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MEASUREMENT OF RADIUM AND THORIUM ISOTOPES IN ENVIRONMENTAL SAMPLES BY ALPHA-SPECTROMETRY

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A new method for the determination of low-level radium and thorium isotopes in environmental samples by α -spectrometry is described. Thorium and radium isotopes were chemically separated from the same sample, by using the same tracer (^{229}Th). Two different ways were explored for the concentration process in water samples, obtaining a chemical yield for Ra isotopes between 70–90% in both cases using KMnO_4 as carrier and BaCl_2 and FeCl_3 , respectively. The method can also be directly applied for uranium measurements, but in this case there is a limitation on the range of uranium isotopes that can be analyzed.

Several methods have been described in the literature on the determination of radium isotopes in environmental samples. The most common method is the radon emanation method.¹ However this method is relatively slow, requiring an ingrowth time of 20 days, being applicable only to ^{226}Ra measurement. The same problem is found in direct γ -ray spectrometry which is limited to the determination of ^{226}Ra , the only radium isotope which is γ -emitter.

More recently, different authors have described methods for Ra isotope measurements based on α -spectrometry, by using co-precipitation with barium deposited onto a membrane filter.^{2,3} However, these methods imply a poor energy resolution (60 keV FWHM) in the best case.

Nevertheless, α -spectrometry seems to be the more suitable in determining Ra isotope concentrations⁴ having higher sensitivity, internal calibration by means of isotopic tracers, ^{226}Ra measurement without an in-growth period for ^{222}Rn . However, several problems are found when using α -spectrometry for Ra measurements. One of them is to isolate Ra from the other chemically similar (Ca, Ba, Sr) elements. Other problem to be solved is to separate Ra isotopes from Th isotopes in order to avoid any interference in the energy spectrum.

The method reported here overcomes the problems mentioned above and allow, at the same time, the determination of the activities of Th and Ra isotopes.

Different tracers can be added in order to determine the chemical yield. We have used ^{229}Th as tracer. Some authors use ^{223}Ra as tracer,^{5,6} but these procedures are lengthy and slowly. However, if ^{224}Ra (3.7 d) is to be measured, we need to develop a fast radiochemical method. ^{225}Ra is used in Reference 4 but this tracer do not allow the internal calibration of Thorium isotope measurements. In our case we have selected ^{229}Th as tracer for the reasons as follows: (1) ^{225}Ra as a daughter product of ^{229}Th can be used to monitoring Ra chemical yield, (2) both ^{229}Th and ^{225}Ra do not occur naturally and are, therefore, not present in environmental samples, (3) the energy of the α -emissions of these isotopes does not interfere with the emissions of the isotopes we are interested in (Ra and Th), and (4) the activity of ^{225}Ra can be easily measured by determining the ^{217}At peak (7.07 MeV) as described in chapter for calculation of radium activity. ^{225}Ra (14.8 d) is a β -emitter and decays to ^{225}Ac , which in turn decays to a series of short-lived α -emitting daughters, of which only ^{227}At can be conveniently measured without interfering with other radionuclide emissions of interest.

The proposed method can be divided in three main steps (for the first step we have explored two different ways):

- 1a. Preconcentration of the sample by means of KMnO_4 as carrier;
- 1b. preconcentration of the sample using Ba^{2+} and Fe^{3+} as carriers;
2. purification with TBP (tributyl phosphate) and ion exchange resin;
3. electrodeposition from ethanol solution⁴ for Ra isotope measurements and SO_4H_2 solution⁷ for Th isotope measurements.

Alternatively, this method can be directly applied for uranium measurements if one accepts a limitation on the range of uranium isotopes analyzed. In this case it is necessary to replace ^{229}Th tracer by ^{233}U . In this way uranium, thorium and radium isotopes can be measured using the same sample. However, ^{234}U isotope could not be easily measured due to energy interferences between ^{233}U α -emissions ($E_{\alpha 0} = 4824$ keV, 84.2%, $E_{\alpha 1} = 4783$ keV, 13.2%) and ^{234}U emissions ($E_{\alpha 0} = 4776$ keV, 72.5%).⁸

The chemical yield obtained by our method ranges from 70% to 90% for Ra isotopes independently of the preconcentration process considered (see above). On the other hand, for thorium isotopes the chemical yield varies between 80% and 90% using the KMnO_4 for the preconcentration process, being slightly worse (70% to 80%) if BaCl_2 and FeCl_3 are used as carriers.

Experimental

Based on preliminary experiments,^{9,10} the following analytical method has been developed for environmental samples.

Preconcentration

Soil samples: The proposed method can be applied to soil samples. A few grams (1–5 g) of soil sample is necessary to carry out the procedure, although it depends on the expected concentration on Ra and Th isotopes on the sample and the accuracy that we want to obtain in the measurement. The soil sample after adding the tracer (^{229}Th or alternatively ^{233}U if we want to measure uranium isotopes with the constraint explained above), is necessarily digested, as it is usually described in the literature.^{5,11} Once the soil sample has been digested the residual sample is filtered and evaporated to dryness. The residue is then dissolved in 50 ml 5M HNO_3 . Finally, the sample is purified with TBP and ion exchange resin, as described in the next section.

Water samples: For the preconcentration of water samples, we have studied two different methods. In both cases the amount of water sample used was about 10 liters. First of all, as in the case of soil samples, the tracer was added (^{229}Th or ^{233}U , if uranium measurements must also be done). Then the water is acidified to pH 2 and filtered in order to separate the organic and suspended matter (pore size 2.5 μm). At this point two different procedures have been explored.

(1) Preconcentration with BaCl_2 and FeCl_3

The method (see Fig. 1) is based in using BaCl_2 and FeCl_3 as carriers, and can be summarized as follows:

- (a) Add 10 mg of Ba^{2+} and 10 mg of Fe^{3+} (from a BaCl_2 and FeCl_3 dissolution) per liter of sample.
- (b) Heat (50 °C) while stir for 30 minutes. This step allow to eliminate Rn and at the same time will favour the $\text{SO}_4\text{Ba/Ra}$ precipitation.
- (c) Add 1 ml $(\text{NH}_4)_2\text{SO}_4$ per liter sample (from a saturated ammonium sulphate dissolution, 100 g $(\text{NH}_4)_2\text{SO}_4$ /liter) and stir again.
- (d) Add concentrated H_2SO_4 slowly until complete precipitation of $\text{SO}_4\text{Ba/Ra}$. Completing the precipitation stir for 30 minutes. Mix well and allow to stand for 2 hours.
- (e) Filter the precipitate on Millipore HASP02500 (pore size 0.45 μm). Here, the aqueous phase contains Th/U. The process that are necessary to carry out on this aqueous phase will be described below, in steps (h) to (k).
- (f) Dissolve the precipitate with 25 ml 5M HCl and evaporate to dryness.
- (g) Dissolve the residue obtained in the previous step with 50 ml 5M NO_3H . Finally, purify the sample with TBP and ion exchange resin, as described in the next section for Ra analysis.

Concerning the Th/U content in the aqueous phase of step (e), the processes followed are co-precipitation with adding Fe^{3+} forming iron hydroxide at pH 8.^{12,13} This process is as follows:

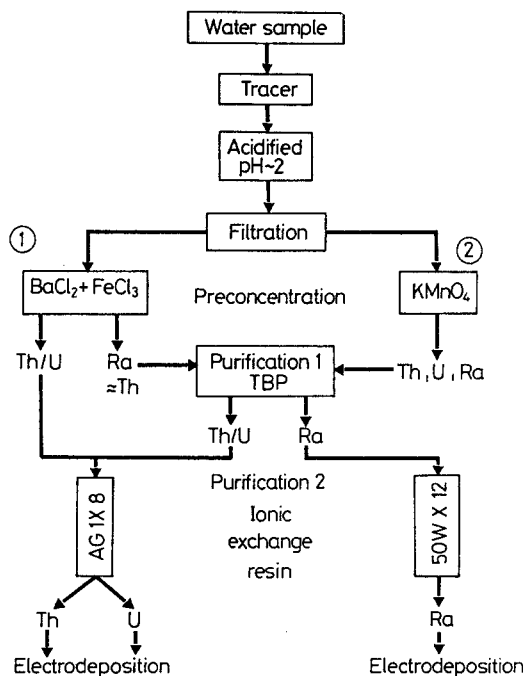


Fig. 1. General diagram of the water sample preparation procedure

- (h) Neutralize with ammonia to pH 8 while stirring. Fe, U, Th and other actinides precipitate in hydroxide form at this pH.
- (i) Filter (pore size 2.2 μm), and reject aqueous phase.
- (j) Wash the filter with 25 ml 8M ClH. Separate the iron from uranium, thorium and other actinides by addition of isopropyl ether,¹³ reject organic phase.
- (k) Evaporate to dryness and dissolve in 7 ml 8M NO_3H .

Finally, purify the residue (after adding to the solution containing Th coming from the purification with TBP as will be described below, see Fig. 1) for Th/U with anion exchange resin, as described in the section dealing with the purification with ion exchange resin.

(2) Preconcentration with KMnO_4

The second procedure studied for the preconcentration, using KMnO_4 as carrier, can be summarized as follows:

- (a) Add 1 ml 0.2M KMnO_4 per liter of sample and stir for 30 minutes.
- (b) Neutralize with ammonia to pH 8.

- (c) Add 1 ml 0.3M MnCl_2 per liter sample, stir during 2 hours and allow to stand for 12 hours.
- (d) Separate the precipitate by centrifuging and reject the aqueous phase.
- (e) Wash the precipitate with 50 ml from a solution of hydroxylammonium chloride.
- (f) Evaporate to dryness and dissolve in 50 ml 5M HNO_3 .

Finally, purify the sample with TBP, where the Ra will be separated from Th/U as described in the next section.

Purification

The solution obtained in the previous step (preconcentration) contain other interfering radionuclides, that must be eliminated. The purification process allow to eliminate them not to interfere in the final spectrum. This process must be carried out very carefully in order to extract as much as possible of the interfering elements, but at the same time removing the minimum amount of the isotopes of interest. In our case we have divided the purification process in two main steps: first consists of the separation of Th/U from Ra with TBP and in the second one the isotopes of interest are finally separated by means of ion exchange resin.

Purification with TBP: In this process the Th/U isotopes are separated from the Ra isotopes. The residue obtained for Th/U analysis by preconcentration with FeCl_3 (see Fig. 1) does not need to be washed with TBP. However, as it will be pointed out below, some amount of Th is obtained after purification with TBP in the solution for Ra analysis (if preconcentrated with BaCl_2). Thorium isotopes obtained in this way is added to the solution for Th/U analysis which has not been purified with TBP (see Fig. 1). The purification process with TBP can be summarized as follows:

- (a) Wash the solution with 50 ml TBP.
- (b) Shake for 5 minutes and separate [if ^{229}Th (^{225}Ra) is used as tracer, record the time of Th/Ra separation] aqueous phase for radium analysis and organic phase for Th/U analysis.

Aqueous phase (Ra analysis): The aqueous phase obtained previously in step (b) must be evaporated to dryness. In this point the purification process with TBP is finished for Ra analysis if we have used the preconcentration process 1 (see Fig. 1, carriers Ba and Fe). The next step consists of the purification with cation exchange resin. This cation exchange resin process is described in the section dealing with the purification with ion exchange resins. However, if the preconcentration process 2 (see Fig. 1) with KMnO_4 carrier has been accomplished, some amount of Ba must be added. This process is similar to that described for the preconcentration with $\text{BaCl}_2 + \text{FeCl}_3$, and is described below:

- (1) Add 10 mg of Ba²⁺ per liter of sample in BaCl₂ form.
- (2) Heat (50 °C) while stir for 30 minutes.
- (3) Add conc. SO₄H₂ slowly until complete precipitation of SO₄Ba/Ra. Stir for 30 minutes. Mix well and allow to stand for 2 hours.
- (4) Filter the precipitate on Millipore HASPO2500 (pore size 0.45 μm).
- (5) Dissolve the precipitate with 25 ml 5M ClH and evaporate to dryness.

We added the steps (1) to (5) above, because we have found that during these processes Ra isotopes absorb more efficiently in the cation exchange resin. The increase in the chemical yield when these processes are used is about 25%. Once the purification with TBP has been carried out, the residue for Ra analysis is ready to be passed through the cation exchange resin, as described in the relevant section.

Organic phase (Th/U analysis)

The organic phase obtained in step (b) above, contains Th/U isotopes to be analyzed. The processes to be done with this organic phase are the followings:

- (1) Wash the organic phase with 25 ml 0.5M C₂H₂O₄. Shake for 5 minutes and separate both phases.
- (2) Repeat the step (1) with another 25 ml 0.5M C₂H₂O₄ to separate all uranium and thorium. Reject organic phase.
- (3) Evaporate to dryness. Dissolve in 10 ml 8M NO₃H if the preconcentration process 2 (KMnO₄ as carrier) has been followed. Dissolve in 3 ml 8M NO₃H if preconcentration process 1 (Fe and Ba as carriers) has been done.

As it was explained, in the last case some amount of thorium is present in the sample obtained by preconcentration with BaCl₂ (see Fig. 1). The thorium is now separated with TBP from radium and the solution obtained in must be added at the end of this step to that one obtained by FeCl₃ preconcentration by the water samples.

- (4) Continue Th/U purification process with anion exchange resin as described in the next section.

Purification with ion exchange resin:

Thorium and uranium separation by anionic exchange resin.

The steps to be done are the followings:

- (a) Prepare an anion exchange column (Bio-Rad AG1-X8, 100–200 mesh, chloride form 100 mm height, 10 mm diameter) by washing with 100 ml 8M HNO₃. The flow rate is 0.8–1.0 ml/min.
- (b) Transfer the solution of Th and U into the column. Thorium is absorbed and uranium is eluted.

- (c) Wash the column with 100 ml 8M HNO₃ to elute all uranium.
At this point the dissolution containing uranium is ready to be electrodeposited by evaporating it to 1 ≈ 5 ml (²³³U should be added as tracer if uranium isotopes must be measured). However, a better resolution (improvement ≈ 20%) without significant losses of uranium (≤ 2%) can be achieved with a re-purification of uranium, described below.
- (d) Prepare another column with 100 ml 9M HCl and pass the solution containing uranium through the resin.
- (e) Wash the column with 100 ml 9M HCl to remove any amount of thorium.
- (f) Pass through the column 100 ml 7.2M HNO₃ to remove uranium. Discard the first 25 ml containing rest of Fe and eventually Mn (no uranium has been observed in this volume fraction as a consequence of the different emigration velocities through the resin for Fe and U ions).
- (g) Evaporate the 75 ml solution containing uranium to 1 ≈ 5 ml and electrodeposit as described in the section describing thorium and uranium electrodeposition.
- (h) Elute Th from the first column with 100 ml 10M HCl. Evaporate the dissolution to 1 ≈ 5 ml and electrodeposit Th exactly in the same way as the uranium isotopes.

Radium separation by cationic exchange resin

The technique described in this step is similar to that reported in Reference 14.

- (a) Prepare a cation exchange column (Bio-Rad AG50WX8, 200–400 mesh sodium form, 50 mm length and 10 mm diam.). Wash the resin with 50 ml 4M NaCl at a flow rate of 1 ml/min.
- (b) Pass through the column 20 ml of distilled water.
- (c) Condition the resin to pH 5 by passing 60 ml of saturated boric acid solution of pH 5.
- (d) The solution which was evaporated to dryness in the previous process (purification with TBP) is dissolved in 10 ml 0.05M CyDTA (cyclohexane-diaminetetraacetic acid), pH 5.
- (e) Pass the solution through the column at a flow rate of 0.5 ml/min.
- (f) Wash the column with 20 ml of saturated boric acid solution at pH 8.5.
- (g) Remove the barium by passing through the column 50 ml 0.05M CyDTA at pH 8.5.
- (h) The remaining CyDTA is removed from the column with 60 ml of 0.5M HCl.
- (i) Finally, elute radium isotopes with 40 ml 3M NO₃H. Evaporate the solution at low heat to dryness and electrodeposit as described in the next section.

Electrodeposition

The electrodeposition cell we have used is the same for the three elements considered (Ra, Th and U) and is described by HALLSTADIUS.⁷

Electrodeposition of radium: The residue obtained in the previous step goes to the electrodeposition process.⁴ The electrodeposition consists of the following steps:

- (1) Dissolve the residue in 0.5 ml 0.1M HNO₃, 9 ml ethanol and 1 ml 0.05M HCl.
- (2) Transfer the residue to an electrodeposition cell described in References 7 and 15. The distance between cathode and anode is 2 mm and the residue is electrodeposited onto a disc stainless steel 2.5 cm in diameter.
- (3) Electrolyze at 120 mA for 30 min. Add 0.5 ml of concentrated ammonia 1 minute before stopping.
- (4) Remove the disc and dry the planchet by heating it slightly.

Once the electrodeposition process is finished, the planchet is ready to be placed in the α -spectroscopy system.

Electrodeposition of thorium and uranium: The electrodeposition process is the same for Th and U radionuclides. The process reported in the literature,^{7,15} was established. The steps are the followings:

- (a) Add 1 ml 0.3M Na₂SO₄ to the solution obtained in the previous process (purification with anionic exchange resin).
- (b) Evaporate to dryness. Add 300 μ l of conc. H₂SO₄.
- (c) Warm and stir beaker until the residue is completely dissolved.
- (d) Add 4 ml distilled water and two drops of 0.2% thymol blue.
- (e) Add conc. NH₃ to a yellow-yellow/orange colour.
- (f) Pour the solution into the electrodeposition cell and rinse the beaker with 5 ml 1% H₂SO₄.
- (g) Electrolyze at 1.2 A for 1 hour. Add 1 ml of concentrated NH₃ 1 minute before stopping.
- (h) Rinse the planchet with acetone. Remove the disc and dry the planchet by heating it slightly.

Once the electrodeposition process is finished, the planchet is ready to be placed in the α -spectroscopy system.

Calculation of activities

Calculation of radium activity

The chemical yield for Ra recovery is calculated as follows: Let A_0 the activity of ²²⁵Ra after the separation from ²²⁹Th at time t_0 , its activity A_1 at the time when build-up of ²²⁵Ac begins is given by:⁴

$$A_1 = A_0 \exp \{ -\lambda_1(t_1 - t_0) \} \quad (1)$$

where λ_1 is the decay probability of ^{225}Ra . The subsequent activity of ^{225}Ac at any time, $A(t)$, is then given by:

$$A(t) = \frac{\lambda_2 A_1 [\exp \{ -\lambda_1(t - t_1) \} - \exp \{ -\lambda_2(t - t_1) \}]}{\lambda_2 - \lambda_1} \quad (2)$$

where λ_2 is the decay constant of ^{225}Ac .

Integrating over the counting period from t_2 to t_3 we obtain:

$$A(t_2, t_3) = A_1 \frac{\lambda_2}{(\lambda_2 - \lambda_1)(t_3 - t_2)} \cdot \left\{ \frac{1}{\lambda_1} [\exp(-\lambda_1(t_2 - t_1)) - \exp(-\lambda_1(t_3 - t_1))] - \frac{1}{\lambda_2} [\exp(-\lambda_2(t_2 - t_1)) - \exp(-\lambda_2(t_3 - t_1))] \right\} \quad (3)$$

Hence, the recovery of ^{225}Ra is $A_{\text{At}}/A(t_2, t_3)$ were A_{At} is the measured activity of ^{217}At .

Once the chemical yield is calculated, the Ra isotopes activity can be obtained. The ^{224}Ra and ^{226}Ra are measured by α -spectrometry immediately after the electrodeposition in order to obtain the maximum counts for ^{224}Ra as well as minimizing the ingrowth of ^{226}Ra daughter ^{222}Rn (half-life 3.82 days).

The ^{228}Ra activity can be measured through its decay product ^{224}Ra after the disc with the electrodeposited radium has been kept for a sufficiently long period of time to allow the ^{228}Th to grow in, and can be calculated using the following equation:

$$A_{228\text{Ra}} = A_{224\text{Ra}} \frac{\lambda_{228\text{Th}} - \lambda_{228\text{Ra}}}{\lambda_{228\text{Th}} [e^{-\lambda_{228\text{Ra}}t} - e^{-\lambda_{228\text{Th}}t}]} \quad (4)$$

where t is the ingrowth time since the preparation of the radium source, being A_i and λ_i the activity and decay constant for isotope i .

Calculation of thorium and uranium activities

Chemical yield of thorium can be easily calculated by determining the ^{229}Th peak area. Activity of natural occurring Th isotopes (^{232}Th , ^{230}Th and ^{228}Th) can then be calculated.

Similarly, chemical yield of uranium can be calculated from ^{233}U peak area. However, a large amounts of ^{233}U as tracer should be added in order to minimize errors

associated in the determination of ^{233}U peak area as a consequence of ^{234}U natural occurring interference. As it was already pointed out, in this case ^{234}U activity cannot be easily determined. Once uranium chemical yield is determined, ^{238}U and ^{235}U activities can be calculated.

Results and discussion

The method proposed has been applied to different natural water and soil samples. The water samples were divided in two aliquots and the two proposed preconcentration processes for water samples were carried out. The yields shown in Table 1 were obtained. The FWHM varies in all cases between 20–23 keV, independently of the preconcentration process followed, with a silicon barrier detector of 19 keV intrinsic resolution and a distance source-detector of 12 mm. As it can be seen in Table 1, the recovery yields are slightly worse in the case of soil samples as it can be expected, mainly due to inefficient digestion of such samples. No differences have been observed between chemical yields obtained by KMnO_4 and $\text{BaCl}_2 + \text{FeCl}_3$ preconcentration processes in the Ra isotopes measurements. However, slightly differences between these preconcentration methods (about $\approx 10\%$) have been observed in Th and U determination (Table 1). Nevertheless, authors recommend $\text{BaCl}_2 + \text{FeCl}_3$ preconcentration method if only Ra isotopes activities must be determined because, in our opinion, this preconcentration method is more easy to be carried out than the other one considered (KMnO_4 as carrier). The last preconcentration process is recommended

Table 1
Radium, thorium and uranium recovery yield, in %

Element	Ra		Th		U		
	KMnO_4	$\text{BaCl}_2 + \text{FeCl}_3$	KMnO_4	$\text{BaCl}_2 + \text{FeCl}_3$	KMnO_4	$\text{BaCl}_2 + \text{FeCl}_3$	
Water sample	1	80	83	70	82	72	
	2	86	84	75	87	74	
	3	90	88	85	76	76	
	4	72	75	90	79	90	80
	5	85	87	88	78	89	77
Soil sample	1	71		72		71	
	2	75		77		78	
	3	80		75		75	
	4	74		70		71	
	5	75		74		73	

if Th and/or U activities must be determined together with Ra activity since more efficient recovery is achieved in this case for Th and U isotopes.

With the method reported in this work is possible to determine low-level activities of radium, thorium (and uranium, if one accepts a limitation on the range of uranium isotopes analyzed) isotopes in environmental samples by α -spectrometry. Typical recovery yields between 70–90% for Ra isotopes are obtained with a FWHM of 20 – 23 keV independently of the preconcentration process followed.

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