RESL TECHNICAL PROCEDURE

CHEM-TP-SR.1

DETERMINATION OF STRONTIUM-90 IN SOIL, WATER, AND FILTER SAMPLES

Preparer: D.S.	Date 1-28-98	Independent Review:	Date 4-21-98
ES&H Review:	Date 2/2/98	RadCon Review: R. Scovill	Date 2/2/98
QA Review:	Date 1/28/98	Supervisor Approval: M. Marlette	Date 4/21/98

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PURPOSE

The purpose of this procedure is to describe a method for determination of strontium-90 in a variety of sample types. The method uses total sample dissolution and will handle samples that contain abnormally high concentrations of calcium. The detection limits for 1 g solid and 150 mL liquid samples are 0.5 pCi/g and $3*10^{-3}$ pCi/mL respectively. The accuracy of the determination is as good as the precision of the measurement of the specific sample will allow. If greater sensitivity is required, which is unnecessary except for very special situations, the procedure can be scaled up to 10 g samples of soil and 2-L water samples. The reagents on the sample dissolution of solids should be scaled up by a factor of ten, the strontium carrier and the EDTA by a factor of four. The large water samples should be evaporated to small volumes, transferred to platinum dishes, taken to dryness and dissolved as 10 g soil samples.

APPLICABILITY

This procedure is applicable to soil, water, air filters and a variety of other sample types.

RESPONSIBILITIES

RESL staff responsible for implementing this procedure are:

Analysts

DEFINITIONS

None.

PROCEDURE

1 **ABSTRACT** One gram of soil is dissolved in potassium fluoride and pyrosulfate fusions to guarantee total sample dissolution. The pyrosulfate cake is dissolved and strontium precipitated as the sulfate. For water samples, the strontium is separated from the bulk of the solution by direct precipitation as the sulfate. Air filter and organic samples are wet ashed and then treated as soil samples. The strontium sulfate is dissolved in EDTA and reprecipitated to separate yttrium-90, other lanthanides and the actinides. The strontium sulfate is redissolved in EDTA, and set aside for yttrium-90 ingrowth. After ingrowth, the yttrium is precipitated as the hydroxide, dissolved in hydrochloric acid, and precipitated as the oxalate. The oxalate is filtered on a glass fiber filter paper and counted in a low background beta counter. Overall chemical yields are better than 96% for yttrium and better than 90% for strontium depending on the concentration of calcium in the sample.

This procedure is a modified version of that written by others (*Martin*), giving higher yields and shorter analysis time.

2 SAFETY PRECAUTIONS

2.1 Follow laboratory safety addressed in ABC-AP-02 and ACB-AP-04.

2.2 Wear proper eye protection (ACB-AP-03).

2.3 Refer to ACB-AP-06 when handling perchloric acid, a strong acid and a powerful oxidizing agent.

2.4 Dispose of all wastes into appropriate satellite accumulation containers.

2.5 Conduct work in accordance with the requirements of the radiation work permit.

3 REAGENTS

3.1 **Sodium Ethylenediaminetetraacetate, 0.25M (EDTA)** Dissolve 73 g of ethylenediaminetetraacetic acid in 50 mL of 50% NaOH and ~500 mL of water. Dilute to 1 L with water and adjust the pH to 11.1. Filter through a 0.45 µM DM-450 membrane filter (Gelman Sciences Ann Arbor, MI).

3.2 **Lithium Sulfate 10%** Add 50 mL of concentrated sulfuric acid to a 1-L polypropylene (PP) bottle containing 200 mL of water. Dissolve 76.4 g of lithium hydroxide monohydrate in 700 mL of water in a 1-L beaker. Add the lithium hydroxide solution to the sulfuric acid solution. Swirl the solution to mix thoroughly. Alternatively, if anhydrous lithium sulfate is available, then add 100 g anhydrous lithium sulfate and dilute to 1 L with water.

3.3 **Strontium Carrier, 100 mg/mL** Add 300 mL of water to a 1-L Erlenmeyer flask containing 85.1 g of reagent grade strontium carbonate. While swirling the solution continuously, slowly add concentrated nitric acid until the strontium carbonate has dissolved. This will take ~90 mL. Transfer the solution quantitatively to a volumetric flask, dilute to 500 mL with water. Transfer the solution to two 250-mL glass bottles with polyethylene lined screw caps.

3.4 **Strontium Carrier, 5 mg/mL** Dilute 5 mL of the 100 mg/mL strontium carrier to 100 mL with 1% nitric acid.

3.5 **Yttrium Carrier, 10 mg/mL** Dissolve 6.356 g of 99.9% Y_2O_3 in 20 mL of hot concentrated HNO_3 and dilute to 500 mL with water in a volumetric flask. Transfer the solution to two 250-mL glass bottles with polyethylene lined screw caps.

3.6 **Strontium Tracer** Prepare a solution of Sr^{85} in 1% HNO_3 at an activity of ~10^4 cpm/mL.

3.7 **Sodium Hydroxide, 50%** Dissolve 500g of solid sodium hydroxide pellets in 750 mL of water in a 2-L beaker. Dilute to a final volume of 1 L and transfer to a 1-L PP bottle.

3.8 **Bromocresol Green, 0.04% (BCG)** Dissolve 40 mg of the sodium salt of bromocresol green in 100 mL of water.

3.9 **Thymol Blue, 0.04% (TB)** Dissolve 40 mg of the sodium salt of thymol blue in 100 mL of water.

3.10 **Nitric Acid, 4M** Dilute 250 mL of concentrated nitric acid to 1 L with water.

3.11 **Oxalic Acid, 2%** Dissolve 10 g of oxalic acid in 500 mL of water in a 500-mL wash bottle.

3.12 **Lithium Sulfate, 5%** Dilute 250 mL of 10% lithium sulfate to 500 mL with water in a 500-mL wash bottle.

3.13 **Sodium hydroxide, 0.25M** Dilute 10 mL of 50% sodium hydroxide to 500 mL in a 500-mL wash bottle.

4 WEIGHING FACTOR FOR YTTRIUM OXALATE

4.1 To a 50-mL conical polymethylpentene (PMP) centrifuge tube, add 5 mL of 4M HNO_3, 1 mL of 10 mg/mL yttrium carrier, 5 mL of 5% oxalic acid, three drops of 0.04% TB, and dilute to 20 mL with water.

4.2 Swirl the solution until thoroughly mixed.

4.3 Add concentrated NH_4OH dropwise until the red color of the indicator just fades to pink (pH 2).

4.4 Heat the solution in a boiling water bath for five minutes, cool, and filter on a well washed, tared 25-mm glass fiber filter paper in an all glass filtering chimney.

4.5 Wash the precipitate with 5 mL of 2% oxalic acid at a pH of 2, then with 5 mL of acetone.

4.6 Dry the precipitate at a distance of ~4" from a 250-watt infrared lamp for five minutes and weigh.

4.7 Several aliquots of the yttrium carrier solution should be taken through the procedure to determine the reproducibility of the weighing form that will be used to determine the yttrium yield. Work with Y^{88} has shown the yield of yttrium oxalate in the procedure listed above to be 99.93 ± 0.02%. With complete recovery, the weight obtained with 10 mg of yttrium carrier should be very close to the theoretical values of 34 mg for yttrium oxalate nonahydrate. Use the weight of the experimentally determined weighing form to correspond to 100% yield. This will alleviate any inaccuracies in concentration that occurred in making the carrier solution. If there is any question as to the completeness of the precipitation, Y^{88} should be used and the minor fraction counted to determine a yttrium yield that will be used to calculate the weight of the oxalate precipitate that corresponds to 100% yield.

5 DETERMINATION OF COUNTING EFFICIENCY FOR YTTRIUM-90 ON YTTRIUM OXALATE

5.1 To a 50-mL conical PMP centrifuge tube, add 5 mL of 4M nitric acid, 1 mL of 10 mg/mL yttrium carrier, 1.0 mL of 5 mg/mL strontium carrier, 1 mL of a standard solution of Sr^{90} at an activity of $.3*10^4$ dpm/mL, 5 mL of 5% oxalic acid, three drops of 0.04% TB, and dilute to 20 mL with water.

5.2 Swirl the centrifuge tube to mix the solution thoroughly and add concentrated ammonium hydroxide dropwise until the red color of the indicator just fades to pink (pH 2).

5.3 Record the time as the beginning of the Y^{90} decay.

5.4 If the indicator endpoint is overshot and a yellow solution is obtained, quickly add hydrochloric acid dropwise to the first permanent pink color. If more than three drops of hydrochloric acid had to be added, strontium oxalate might have precipitated, contaminating the yttrium oxalate. Discard the solution and start over.

5.5 Heat the solution in a boiling water bath for five minutes, cool, and centrifuge for five minutes. Decant and discard the supernate.

5.6 Wash the precipitate with a forceful jet of 5 mL of a 2% solution of oxalic acid directed from a wash bottle. Centrifuge, decant and discard the supernate.

5.7 Flip the centrifuge tube sharply to break up the packed precipitate and add 5 mL of 4M nitric acid. Heat in a boiling water bath until the precipitate has dissolved.

5.8 Cool the solution in a bath of cold, running tap water and add 5 mL of 5% oxalic acid, three drops of TB, and dilute to 20 mL with water. Precipitate yttrium oxalate with ammonium hydroxide at a pH of 2.

5.9 Mount the strontium-free yttrium oxalate nonahydrate precipitate on a tared 25-mm glass fiber filter paper in an all glass filtering chimney. Wash the precipitate with 5 mL of 2% oxalic acid and then with 5 mL of acetone.

5.10 Dry the precipitate at a distance of ~4" from a 250-watt infrared lamp for five minutes.

5.11 Weigh the precipitate to determine the yttrium yield. Count the mounted precipitate in the low background beta counter to determine the counting efficiency of Y^{90} as 34 mg of yttrium oxalate nonahydrate.

5.12 Record the time at which half of the counting time has elapsed as the end of the Y^{90} decay.

6 SOIL SAMPLES

6.1 To one gram of soil in a 60-mL platinum dish, add 0.5 mL of HNO_3 and 0.5 mL of HF. Prewetting the soil with water may be necessary if the evolution of CO_2 is vigorous enough to cause some loss of the sample due to spraying.

6.2 After the evolution of CO_2 has ceased, add 1 mL of 100 mg/mL Sr carrier and 1 mL of Sr^{85} tracer.

6.3 Add an identical 1-mL aliquot of tracer to a counting bottle containing 20 mL of 1% HCl to serve as a standard.

6.4 Heat the platinum dish on the hot plate until the soil is almost dry, taking care not to lose any tracer by splattering.

6.5 Cool, and add 2 g of anhydrous potassium fluoride and 1.3 g of potassium hydrogen fluoride.

6.6 Mix the potassium fluorides and soil thoroughly with a Teflon stirring rod.

6.7 Place the dish on a ring stand and fuse over the full heat of a Fisher blast burner until a clear melt is obtained.

6.8 Cool the melt to room temperature and add 4 mL of H_2SO_4 slowly and with enough cooling to prevent the solution from frothing over the sides of the dish. When the dissolution becomes vigorous enough for the solution to froth over the sides of the dish, cool the dish in a bath of cold running water until the reaction slows, then reheat. When most of the cake has dissolved, the vigorous reactions will subside enough so that the dish can be placed on the full heat of the bare hot plate.

6.9 Heat the dish on a hot plate until the potassium fluoride cake has dissolved and the transposition has been completed.

6.10 After all of the potassium fluoride cake has transposed, add 2 g of anhydrous Na_2SO_4, swirl to mix and heat over a small flame of the blast burner until the evolution of sulfuric acid fumes have slowed and a clear red pyrosulfate fusion is obtained.

6.11 Remove the dish from the heat and swirl the melt high onto the sides of the dish until the melt solidifies. Cool the cake to room temperature. **Note:** *Do not quench the dish in cold water. This practice will decrease the life of the platinum dish.*

6.12 To remove the cake from the dish, gently flex the sides of the dish, this will fracture the cake and with minor tapping the cake will release itself from the dish.

6.13 Dissolve the pyrosulfate cake in a boiling solution of 50 mL of water, 5 mL of concentrated HCl, and 6 g of anhydrous lithium sulfate in a 250-mL Erlenmeyer. **Note:** *Strontium and barium sulfates will precipitate at this point, but most of the calcium will remain in solution.*

6.14 Continue to boil the solution for fifteen minutes to hydrolyze condensed phosphates. Continue under SEPARATION OF STRONTIUM SULFATE (Section 10).

7 WATER SAMPLES

7.1 Add 500 mL of the water sample and 1 mL of 0.04% TB to a 1-L beaker. If the solution is blue or yellow, add concentrated nitric acid to the red endpoint of the indicator. If the solution is red, continue with the next step.

7.2 Add 5 mL of nitric acid, 1 mL of the 100 mg/mL strontium carrier and 1 mL of Sr^{85} tracer.

7.3 Add an identical 1-mL aliquot of tracer to a counting bottle containing 20 mL of 1% nitric acid to serve as a standard.

7.4 Evaporate the solution to ~ 100 mL and transfer it quantitatively to a 250-mL Erlenmeyer flask.

7.5 Evaporate the solution to ~50 mL.

7.6 Add 6 g of anhydrous lithium sulfate. Boil the solution for 10 minutes.

7.7 Continue under SEPARATION OF STRONTIUM SULFATE (Section 10).

8 ORGANIC AIR FILTERS

8.1 Transfer up to one four inch filter paper to a 250-mL Erlenmeyer flask. Add 1 mL of strontium carrier, 1 mL of Sr^{85} tracer, 10 mL of H_2SO_4 and 10 mL of HNO_3 acid.

8.2 Add an identical 1-mL aliquot of tracer to a counting bottle containing 20 mL of 1% HCl to serve as a standard.

8.3 Heat the Erlenmeyer on a hot plate until the nitric acid has oxidized the easily oxidizable organic material.

8.4 Continue to heat until the excess nitric acid has been driven off and the sulfuric acid has charred the filter paper.

8.5 While swirling the flask, add 1 mL of nitric acid to oxidize the charred organic matter. After the reaction subsides, repeat the 1 mL additions of nitric acid until the solution has either lightened in color or until the nitric acid has no more effect on oxidizing the filter.

8.6 Repeat Steps 8.4-8.5 until the solution no longer chars when fumed with sulfuric acid.

8.7 Add 1 mL of perchloric acid dropwise to the hot concentrated sulfuric acid to oxidize the remaining hard to oxidize organic material.

CAUTION!! ***If the perchloric acid is added while the solution still contains carbon or while the solution is very dark in color a VERY vigorous reaction or EXPLOSION can result!! Never add perchloric acid to a sample without first pretreating the sample extensively with nitric acid. Use perchloric acid only as a last resort to oxidize the most difficult to oxidize organic material, and only after extensive treatment of repeatedly charring with sulfuric acid and then oxidizing with nitric acid!***

8.8 Evaporate the sulfuric acid to .5 mL and transfer the solution quantitatively to a 60-mL platinum dish.

8.9 Evaporate the solution to dryness and proceed with the soil procedure.

9 GLASS FIBER FILTERS

Treat as a one gram soil sample (Section 6).

10 SEPARATION OF STRONTIUM SULFATE

10.1 Transfer the precipitated solution to a 100-mL glass centrifuge tube with a 5% solution of lithium sulfate and centrifuge five minutes. Decant and discard the supernate.

10.2 Wash the precipitate with 5% lithium sulfate and centrifuge for five minutes. Discard the wash.

10.3 Add 10 mL of 0.25M EDTA, three drops of TB and heat in a boiling water bath until the precipitate has dissolved completely.

10.3.1 If the solution fades from blue during the dissolution, add 50% sodium hydroxide dropwise to the blue endpoint of the TB.

10.3.2 In a sample that contains a high concentration of calcium, more EDTA will have to be used to dissolve the entire precipitate. Do not use more EDTA than is necessary to dissolve the precipitate completely or a loss of strontium will result.

10.3.3 If ferric hydroxide precipitates, and after all of the sulfate precipitate has been dissolved, centrifuge and decant the solution to another 100-mL centrifuge tube. Discard the hydroxide precipitate.

10.4 Swirl the solution, and add 10 mL of 10% lithium sulfate and three drops of bromocresol green (BCG).

10.5 Add HCl dropwise until the solution turns green, then add .3 mL of glacial acetic acid to the yellow end point of the bromocresol green to precipitate strontium sulfate (pH of 4). Record this time as the start of the Y^{90} ingrowth.

10.5.1 If the acidity of the solution is increased much further, calcium sulfate will precipitate with the strontium sulfate and might not dissolve in the limited amount of EDTA in the subsequent dissolution. If the pH of the solution is much higher than four, the strontium sulfate will be precipitated incompletely. If there is any question as to the completeness of precipitation, decant the supernate into a counting bottle and count before discarding.

10.6 Heat the precipitated solution in a boiling water bath for five minutes, cool, and centrifuge at 2000 rpm. Decant and discard the supernate.

10.7 Add 1 mL of 10 mg/mL yttrium carrier to the $SrSO_4$ precipitate. Swirl the centrifuge tube to suspend the precipitate, add 10 mL of 0.25M EDTA, three drops of thymol blue, and 50% sodium hydroxide dropwise to the blue endpoint of the indicator.

10.8 Place the centrifuge tube in a bath of boiling water for five minutes to dissolve the precipitate completely.

10.9 Cool the solution in a cold water bath, and transfer it quantitatively to a counting bottle. Adjust the height of the sample with water to the same height as that of the standard.

10.10 Count the solution and the Sr^{85} standard to determine the strontium yield.

10.11 Transfer the solution to a 50-mL PMP centrifuge tube, seal the top of the tube with parafilm to prevent evaporation and set aside for at least five days to permit Y^{90} to ingrow to .75% of equilibrium with the Sr^{90}.

10.12 After Y^{90} ingrowth add two 2.5 g portions of KOH. Heat in a boiling water bath for fifteen minutes to ensure complete precipitation of yttrium hydroxide. Record this time as the end of the Y^{90} ingrowth.

10.13 Centrifuge the solution for five minutes while still hot. Decant the supernate into a counting vail (storage of the strontium fraction permits remilking the solution for a second set of Y^{90} counts if necessary).

10.14 Wash the precipitate with 10 mL of 0.25M sodium hydroxide. Centrifuge, decant and discard the wash.

10.15 Dissolve the hydroxide precipitate in 5 mL of 4M nitric acid.

10.16 Swirl the solution and add three drops of thymol blue and 5 mL of 5% oxalic acid. Add NH_4OH dropwise with swirling to the last shade of pink, but not to the yellow endpoint of the indicator (pH 2).

10.17 Heat in a boiling water bath for five minutes, cool, and centrifuge for five minutes. Decant and discard the supernate.

10.18 Add 5 mL of 4M HNO_3 to the centrifuge tube to dissolve the yttrium oxalate.

10.19 Add 5 mL of 5% oxalic acid and three drops of thymol blue.

10.20 Add NH_4OH dropwise to the pink endpoint of the indicator to reprecipitate yttrium oxalate.

10.21 Heat the precipitated solution in a boiling water bath for five minutes. Cool, and filter the precipitate on a well washed, tared, 25-mm glass fiber filter paper in an all glass filtering chimney.

10.22 Wash the precipitate with 5 mL of 2% oxalic acid at a pH of 2 followed by 5 mL of acetone.

10.23 Dry the precipitate at a distance of 4" from a 250-watt infrared lamp for five minutes.

10.24 Weigh the dried filter paper to determine the yttrium yield.

10.25 Mount the filter paper in a sample holder and count in a low background beta counter for a time long enough to obtain the statistical precision desired. Record the time at which half of the count time has elapsed as the end of the Y^{90} decay.

REFERENCES

D. B. Martin, *Anal. Chem.*, 51, 1968-72 (1979)

C. W. Sill, D. S. Sill, Determination of Alpha Emitters in Soil, EG&G Idaho Inc., Idaho Falls, Idaho 83415 (1994)

RESL-TP-IH.2 General Laboratory Safety
RESL-TP-IH.1 Eye Protection Requirements
RESL-TP-IH.4 Handling of Corrosive Chemicals
RESL-TP-IH.6 Handling Perchloric Acid
RESL-TP-IH.9 Handling Hydrofluoric Acid

QUALITY RECORDS

None.

Attachment 1
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CALCULATIONS

Sr-90, uCi/g = (Y-YB)/(CTY*CEY*g*SY*YY*YG*YD*2.22 E6)

$$S^2 \text{Sr-90} = \text{SQR}(A^2+B^2+C^2+D^2+E^2+F^2+G^2)*\text{Sr-90}^2$$

Where: A = SQR(Y+YB)/(Y-YB)
B = SCEY/CEY
C = SG/g
D = SSY/SY
E = SYY/YY
F = SYG/YG
G = SYD/YD

And: Y = Gross counts of Y-90
YB = Background of Y-90
CTY = Count time
g = Sample size
SG = Standard deviation of the sample size
SY = Strontium Yield
SSY = St. Dev. of SY
YY = Yttrium yield
SYY = St. Dev. of YY
YG = Yttrium growth = 1-exp-(Ln 2 * T1/64)
SYG = Standard Deviation YG = $(\text{Ln } 2 * T1/64) * \text{SQR}((ST1/T1)^2 + (.1/64)^2)$
YD = Yttrium decay = exp-(Ln 2 * T2/64)
SYD = Standard Deviation of YD = (Ln 2 * T2/64) *SQR((ST2/T2)2 + (.1/64)2)
T1 = Time of Y-90 ingrowth in hours
ST1 = Standard Deviation of T1
T2 = Time of Y-90 decay in hours
ST2 = Standard Deviation of T2
CEY = counting efficiency of Y-90 on yttrium oxalate
SCEY = Standard Deviation of CEY
SQR( )= square root of the quantity in the ( )
exp-( ) = the antilog of minus the quantity in the ( )