

^{226}Ra and ^{228}Ra determination in environmental samples by alpha-particle spectrometry

J. L. Aguado,¹ J. P. Bolivar,¹ R. García-Tenorio^{2*}

¹ Departamento de Física Aplicada, Universidad de Huelva, Facultad de Ciencias Experimentales, Campus El Carmen 21071, Huelva, Spain

² Departamento de Física Aplicada II, Universidad de Sevilla, E.T.S.A., Avda. Reina Mercedes 2, 41012 Sevilla, Spain

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A complete methodology for ^{226}Ra and ^{228}Ra determination by alpha-particle spectrometry in environmental samples is being applied in our laboratory using ^{225}Ra as an isotopic tracer. This methodology can be considered highly suitable for the determination of these nuclides when very low absolute limits of detection need to be achieved. The ^{226}Ra determination can be performed at any time after the isolation of the radium isotopes from the analyzed samples while the ^{228}Ra determination needs to be carried out at least six months later through the measurement of one of its grand-daughters. The method has been validated by its application to samples with known concentrations of these Ra nuclides, and by comparison with other radiometric methods.

Introduction

^{226}Ra ($T_{1/2}=1600$ years) is a radionuclide of the ^{238}U series and is one of the most important isotopes to be determined in environmental samples among the naturally occurring radionuclides, since it is potentially dangerous to human beings even at low concentration levels, and at the same time due to its important role in several environmental and earth science investigations.¹

^{226}Ra is mainly an α -nuclide ($E_{\alpha 1}=4.781$ MeV, 94.5% and $E_{\alpha 2}=4.598$ MeV, 5.5%), however, it also emits a low intensity γ -photon ($E_{\gamma}=186.2$ keV, 3.5%). Therefore, its determination can be carried out through the direct measurement of one or more of these emissions. Moreover, a series of short-life radionuclides (^{222}Rn , ^{218}Po , ^{214}Pb , ^{214}Bi , ^{214}Po) by the ^{226}Ra α -decay makes additionally possible the indirect determination of ^{226}Ra through the measurement of one of their daughters, once the secular equilibrium can be assured.

^{228}Ra , ($T_{1/2}=5.75$ years), is a member of the thorium series, and is even more radiotoxic than ^{226}Ra .² However, and in comparison with the former, there is a clear lack of data concerning ^{228}Ra levels in environmental samples, probably due to the fact that its measurement cannot be considered straightforward. Nevertheless, if in addition to their radiological concern, we bear in mind that the analysis of $^{228}\text{Ra}/^{226}\text{Ra}$ isotopic ratios is extremely useful in geochemical oceanic and hydrological research,^{3,4} it can be concluded that the possessing of efficient methodologies for the determination of both radioisotopes is essential in an environmental radioactivity laboratory.

A very good compilation of conventional radiometric methods for the analysis of ^{226}Ra in environmental samples can be found elsewhere.⁵ These methods differ concerning the reachable detection limit, selectivity,

analytical effort and reproducibility, and are based either on the measurement of ^{226}Ra via its α -particles or γ -emission, or through the measurement of its progenies when secular equilibrium is reached.^{2,6,7}

The radiometric methods found in the literature for the determination of ^{228}Ra in environmental samples are more limited. This radionuclide only emits weak β -particles (39 keV, 60%, and 14.5 keV, 40%), and therefore, its direct measurement with a good sensitivity is relatively difficult. For this reason, its determination is generally performed through the measurement of some of its progenies: either through the γ -emissions associated to the more energetic β -particles of ^{228}Ac or through the α -particles emitted by ^{224}Ra .

As a general policy, if, in addition to ^{226}Ra , we are also interested in the ^{228}Ra determination, then it is clear that we must try to avoid the necessity of applying two different measurement techniques and of preparing two different Ra sources from the same sample. This reduces the applicable radiometric methodologies to a limited number:^{2,7–9} gamma-ray spectrometry, liquid scintillation counting and alpha-particle spectrometry.

The major advantage of the determination of ^{226}Ra and ^{228}Ra by alpha-particle spectrometry is the low limit of detection that can be achieved for both Ra nuclides, which allows the precise determination of activities in the order of mBq.¹⁰ However, although the ^{226}Ra can be determined after the deposition of the isolated Ra, it is necessary to wait at least six months for the growth of the progeny ^{228}Th for the proper ^{228}Ra determination by α -spectrometry.

This work is devoted to the exposition and validation of the complete methodology currently applied in our laboratory for the determination of ^{226}Ra and ^{228}Ra in environmental samples by α -particle spectrometry.

* E-mail: gtenorio@us.es

Experimental

Radiochemical method

The determination of the aforementioned Ra isotopes by α -particle spectrometry demands a laborious radiochemical procedure and, consequently, the use of a yield tracer, in order to quantify the possible losses of the Ra isotopes after the application of the different radiochemical steps. It is no trivial to find a suitable yield tracer for the determination of ^{226}Ra and ^{228}Ra in environmental samples by α -particle spectrometry. In fact it is impossible to find the ideal nuclide: a radioisotope of Ra not present in the environment, with a half-life long enough to allow its proper measurement and with α -emissions which do not interfere with those produced by the natural Ra isotopes and their progenies. Bearing these facts in mind, after the careful analysis of the different possibilities,⁵ it was decided to use ^{225}Ra ($T_{1/2}=14.8$ days) as yield tracer. This is a beta-emitter which does not exist in the environment, and is available for us in secular equilibrium with its progenitor, ^{229}Th ($T_{1/2}=7.34\cdot 10^3$ years).¹¹ Using this tracer, the determination of the radiochemical yield is performed through the measurement of one of its short half-life α -emitter progenies, ^{217}At , since its α -emission does not interfere with those emitted by the final Ra source.

The radiochemical method, with some modifications and adjustments, follows that originally developed by HANCOCK and MARTIN,¹² and has been analyzed and refined in detail in order to minimize possible interferences, artefacts, as well as limits of detection. It is based on three main steps: (a) dissolution of the matrix (if it is solid) and/or Ra pre-concentration, (b) removal of interfering elements for the isolation of the Ra-isotopes, and (c) deposition of the Ra-isotopes in thin layers for their proper measurements. These steps are detailed in the following paragraphs.

Step a: Dissolution and/or Ra pre-concentration: The solid samples (soils, sediments, vegetables, etc) after its drying, grinding and homogenization, and after the addition of the tracer, are dissolved by microwave digestion (20 mL HF, 7.5 mL HNO_3 and 10 mL HClO_4 per gram of sample). The filtered solutions are then dried and conditioned in 0.1M HNO_3 (100 mL). The liquid matrices, on the other hand, are initially evaporated to dryness after the addition of the tracer, and the residue is later redissolved with 5 mL conc. HNO_3 , and conditioned, in a similar way to the solid samples, 100 mL 0.1M HNO_3 (Solution A). Later on, and in both cases (solid or liquid matrix), the Ra isotopes are pre-concentrated from the Solution A by co-precipitation with Pb as sulphate, $\text{Pb}(\text{Ra})\text{SO}_4$. In the co-precipitation process, the Th and Ac are co-precipitated in addition to

the Ra, while the majority of U remains in the supernatant. Consequently, at this stage we assume that the progenitor (^{229}Th) and the progeny (^{225}Ac) continue to be in secular equilibrium with the yield tracer ^{225}Ra .

The co-precipitation of Ra with Pb as sulphate is performed by adding first 1 mL of H_2SO_4 (98%) and 2 g of K_2SO_4 to Solution A. Then, by adding drop-wise 1 mL 0.24M $\text{Pb}(\text{NO}_3)_2$ the lead sulphate is formed and precipitated. This precipitate, isolated either by centrifugation or filtration, is finally washed with 20 mL of K_2SO_4 0.1M/ H_2SO_4 0.2M.

Step b: Ra isolation and purification: The Pb-Ra precipitate coming from the previous step is dissolved, and then passed sequentially through two exchange resins for Ra isolation and purification. Specifically, the $\text{SO}_4\text{Pb}(\text{Ra})$ precipitate is first dissolved with 5 mL EDTA 0.1M pH 10 and 2 drops of NH_3 , and then passed through an anion-exchange column, Biorad AG1-X8, 5 cm in height and 7 mm diameter, which does not need to be previously conditioned. The resulting eluate from this step is preserved, and added to that resulting from the posterior washing of the column with 13 mL of EDTA 0.01M pH 10.

In the anion-exchange processes, the Th, the sulphate ions and a fraction of Ac are retained in the column, while all the Ra passes without interaction through the column. The Ra isotopes are present then in the composed eluate, which is afterwards conditioned by adding 1 mL of 5M NH_4AC and by adjusting its pH to 4.5 with HNO_3 (Solution B).

At this stage, the time of the Ra elution from the anion-exchange need to be recorded, since from the moment the ^{225}Ra is isolated from its progenitor ^{229}Th , it starts to decay with its own half-life.

In the eluate obtained from the anion-exchange column, and in addition to the Ra, other interfering elements are present such as Pb used for the coprecipitation, a fraction of Ac, some remaining traces of U and Po, and others from the Group II (Ca, Sr, Ba). All these Ra-accompanying elements are removed by using a second exchange column, which in this case is of cationic type (Biorad AG50W-X12, 8 cm in height and 7 mm diameter). This column is conditioned by its sequential washing with 15 mL of 1.5M NH_4AC and 15 mL of 0.25M NH_4AC at pH 4.5, while its volume flux needs to be adjusted to 0.8–1 mL/min by adapting a Teflon tube (40 cm length, 2 cm diameter) to its mouth. Then, the solution coming from the previous ion-exchange step (Solution B) is passed through the conditioned cationic column at the fixed flow, where the Ra and the Ac, among others, are retained very efficiently. The Ac is then eluted by washing the column with 50 mL of 0.1M $\text{NH}_4\text{AC}/\text{HNO}_3$ (at the same time the Pb and the remaining traces of U and Po are eluted), while more than 99.5% of the Ba is removed by an additional

washing of the column with 40 mL 2.5M HCl. Finally, the isolated Ra is eluted from the column by adding 25 mL of 6M HNO_3 (Solution C).

The time when the elution of the Ac from the cationic column is carried out also needs to be recorded. At this time, the direct progeny of ^{225}Ra is removed, fact that needs to be considered for a correct determination of the radiochemical yield since it will be determined through the α -emission of one of the ^{225}Ra progenies, ^{217}At .

Step c: Ra deposition in thin layers: As a final step, Solution C is conditioned for the Ra quantitative deposition in thin layers by electrodeposition. This electrodeposition is carried out in the following way: (a) Solution C is brought to dryness, (b) the resulting residues are re-dissolved in 1 mL of 0.1M HNO_3 and transferred with 9 mL of ethanol into an electrodeposition cell, and (c) the radium deposition is provoked onto stainless steel planchets by inducing a current intensity of 0.1 A for 30 minutes.¹³ This current is produced by using a platinum wire as an anode, separated by about 2 mm from the stainless planchets which act as a cathode.

Immediately after the interruption of the current, the liquid should be discharged from the electrodeposition cell and the formed electrodeposited Ra should be dried only with hot air. The thin Ra deposit formed is so weakly bound to the stainless steel support that any washing could destroy it, at least partially.

Once the electrodeposited Ra source has been prepared, it is ready to be measured by α -particle spectrometry.

^{226}Ra and ^{228}Ra activity determination

In our case, the counting of the prepared Ra sources has been carried out using an α -spectrometric system (Soloist-U050, EG&G Ortec) formed by eight chambers, each one equipped with a 450 mm² passivated implanted silicon detector (PIPS). Each detection unit has been energy calibrated using proper standard sources. The routine environmental counting is performed by placing the stainless steel planchets containing the Ra deposits at a distance of 5 mm from the detector. Under these conditions, the absolute efficiency in each chamber is approx. 25%.

In Fig. 1 a typical Ra α -spectrum corresponding to the counting of one environmental Ra sample, and covering the energy range of 4–8 MeV, is shown. The counting was performed three days after the application to the environmental matrix of the previously described

radiochemical method. This spectrum contains a complex set of peaks, some of them overlapping, corresponding to the different natural Ra isotopes and their short half-life daughters, and to some of the short half-life daughters of the ^{225}Ra tracer.

Of the four Ra-isotopes found in the nature, three, ^{226}Ra ($T_{1/2}$ = 1600 years), ^{224}Ra ($T_{1/2}$ = 3.66 days) and ^{223}Ra ($T_{1/2}$ = 11.43 days) are α -emitters, while the fourth, ^{228}Ra ($T_{1/2}$ = 5.75 years) is a β -emitter. Few days after the isolation of the Ra isotopes from the environmental matrix, contributions only from the three Ra α -emitters and their short half-life progenies can be expected in the α -spectrum, since although ^{228}Ra decays, after producing ^{228}Ac ($T_{1/2}$ = 6.13 h, β -emitter), into ^{228}Th (which is an α -emitter), the contribution of this last nuclide to the α -spectrum is negligible due to its long half-life ($T_{1/2}$ = 1.9 years). By other hand, the contribution of ^{223}Ra and daughters is expected, in general, to be relatively small in comparison with ^{226}Ra and daughters due to the scarcity in nature of its progenitor, ^{235}U , in relation with the ^{226}Ra progenitor (^{238}U).

In the spectrum of Fig. 1 and in addition to the two peaks free of interferences, corresponding to the two main α -emissions of ^{226}Ra (4.60 MeV, 5% and 4.78 MeV, 95%, marked in black), appear: (a) the alpha-peaks corresponding to the ^{226}Ra daughters, marked also in black, which have not reached the secular equilibrium with its progenitor when the counting shown in Fig. 1 was performed. However, the manifestation of this equilibrium should not be expected in the α -spectrum independent from the time elapsed between the preparation of the source and the performance of the counting, owing to the diffusion of a fraction of the ^{222}Rn from the Ra source,¹⁴ (b) the isolated alpha-peak of ^{217}At , marked with dashed lines, and used for the determination of the radiochemical yield, as ^{225}Ra daughter, taking into account that in the decay scheme of this Ra nuclide no Rn isotopes exist which produce any uncontrolled disequilibria through diffusion between the members of its series, and (c) a set of additional peaks, mostly formed by interfering contributions of several radionuclides (either Ra isotopes or Ra daughters) which not allow in particular the proper and accurate determination of the ^{224}Ra and ^{223}Ra concentrations in the environmental sample analyzed. In fact, the direct ^{223}Ra and ^{224}Ra α -emissions are not isolated, and in the case of ^{224}Ra , it is not possible to find any α -peak free of interferences corresponding to one of its progenies.

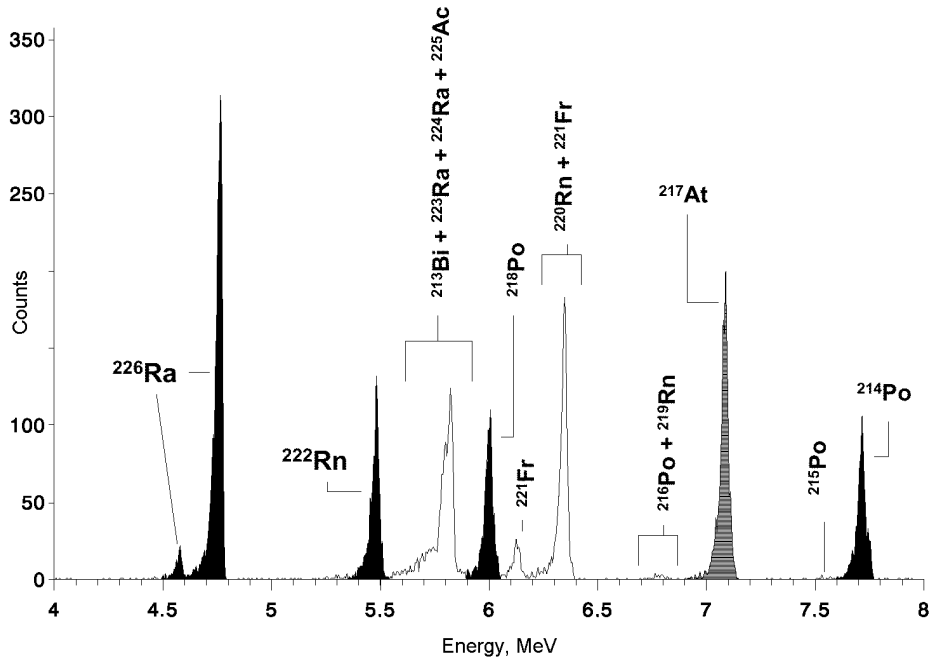


Fig. 1. Alpha-spectrum obtained after the counting of an electrodeposited Ra source obtained from an environmental sample. Counting was performed 3 days after electrodeposition. Black areas correspond to ^{226}Ra and daughter peaks. ^{225}Ra tracer daughter, ^{217}At , is also marked

It is also interesting to remark that the resolution of the ^{226}Ra α -peaks is excellent, with a FWHM for the main peak (4.78 MeV) of 25 keV, although this value can vary slightly depending on the type of environmental sample analyzed. Nevertheless, this resolution is generally lower than 40 keV as has been verified through the application of the proposed methodology to a wide set of different environmental samples.

The radiochemical yield of the procedure, R , is determined by the expression:

$$R = \frac{N_{At}}{\varepsilon N_2(t_0, t_1, t_2, t_3)} \quad (1)$$

where ε is the absolute ^{226}Ra detection efficiency of the α -spectrometric system used, N_{At} are the ^{217}At counts measured from the α -spectrum in the 7.07 MeV isolated peak, and $N_2(t_0, t_1, t_2, t_3)$ represents the theoretical number of ^{217}At disintegrations expected in the sample during the measuring time interval assuming that the total recovery of the chemical procedure is 100%. The value of the absolute ^{226}Ra detection efficiency, ε , is determined independently by measuring calibration sources under the same geometric conditions as the Ra sources. The value of N_{At} is taken directly from the measured α -spectrum, and the value of $N_2(t_0, t_1, t_2, t_3)$ is calculated by using Bateman's equations. In particular, the value of this last parameter, $N_2(t_0, t_1, t_2, t_3)$, is obtained by the expression:

$$N_2(t_0, t_1, t_2, t_3) = \left(\frac{A_0 e^{-\lambda_1(t_1-t_0)} \lambda_2}{\lambda_2 - \lambda_1} \right) \left(\frac{1}{\lambda_1} \left[e^{-\lambda_1(t_2-t_1)} - e^{-\lambda_1(t_3-t_1)} \right] - \frac{1}{\lambda_2} \left[e^{-\lambda_2(t_2-t_1)} - e^{-\lambda_2(t_3-t_1)} \right] \right) \quad (2)$$

where t_0 and t_1 indicate the $^{229}\text{Th}/^{225}\text{Ra}$ and $^{225}\text{Ra}/^{225}\text{Ac}$ separation times, respectively, t_2 and t_3 are the times when the α -measurement starts and finishes, A_0 is the $^{229}\text{Th}(^{225}\text{Ra})$ activity added to the sample, and λ_1 and λ_2 are the decay constants of ^{225}Ra and ^{225}Ac , respectively. Based on the radiochemical yield calculation, the ^{226}Ra activity concentration in the measured sample (Ra source) is easily determined by the expression:

$$A_e(^{226}\text{Ra}) = \frac{N_{Ra} N_2(t_0, t_1, t_2, t_3)}{N_{At} m (t_3 - t_2)} \quad (3)$$

where N_{Ra} represents the ^{226}Ra counts obtained from its direct emissions in the α -spectrum, and m is the quantity of sample (in mass or volume).

After the ^{226}Ra determination, the re-counting of the Ra sources at least six months after their preparation also makes it possible to determine their ^{228}Ra content.

In the time interval elapsed between the preparation of the sample and the mentioned re-counting, the ^{223}Ra , ^{224}Ra and ^{225}Ra nuclides initially deposited and their progenies have disappeared from the source, and consequently the structure of the α -spectrum is simpler.

In this spectrum, only the ^{226}Ra α -peaks and those corresponding to their progenies remain, however, the contribution of several daughters of ^{228}Ra (Fig. 2) appear at the same time.

For ^{228}Ra determination it is necessary to wait at least six months from the preparation of the Ra source to allow the sufficient growth of the first α -emitter ^{228}Ra progeny: the ^{228}Th . However, the determination is not performed by the counting of the ^{228}Th α -peak, since it overlaps with the ^{222}Rn peak. This is carried out by means of the ^{224}Ra α -peak, which appears isolated after the decay of the short half-life Ra isotopes that were initially present in the source (Fig. 2).

Six months after the Ra electrodeposition, the ^{228}Th reaches more than 15% of the initial electrodeposited activity of ^{228}Ra , and the ^{224}Ra is in secular equilibrium with the ^{228}Th . The maximum percentage of ^{228}Th would be observed, in relation with the initial activity of its progenitor ^{228}Ra , 4.5 years after the electrodeposition (57%).

The ^{224}Ra , and consequently the ^{228}Th activity concentration associated to the prepared source, can be calculated from the new α -spectrum through the expressions:

$$A_e(^{224}\text{Ra}) = A_e(^{228}\text{Th}) = \frac{N_{224}}{R \varepsilon P_\alpha m t_R} = \frac{N_{224}}{0.95 N_{226}} A_e(^{226}\text{Ra}) \quad (4)$$

where N_{224} is the number of counts in the ^{224}Ra α -peak (5.68 MeV, $P_\alpha=0.95$), m is the amount of environmental sample treated (in mass or volume), t_R is

the counting time in the α -system, R is the chemical yield determined in the first counting of the Ra-source, and ε is the absolute counting efficiency. N_{226} is the number of counts in the ^{226}Ra α -peaks, while $A_e(^{226}\text{Ra})$ is the activity concentration of ^{226}Ra determined in the first measurement.

Afterwards, the ^{228}Ra specific activity, initially associated to the Ra-source, can be calculated, by using Bateman's equations, through the expression:

$$A_e(^{228}\text{Ra}) = A_e(^{228}\text{Th}) \frac{\lambda_{\text{Th}} - \lambda_{\text{Ra}}}{\lambda_{\text{Th}} (1 - e^{-t_A (\lambda_{\text{Th}} - \lambda_{\text{Ra}})})} \quad (5)$$

where λ_{Th} and λ_{Ra} are the decay constants of ^{228}Th and ^{228}Ra , respectively, and t_A is the time passed from the electrodeposition of the source until the re-counting of the sample.

The methodology proposed for ^{226}Ra and ^{228}Ra determination by α -particle spectrometry in environmental samples allows reaching very low limit of detection (LLD). These LLD values have been determined by applying the radiochemical procedure to blank samples, by continually measuring them in the α -spectrometric system under standard conditions for 48 hours, and by assuming average radiochemical yields of 40% and 70% for solid and liquid samples, respectively.

LLD values as low as 0.4 mBq (liquid samples) and 0.7 mBq (solid samples) are obtained for ^{226}Ra , while in the case of ^{228}Ra the LLD values are higher, 3 mBq (liquids) and 5 mBq (solids). These LLD values indicate the possibility of determining both nuclides at the mBq level by applying the proposed methodology.

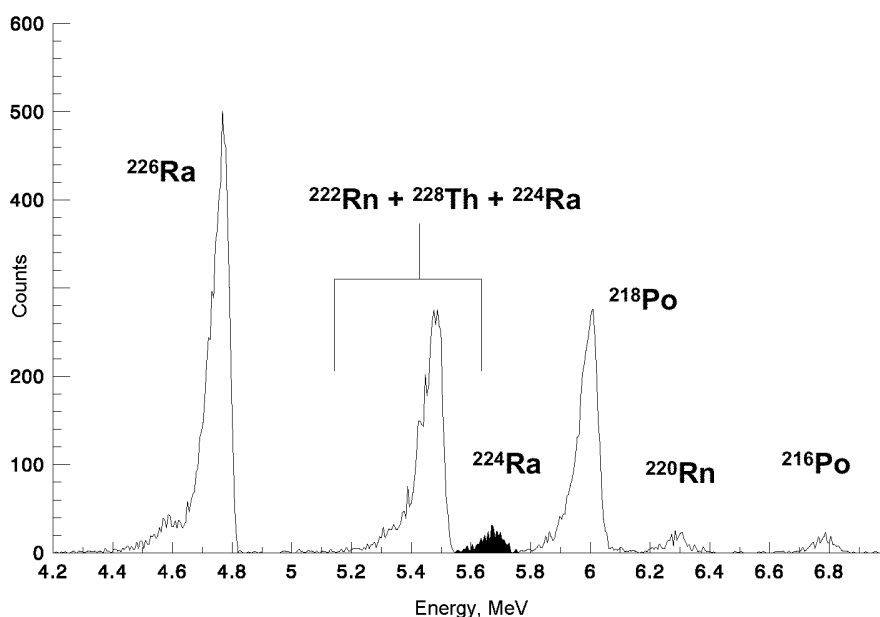


Fig. 2. Alpha-particle spectrum obtained for ^{228}Ra determination in environmental samples, six months after source preparation. The 0.95 intensity ^{224}Ra peak area used for ^{228}Ra determination is marked

Countermeasures to be adopted for a proper ^{226}Ra and ^{228}Ra determination

The expression of $N_2(t_0, t_1, t_2, t_3)$, used for the determination of the radiochemical yield, and consequently for the ^{226}Ra and ^{228}Ra activity concentrations, has been obtained by assuming that at time t_0 all the Th has been removed from the sample (Hypothesis A), that at time t_1 all the ^{225}Ac ("old Ac") has also been removed, and starts to grow from zero (producing the "fresh" Ac) (Hypothesis B), and that in the electrodeposition step there is no discrimination between Ra and the "fresh" Ac formed (Hypothesis C).

The incomplete removal of the Th at time t_0 , would induce the non-decay of a fraction of the ^{225}Ra with its own half-life from this time, while the incomplete isolation of the Ra from Ac in the cation-exchange column step would induce the presence of some "old" Ac in addition to the "fresh" Ac in the final counting deposit. In both cases the radiochemical yield would be overestimated. In addition, the determination of the radiochemical yield would be erroneous, if, after the formation of a fraction of "fresh" ^{225}Ac in the isolated Ra solution, some discrimination occurred in its electrodeposition in relation with radium. The accurate determination of the ^{226}Ra activities in the environmental samples by the proposed method then demands either the verification of the three hypotheses (Hypotheses A, B and C) or the adoption of some countermeasures to minimize as much as possible the impact of their non-verification in the Ra determinations.

The effects of an incomplete verification of Hypothesis B can be largely mitigated by performing the first counting of the sample by α -particle spectrometry some days (approx. twenty days) after the electrodeposition of the source since if the $^{225}\text{Ra}/^{225}\text{Ac}$ separation in the cationic column was not good, and therefore, some "old" Ac remains in the Ra-source, with time its contribution to the total ^{225}Ac ("old" plus "fresh") will be smaller, and practically zero after twenty days. The effects of the incomplete verification of Hypothesis C can be also mitigated by performing the electrodeposition step immediately after the Ra elution from the cationic column, since in this way the growth of the ^{225}Ac before the electrodeposition would be prevented, as would be the possible fractionation between Ra and Ac in this step.

Various tests have been performed to evaluate the importance of these two mitigation strategies. First of

all, the necessity of carrying out the Ra electrodeposition step just after the Ra isolation was clearly deduced by observing that even if the electrodeposition procedure is quantitative for Ra and Ac, the electrodeposition yield is not the same for both elements (some fractionation occurs). In addition, the need to wait at least twenty days for the performance of the counting was checked by repeating the counting of some environmental Ra-sources several times (in the interval of 0–30 days), scanning in each case the time elapsed between the electrodeposition and counting. In only a few samples were obtained in all the repeated measurements internally coherent ^{226}Ra results during the 30 days. In most cases when the time elapsed between electrodeposition and counting was short, slightly lower ^{226}Ra values were found than when the time elapsed exceeded 20 days (Fig. 3). This fact indicates the original presence in the environmental Ra-sources of some "old" Ac (in general <20%) not removed by the cation-exchange column, which results in an overestimation in the determination of the radiochemical yield, and consequently, in an underestimation of the ^{226}Ra specific activities especially when the time elapsed between the Ra-source preparation and the counting is short. When the Ra-sources are measured at least 20 days after their separation, the contribution of the remaining "old" Ac fraction to the total Ac is minimal; hence, coherent ^{226}Ra results from the repeated counting of the sample are obtained in all tests under this condition.

On the other hand, the validity of Eqs (4) and (5) for the determination of the ^{228}Ra content in the analyzed environmental samples is based on two hypotheses that can be considered as sufficiently verified. The first hypothesis is that there is no process which alters the theoretical expected growth of the ^{228}Ra progenies in the Ra source, a fact which can be assumed since no Rn isotope exists in its decay chain. And the second hypothesis is that the Th originally present in the environmental sample is totally eliminated by the radiochemical method, and consequently no ^{228}Th is initially present in the Ra source after its electrodeposition, a fact that was checked and verified by applying the described Ra radiochemical procedure to some synthetic samples doped with this element. This second hypothesis needs to be fulfilled since the expression used for ^{228}Ra determination is obtained by assuming that the ^{228}Th grows from zero after the electrodeposition.

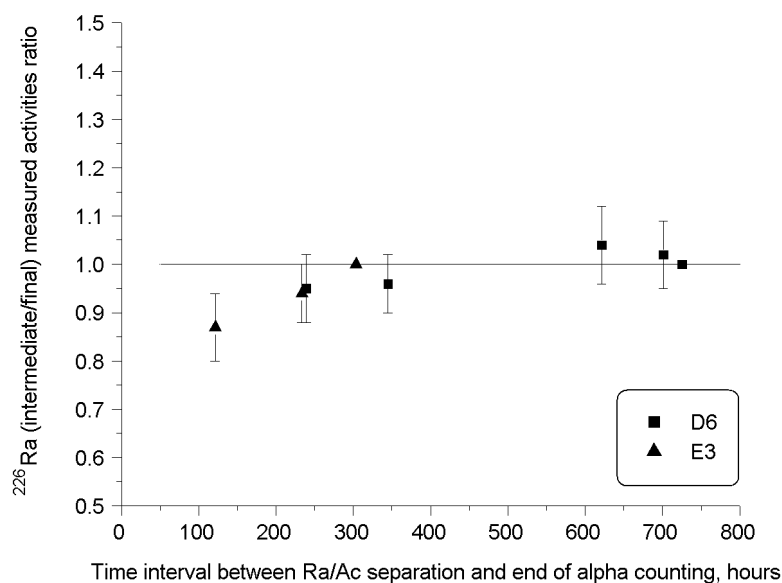


Fig. 3. Evolution of the ^{226}Ra activity concentration determined in two sediment samples (codes D6 and E3, respectively) when the time interval elapsed between the Ra/Ac radiochemical separation and the end of the counting is increased. For each sample, the ^{226}Ra activity concentrations have been normalized to the final ^{226}Ra value obtained after the counting of the corresponding source 30 days after Ra/Ac separation in the cationic column

Validation

Various approaches and exercises have been carried out for ^{226}Ra and ^{228}Ra determination in environmental samples in order to validate the proposed methodology as a whole, and consequently, to validate all the hypothesis and/or associated countermeasures. Indeed, in all the cases, the previously commented countermeasures have been applied: the Ra was immediately electrodeposited after its isolation, and the first measurement for ^{226}Ra determination was carried out at least 20 days after the electrodeposition.

In particular, for the validation of the methodology used for the determination of the ^{226}Ra content in environmental samples, the following checks were performed:

Measurements of standard ^{226}Ra synthetic water solutions

Two aliquots of distilled water were spiked with known amounts of ^{226}Ra (coming from standard solutions) in order to produce two synthetic Ra samples. With these aliquots, the complete radiochemical method for Ra isolation, purification and deposition was applied. The results obtained for the two ^{226}Ra synthetic samples are compiled in Table 1. In this table, the ^{226}Ra initially added for their production are also indicated, making possible to observe that the determined values are in very good agreement with the referenced ones.

Table 1. Results of the ^{226}Ra activity concentrations, (in $\text{Bq}\cdot\text{L}^{-1}$), obtained by applying the whole procedure to two standard ^{226}Ra synthetic water solutions

Sample	Reference value	Measured value
A	173.5 ± 1.7	179.4 ± 12.3
B	34.7 ± 0.3	35.6 ± 2.4

Freshwater intercomparison exercise

We have also participated in an international intercomparison exercise (SUBATECH998, coordinated by Dr. ABBE, CNRS, France) for the determination of the ^{226}Ra content in a filtered and acidulated aqueous sample, by applying the complete methodology to one of the aliquots.

In our water aliquot, a ^{226}Ra specific activity of 2.00 ± 0.15 Bq/L was obtained, a value in total agreement with the average confident value (16 laboratories) obtained from the intercomparison exercise, that was 2.00 ± 0.19 Bq/L.

Comparison with γ -ray spectrometry

Finally, the methodology presented in this paper has been checked by means of its application to river sediment samples in which the ^{226}Ra activity concentrations had been previously determined by a validated γ -ray spectrometry procedure.

This comparison was carried out through the application of both ^{226}Ra methodologies (α and γ) to a total of 19 sediment samples. The results are compiled in Fig. 4. In this figure and for each sample, the α - ^{226}Ra values are plotted against the γ - ^{226}Ra values.

As can be observed, the agreement between the results obtained through the two radiometric techniques is quite satisfactory. In fact, a very good lineal correlation coefficient ($r=0.977$) is obtained. Nevertheless, the slope of the fitted straight line is slightly higher than one, indicating a slight tendency to obtain higher ^{226}Ra values by α -particle spectrometry than by γ -ray spectrometry in most of the samples.

After a careful study of all the different factors that could explain the existence of this tendency, it was

concluded that the ^{226}Ra γ -ray determinations were, in general, slightly underestimated due to some small ^{222}Rn diffusion from the sample. Hence, it is worth mentioning that the ^{226}Ra determination by γ -ray spectrometry was carried out though one of the γ -emissions of one of its progenies (^{214}Pb).

Some of the previously indicated riverbed sediment samples were also used for checking the methodology described in this paper for ^{228}Ra determination by α -particle spectrometry. In fact, some of the Ra-sources previously measured by this technique for ^{226}Ra determinations were re-measured after six months for the determination of ^{228}Ra . The ^{228}Ra α -results were then compared with those obtained for the same nuclide by γ -ray spectrometry, as shown in Fig. 5.

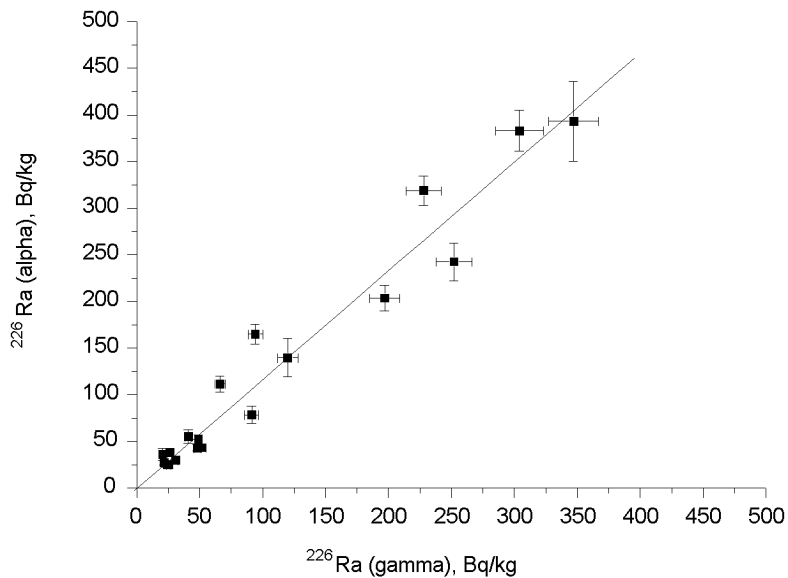


Fig. 4. Alpha-particle spectrometry versus gamma-ray spectrometry determinations of ^{226}Ra in aliquots of the same river sediment samples

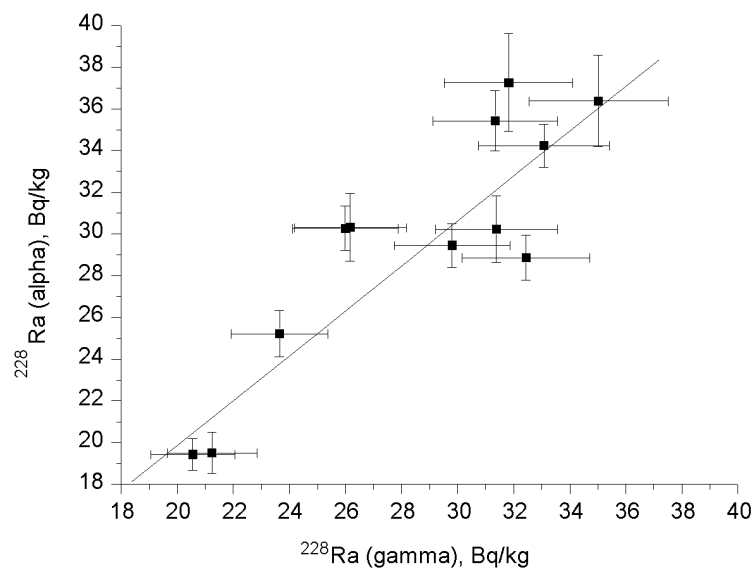


Fig. 5. Alpha-particle spectrometry versus gamma-ray spectrometry determinations of ^{228}Ra in aliquots of the same river sediment samples

The agreement between the results obtained through the two radiometric techniques is satisfactory, (correlation coefficient = 0.91; slope of the line = 1.1 ± 0.1). However, in this case it is possible to see that there is no tendency to underestimate by the γ -spectrometric measurements, a fact which reinforces the theory given previously for the explanation of the γ -ray ^{226}Ra results. In the ^{228}Ra comparison the γ -underestimation is not observed since the determination is performed through the measurement of one progeny (^{228}Ac) which is not a daughter of any isotope of radon.

Conclusions

The method applied in our laboratory for the determination of ^{226}Ra and ^{228}Ra in various environmental matrices by α -particle spectrometry has been fully described. It stands out due to the low limits of detection that can be achievable for both nuclides and because it allows the determination of both Ra isotopes using only one radiometric technique after obtaining only one counting source from the treated aliquot.

The method is comprised of several steps: radiochemical isolation and purification of the Ra isotopes from the environmental matrices; selection of the proper tracer yield; interpretation and analysis of the obtained α -spectra; and, finally, activity determinations.

Special efforts have been devoted to analyzing the magnitude and influence of possible interferences and/or artefacts which can lead to erroneous determinations of the Ra activity concentrations. Several countermeasures have been adopted and evaluated to avoid and minimize the influence of these possible interferences. In particular, it has been concluded that Ra needs to be electrodeposited immediately after its isolation in the ion-exchanger columns, and the final Ra source must be counted at least 20 days after the electrodeposition for ^{226}Ra determination.

The whole procedure has been validated successfully through its application to reference samples, the participation in inter-comparison exercises, and by determining the ^{226}Ra and ^{228}Ra content in samples where both isotopes have been previously determined by alternative radiometric techniques.

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