

Separation of Sr from Ca, Ba and Ra by means of $\text{Ca}(\text{OH})_2$ and $\text{Ba}(\text{Ra})\text{Cl}_2$ or $\text{Ba}(\text{Ra})\text{SO}_4$ for the determination of radiostrontium

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Abstract

A simple procedure is developed to separate Sr from a large amount of Ca, which relies on the insolubility of $\text{Ca}(\text{OH})_2$ in alkaline solution. Calcium is quantitatively separated from Sr and more than 95% of Sr is recovered from a sample with as much as 50 g of Ca and a Ca/Sr mole ratio of 250. A new procedure for the separation of Sr from Ba and Ra is also investigated, which is based on the difference in solubility of the chlorides of Sr, Ba and Ra in HCl media. In 9.5 mol l^{-1} HCl or 7.5 mol l^{-1} HCl–10% acetone media, >97% of Ba and Ra can be removed by $\text{Ba}(\text{Ra})\text{Cl}_2$ precipitation, and >94% of Sr was recovered. In the determination of ^{90}Sr by measuring ^{90}Y , the separation of Ra and Ba can easily be carried out by precipitation of Ba and Ra as $\text{Ba}(\text{Ra})\text{SO}_4$, while Y can be quantitatively recovered in the solution. By this method, a further separation of ^{90}Y from radiostrontium can be completed. The new separation procedure has been successfully used for the determination of ^{90}Sr in samples with high Ca content, such as 45 l of seawater and 200 l of drinking water. The analytical quality of the results is comparable to that of the traditional method using fuming nitric acid and BaCrO_4 precipitation.

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1. Introduction

Radiostrontium (^{90}Sr and ^{89}Sr) has been released to the environment by global fallout following atmospheric nuclear explosions, by nuclear waste discharges and fallout from the Chernobyl accident. As it has a short half-life (50.5 days), ^{89}Sr quickly decays to undetectable levels, while ^{90}Sr is radiologically more important because of its longer half-life (28.78 years) and accumulation in bone tissue. Radiostrontium can also be used as an oceanographic tracer to investigate the movement of water mass in the ocean [1–3]. Cost-effective and relatively simple procedures

for determination of radiostrontium are desirable for radioecology, environmental radioactivity and oceanographic studies, which often require the analysis of a large number of samples. Both ^{90}Sr and ^{89}Sr are β^- emitters. Determination by direct measurement of ^{90}Sr and ^{89}Sr or the short-lived daughter ^{90}Y (also a pure β^- emitter) using a proportional counter or liquid scintillation counter requires previous chemical separation and preconcentration in order to avoid interference from other radionuclides and problems from self-absorption due to the presence of calcium in the sample. In various analytical procedures for ^{90}Sr , a more time-consuming and expensive step is the separation of Sr from Ca, Ba and Ra. Many techniques for separation of strontium from matrices have been reported, such as liquid–liquid extraction using

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a crown ether [4,5], liquid membrane extraction [6], extraction chromatography [7] using Sr–Spec resin [8,9], ion-exchange [9–13] and strontium rhodizonate and CaHPO_4 precipitation [13,14]. But they cannot be used for the separation of Sr from a large amount of Ca. One general method based on the insolubility of strontium nitrate in strong nitric acid is still widely used for separation of Sr from Ca [15]. For the analysis of some samples with a high calcium content such as a large volume of seawater ($\sim 50\text{ l}$) and drinking water ($\sim 200\text{ l}$), more than 3 l of fuming nitric acid has to be used for this separation. It is time-consuming, expensive and destructive to laboratory apparatus, also hazardous for the operator.

Strontium is usually separated from isotopes of barium by BaCrO_4 precipitation [15], but the operation is difficult and time-consuming due to critical control of pH of the solution and removal of excess Cr afterwards. It was supposed that naturally occurring isotopes of radium (^{226}Ra , ^{228}Ra) could also be removed with Ba in this step. This is important for analysis of low-level environmental samples, because radium is the main contributor to radioactivity in these samples, with activity levels higher than those of ^{90}Sr and ^{89}Sr . However, no detail of the separation efficiency of Ra by Ba(Ra)CrO_4 method is available.

Patti and Hernandez [16] used Ca(OH)_2 precipitation to separate Ca from Sr for the preparation of a calcium salt with a low concentration of strontium, but no decontamination of Ca from Sr was investigated and no application of this method for the determination of radiostrontium was reported. In the present work, the separation of Sr from a large amount of Ca by Ca(OH)_2 precipitation is investigated for the determination of radiostrontium. We noticed that the solubilities of SrCl_2 and BaCl_2 are different in different concentrations of hydrochloric acid. By using this feature, the separation of Sr from Ba and Ra is investigated.

The determination of ^{90}Sr is usually carried out by measuring its short-lived daughter ^{90}Y , and the concentration of ^{89}Sr is calculated by the difference between the total radioactivity of isotopes of strontium and ^{90}Sr measured by ^{90}Y . Ba(Ra)SO_4 precipitation is widely used for the separation of Ra from various matrices, while $\text{Y}_2(\text{SO}_4)_3$ is soluble. Thus, this feature can be used to separate Ba and Ra, if only ^{90}Sr need to be determined. Meanwhile, ^{90}Sr can also be

precipitated with Ba(Ra)SO_4 as SrSO_4 and is further decontaminated. In this work, the separation of Y from Ba, Sr and Ra by Ba(Ra)SO_4 precipitation is also investigated.

2. Experimental

2.1. Chemical reagents

All chemicals used in the experiment were analytical-grade reagents. ^{133}Ba tracer was purchased from Eckert & Ziegler Co. (Valencia, CA 91355) and diluted to 3020 Bq ml^{-1} in 1 mol l^{-1} HCl. ^{226}Ra (INST-SRM-4967) was purchased from the National Institute of Standards and Technology (NIST, Gaithersburg, MA 20899) and diluted to 33 Bq ml^{-1} in 1 mol l^{-1} HCl. ^{85}Sr tracer was purchased from Isotope Products Laboratories (3017N San Fernando Blvd, Burbank, CA 91504) and diluted to 2100 Bq ml^{-1} in 1 mol l^{-1} HCl.

2.2. Samples

Seawater samples were collected in Danish waters from Hesselø in Kattegat and Møen in the Baltic Sea. The drinking water samples were collected at different locations in Denmark.

2.3. Analytical procedure

2.3.1. Separation of strontium from calcium by Ca(OH)_2 precipitation

Fifty grams of calcium as $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and 0.33 g of strontium as $\text{SrCl}_2 \cdot 2\text{H}_2\text{O}$ was taken in a 5 l beaker, and 2.5 l of 0.3 mol l^{-1} HCl was added to dissolve them. Then 1050 Bq of ^{85}Sr tracer was added, and the solution was stirred for 5 min. Next 6 mol l^{-1} NaOH was added to give a NaOH concentration of 0.2 mol l^{-1} , and the calcium was precipitated as Ca(OH)_2 . The slurry was transferred to a centrifuge tube and centrifuged to separate the Ca(OH)_2 precipitate at 3000 rpm for 10 min. The precipitate was washed with 0.2 mol l^{-1} NaOH and the washings were combined with the supernatant. A few drops of 6 mol l^{-1} NaOH were added to the supernatant to check if Ca is completely precipitated. Na_2CO_3 was added to the hot supernatant and the SrCO_3

precipitate separated by centrifugation. The radioactivity of ^{85}Sr in the $\text{Ca}(\text{OH})_2$ and SrCO_3 fractions were measured by a NaI well detector.

Calcium in the supernatant, which was not precipitated, was measured gravimetrically as $\text{CaC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$. In this case, no Sr carrier was added to the original solution.

2.3.2. Separation of Sr from Ba by BaCl_2 precipitation

A solution (2 ml) containing 15 mg of Ba^{2+} and 0.3 g of Sr^{2+} was taken in a 100 ml centrifuge tube, and 0.5 ml of 3020 Bq ml^{-1} ^{133}Ba and 0.5 ml of 2100 Bq ml^{-1} ^{85}Sr tracers were added. Then 12 mol l^{-1} HCl, deionized water and acetone were added to give a range of HCl and acetone concentrations, with a total volume of 40 ml. The suspension was stirred for 2 min, and centrifuge at 3000 rpm for 10 min. The supernatant was transferred to another centrifuge tube, the precipitate was dissolved in water and transferred to a 25 ml polythene counting vial for measurement.

Next, 15 mg of Ba^{2+} was added to the supernatant. After stirring for 2 min, the precipitate was separated by centrifugation. The supernatant was transferred to a counting vial for measurement, the precipitate was dissolved in water and transferred to another counting container. The radioactivity of ^{85}Sr and ^{133}Ba in the supernatant and precipitate fractions were measured with a HpGe detector by counting the 356 keV γ -rays of ^{133}Ba and the 514 keV γ -rays of ^{85}Sr .

2.3.3. Separation of Sr from Ra by $\text{Ba}(\text{Ra})\text{Cl}_2$ precipitation

The procedure is the same as that for the separation of Sr from Ba, except that 1.0 ml of 33 Bq ml^{-1} ^{226}Ra was added instead of ^{85}Sr and ^{133}Ba tracers. The radioactivity of ^{226}Ra in the precipitate and supernatant was measured with a Ge detector by counting the 185 keV γ -rays of ^{226}Ra .

2.3.4. Separation of Sr from Ra by $\text{Ba}(\text{Ra})\text{CrO}_4$ precipitation

A solution (2 ml) containing 15 mg of Ba^{2+} and 0.3 g of Sr^{2+} was taken in a beaker, 1.0 ml of 33 Bq ml^{-1} ^{226}Ra , was added, the pH of the solution was adjusted to 4–6, 10 ml of $\text{HAc-NH}_4\text{Ac}$ buffer (pH 5.5) was added and the solution heated on a

hotplate to near boiling. A 1.0 ml of 0.3 mol l^{-1} Na_2CrO_4 was added to the solution, and the mixture heated for 30 min. The suspension was cooled to room temperature, and filtered through a $0.45 \mu\text{m}$ membrane with suction. The precipitate was washed with 3 ml of water, and the washings were combined with the filtrate. The precipitate on the filter was transferred to a counting container for measurement. Fifteen milligrams of Ba^{2+} and 1.0 ml of 0.3 mol l^{-1} Na_2CrO_4 were added to the filtrate, which was heated on a hotplate for 30 min. After cooling to room temperature, it was filtered through a $0.45 \mu\text{m}$ membrane. The precipitate was washed with 3 ml of water, the precipitate on the filter was transferred to a counting vial and the filtrate was transferred to another container for measurement. ^{226}Ra in the precipitate and supernatant was measured with a HpGe detector.

2.3.5. Separation of Y from Ba by BaSO_4 precipitation

$\text{SrCl}_2 \cdot \text{H}_2\text{O}$ (1 g) and 28.66 mg of $\text{Y}_2(\text{C}_2\text{O}_4)_3 \cdot \text{H}_2\text{O}$ was taken in a centrifuge tube and dissolved in 60 ml of 0.4 mol l^{-1} HCl. Ammonia solution was added to adjust the pH to >10 and the mixture heated for a while; a $\text{Y}(\text{OH})_3$ precipitation was formed. The mixture was centrifuged and the supernatant transferred to a beaker. One millilitre of 6 mol l^{-1} HNO_3 was added to the centrifuge tube to dissolve the $\text{Y}(\text{OH})_3$ precipitate and the sample was transferred to a smaller tube. Wash the larger tube with 0.1 mol l^{-1} HNO_3 and combine the washings with the solution to make the total volume 20 ml. Five milligrams of Sr^{2+} carrier was added to the solution and the mixture stirred. Twenty-five percent ammonia solution was added to adjust the pH to >10 , the suspension allowed to stand for 10 min and the precipitate was separated by centrifugation. One millilitre of 6 mol l^{-1} HNO_3 was added to dissolve the precipitate and to adjust the volume to 20 ml. Five milligrams of Ba^{2+} carrier and 2 mg of Sr^{2+} carrier were added, the mixture stirred for 1 min. One millilitre of 2 mol l^{-1} H_2SO_4 was added, the mixture stirred to form BaSO_4 and SrSO_4 , and centrifuged to separate the precipitate. The supernatant was transferred to another centrifuge tube, and 25% ammonia solution was added to adjust the pH to >10 . After stirring, and standing for 5 min, the mixture was centrifuged to separate the precipitate. Five drops of 6 mol l^{-1} HNO_3 were added to dissolve the sample, 20 ml of

8% $\text{H}_2\text{C}_2\text{O}_4$ solution was added, and the mixture was stirred and heated. The solution was passed through a filter, and the $\text{Y}_2(\text{C}_2\text{O}_4)_3 \cdot \text{H}_2\text{O}$ precipitate on the filter was washed with water and ethanol. The precipitate was dried and weighed to calculate the chemical yield of Y.

2.3.6. Separation of Y from Ba by BaSO_4 precipitation using ^{133}Ba tracer

A solution (20 ml) containing 3.0 mg of Y^{2+} , 2.5 mg of Ba^{2+} and 3.0 g of Sr^{2+} was taken in a beaker, 1.0 ml of 2100 Bq ml^{-1} ^{133}Ba was added and stirred for 3 min. A total of 1.0 ml of 2 mol l^{-1} H_2SO_4 was added and stirred for 2 min. The suspension was filtered through a $0.45 \mu\text{m}$ membrane and washed with 5 ml of 0.5 mol l^{-1} H_2SO_4 . The precipitate on the filter was transferred to a counting vial; the filtrate was transferred to another container for measurement of ^{133}Ba .

2.3.7. Separation of Y from Ra by Ba(Ra)SO_4 precipitation

The procedure was the same as that for separation of Y from Ba, except 1.0 ml of 33 Bq ml^{-1} ^{226}Ra tracer was added instead of ^{133}Ba tracer.

2.3.8. Determination of ^{90}Sr in seawater and drinking water

2.3.8.1. Procedure for determination of ^{90}Sr in 45 l of seawater. Transfer 45 l of seawater to a 100 l flask, add ^{85}Sr tracer and 1 g of $\text{SrCl}_2 \cdot \text{H}_2\text{O}$. Stir for 10 min. Adjust the pH to 8–10 using NaOH. Heat to boiling. Add 1–1.5 l of 2 mol l^{-1} $(\text{NH}_4)_2\text{CO}_3$ and stir with a rod for 1 min (do not use air bubbles). Cover the vessel with a glass disc. Stand overnight. Discard the supernatant. Dissolve the precipitate of $\text{SrCO}_3/\text{CaCO}_3$ in 1000 ml of 4 mol l^{-1} HNO_3 . Wash the vessel twice with 500 ml of H_2O each time. Combine the washings with the dissolved precipitate in a beaker. Add 10 mg of Fe^{3+} , heat to boiling to completely dissolve the material and cool to room temperature. Add 6 mol l^{-1} NaOH to adjust the pH to 10, add more 6 mol l^{-1} NaOH to make the concentration of NaOH to be 0.2 mol l^{-1} and stir for 1 min (until there is no white precipitate in the supernatant). Transfer the sample to a 250 ml centrifuge tube and centrifuge. Transfer the supernatant to another beaker. Wash the precipitate with 150 ml of 0.2 mol l^{-1} NaOH, and combine the

washings with the supernatant. Heat the solution to boiling. Add Na_2CO_3 to the solution (5 g of Na_2CO_3 per 100 ml of solution). Stir and heat the sample on a 250°C hotplate for 1 h. Cool, centrifuge to separate the precipitate, and discard the supernatant. Add 10 ml of 8 mol l^{-1} HNO_3 to dissolve the precipitate. Repeat the procedure from addition of 6 mol l^{-1} NaOH. Dissolve the precipitate with 4 ml of 6 mol l^{-1} HNO_3 . Add 5 mg of Fe^{3+} , stir and add NaOH to adjust the pH to 10. After centrifuging, transfer the supernatant to another tube. Add 12 mg of Y^{3+} carrier and 5 mg of Ba^{2+} carrier to the supernatant.

Take part of the solution to measure the chemical yield of strontium, $Y = (C_p W g_2)/(C_{st} W_1 g_1)$, where W is the total weight of solution, W_1 the weight of solution taken and measured, C_p the measured counts of strontium tracer in the sample, g_1 the amount of tracer added to the sample, g_2 the amount of tracer in the standard, and C_{st} is the counts for the standard.

Combine the solutions after measurement, and leave the solution for 3 weeks for growth of the daughter nuclide ^{90}Y . Add NH_3 to the solution to adjust the pH to >10 and heat for a few minutes. Centrifuge to separate the precipitate. Add 1 ml of 6 mol l^{-1} HNO_3 to dissolve the precipitate and transfer the sample to a smaller tube. Wash the larger tube with 0.1 mol l^{-1} HNO_3 and combine the washings with the dissolved material to make the final volume 20 ml. Add 5 mg of Ba^{2+} carrier and 2 mg of Sr^{2+} carrier to the solution, and stir for 1 min. Add 1 ml of 2 mol l^{-1} H_2SO_4 and stir to precipitate BaSO_4 and SrSO_4 . Centrifuge to separate the precipitate and transfer the supernatant to another tube. Add 25% ammonia solution to the supernatant to adjust the pH to >10 , stir, and leave for 5 min. Centrifuge to separate the precipitate, and discard the supernatant. Add five drops of 6 mol l^{-1} HNO_3 to dissolve the precipitate. Add 20 ml of 8% $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ solution, stir and heat. After cooling to the room temperature, filter and wash the precipitate twice with water and ethanol. Dry and weigh the $\text{Y}_2(\text{C}_2\text{O}_4)_3 \cdot \text{H}_2\text{O}$ to calculate the chemical yield of Y. Measure the radioactivity of ^{90}Y using an anti-coincident gas flow GM counter (Risø).

2.3.8.2. Determination of ^{90}Sr in 200 l of drinking water and lake water. Transfer the first 100 l of water to a 200 l flask, add 30 g of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$, ^{85}Sr tracer and 1 g of $\text{SrCl}_2 \cdot \text{H}_2\text{O}$, and stir for 10 min.

Adjust the pH to 8–10 with 25% ammonia solution. Heat to boiling. Add 2 l of 2 mol l^{-1} $(\text{NH}_4)_2\text{CO}_3$ and stir for 1 min (do not use air bubbles). Cover the vessel with a glass disc. Allow to stand overnight or over a weekend. Siphon off the supernatant, and dissolve the precipitate of SrCO_3 in 1000 ml of 4 mol l^{-1} HNO_3 .

Add the second 100 l of water to the large flask, stir for 10 min with air bobbles. Adjust the pH to 8–10 with 25% ammonia solution. Heat to boiling. Add 2 l of 2 mol l^{-1} $(\text{NH}_4)_2\text{CO}_3$ and stir for 1 min (do not use air bubbles). Cover the vessel with a glass disc. Allow to stand overnight or over a weekend. Siphon off the supernatant, and dissolve the precipitate of SrCO_3 in 1000 ml of 4 mol l^{-1} HNO_3 . Wash the flask twice with 500 ml of water each time. Combine the washings and the dissolved precipitates. The volume of the solution is ca. 3 l. Add 10 mg of Fe^{3+} to the solution. Then follow the procedure as for seawater.

3. Results and discussion

Table 1 shows the separation of Sr from Ca by $\text{Ca}(\text{OH})_2$ precipitation from alkaline solution. In 0.2 mol l^{-1} NaOH , >99% of Ca can be removed by one precipitation, with >95% of Sr remaining in the solution. The concentration of Ca in the solution does not significantly affect the separation of Sr from Ca in a solution containing $\leq 50 \text{ g}$ of Ca (or a Ca concentration of 20 g l^{-1}) or a Ca/Sr mole ratio of 160. Baratta and Knowles [17] investigated the separation of Sr and Ca by $\text{Sr}(\text{NO}_3)_2$ in a strong nitric acid medium using a radioactive tracer. Their results show that at 64–67% nitric acid, 95–100% of Sr was recovered, while 90–94% of Ca was removed. It can be seen that the separation efficiency of Sr from Ca by $\text{Ca}(\text{OH})_2$ in this work is similar to that achieved by $\text{Sr}(\text{NO}_3)_2$ precipitation using fuming nitric acid. However, the operation of $\text{Ca}(\text{OH})_2$ precipitation is

easier, cheaper and less risky compared with the use of fuming nitric acid, especially for samples with a high calcium content. For analysis of seawater with a low ^{90}Sr concentration, normally as much as 45 l need to be treated to achieve low detection limits. As the calcium content could be >18 g, as much as 2 l of fuming nitric acid need to be added to separate Sr from Ca. Handling of such a large amount of fuming nitric acid is difficult and risky. When using $\text{Ca}(\text{OH})_2$ precipitation, the operation is easier and safer. By double precipitation of $\text{Ca}(\text{OH})_2$, >99.9% of Ca can be removed. For a sample containing 20 g of Ca <20 mg of Ca remains, which is much less than the Sr content of the samples ($\sim 350 \text{ mg}$). In addition, many interfering nuclides, such as uranium, thorium, transuranic elements and rare earth elements will also precipitate with $\text{Ca}(\text{OH})_2$ and are separated from Sr.

Table 2 shows the separation of Sr from Ba by BaCl_2 precipitation in HCl. Both BaCl_2 and SrCl_2 are soluble in water and dilute HCl, but not in concentrated HCl; their solubility varies with the concentration of HCl. In 9.5 mol l^{-1} HCl, >97% of Ba can be removed by BaCl_2 precipitation, while $\sim 94\%$ of Sr remains in the solution. This separation efficiency is similar to that using BaCrO_4 precipitation (Table 2).

Addition of acetone can promote the precipitation of BaCl_2 at lower HCl concentration. The results (Table 3) show that in 10% acetone, 95% of the Ba can be precipitated at 7.5 mol l^{-1} HCl and $\sim 94\%$ Sr is recovered in the solution. Thus, a 7.5 mol l^{-1} HCl–10% acetone medium can also be used to separate Sr from Ba, and, in this condition, HCl is less volatile.

Barium-133 has been present in the environment due to atmospheric fallout from nuclear weapons testing in 1950s and 1960s, but it has decayed to insignificant levels now. The separation of Ba in the procedure is also used for the separation of radium isotopes (^{226}Ra , ^{228}Ra), because radium and barium have very similar chemical properties and ^{226}Ra is a

Table 1
Separation of Sr from Ca by $\text{Ca}(\text{OH})_2$ precipitation

No.	^{85}Sr added (Bq)	Ca added (g)	^{85}Sr (Bq)		Recovery of Sr (%)	Ca in supernatant (g)	Ca decontamination (%)
			Precipitation	Supernatant			
1	1050	50.00	31.6	1058.4	97.0	0.18	99.5
2	1050	31.00	38.1	1037.7	96.4	0.14	99.5
3	1050	10.00	30.6	1029.6	97.1	0.07	99.3

Table 2

Separation of Sr from Ba by BaCl₂ and BaCrO₄ precipitation

[HCl] (mol l ⁻¹)	Tracers added (Bq)		Supernatant (Bq) ^a		Precipitate (Bq) ^a		Recovery of Sr (%)	Decontamination of Ba (%)
	⁸⁵ Sr	¹³³ Ba	⁸⁵ Sr	¹³³ Ba	⁸⁵ Sr	¹³³ Ba		
8.5	1050	1510	1058.4 ± 15.9	918.8 ± 14.2	2.0 ± 3.4	604.2 ± 19.4	99.8 ± 0.3	40.0 ± 1.3
9.0	1050	1510	1036.4 ± 24.8	484.7 ± 18.4	2.1 ± 2.4	1025.9 ± 27.3	98.8 ± 0.3	67.9 ± 1.8
9.5	1050	1510	998.6 ± 18.7	43.8 ± 9.4	62.4 ± 5.9	1420.9 ± 21.5	94.1 ± 0.6	97.1 ± 1.4
10.0	1050	1510	719.3 ± 16.2	40.5 ± 7.2	331.2 ± 11.1	1467.7 ± 19.2	68.5 ± 1.5	97.3 ± 1.3
10.5	1050	1510	309.7 ± 12.8	28.6 ± 4.2	743.4 ± 18.4	1543.1 ± 28.2	29.5 ± 1.3	98.1 ± 2.7
11.0	1050	1510	221.5 ± 16.2	7.9 ± 4.8	846.3 ± 21.2	1499.2 ± 19.2	21.1 ± 1.1	99.5 ± 1.3
BaCrO ₄	1050	1510	1038.1 ± 17.6	15.3 ± 5.7	49.0 ± 7.8	1496.2 ± 18.1	95.3 ± 0.7	99.0 ± 0.4

^a Average and standard deviation of two determinations.

Table 3

Separation of Sr from Ba by BaCl₂ precipitation in HCl–10% acetone medium

[HCl] (mol l ⁻¹)	Tracers added (Bq)		Supernatant (Bq) ^a		Precipitate (Bq) ^a		Recovery of Sr (%)	Decontamination of Ba (%)
	⁸⁵ Sr	¹³³ Ba	⁸⁵ Sr	¹³³ Ba	⁸⁵ Sr	¹³³ Ba		
7.0	1050	1510	1045.8	496.8	4.2	1037.4	99.6	67.1
7.5	1050	1510	984.9	65.2	65.6	1439.0	93.8	95.7
8.0	1050	1510	823.2	27.2	224.7	1485.8	78.4	98.2
8.5	1050	1510	516.6	14.8	539.7	1531.1	49.2	99.0
9.0	1050	1510	205.8	8.2	851.6	1493.4	19.6	99.5

^a Average and standard deviation of two determinations.

major component of naturally occurring radionuclides and needs to be separated for the determination of radiostrontium at low levels. Table 4 shows the separation of Sr from Ra by Ba(Ra)Cl₂ precipitation. At 9.5 mol l⁻¹ HCl, ~97% Ra can be removed from the solution. If this precipitation procedure is repeated, the decontamination of Ra can be >99%. This result is similar to that using Ba(Ra)CrO₄ precipitation which is used in the traditional analytical procedure for radiostrontium determination [15]. Compared

with Ba(Ra)CrO₄ precipitation, the procedure using Ba(Ra)Cl₂ precipitation is easier and quicker, because the concentration of HCl is easily adjusted and no operation is needed to remove external elements such as Cr in the BaCrO₄ procedure.

Ba(Ra)SO₄ precipitation is very effective and specific for the separation of Ra and Ba from other elements, and has been widely used for the determination of Ra [18]. But it cannot be used to separate Ba and Ra from Sr and Ca due to the low solubility of

Table 4

Separation of Sr from Ra by Ba(Ra)Cl₂ and Ba(Ra)CrO₄ precipitation

Medium (mol l ⁻¹)	²²⁶ Ra added (Bq)	²²⁶ Ra in precipitate (Bq) ^a		²²⁶ Ra in supernatant (Bq) ^a	Decontamination of Ra (%)	
		First	Second		Once	Twice
NaCrO ₄	33.0	32.37 ± 1.25	0.85 ± 0.36	0.30 ± 0.39	98.1 ± 2.8	99.1 ± 1.2
HCl						
9.0	33.0	22.28 ± 1.62	9.48 ± 0.94	0.84 ± 0.42	67.5 ± 4.9	97.4 ± 1.3
9.5	33.0	32.1 ± 0.69	1.3 ± 0.42	0.29 ± 0.32	97.3 ± 2.1	99.1 ± 1.0

^a Average and standard deviation of two determinations.

Table 5

Separation of Y from Ba and Sr and Ra by BaSO₄ + SrSO₄ or Ba(Ra)SO₄ precipitation

Tracer	Added	Supernatant	Precipitate	Recovery of Y (%)	Decontamination of Sr, Ba, Ra (%)
Y (mg)	11.10	10.95 ± 0.22		98.6 ± 2.0	
⁸⁵ Sr (Bq)	1050	8.7 ± 2.4	1042 ± 38		99.2 ± 0.2
¹³³ Ba (Bq)	1510	2.2 ± 1.8	1511 ± 21		99.9 ± 0.1
²²⁶ Ra (Bq)	33.0	0.14 ± 0.26	32.87 ± 0.47		99.6 ± 1.4

Table 6

Analysis of seawater and drinking water for ⁹⁰Sr by the developed procedure and the traditional procedure using fuming nitric acid and BaCrO₄ precipitation

Sample	Volume (l)	Location	New procedure			Traditional fuming HNO ₃ procedure		
			Recovery (%)		Concentration of ⁹⁰ Sr (Bq m ⁻³)	Recovery (%)		Concentration of ⁹⁰ Sr (Bq m ⁻³)
			Sr	Y		Sr	Y	
Seawater	45	Hesslø	78.9	86.5	2.297	41.2	73.2	2.419
Seawater	45	Møen	80.0	92.9	11.727	78.5	89.5	12.174
Drinking water	200	Hvidsten	85.5	82.8	0.0442	68.5		0.0692
Drinking water	200	Fåretofte	79.2	86.8	0.0231	74.1		0.0398
Drinking water	200	Robbedale	79.2	86.4	0.0616	61.9		0.0747
Drinking water	200	Blykober	65.8	88.7	0.0329	69.4		0.0607

the sulphates of Sr and Ca. However, ⁹⁰Sr is usually determined by measuring its short-lived daughter nuclide ⁹⁰Y, and Y₂(SO₄)₃ is water soluble. Thus, the precipitation of Ba(Ra)SO₄ can be used to remove Ba and Ra from Y if only ⁹⁰Y is to be determined. Meanwhile, the separation of ⁹⁰Y from its mother nuclide ⁹⁰Sr and other isotopes of strontium such as ⁸⁹Sr and ⁸⁵Sr tracer can be also carried out in this step. Table 5 shows the separation of Y from Ba, Ra and Sr by sulphate precipitation; >99.5% Ba and Ra, and >99% Sr can be removed by this method, while >98.5% Y remained in the solution. It can be seen that the decontamination of Ba and Ra by this method is more effective than by Ba(Ra)CrO₄ and Ba(Ra)Cl₂ precipitation. But for the determination of both ⁹⁰Sr and ⁸⁹Sr, this method cannot be used because it cannot separate Ba and Ra from Sr. Therefore, it is recommended that the procedure of Ba(Ra)Cl₂ precipitation is used for the determination of both ⁹⁰Sr and ⁸⁹Sr, and the Ba(Ra)SO₄ procedure for the determination of ⁹⁰Sr only.

The new analytical procedure has been applied to analyses of seawater and drinking water samples in our laboratory. Table 6 compares the analytical results obtained by the new procedure and the traditional

procedure using fuming nitric acid and BaCrO₄ precipitation. They are in good agreement, especially for seawater samples. The differences between the results of the two methods for some drinking water samples are probably attributed to the large counting uncertainties at these low levels. The detection limit of our β counter (anti-coincidence gas flow GM counter) is 5–10 mBq, or 0.02–0.05 Bq m⁻³ for 200 l samples. The analytical error at this level is >50%. The lower results of the drinking water samples obtained with the new procedure could also be due to better decontamination of interfering nuclides such as ²²⁶Ra.

4. Conclusions

The separation of Sr from a large amount of Ca is successfully carried out by Ca(OH)₂ precipitation; the decontamination factor for Ca is >10³ when using double precipitation. For the determination of radiostrontium, the procedure is easier, less risky and much cheaper than the traditional method using fuming nitric acid.

At 9.5 mol l⁻¹ HCl or 7.5 mol l⁻¹ HCl–10% acetone, Sr can be separated from Ba and Ra. The

separation efficiency is similar to that of the BaCrO₄ precipitation method, but the procedure is easier and quicker.

For the determination of ⁹⁰Sr, a more effective and specific separation of Ba and Ra can be achieved by Ba(Ra)SO₄ precipitation. This procedure can be used simultaneously for separation and further purification of ⁹⁰Y from radiostrontium.

The procedure of Ca(OH)₂ precipitation combined with Ba(Ra)SO₄ has been successfully applied for ⁹⁰Sr analysis of 45 l seawater and 200 l drinking water samples.

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