 1983	$105 \pm 8$	$25 \pm 5$	$196 \pm 19$	$361 \pm 31$	2	$613 \pm 51$	56
R2	Apr. 1983	$23 \pm 2$	$12 \pm 5$	$48 \pm 7$	$128 \pm 12$	1	$144 \pm 14$	92
R3	Apr.-May 1983	$193 \pm 14$	$28 \pm 9$	$307 \pm 24$	$923 \pm 76$	6	$1049 \pm 87$	52

Table 2.  $^{226}\text{Ra}$  and actinide  $\alpha$ -emitter activities measured in some drinking water samples (D) and lake water samples (L) (No significant  $^{224}\text{Ra}$  activity was found). For comparison, total  $\alpha$  activity is given. The latter was determined following the method of Ref. (5)

Sample	Sampling date	Activity (mBq/L)				$t$ (days)
		$^{226}\text{Ra}$	Actinides	Total		
D1	2-16-84	$1.7 \pm 0.6$	$14 \pm 4$	$19.0 \pm 2.9$	4	
D2	4-16-84	$4.3 \pm 0.8$	$20 \pm 3$	$23.5 \pm 3.1$	32	
D3	7-13-84	$1.7 \pm 0.6$	$16 \pm 3$	$7.9 \pm 2.5$	22	
L1	2-16-84	$1.8 \pm 0.6$	$6 \pm 3$	$17.1 \pm 3.1$	9	
L2	4-16-84	$0.3 \pm 0.5$	$9 \pm 3$	$13.5 \pm 3.9$	16	
L3	7-13-84	$0.6 \pm 0.4$	$6 \pm 2$	$4 \pm 3$	19	

The activities found in different rainwater samples are given in Table 1. They have been collected since December 1982 at the University of Seville. The results show a considerable presence of  $^{226}\text{Ra}$ , quite similar to those from actinides, and significant  $^{224}\text{Ra}$  activities are also obtained. Total  $\alpha$  activity was measured for one or several days after chemical separation ( $A_1$ ) and after several months ( $A_2$ ); the time that mediated between the preparation and reading of the activity is shown in columns 7 and 9 respectively. It is observed that  $A_2$  is systematically higher than  $A_1$ . This is due to the  $^{226}\text{Ra}$  content in the prepared sample.

To compare the measurements of the total activity (columns 6 and 8) with the sum of the partial measurements (columns 3, 4 and 5), one also has to include the contribution of the descendents of Ra isotopes, which vary with time, as explained in Section 4. Thus after 6 days the activity of the  $^{226}\text{Ra}$  family has increased by a factor  $F_6(6) = 2.99$ , and that of the  $^{224}\text{Ra}$  family by a factor  $F_4(6) = 1.33$ , and after 52 days by factors  $F_6(52) = 4$  and  $F_4(52) \approx 0$ . Therefore, if we look at the most active sample R3, one has to compare the total activity found after 6 days ( $923 \pm 73$ ) with

$$2.99(193 \pm 14) + 1.333(28 \pm 9) + (307 \pm 24) = 921 \pm 50$$

and the activity found after 52 days ( $1049 \pm 87$ ), has to be compared with

$$4(193 \pm 14) + (307 \pm 24) = 1080 \pm 61.$$

Similarly, for the samples R1 and R2 it is straightforward to show that the results of columns 6 and 8 are compatible with those of columns 3-5 within experimental fluctuations.

The  $\alpha$  activities of some drinking water samples (named D) from Seville are given in Table 2. Actinide  $\alpha$  emitter concentrations (column 4 of the Table) are clearly higher than those of  $^{226}\text{Ra}$  (column 3). On the other hand, significant  $^{224}\text{Ra}$  activity was not found in this kind of sample. In general, the specific activities are very low, with relative errors ranging from 15 to 35%. In the last 2 columns of this Table the total  $\alpha$  activity is given for each sample and the time after separation when it was measured.

In the same Table, the results for artificial lake water samples (named L in column 1) are presented. These reservoirs are located around Seville and feed the water treatment plants of the city. Neither  $^{224}\text{Ra}$  nor  $^{226}\text{Ra}$  are significantly present in these waters, with the exception of sample L1. The levels of actinide activities are very low and there are no highly significant differences between these results and those from drinking water samples. Again the data of columns 5 and 6 can be shown to agree with the sum of the activities found separately for Ra (column 3 plus descendents) and actinides (column 4), although the large relative errors make the check more ambig-

Table 3. Values of the parameters appearing in equations (A1) to (A3) for the different Ra families

$i$	$^{226}\text{Ra}$ $h_i$	$n = 4$ $t_i$ (min $^{-1}$ )	$^{226}\text{Ra}$ $h_i$	$n = 7$ $t_i$ (min $^{-1}$ )	$^{226}\text{Ra}$ $h_i$	$n = 8$ $t_i$ (min $^{-1}$ )	$^{226}\text{Ra}$ $h_i$	$n = 4$ $t_i$ (min $^{-1}$ )
0	4.1516	1.315E-4	7.50475	2.292E-7	5.01441	8.2365E-10	4.002	4.2098E-5
1	-2.00308	0.748001	3.28E-4	0.001885	-3.00965	1.2589E-4	-2.0005	10.5022
2	0.002705	277.259	-7.52839	6.889E-7	5.79E-4	0.222877	4.497E-4	23364.5
3	-1.2902	0.001086	0.0235	1.315E-4	0.02149	0.0258637	-1.06	0.0192008
4	0.07606	0.011448	*	0.748001	-0.0124	0.0348315	0.065	0.323901
5	—	—	*	277.259	*	253590	—	—
6	—	—	-0.0002284	0.0010867	-1.03278	5.90962E-8	—	—
7	—	—	*	0.011448	-9.8E-5	9.60208E-5	—	—
8	—	—	—	—	0.01845	3.4788E-6	—	—

\* Negligible ( $|h_i| < 10^{-7}$ ).

uous in these cases, than for the rain samples of Table 1.

## 6. Summary and Conclusions

Most environmental laboratories devote a large part of their work to the determination of  $\alpha$  activity in water. As a first stage the measurement of total  $\alpha$  activity is currently used. Since these results are difficult to interpret, other methods are needed that could broaden and qualify the information obtained.

In this work a method is given for the separate measurement of Ra and actinide  $\alpha$  emitters from the same environmental water sample. Ra is first recovered by coprecipitation with Ba, and later the actinides with Fe. In addition, a study of the temporal evolution of Ra activity gives the isotopic composition of the extracted Ra, i.e.  $^{226}\text{Ra}$  and  $^{224}\text{Ra}$  concentrations. The details of this study have been carefully determined.

With this easy procedure more and better information than simple, gross  $\alpha$  determination, is extracted from each water sample. Moreover, in some cases, this method can easily compete with others of greater sophistication.

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## APPENDIX

The total  $\alpha$  activity originated by a whole family at a time  $t$  after the isolation of the parent Ra isotope, is deduced from Bateman's equations (see for example Ref. 4) and can be expressed as

$$A_T = A_0 \sum_{i=0}^n b_i \exp(-\lambda_i t) \quad (\text{A1})$$

where  $A_0$  is the initial activity of the parent ( $\beta$  for  $^{228}\text{Ra}$ ,  $\alpha$  for the others) and the coefficients  $b_i$  can be written

$$b_i = \frac{\lambda_i}{\lambda_0} \sum_{k=i}^n r_k \prod_{j=\bullet}^k \lambda_j / (\lambda_j - \lambda_i) \quad (\text{A2})$$

Here  $n$  is the number of radioactive descendants considered ( $^{207}\text{Tl}$  and  $^{208}\text{Tl}$  need not be computed, as no  $\alpha$  emission follows, and  $^{212}\text{Po}$  because of its extremely short life is "embodied" in  $^{212}\text{Bi}$  as if the latter had 100% alphas),  $r_k$  is the fraction of  $\alpha$  emission by the  $k$ th descendant ( $r_k = 0$  for  $\beta$  emitters,  $r_k = 1$  for  $\alpha$  emitters). By the symbol  $\prod'$  we mean a product where the factor  $j = i$  is excluded with the complementary convention

$$\prod'_{j=0}^{\bullet} = 1.$$

The values of  $n$ ,  $b_i$  and  $\lambda_i$  are tabulated in Table 3 for the chains originated by each Ra isotope.

The number of counts detected in the interval from  $t$  to  $t + \Delta t$  is

$$R = R_0 \sum_{i=0}^n \frac{b_i}{\lambda_i} \exp(-\lambda_i t) [1 - \exp(-\lambda_i \Delta t)] \quad (\text{A3})$$

where  $R_0 = \varepsilon A_0$  and  $\varepsilon$  is the efficiency of the counting system.