Direct strontium determination in aqueous samples – Version 1.0 – 14/09/15 - TKI

Summary

1 Scope

This procedure describes a method for the direct separation and measurement of Sr-89 and Sr-90 in aqueous samples (drinking water, mineral water and ground water samples with limited mineral content).

2 Summary of Method

Radioactive strontium is concentrated and separated using TK100 Resin prior to gas proportional counting, liquid scintillation counting or Cerenkov counting. TK100 resin is used to concentrate strontium from 250 – 500 mL aqueous samples and to subsequently separate it from matrix elements and other beta emitters. Stable strontium and/or strontium-85 tracer are used to monitor method yields and correct results to improve precision and accuracy.

3 Significance of Use

This method is a rapid and reliable method for measurement of strontium in aqueous samples.

4 Interferences

4.1 The presence of elemental strontium in the sample may bias the gravimetric yield determination. If it is suspected that natural strontium is present in the sample, its concentration should be determined by a suitable means and the yield calculation appropriately modified.

4.2 Strontium must be separated from interfering isotopes of other elements to enable measurement by beta counting.

4.3 A rinse with 8M HNO_3 is used to effectively remove barium-140, yttrium-90 and potassium-40 isotopes as well as other matrix interference's.

5 Apparatus

5.1 Analytical balance- 0.0001 g sensitivity

5.2 Vacuum box

5.3 Cartridge reservoirs - 20 mL or similar

5.4 Beta detector -gas proportional counter, liquid scintillation or Cerenkov counter

5.5 Counting dishes - 50.8 mm diameter, 6.4 mm deep flat bottom, cupped planchet. – GPC option only

5.6 Liquid scintillation vials

5.7 Fume hood

5.8 Gamma pulse height analyzer - Sr-85 tracer only

5.9 Filter- 0.45 micron

5.10 Fume hood

5.11 Hotplate

5.12 Plastic Petri dishes, 5-1/2 x 1 cm

6 Reagents

6.1 Unless otherwise indicated, all references to water should be understood to mean deionized distilled water.

6.2 Acetone

6.3 Nitric acid (15.7 M)- concentrated HNO_3 (sp gr 1.42)

6.4 Ethyl alcohol -USP, 100%

6.5 Liquid scintillation cocktail (LSC counting only)

6.6 Nitric acid (15.7M) - concentrated nitric acid

6.7 Nitric acid solution (0.01M) - Add 0.64 mL of concentrated nitric acid (sp gr 1.42) to 950 mL of water and dilute to 1 liter with water.

6.8 Nitric acid solution (0.05M) - Add 3.2 mL of concentrated nitric acid (sp gr 1.42) to 900 mL of water and dilute to 1 liter with water. For gravimetric yield determination only.

6.9 Hydrochloric acid (12M) - concentrated hydrochloric acid

6.10 Hydrochloric acid (2M) -Add 167 mL of concentrated HCl to 800 mL of water and dilute to 1 liter with water.

6.11 Nitric acid solution (8M) - Add 510 mL of concentrated nitric acid (sp gr 1.42) to 400 mL of water and dilute to 1 liter with water.

6.12 TK100 Resin -prepacked 2mL column (~ 0.7 grams resin), or smaller particle size (50-100 mm) in appropriate size column. Pre-packed cartridges may also be used. Refer to VBS01, Setup and Operation Instructions for Eichrom's Vacuum Box System (VBS)

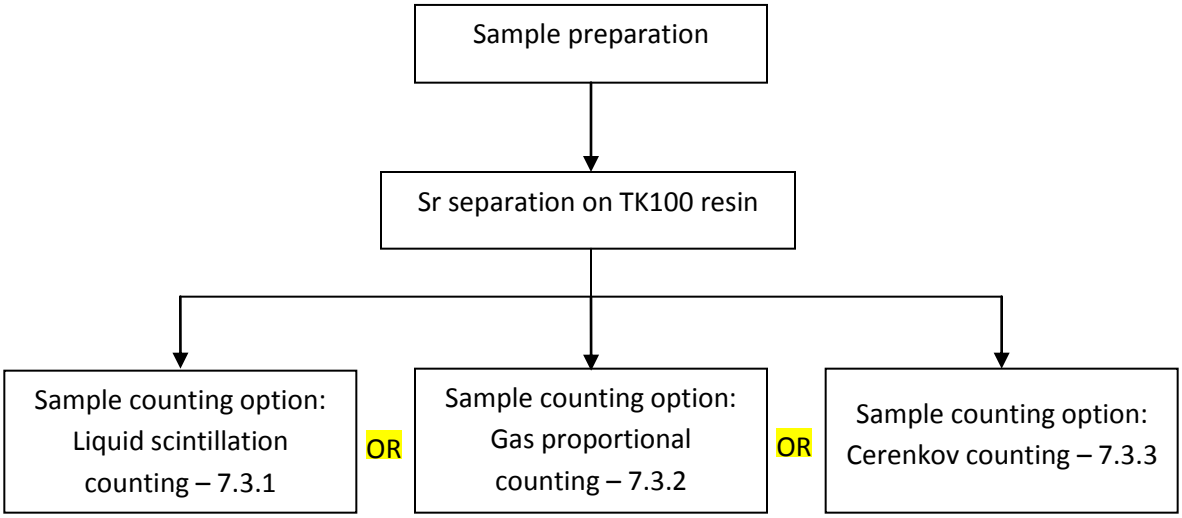
6.13 Sr-85 tracer and/or standards

6.14 Strontium (Sr) carrier (5 mg/mL), gravimetric - Dissolve 12.1 grams $Sr(NO_3)_2$ in water and dilute to 1 liter with water.

Note: In case of spectrometric yield determination concentration of the Strontium carrier solution can be adjusted to lower quantities of Sr.

7 Procedure

7.1 Synopsis



7.2 Strontium Separation using TK100 Resin:

7.2.1 If samples larger than 250 – 500 mL are analyzed, evaporate the sample to approximately 500 mL.

7.2.2 Measure the sample volume using a standard graduated cylinder (or equivalent) and transfer volume to an appropriate size plastic bottle or volumetric flask.

7.2.3 If necessary filter the sample

7.2.4 Acidify the sample to pH 2 using concentrated nitric acid.

Note: Alternatively the sample can be loaded without acidification (pH ≤ 8)

7.2.5 Add 1 ml of 5 mg/ml strontium carrier (for gravimetric yield determination option, for spectrometric yield determination lower amounts may be added) or strontium-85 tracer (for gamma and LSC "3 window method" yield determination option) into each sample aliquot.

7.2.6 Place columns or cartridges on vacuum box. Attach suitable reservoirs.

7.2.7 Ensure that a suitable container is below each column/cartridge.

7.2.8 Add 5 ml of 0.01 M HNO_3 to each column/cartridge to condition resin.

7.2.9 Adjust flow rate to 5 - 10 mL/min.

7.2.10 Load each sample onto the appropriate column and allow to drain.

7.2.11 Add 20 ml of 8 M HNO_3 to each column to rinse.

7.2.12 Discard the feed and rinse solutions collected.

7.2.13 Place fresh LSC vial below each column/cartridge.

7.2.14 Add 15 ml of 2 M HCl to each column to elute strontium.

Note: Alternatively 0.1M EDTA solution might be used, however Pb-210 present on the column/cartridge might be co-eluted

7.2.15 Cap and shake Sr eluate for homogenization.

7.3 Sample preparation for counting

7.3.1 Liquid scintillation counting option:

7.3.1.1 Case of yield determination via Sr-85 (γ or LSC "3 window method"):

7.3.1.1.1 Withdraw 10 mL and transfer into fresh LSC vial

7.3.1.1.2 Add 10 mL of liquid scintillation cocktail to the withdrawn aliquot, cap and shake

7.3.1.1.3 Count sample on liquid scintillation counter using 2 or 3 window method. It is advisable to count the sample several times over time in order to follow Y-90 ingrowth.

7.3.1.2 Case of yield determination via spectrometry (ICP-MS, AAS,…):

7.3.1.2.1 Homogenize eluate and withdraw appropriate sample aliquot for yield determination by spectrometry, then withdraw a 10 mL aliquot and transfer into fresh LSC vials

7.3.1.2.2 To the withdrawn aliquot add 10 mL of liquid scintillation cocktail, cap and shake

7.3.1.2.3 Count sample on liquid scintillation counter using 2 or 3 window method. It is advisable to count the sample several times over time in order to follow Y-90 ingrowth.

7.3.1.3 Case of yield determination via gravimetry:

7.3.1.3.1 For each sample analyzed, clean a counting dish by moistening a paper towel with ethanol, wiping the dish and letting it dry.

7.3.1.3.2 Weigh the counting dish(s) on an analytical balance and record the weight.

7.3.1.3.3 Place each counting dish on a hot plate under a heat lamp in a hood.

7.3.1.3.4 Evaporate the eluate from 7.2.14 onto each dish in successive 3 mL volumes.

7.3.1.3.5 Allow each 3 mL volume to evaporate to near dryness between additions.

7.3.1.3.6 Rinse the vial containing the column strip solution with 2 mL of 0.05M HNO_3 and transfer to the counting dish.

7.3.1.3.7 After all the solution has evaporated to dryness, cool each dish.

7.3.1.3.8 Reweigh each counting dish, and record the weight.

7.3.1.3.9 Redissolve residue in 4 mL 0.05M HNO_3, transfer solution into LSC vial

7.3.1.3.10 Rinse dish two times with 3 mL 0.05M HNO_3, transfer solution into LSC vial

Note: Alternatively the Sr can be precipitated as $SrCO_3$ and filtered using a weighed filter. The filter is then dried and weighed, the weight is recorded. The $SrCO_3$ precipitate is redissolved in 10 mL 0.05M HNO_3.

7.3.2 Gas Proportional Counting Option:

Note: Gas proportional counting provides lower detection limits than liquid scintillation counting or Cerenkov counting.

7.3.2.1 For each sample analyzed, clean a counting dish by moistening a paper towel with ethanol, wiping the dish and letting it dry.

7.3.2.2 Weigh the counting dish(s) on an analytical balance and record the weight.

7.3.2.3 Place each counting dish on a hot plate under a heat lamp in a hood.

7.3.2.4 Evaporate the eluate from 7.2.14 onto each dish in successive 3 mL volumes.

7.3.2.5 Allow each 3 mL volume to evaporate to near dryness between additions.

7.3.2.6 Rinse the vial containing the column strip solution with 2 mL of 0.05M HNO_3 and transfer to the counting dish.

7.3.2.7 After all the solution has evaporated to dryness, cool each dish.

7.3.2.8 Reweigh each counting dish, and record the weight.

7.3.2.9 Count samples sufficient time to achieve the desired counting statistics and minimum detectable concentration.

7.3.2.10 After total strontium has been counted, set planchets aside in a safe place during the Y-90 ingrowth period.

Note: Alternatively Y-90 can be eluted from the TK100 column after sufficient ingrowth time with 8M HNO_3 and measured directly

7.3.3 Cerenkov Counting Option:

Note: This option gives somewhat poorer detection limits because of the relatively higher backgrounds of Cerenkov counting. However, it is fast and has virtually no interference between Sr-89 and Sr-90. It has been reported that high ratios of Sr-89/Sr-90 may cause a high bias with the gas proportional counting option. It is advisable to use the Cerenkov counting option in these cases.

7.3.3.1 Pour the column strip solution from step 7.2.14 into the Cerenkov counting vial.

7.3.3.2 Count the samples sufficient time to achieve the desired counting statistics and minimum detectable concentration.

Note: Only Sr-89 is counted here. In order to obtain information on the Sr-90 activity of the sample perform additional measurements over time to follow Y-90 ingrowth. Alternatively Y-90 can be eluted from the TK100 column with 8M HNO_3 after sufficient ingrowth time and measured by Cerenkov counting directly.

7.3.3.3 Measure a blank vial before and after each sample group.

7.3.3.4 Determine yield via γ-counting, spectrometry or gravimetry as described in 7.3.1.1 - 3

7.3.4 Gamma Counting of Strontium-85 Tracer Option:

7.3.4.1 Measure the Sr-85 on the counting dish or in the Sr strip solution using gamma pulse height analysis after counting the sample for beta activity.

7.3.4.2 Count the samples sufficient time to achieve the desired counting statistics (typically <5% rsd).

8 Preparation of Pure Sr-90 and Pure Y-90 for Counter Calibration Sources:

8.1 Add an appropriate volume of calibrated Sr-90 standard solution (in equilibrium with Y-90) to a small beaker, add 1 mL of Sr carrier and evaporate the solution to dryness.

8.2 Redissolve the residue in 5 mL of 8M HNO_3.

8.3 Place a beaker below each column.

8.4 Pipette 5 mL of 8M HNO_3 into each TK100 column to condition resin and allow to drain.

8.5 Ensure that a clean beaker or vial is below the column.

8.6 Transfer the redissolved residue into the appropriate TK100 Resin column by pouring or by using a plastic transfer pipette and allow to drain.

8.7 Add 5 mL of 8M HNO_3 to rinse to the beaker and transfer each solution into the TK100 Resin column and allow to drain.

8.8 Repeat step 8.7.

8.9 Add 5 mL of 8M HNO_3 to the TK100 Resin column and allow to drain.

8.10 Add 15 mL of 2M HCl to the column to strip the Sr-90.

8.11 Prepare the Sr-90 from step 8.10 as appropriate for use as a calibration standard (evaporation on planchet, etc.).

8.12 Prepare the Y-90 in the load plus rinse solutions (steps 8.6 to 8.9) as appropriate for use as a calibration standard.

9 REFERENCES

(1) Banavali, A.D., et al., "Strontium-89/90 Analysis by Eichrom Column Chemistry and Cerenkov Counting," 38th Annual Conference on Bioassay, Analytical and Environmental Radiochemistry. Santa Fe, NM, November, 1992.

(2) Nelson, D.M, "Purification of Strontium in Water before Strontium-89/Strontium-90 Measurement," DOE Methods Compendium, RP500.

(3) Jake Surman, Jackie Pates, Hao Zhang and Steffen Happel: "Development of a new resin for the rapid determination of strontium-90 in environmental waters", oral presentation at the INTERNATIONAL SYMPOSIUM ON ENVIRONMENTAL RADIOACTIVITY, PLYMOUTH (UK), 4-5 September, 2012

(4) J.J.Surman, J.M.Pates, H.Zhang, S.Happel: "Development and characterization of a new Sr selective resin for the rapid determination of 90Sr in environmental water samples", Talanta, 129 (2014) 623–628