1. Scope

This procedure describes a method for the separation and measurement Sr-90 in water samples up to 40 L via its daughter Y-90. Water samples (including sea water) up to 40 L can be analyzed.

2. Summary

Sr-90 is assumed to be in equilibrium with its daughter Y-90. Y-90 is separated using DGA,N resin after concentration from the sample and matrix removal via two consecutive co-precipitation steps. Y-90 is measured after separation on DGA,N resin by gas proportional counting, liquid scintillation counting or Cerenkov counting. Stable yttrium is used to monitor chemical yields and correct results to improve precision and accuracy.

This draft method is entirely based on a method developed, and kindly provided, by Sherrod L. Maxwell (SRNL, Savannah River, USA).

3. Significance of use

This method is a rapid and reliable method for the determination of Sr-90 in large water samples.

4. Interferences

The presence of elemental yttrium in the sample may bias the gravimetric yield determination. If it is suspected that natural yttrium is present in the sample, its concentration should be determined by a suitable means and the yield calculation appropriately modified. The amount of yttrium added, however, is typically much, much higher than any native yttrium in water samples. Y-91 will interfere if present. It is advisable to follow Y-90 decay through repeated measurements. Yttrium must be separated from interfering isotopes of other elements to enable measurement by beta counting. The preconcentration steps reduce interfering isotopes such as K-40, Cs-134, Cs-137 and I-131.The Y-90 separation on DGA,N resin is used to effectively remove K-40, Cs-134, Cs-137, Co-60, Ba-140, La-140, I-131, Sr-89/90 as well as Pb, Bi, U and Th isotopes. Ca is removed on DGA Resin, N along with the La carrier added.

5. Apparatus

- Analytical balance- 0.0001 g sensitivity

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- Centrifuge
- Centrifuge tubes (preferably 500 mL conical tubes)
- Beta detector -gas proportional counter, liquid scintillation or Cerenkov counter
- Counting dishes – GPC option only
- Liquid scintillation vials –PE or glass, e.g. part numbers ME-VIA-PV1 or ME-VIA-GV1 - LSC and Cerenkov option only
- Fume hood
- Heat lamp
- Vacuum Box System- part number AC-24-BOX or AC-12-BOX
- Luer-lock two-way valves – part number AC-12-VALVE
- Cartridge reservoirs-10 mL Cartridge Reservoir, part number AC-25-RV10 or 20 mL Cartridge Reservoir, part number AC-25-RV20
- Stainless steels discs - part number AC-D100-IN25
- Tips, white inner- part number AC-1000-TUBE-PE
- Tips, yellow outer- part number AC-1000-OT
- Filter- 0.45 micron
- Fume hood
- Resolve® filter filtration unit - part number RF-DF25-25PP01– GPC option only
- Hotplate
- Stirring glass rods
- Plastic Petri dishes, 5-1/2 x 1 cm
- Vortex mixer

6. Reagents

a. Reagents

Unless otherwise indicated, all references to water should be understood to mean deionized distilled water. All reagents should be at least of analytical grade.

- Acetone
- Ethanol
- Calcium nitrate (50 mg Ca^{2+} / mL): Dissolve 51.1 g of anhydr. $Ca(NO_3)_2$ in 100 mL of water and dilute to 250 mL with water
- Iron nitrate (50 mg Fe^{3+} / mL): Dissolve 36.2 g of $Fe(NO_3)_3$*$9H_2O$ in 60 mL of water and dilute to 100 mL with water
- Yttrium nitrate (1 mg Y^{3+} / mL): Dissolve 430.8 mg of $Y(NO_3)_3 \cdot 6H_2O$ in 60 mL of water and dilute to 100 mL with water

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- Lanthanum nitrate (10 mg La^{3+} / mL): Dissolve 3.117 g of $La(NO_3)_3 \cdot 6H_2O$ in 60 mL of water and dilute to 100 mL with water
- Cerium nitrate (1 mg Ce^{3+} / mL): Dissolve 309.9 mg of $Ce(NO_3)_3 \cdot 6H_2O$ in 60 mL of water and dilute to 100 mL with water
- Hydrogen peroxide (30%) - H_2O_2
- Ammonium hydroxide - concentrated NH_4OH
- Nitric acid (15.7 M) - concentrated HNO_3
- Hydrochloric acid (12 M) - concentrated nitric acid
- Hydrofluoric acid (28.9 M) – concentrated HF
- Liquid scintillation cocktail – e.g. part number ME-COC-PSHC or ME-COC-GS1 - LSC counting only
- DGA,N Resin- prepacked cartridge, 50-100 µm particle size resin (s grade), part number DN-10- S

b. Preparation of solutions

- 8 M HNO_3: Add 510 mL of concentrated nitric acid to 400 mL of water and dilute to 1 liter with water.
- 0.05 M HNO_3: Add 3.2 mL of concentrated nitric acid to 900 mL of water and dilute to 1 liter with water.
- 3 M HCl: Add 250 mL of concentrated hydrochloric acid to 500 mL of water and dilute to 1 liter with water.
- 3 M HCl: 0.25 M boric acid: Add 250 mL of concentrated hydrochloric acid and15.46g boric acid to 500 mL of water and dilute to 1 liter with water.
- 3 M HCl– 0.25 M HF: Add 250 mL of concentrated hydrochloric acid and 8.65 mL of concentrated hydrofluoric acid to 500 mL of water and dilute to 1 liter with water. Transfer into plastic container.
- 1.5 M HCl: Add 125 mL of concentrated hydrochloric acid to 500 mL of water and dilute to 1 liter with water.
- 0.25 M HCl: Add 21 mL of concentrated hydrochloric acid to 500 mL of water and dilute to 1 liter with water.
- 2 M $Al(NO_3)_3$: 428 g anhydrous aluminium nitrate to 400 mL of water and dilute to 1 liter with water.

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7. Procedure

a. *Sample preparation*

1. If required, filter the sample through a 0.45 micron filter.
2. Aliquot 5 L to 40 L of the sample (or enough to meet required detection limit) into an appropriately sized container.
3. Add 1 mL conc. HCl per L of sample to acidify the sample to pH 2.
4. Add 1 ml of 1 mg/ml yttrium carrier (for yield determination by ICP-MS) and 1 mL of 10 mg/ml lanthanum carrier into each sample.
5. Add 1 mL iron nitrate (50 mg Fe^{3+} / mL) solution per L of sample. Mix sample.
6. Add 1.75 mL conc. ammonium hydroxide (14.5 M) per L of sample while stirring. Supernatant should be ~pH 8.8 – 9. Adjust pH as needed with HCl or NH_4OH. Note time and day as start of Y-90 decay.

⚠ **Note:** The pH should be in the range (<pH 8.8-9) to minimize Ca precipitation. If a slightly different concentrated NH_4OH is used, the volume added should be adjusted accordingly.

7. Mix well. Allow to settle for at least 1 h.
8. Pour or pump off supernatant to approx. 2-4 L.
9. Transfer $Fe(OH)_3$ precipitate into centrifugation tubes (preferably four 500 mL tubes). Centrifuge for 10 min at 2000 rpm. Discard supernatant and replace with fresh aliquot of solution/precipitate. Repeat until all precipitate has been centrifuged, rinsing container with deionized water.
10. Add 100 mL pH 8.8 – 9 water into each tube and shake to dissolve Ca from precipitate. Centrifuge 10 min at 2000 rpm (or higher). Discard supernatant.
11. Add 100 mL 1.5 M HCl into the first tube to dissolve precipitate. Transfer obtained solution into 2nd centrifuge tube to dissolve precipitate. Transfer obtained solution into 3rd tube to dissolve precipitate. Transfer obtained solution into 4th tube to dissolve precipitate. Tube 4 contains the entire $Fe(OH)_3$ precipitate dissolved in 100 mL 1.5 M HCl.

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12. Add 20 mL 1.5 M HCl into 1st tube. Rinse tube and transfer rinsing solution into 2nd tube. Rinse tube and transfer rinsing solution into 3rd tube. Rinse tube and transfer rinsing solution into 4th tube. Repeat two more times fresh 20 mL 1.5 M HCl.
13. Add 1.5 mL Ca carrier solution (75 mg Ca) into 4th tube containing the dissolved precipitate and mix.

⚠ **Important**: The amount of Ca added can be adjusted down to decrease the precipitate size or increased to enhance chemical yield as needed. This will depend on residual Ca which is based on the pH adjustment for the hydroxide precipitation and water rinse. Typically, 75-100 mg Ca is an optimal amount if good Ca removal occurs.

14. Add 50 mL conc. HF and mix well. Allow to sit for 15 min.

⚠ **Remark**: alternatively, NH_4F or NaF might be used

15. Centrifuge for 10 minutes at 2000 rpm. Discard supernatant.

⚠ **Important**: If a LaF_3/CaF_2 precipitate above a volume of ~5-10 Ml occurs, too much Ca may be present. This can occur if the initial hydroxide precipitation pH is higher than pH 9. If this occurs, an option to reduce Ca is to redissolve the precipitate in 100 mL 1.5 M HCl, add 10 mL conc. HF, mix well, wait 10 minutes, centrifuge again and discard supernatant

16. Dissolve residue in 10 mL 3M HNO_3 – 0.25M boric acid and transfer into a 50 ml centrifuge tube. Rinse 500 ml tube with 10 mL conc. HNO_3 , then 10 mL 2M $Al(NO_3)_3$ and transfer rinses to 50 ml tube. Cap and mix well. Centrifuge 5 minutes at 2000 rpm.

⚠ **Note:** The sample may be loaded from the 50 mL tube or transferred to a 100 mL beaker first.

17. In case a solid residue remains, transfer solution into 100 mL beaker. Rinse residue with 3 mL 3 M HNO_3 – 0.25 M boric acid and 2 mL con. HNO_3 and combine rinse with solution step 16.
18. In case there should still be significant residue, rinse residue into glass beaker with 3 mL conc. HNO_3. Add 3 mL 30% H_2O_2 to the sample and evaporate to

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dryness to destroy organic matter. Dissolve residue in 3 mL 3M HNO_3 – 0.25M boric acid and 2 mL conc. HNO_3, warm solution to dissolve residue. Transfer solution into tube/beaker used in step 16.

b. Radiochemical separation

DGA, N resin cartridge preparation

1. Prepare vacuum box following Eichrom method VBS01
2. For each sample to be analyzed place one 2 mL DGA,N cartridge on the vacuum box
3. Connect 20 mL reservoir to each of the cartridges
4. Place appropriately sized beaker or 50 mL centrifuge tube below each cartridge
5. Pipette 5 mL of 8 M HNO_3 into each cartridge, start vacuum and allow solution to drain. Adjust the vacuum pressure to achieve a flow-rate of 1 mL per minute (~1 drop/second)

⚠ **Important:** The flow rates for load and strip solutions should be 1 mL/min; for the rinse solutions 3 mL/min can be used, unless specified otherwise in the step

Yttrium Separation

6. Transfer each redissolved sample (step 17 sample preparation) onto the appropriate DGA,N resin cartridge by pouring or by using a plastic transfer pipette and allow to drain (1 mL/min)
7. Add 5 mL of 8 M HNO_3 to rinse each tube/beaker and transfer each solution into the appropriate DGA,N resin cartridge and allow to drain (1 mL/min)
8. Add 15 mL of 8 M HNO_3 to each cartridge and allow to drain (2 mL/min, Ca removal)
9. Add 20 mL of 0.05 M HNO_3 to each cartridge and allow to drain (~1.5-2 mL/min, La/U removal)
10. Add 15 mL of 3 M HNO_3 – 0.25 M HF to each cartridge and allow to drain (~1.5-2 mL/min, U/Th removal)
11. Add 10 mL of 3 M HCl to each cartridge and allow to drain (~2 mL/min, La/Ca

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removal)

12. Ensure that clean, labelled containers are placed below each cartridge

⚠ **Remark**: For maximum removal of interferences, change column reservoirs and connector tips prior to ^{90}Y elution

13. Pipette 19 mL of 0.25 M HCl into each reservoir and allow to drain to elute the yttrium (1 mL/min or slightly slower). In case of liquid scintillation or Cerenkov counting collect fraction in LSC vial. Adjust volume to exactly 20 mL with 0.25 M HCl

c. Sample measurement

Liquid scintillation counting option

1. Evaporate solution to near dryness. Redissolve in 10 mL 0.1 M HNO_3.
2. Withdraw appropriately sized aliquot from the Y fraction for yield determination via spectrometry
3. Add 10 mL of liquid scintillation cocktail and shake
4. Count sample on liquid scintillation counter. It is advisable to count the sample several times in order to follow Y-90 decay

Cerenkov Counting Option

1. Cap vial and shake to homogenize
2. Withdraw appropriately sized aliquot from the Y fraction for yield determination via spectrometry
3. Count sample on liquid scintillation counter. It is advisable to count the sample several times in order to follow Y-90 decay

Gas Proportional Counting Option

1. Withdraw appropriately sized aliquot from the Y fraction for yield determination via spectrometry
2. Add 100 µL of the Ce carrier solution (100 µg Ce^{3+}) and shake
3. Add 2 mL conc. HF and shake. Allow to sit for 15 min

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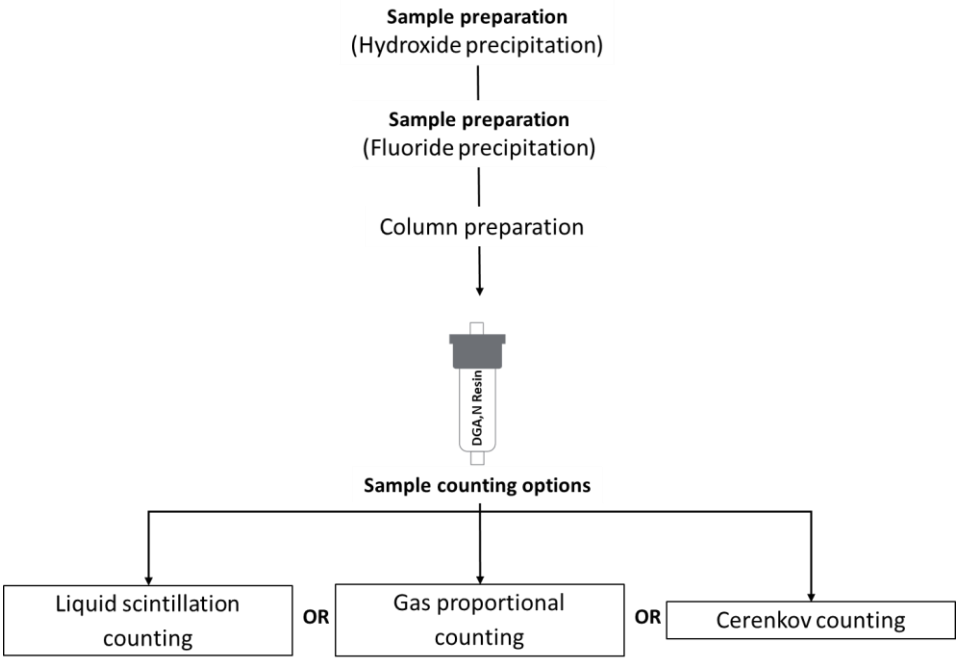
4. Place Resolve® filter filtration unit on yellow outer tip, place on vacuum box. Assure that an empty centrifuge tube (or liner) is placed below the unit. Start vacuum
5. Rinse unit with 2 – 3 mL 95% ethanol. Check for leaks
6. Rinse unit with 2 – 3 mL water
7. Pass solution through filter
8. Rinse centrifuge tube with 5 mL water, transfer onto filtration unit
9. Rinse filter with 2 – 3 mL water, followed by 2 – 3 mL 95% ethanol
10. Stop vacuum. Remove filter from filtration unit, allow to dry and glue on planchet or steel disc

d. Synopsis



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