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Sample pretreatment in the determination of specific alpha emitters in drinking water using [Ba+Fe]-coprecipitation method

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HIGHLIGHTS

- The quantitative recovery in the [Ba+Fe]-coprecipitation method was determined.
- The precipitate treatment is best carried out using a complete destruction method.
- Radium, thorium and plutonium partially coprecipitate with barium sulfate.
- Polonium, uranium and americium remain quantitatively in the acid solution.

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ABSTRACT

The [Ba+Fe]-coprecipitation method is applied to measure gross alpha activity for radiological examination of drinking water in the laboratory. This method collects all the alpha-emitting radionuclides of interest (natural alpha emitters and transuranium elements) in a precipitate on a filter. This paper describes an investigation of sample pretreatment of the precipitate collected by the [Ba+Fe]-coprecipitation method for gross alpha activity determination. The aim of this preliminary work is to be a starting point to develop simple and rapid radiochemical procedures for specific alpha emitters (polonium, radium, thorium, uranium, plutonium and americium), in contrast to the sophisticated, expensive and time-consuming alpha spectrometry method. The sample pretreatment aspects considered include quantitative [Ba+Fe]-coprecipitation, two methods for precipitate treatment (leaching and complete destruction of the filter), and the determination of the alpha-emitting proportions present in the barium sulfate precipitate and acid solution obtained after precipitate treatment. Furthermore, a radiochemical procedure for ²²⁶Ra determination was performed and finally, the sample pretreatment proposed in this work was summarized.

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1. Introduction

Gross alpha activity is one of the parameters to be determined for monitoring the radiological quality of drinking water. In the Spanish Royal Decree on drinking water quality (BOE, 2003), the recommended reference level for gross alpha activity is 0.1 Bq L⁻¹. If gross alpha activity is below the reference level, the drinking water examined is acceptable for human consumption. Otherwise, a specific analysis is required to determine the alpha emitter activity concentration using more sophisticated procedures. The main natural alpha emitters that can be present in drinking water are ²³⁸U, ²³⁴U, ²³²Th, ²²⁶Ra, and ²¹⁰Po, and the artificial ones are

^{239,240}Pu and ²⁴¹Am (Jóbbágy et al., 2010). Therefore, some authors use radiochemical separation and alpha spectrometry for these specific alpha emitters (Montaña et al., 2013). These procedures are expensive and time-consuming, and many times are unnecessary. That is, the limit of detection of these procedures is usually several times below the limit of detection required by regulation.

Gross alpha measurement is one of the simplest radiochemical procedures. Its main advantages are the relatively low costs and simplicity. Two main types of methods are used to measure gross alpha activity: the evaporation method and the [Ba+Fe]-coprecipitation method. In the evaporation method, a water sample aliquot is evaporated to dryness, and a solid thin residue is obtained on a planchet. In the [Ba+Fe]-coprecipitation method, by contrast, the radionuclides from a water aliquot are coprecipitated with a

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mixture of barium sulfate and ferric hydroxide (Suarez-Navarro et al., 2002). The precipitate is collected on a filter, which is placed on a planchet. The minimum detectable activity (MDA) achieved with the [Ba+Fe]-coprecipitation method is one order of magnitude lower than that for the evaporation method under the same measuring conditions (Montaña et al., 2012).

Although iron and barium carrier solutions of 5 mg mL^{-1} were sufficient to recover transuranic (Ballestra and Fukai, 1983) and radium (Barker and Thatcher, 1957) nuclides quantitatively in the [Ba+Fe]-coprecipitation method, no specific values for the recovery of alpha-emitting nuclides were found in the literature (APHA-AWWA-WEF, 1999; EPA, 1984). On the other hand, two sample procedures were investigated for treatment of the precipitate from the filtration in the [Ba+Fe]-coprecipitation method for gross alpha activity determination. Leaching was done with HCl, and the complete destruction of the filter was accomplished using a mixture of aqua regia and HClO_4 . After the application of the selected procedure for precipitate treatment, a barium sulfate precipitate and an acid solution were obtained, and the alpha-emitting proportions in both fractions were determined. Knowledge of these proportions is necessary to develop simple and fast radiochemical separations for specific alpha-emitting radionuclides in drinking water using the precipitate collected in the gross alpha [Ba+Fe]-coprecipitation method. Gross alpha activity and specific alpha-emitting radionuclides may be determined either using ZnS(Ag) scintillation detector or a gas-flow proportional counter.

A radiochemical procedure for ^{226}Ra determination was performed and the accuracy of the proposed method was evaluated through participation in an International Atomic Energy Agency (IAEA) intercomparison of synthetic and natural water samples. Finally, a radiochemical procedure for the recovery of other alpha emitters in the barium sulfate precipitate was optimized.

2. Materials and methods

2.1. Materials and equipment

Laboratory apparatus. The following components were used in the vacuum filtration: $0.45 \mu\text{m}$ filters made of cellulose nitrate (Millipore, France), a special glass material for filtration (Millipore, France), and a vacuum pump (Schott, Germany). Other equipment included hotplates with temperature control, a centrifuge (Selecta, Spain), and commercially available stainless steel planchets (diameter: 5 cm).

Measurements were carried out in a Berthold LB770-2 gas-flow proportional counter. This system is provided with 10 ultra-flat flow proportional detector tubes having thin aluminized plastic windows located directly above the planchet counter, allowing the simultaneous measurement of 10 samples. The detector background readings are reduced by means of a large-area flow counter, and the use of a passive shield of 10 cm thick machined lead bricks surrounding the counter tubes. The counting gas is a mixture of 90% argon and 10% methane (P-10 gas). The detectors are polarized at the same high voltage (HV) of 1625 V.

2.2. Reagents

All of the chemicals used were of analytical reagent grade. High-quality deionized water with a conductivity of $10 \mu\text{S cm}^{-1}$ was used.

The following reagents were employed in the various methods in this study:

- [Ba+Fe]-coprecipitation method: H_2SO_4 , HNO_3 (Merck, Germany), Bromocresol Purple indicator, $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (Panreac, Spain).
- Precipitate treatment in the [Ba+Fe]-coprecipitation method: HCl and H_2SO_4 (Merck, Germany) for the leaching method and a mixture of HCl, HNO_3 , HClO_4 and H_2SO_4 (Merck, Germany) and H_2O_2 (Panreac, Spain) for the complete destruction method.
- Purification of the barium sulfate precipitate: CH_3COOH , NH_4OH , HCl, H_2SO_4 , HNO_3 (Merck, Germany), EDTA, Na_2SO_4 , phenolphthalein, Methyl Orange (Panreac, Spain).
- Plutonium and thorium recovery: NaOH (Panreac, Spain), ZrO_2 (Merck, Germany), and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (Panreac, Spain).

Six alpha standard solution (^{210}Po , ^{226}Ra , ^{230}Th , ^{234}U , ^{235}U , ^{238}U , ^{239}Pu and ^{241}Am) and beta-gamma standard solution (^{234}Th) were provided by Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas, Madrid, Spain (CIEMAT).

2.3. [Ba+Fe]-coprecipitation method

Sample preparation for gross alpha activity determination in drinking water using the [Ba+Fe]-coprecipitation method is summarized below.

A 500 mL water sample was filtered using the vacuum filtration system. 20 mL of H_2SO_4 was added and the sample was boiled for 3 min to eliminate the Rn and CO_2 . The sample was then cooled to room temperature and allowed to stand for 60 min. The sample was heated to 50°C and then 1 mL of the Ba^{2+} carrier was added to the sample while it was stirred. The barium sulfate precipitate formed was stirred for 30 min to 50°C to obtain optimum precipitate formation. The sample was then cooled to room temperature. To coprecipitate the actinides, 1 mL of Fe^{3+} carrier was added to the solution and NH_4OH was added dropwise until the precipitate was produced. Bromocresol Purple indicator was used to control the pH of the precipitation (about 6.8). Then the solution was stirred for 30 min at room temperature to produce finer precipitate particles. The precipitate was then deposited onto a filter, using the vacuum filtration system. Finally, the filter with the precipitate was placed on the planchet and then dried under an infrared lamp. The planchet was placed in a desiccator for two days, then was weighed and counted.

2.4. Activity calculation

The activity was calculated with the following expression:

$$A = \frac{c - b}{60E f_a} \quad (1)$$

where A is the activity in Bq, c is the count rate of the source in counts per minute (cpm), b is the background count rate in cpm, 60 is the factor to transform the cpm in cps, E is the ^{241}Am efficiency, and f_a is the self-absorption factor. The uncertainty associated with the activity was estimated with the following expression:

$$u(A) = kA \sqrt{\frac{1}{c} + \frac{1}{b} + \left(\frac{u(E)}{E}\right)^2} \quad (2)$$

where k is the coverage factor.

3. Experimental studies

3.1. Method for determining the [Ba+Fe]-coprecipitation recovery

The [Ba+Fe]-coprecipitation method recovery was determined by a double [Ba+Fe]-coprecipitation. In the first [Ba+Fe]-coprecipitation, two fractions were obtained: (i) the filter, where the precipitated was collected and (ii) the filtrate, which was used for a second [Ba+Fe]-coprecipitation. The recovery was determined with the following expression:

$$R(\%) = 100 \frac{A_1}{A_1 + A_2} \quad (3)$$

where R is the recovery, and A_1 and A_2 are the activities of the filter in the first [Ba+Fe]-coprecipitation and in the second [Ba+Fe]-coprecipitation, respectively. Self-absorption curves were not necessary because the same precipitate was deposited in the filter in the first and second [Ba+Fe]-coprecipitation. Samples were measured in a proportional counter. This assay was performed in duplicate with each of the six standard solutions.

3.2. Comparison of two precipitate treatment methods

Two precipitate treatment methods were investigated: method (A) leaching with HCl; and method (B) complete destruction of the filter using a mixture of mineral acids including nitric, hydrochloric and perchloric acids, with hydrogen peroxide. Methods A and B are schematically presented in Fig. 1. Both methods were modified by adding H_2SO_4 .

3.2.1. Method A (leaching method)

[Ba+Fe]-coprecipitation method was applied in duplicate to 500 mL water samples without standards. The two filters obtained were attached to the wall of the beaker with deionized water and precipitate was leached from both filters with concentrated HCl. After the leaching, the iron hydroxide solution and precipitated barium sulfate were centrifuged for 5 min at 4300 rpm, then

washed three times with 10% HCl, 1% HCl and deionized water, respectively. This procedure was modified by adding 1 mL of 1 N H_2SO_4 after the leaching. Then, the leachate was stirred for 15 min to 50 °C. After cooling the leachate was allowed to stand 2 h to reach room temperature, and then it was centrifuged as described above. The barium sulfate precipitate was dried and weighed to calculate the chemical yield.

To test the selectivity of the method, the leaching method was applied in duplicate to the sample filters prepared by [Ba+Fe]-coprecipitation using the ^{230}Th , $^{234}\text{U}+^{235}\text{U}+^{238}\text{U}$ and ^{241}Am standard solutions. After leaching, both faces of the filter were measured in a proportional counter to confirm the lack of radioactivity.

3.2.2. Method B (complete destruction method)

The [Ba+Fe]-coprecipitation method was applied in duplicate to 500 mL water samples without standards. Both filters were completely destroyed using a mixture of 15 mL of concentrated HCl, 5 mL of concentrated HNO_3 , 5 mL 70% HClO_4 , with five drops of H_2O_2 . The solution was evaporated and, before reaching dryness, salts were redissolved in 5 mL of concentrated HCl, 1 mL of concentrated HNO_3 , 2.5 mL 70% HClO_4 . This solution was evaporated to dryness, and the residue was dissolved in 10 mL of concentrated HCl. About 50 mL of deionized water was then added to the solution. This procedure was modified by adding 1 mL of 1 N H_2SO_4 at this point. Then, the solution was stirred for 15 min to 50 °C. After cooling the solution for 2 h to room temperature, it was centrifuged for 5 min at 4300 rpm, then washed three times with 10% HCl, 1% HCl and deionized water, respectively. The barium sulfate precipitate was dried and weighed to calculate the chemical yield.

3.2.3. Selected method for the precipitate treatment

Table 1 shows the BaSO_4 chemical yields for the two precipitate treatment methods investigated (with H_2SO_4 addition) in the gross alpha [Ba+Fe]-coprecipitation method.

In the case of the leaching method, the presence of concentrated HCl inhibits the barium sulfate precipitation (Sill, 1980).

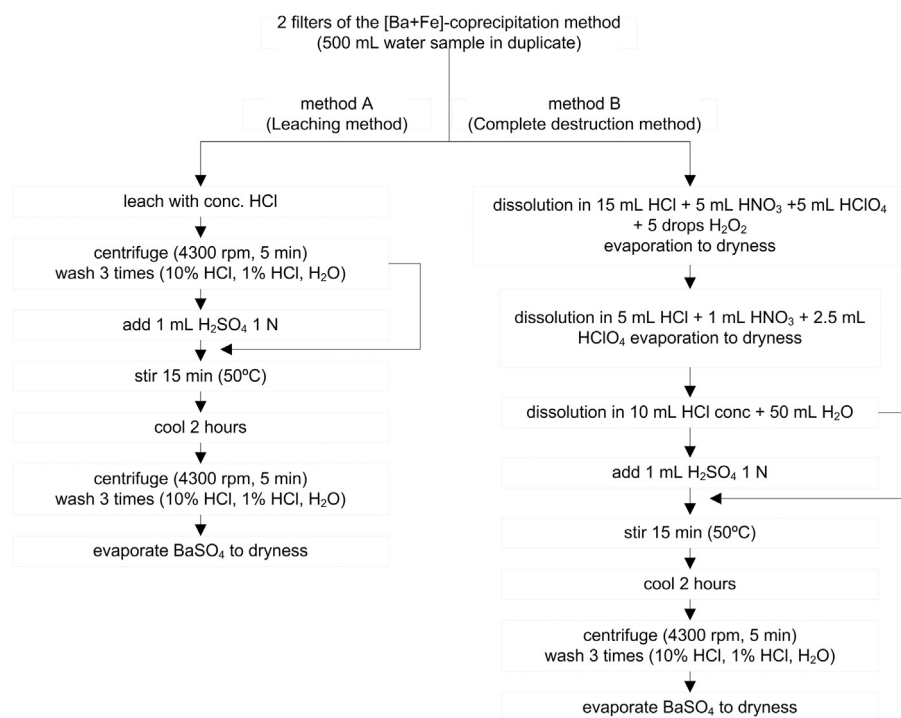


Fig. 1. Methods for the precipitate treatment, where methods A and B were modified by the addition of 1 mL of 1 N H_2SO_4 in the steps indicated in the figure.

Table 1

BaSO₄ chemical yields for the two methods used in the precipitate treatment, with and without H₂SO₄ addition. Each run was performed in duplicate.

Method	Replicates	Weigh of BaSO ₄ (mg)	BaSO ₄ chemical yields (%)
Leaching (method A)	3	3.8 ± 0.8	22.5 ± 4.4
Method A + H ₂ SO ₄	5	11.8 ± 0.5	69.7 ± 2.9
Complete destruction (method B)	6	12.6 ± 0.1	74.84 ± 0.80
Method B + H ₂ SO ₄	6	14.6 ± 0.3	85.3 ± 2.0

Quoted uncertainties correspond to $k=1$.

Also in this method, the lack of radioactivity after leaching was confirmed on both sides of the filters.

In both methods (leaching and complete destruction), the addition of 1 N H₂SO₄ improves the BaSO₄ chemical yields. This result may be due to the presence of H₂SO₄ improving the barium sulfate precipitation. Consequently, the precipitate treatment is best carried out using the complete destruction method (method B) with H₂SO₄ addition.

3.3. Alpha-emitting proportions in barium sulfate precipitate and acid solution

The method for determining the proportions of the alpha emitters ²¹⁰Po, ²²⁶Ra, ²³⁰Th, ²³⁴U + ²³⁵U + ²³⁸U, ²³⁹Pu and ²⁴¹Am in the BaSO₄ precipitate and in the acid solution is schematically shown in Fig. 2.

The [Ba+Fe]-coprecipitation method was applied in duplicate to 500 mL water samples spiked individually with each of the six standard solutions. Several replicates were performed for each alpha emitter. After the application of the complete destruction method (see Section 3.2.2), the proportions of alpha emitters in the barium sulfate precipitate and acid solution were determined.

3.3.1. Alpha-emitting proportions in barium sulfate precipitate

The ²¹⁰Po, ²³⁰Th, ²³⁴U + ²³⁵U + ²³⁸U, ²³⁹Pu and ²⁴¹Am proportions in the BaSO₄ precipitate were determined as follows. The precipitated barium sulfate was centrifuged for 5 min at 4300 rpm and washed three times with 10% HCl, 1% HCl and deionized water, respectively. The precipitate was transferred to a stainless steel planchet, then evaporated to dryness and measured in a proportional counter.

For the determination of the ²²⁶Ra proportion, the barium sulfate precipitate was dissolved by adding 20 mL EDTA 0.25 M, with 5 drops of phenolphthalein, 1 mL of Na₂SO₄ 1 N and NH₄OH, until the solution turned pink in color. The solution was heated to 65 °C, and then CH₃COOH was added to obtain a pH of 5.0 to reprecipitate the BaSO₄, taken as the initial time to correct for daughter growth. The solution was cooled and the precipitate was centrifuged for 5 min at 4300 rpm. In this step, the solution was reserved for the recovery of other alpha emitters. The precipitate was then washed three times with deionized water. Finally, the precipitate was evaporated to dryness on a stainless steel planchet and measured in a proportional counter (IAEA, 2010).

The complete method for determining the proportions of the alpha emitters ²¹⁰Po, ²²⁶Ra, ²³⁰Th, ²³⁴U + ²³⁵U + ²³⁸U, ²³⁹Pu and ²⁴¹Am in the BaSO₄ precipitate is shown in Fig. 3.

3.3.2. Alpha-emitting proportions in acid solution

The ²¹⁰Po, ²³⁰Th, ²³⁴U + ²³⁵U + ²³⁸U, ²³⁹Pu and ²⁴¹Am proportions in the acid solution were determined as follows. The solution was evaporated to dryness and the residue was dissolved in 5 mL of concentrated HNO₃. Finally, the solution was again evaporated to dryness on a stainless steel planchet and measured in a proportional counter.

For the determination of ²²⁶Ra proportion in the acid solution, a radiochemical procedure was performed (APHA-AWWA-WEF, 1999) adding 1 mL of concentrated HCl, 5 mL of Ba²⁺ carrier (6.4 mg mL⁻¹) and 1 mL of Pb²⁺ carrier (195 mg mL⁻¹) to acid solution. The solution was boiled, then 1 mL of Methyl Orange and

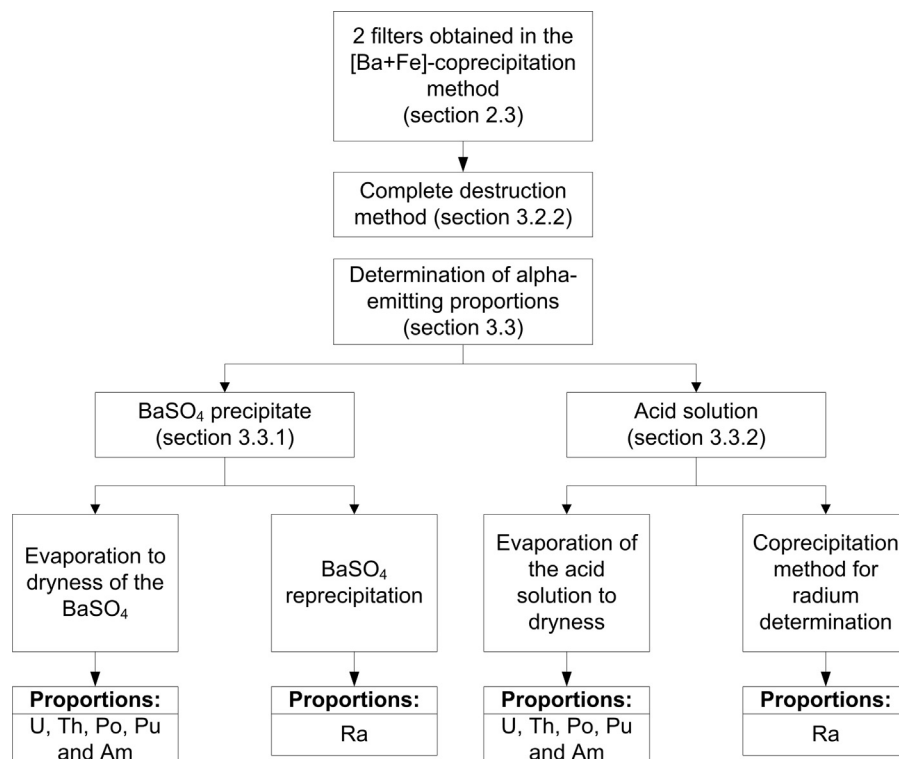


Fig. 2. Schematic method for determining alpha emitter proportions in the BaSO₄ precipitate and in the acid solution using complete destruction method.

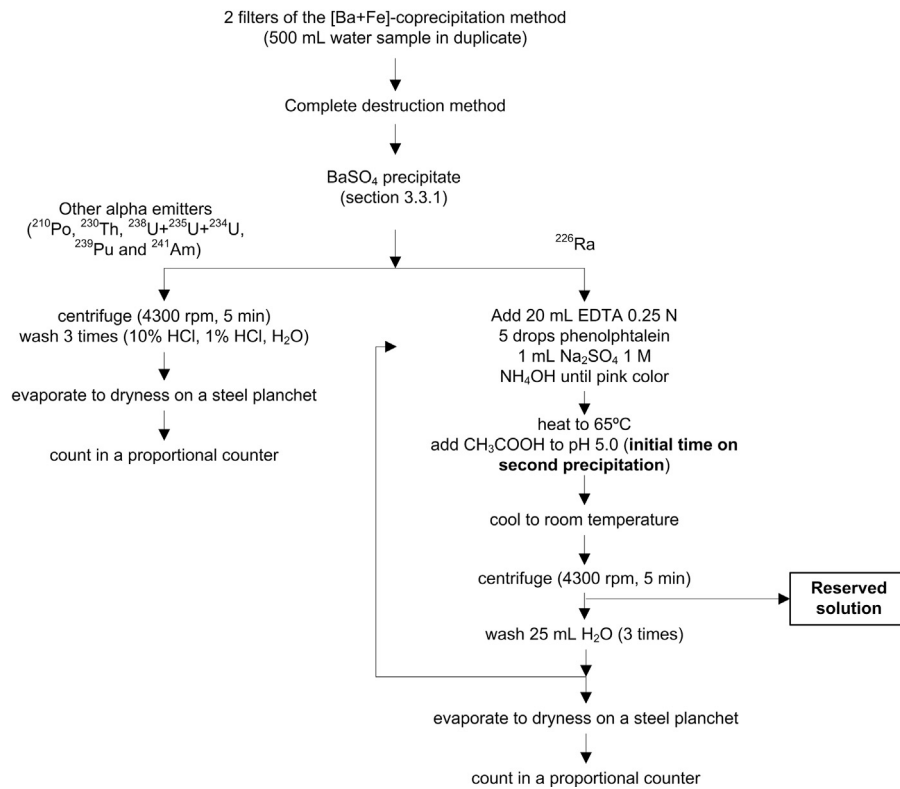


Fig. 3. Method for determining alpha emitter proportions in the BaSO₄ precipitate obtained from the precipitate treatment in the gross alpha [Ba+Fe]-coprecipitation method.

H₂SO₄ (1:1 v/v) was added until the solution turned red. This was allowed to stand overnight, and was then centrifuged. The supernatant was discarded, and the BaSO₄ precipitate was dissolved in 20 mL of EDTA 0.25 M with 3 drops of phenolphthalein, and NH₄OH was added until the solution turned red. The solution was heated to 65 °C, and then CH₃COOH was added to obtain a pH of 5.0 to reprecipitate the BaSO₄, taken as initial time to correct for daughter growth. The solution was cooled, the precipitate was centrifuged for 5 min at 4300 rpm, and then washed three times with deionized water. Finally, the precipitate was evaporated to dryness on a stainless steel planchet, and measured in a proportional counter.

The complete method for determining the proportions of the alpha emitters ²¹⁰Po, ²²⁶Ra, ²³⁰Th, ²³⁴U+²³⁵U+²³⁸U, ²³⁹Pu and ²⁴¹Am in the acid solution is shown in Fig. 4.

3.3.3. Expressions for the determination of alpha emitter proportions

The alpha-emitting proportions in the barium sulfate precipitate and acid solution were determined from the following expressions:

$$P_p(\%) = 100 \frac{A_p}{A_p + A_d} \quad (4)$$

$$P_d(\%) = 100 \frac{A_d}{A_p + A_d} \quad (5)$$

where P_p and P_d are the proportions in the BaSO₄ precipitate and in the acid solution, respectively, and A_p and A_d are the activities expressed in Bq in the BaSO₄ precipitate and in the acid solution, respectively, for each of the six standards. Activities were calculated using Eq. (1), where self-absorption factors obtained from literature were used to calculate the activity in the two fractions for each of the six standards (Semkow et al., 2005).

3.4. ²²⁶Radium determination

The method for the determination of the ²²⁶Ra proportion in the barium sulfate precipitate described in Section 3.3.1 (see Fig. 3) was used to perform the specific ²²⁶Ra analysis in drinking water.

This separation procedure was applied to a standard solution containing ²²⁶Ra to determine the radiochemical yield using BaSO₄ as a non-radioactive tracer, and it was applied to standard solutions containing ²³⁰Th, ²³⁹Pu and ²⁴¹Am to determine the radiochemical separation factors for these specific alpha emitters.

The activity of ²²⁶Ra was determined with the following expression:

$$A_{Ra226} = \frac{c - b}{60 E f_a f_c r V} \quad (6)$$

where A_{Ra226} is the activity of ²²⁶Ra in Bq L⁻¹, c is the count rate of the sample in cpm, b is the background count rate in cpm, 60 is the factor to transform the cpm in cps, E is the ²⁴¹Am efficiency, f_a is the self-absorption factor, f_c is the correction factor due to contribution from α -emitter descendants of ²²⁶Ra, r is the radiochemical yield, and V is the sample volume in L.

Self-absorption factors were obtained from an alpha absorption curve. A set of sources with different thicknesses ranging from 1 to 50 mg were prepared using sodium nitrate as a substrate. The sources were spiked with known quantities of a calibrated solution of ²⁴¹Am.

The correction factor (f_c) was calculated using Bateman's equations (Jia and Jia, 2012) using the following expression:

$$f_c = 4 - 3e^{-\lambda t} \quad (7)$$

where λ is the decay probability for ²²²Rn, and t is the time elapsed since the BaSO₄ precipitation and measurement (see Section 3.3.1 and Fig. 3).

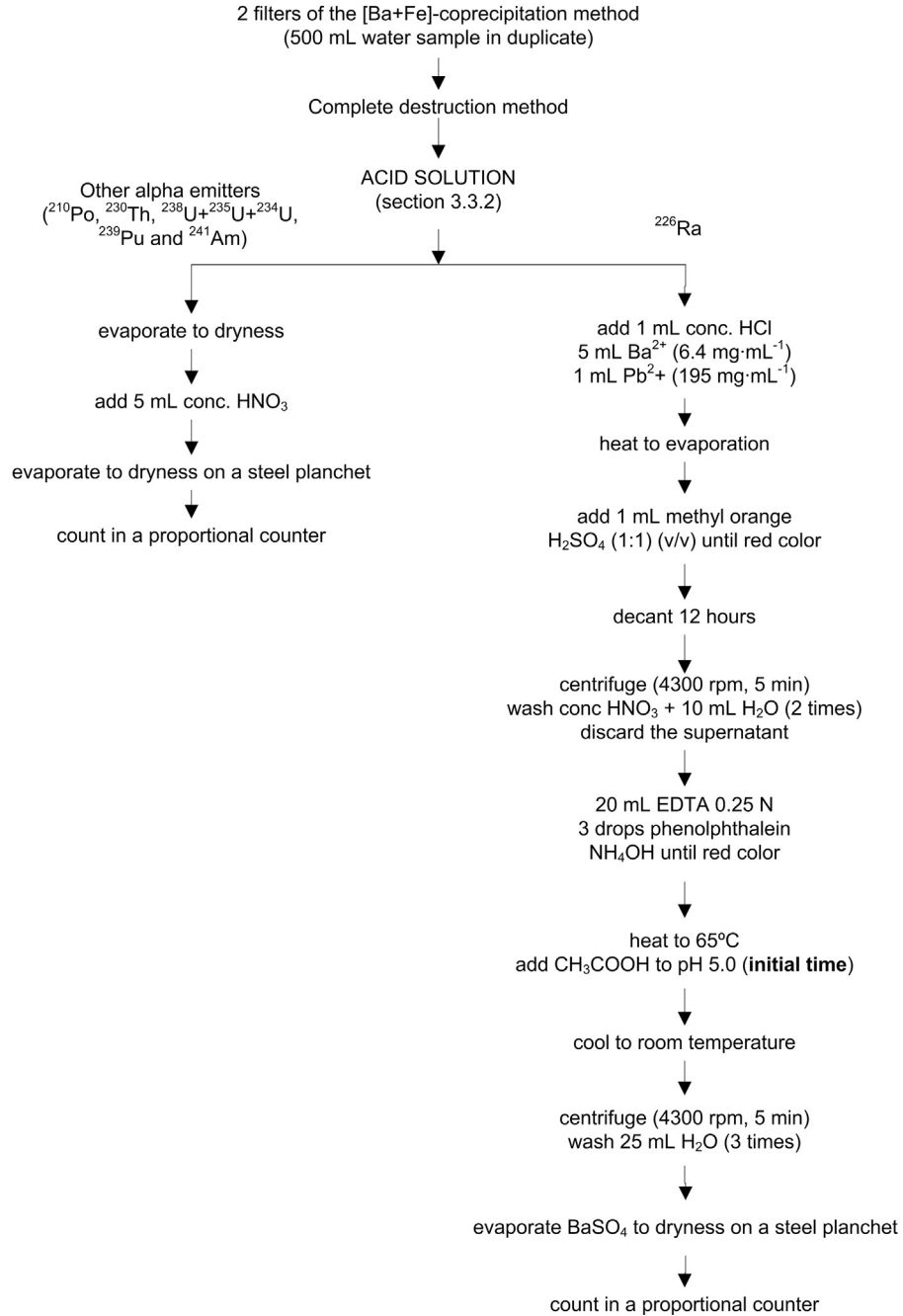


Fig. 4. Method for determining alpha emitter proportions in the acid solution obtained from the precipitate treatment in the gross alpha [Ba + Fe]-coprecipitation method.

The uncertainty associated with the activity of ^{226}Ra was estimated with the following expression:

$$u(A_{\text{Ra}226}) = kA_{\text{Ra}226} \sqrt{\frac{1}{c} + \frac{1}{b} + \left(\frac{u(E)}{E}\right)^2 + \left(\frac{u(r)}{r}\right)^2 + \left(\frac{u(V)}{V}\right)^2} \quad (8)$$

where k is the coverage factor.

The minimum detectable activity of ^{226}Ra ($MDA_{\text{Ra}226}$) can be estimated as (Currie, 1968):

$$MDA_{\text{Ra}226} = \frac{3.29 \sqrt{\frac{b}{t_m} + \frac{b}{t_b}} + 2.7 \left(\frac{1}{t_m} + \frac{1}{t_b}\right)}{60E f_d f_c r V} \quad (9)$$

where t_m and t_b are the sample and background measuring times in minutes, respectively.

In order to assess the method, two types of water were analyzed: three natural water samples of low salinity and two synthetic waters with high salinity (mine discharge water). The samples were provided by the IAEA during an international intercomparison exercise, "AQCS Proficiency Test, Determination of Radium and Uranium Radionuclides in Water, 2003".

3.5. Optimization of thorium and plutonium recovery from barium sulfate precipitate

Barium sulfate precipitate contains thorium and plutonium alpha emitters (see Section 4.2, and Table 3). The reserved solution obtained from the determination of the ^{226}Ra proportion in the barium sulfate precipitate (see Section 3.3.1 and Fig. 3) was used to recover both alpha emitters in order to add them to the acid

Table 2

Recoveries in the [Ba+Fe]-coprecipitation method for the six alpha emitter standard solutions. This assay was performed in duplicate.

Alpha-emitting	Recovery (%)
²¹⁰ Po	98.9 ± 7.0
²²⁶ Ra	99.7 ± 7.5
²³⁰ Th	99.6 ± 4.4
²³⁴ U + ²³⁵ U + ²³⁸ U	98.6 ± 5.5
²³⁹ Pu	100 ± 11
²⁴¹ Am	100 ± 16

Quoted uncertainties correspond to $k=1$.

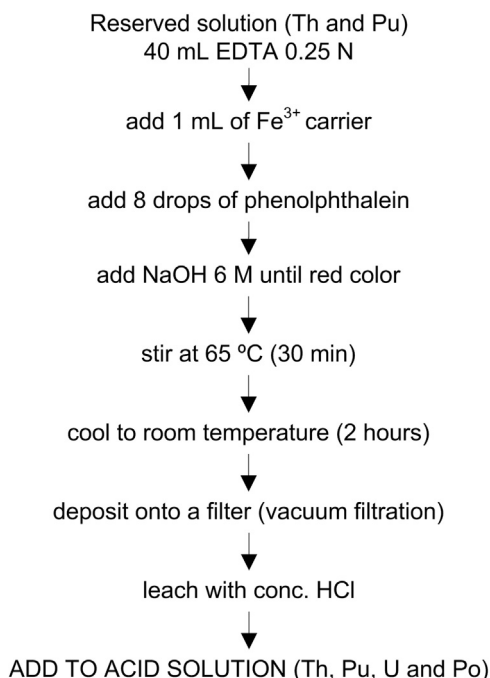


Fig. 5. Method for plutonium and thorium recovery from barium sulfate precipitate method using the reserved solution (see Fig. 3).

Table 3

Alpha emitter proportions in the BaSO₄ precipitate and the acid solution.

Alpha-emitting	Replicates	Proportions (%)	
		BaSO ₄ precipitate	Acid solution
²¹⁰ Po	5	0.8	99.2
²²⁶ Ra	5	96.0	4.0
²³⁰ Th	5	50.8	49.2
²³⁴ U + ²³⁵ U + ²³⁸ U	2	0.2	99.8
²³⁹ Pu	5	16.0	84.0
²⁴¹ Am	2	3.1	96.9

Table 4

²²⁶Ra intercomparison exercise with the IAEA.

Sample reference	IAEA activity (Bq)	Laboratory activity (Bq)
IAEA-423 ^a	8.7 ± 0.14	9.33 ± 0.82
IAEA-431 ^a	24.9 ± 0.39	23.7 ± 1.3
IAEA-426 ^b	6.5 ± 2.7	7.45 ± 0.42
IAEA-427 ^b	65 ± 17	68.4 ± 7.8
IAEA-428 ^b	3.6 ± 1.1	3.00 ± 0.18

The uncertainties are expressed for $k=2$.

^a Synthetic sample.

^b Sample of natural origin.

solution fraction obtained after the complete destruction method. The acid solution fraction was used to continue specific analysis of the individual alpha emitters (thorium, plutonium, uranium and polonium). Prior to the complete destruction of the filters, ²⁴¹Am was measured by gamma spectrometry (Suarez-Navarro, 2009).

Several conditions (dilution, carrier, resting time, double precipitation, temperature and pH) were varied to optimize the recovery of thorium and plutonium from barium sulfate precipitate. The selected method (Fig. 5) was applied to 10 replicates containing ²³⁴Th for the determination of the radiochemical yield recovery using gamma spectrometry, and it was applied to 10 replicates containing ²³⁹Pu. Finally, a radiochemical yield for the recovery of thorium and plutonium was calculated.

4. Results and discussion

4.1. Method for determining the [Ba+Fe]-coprecipitation recovery

Table 2 shows the recoveries in the [Ba+Fe]-coprecipitation method for the six standard solutions. Recoveries ranged from 98.6% to 100%, therefore quantitative recovery of the [Ba+Fe]-coprecipitation method may be assumed for all the alpha emitters, as was found in the international literature. Recovery was below 100% in some cases; this is because the alpha counting efficiency in the proportional counter was determined using ²⁴¹Am.

4.2. Alpha-emitting proportions in the barium sulfate precipitate and acid solution

Table 3 shows the alpha-emitting proportions in the BaSO₄ precipitate and the acid solution. The alpha-emitting proportions in the barium sulfate precipitate and acid solution depend on the oxidation state and the presence of potassium and sodium ions (Kimura et al., 1986). In general, alpha emitters in the ter- and quadrivalent states can be carried quantitatively in the BaSO₄ precipitate (Sill and Willis, 1966). Nevertheless, under the conditions described in the methodology used in the work, a specific explanation is necessary for each alpha emitter.

Polonium scarcely precipitates at all with barium sulfate in the presence of hydrochloric acid (Sill, 1978). Thus, the polonium remains in acid solution.

Radium precipitates quantitatively in BaSO₄. Nevertheless, a small proportion of radium is present in the acid solution due to HCl inhibiting formation of the BaSO₄ precipitate (Sill, 1980).

The only oxidation state of thorium in solution is the quadrivalent state. Nevertheless, the presence of sodium and potassium ions is indispensable for the quantitative coprecipitation of thorium (Kimura and Kobayashi, 1985).

The most stable oxidation states of uranium in solution are the quadri- and hexavalent states. The complete destruction method oxidizes uranium to the hexavalent state due to the presence of HClO₄ and the iron carrier. Thus, the uranium remains in acid solution (Betts, 1955).

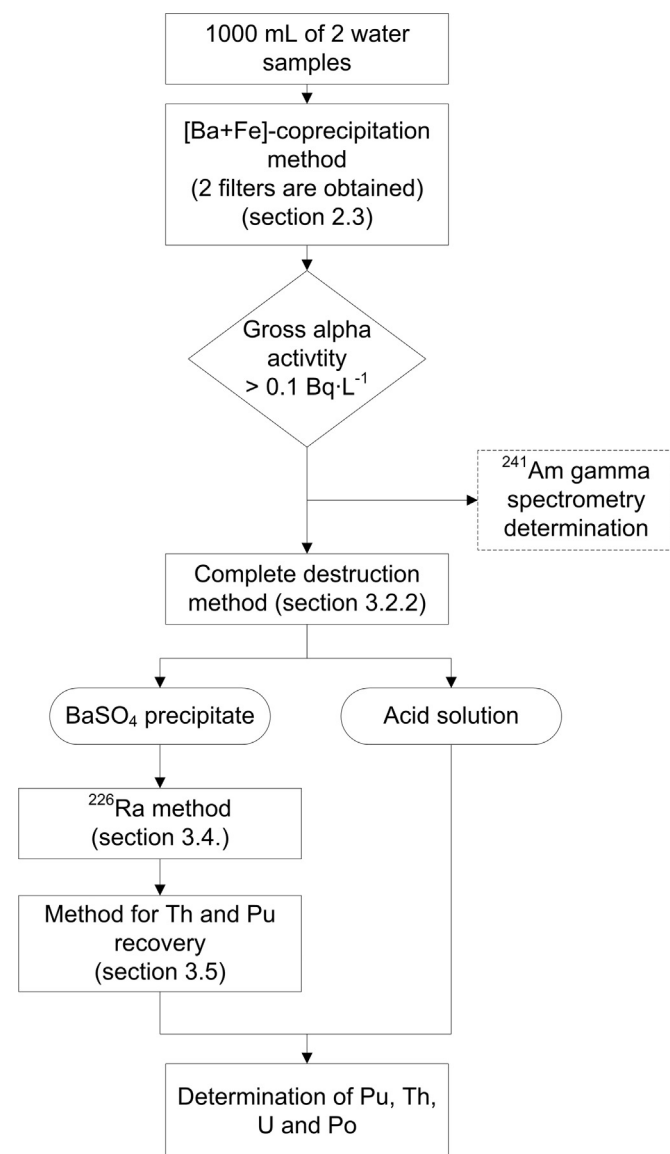
Plutonium is stable in acid solution in the ter-, quadri- and hexavalent states. In the complete destruction method, the plutonium oxidizes quantitatively to the penta- and hexavalent states, but if the evaporation to dryness is too rapid, some of the hexavalent plutonium is decomposed thermally to the quadrivalent state (Sill, 1980).

The most stable oxidation state of americium in solution is tervalent. This element should coprecipitate with barium sulfate in the presence of sodium and potassium ions. Nevertheless, in our conditions with the absence of these ions and in highly acidic media, the coprecipitation is low (Kimura et al., 1986).

Table 5

Thorium and plutonium recovery optimization from barium sulfate precipitate by varying several conditions.

Method	Varied condition	Weighted average recovery ^a (%)
1	Dilution to 250 mL instead 40 mL from reserved solution	56.8
2	Zirconium carrier instead of iron hydroxide	68.0
3	Increase resting time 2 h after precipitation	69.3
4	Double precipitation instead single precipitation	57.2
5	Resting time 2 hours and precipitation at 65 °C	80.6
6	Resting time 2 h and pH of the solution between 12.5 and 12.6	53.6
7	Resting time 2 h, precipitation at 65 °C and pH between 12.5 and 12.6	76.4

^a Weighted average recovery was calculated by weighting with the percentage obtained in Table 3 for ²³⁰Th and ²³⁹Pu tracers.**Fig. 6.** Proposed method for sample pretreatment in the determination of specific alpha emitters in drinking water using [Ba+Fe]-coprecipitation.

4.3. ²²⁶Ra determination

The chemical yield of the radiochemical separation process was 98.7%. The results obtained for the radiochemical separation factors were greater than 99% (99.9% for ²⁴¹Am, 99.8% for ²³⁰Th and 99.2% for ²³⁹Pu). These data confirm the selectivity and effectiveness of the separation procedure for ²²⁶Ra determination.

The results obtained in the intercomparison exercise are presented in Table 4. As noted, all results were statistically indistinguishable, confirming the accuracy of the proposed method.

4.4. Optimization of thorium and plutonium recovery from barium sulfate precipitate

Table 5 lists the thorium and plutonium results obtained with the 7 tested variations of the method. Weighted average recoveries were calculated by weighting with the percentage obtained in Table 3 for both radionuclides. Best results were obtained from the method variation number 5, where precipitation was performed at 65 °C with cooling to room temperature over 2 h after precipitation.

The radiochemical recovery obtained for thorium and plutonium from the reserved solution of the BaSO₄ precipitate fraction was 93.6% and 63.3%, respectively. Both results were similar to the weighted average recovery obtained previously in Table 5 for the selected method.

The addition of these radiochemical recoveries to the acid solution proportions (Table 3) gives a total recovery of 96.7% for thorium and 94.1% for plutonium to follow-up chemical procedures for specific analysis of the individual alpha emitters.

4.5. Proposed method for sample pretreatment

The proposed method for sample pretreatment in the determination of specific alpha emitters in drinking water is summarized in Fig. 6. The method started by determining gross alpha activity using the [Ba+Fe]-coprecipitation method. If gross alpha activity was above the reference level, the filters were measured by gamma spectrometry to determine ²⁴¹Am activity. Then, the filters were treated with the complete destruction method (Section 3.2.2.) and two fractions were obtained: barium sulfate precipitate and acid solution. ²²⁶Ra activity was obtained by the method described in Section 3.4. Finally, Th and Pu recovered from barium sulfate (Section 3.5) were added to acid solution fraction.

5. Conclusions

The quantitative recovery in the [Ba+Fe]-coprecipitation method was determined using all the alpha-emitting radionuclides of interest (natural alpha emitters and transuranium elements). Recoveries varied from 98.6% to 100%, depending on the type of alpha emitting isotope.

Two precipitate treatment methods (leaching and complete destruction) were used in the [Ba+Fe]-coprecipitation method for gross alpha activity determination. The best results were obtained for the method involving the complete destruction of the filter by adding 1 N H₂SO₄ to the solution. Therefore, this method was used for precipitate treatment.

Under our conditions, radium, thorium and plutonium partially coprecipitate with barium sulfate, and polonium, uranium and americium remain quantitatively in the acid solution. Knowledge of the behavior of the alpha emitters and their proportions in the barium sulfate and acid solution is necessary to develop simple and fast radiochemical separations for specific alpha-emitting radionuclides in drinking water using the precipitate collected in the [Ba+Fe]-coprecipitation method for gross alpha activity determination.

For the determination of ^{226}Ra in drinking water from barium sulfate precipitate, a radiochemical procedure was developed. The proposed method allows the quantitative and selective determination of ^{226}Ra in water samples. The accuracy of the method was successfully evaluated through participation in the IAEA inter-comparison of synthetic and natural water samples.

As thorium and plutonium partially coprecipitate with barium sulfate, a method was optimized to recover both alpha emitters from barium sulfate (93.6% and 63.3%, respectively). These proportions obtained from the reserved solution from barium sulfate precipitate were added to acid solution fraction.

Finally, the total proportions of the thorium, plutonium, uranium and polonium in the acid solution in the proposed method for the determination of specific alpha emitters in drinking water were 96.7%, 94.1%, 99.8% and 99.2%, respectively. ^{241}Am was previously determined by gamma spectrometry, prior to the complete destruction of the filters.

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