

Determination of Thorium in Drinking Water
Method 910

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DETERMINATION OF THORIUM IN DRINKING WATER

1. Scope and Application

- 1.1 This method covers the measurements of total alpha and/or beta emitting isotopes of thorium.
- 1.2 Because of its low specific activity, natural thorium (232) is determined by a colorimetric method using arsenazo III reagent.

2. Summary of Method

- 2.1 An acidified aliquot of the sample is heated to boiling. Other actinide elements after adjustment of the valence state using sodium nitrite and thorium are coprecipitated and concentrated on ferric hydroxide at a high pH. Thorium is purified by selective solvent extraction techniques using tri-isooctyl amine (TIOA) and trioctyl phosphine oxide (TOPO). Thorium is coprecipitated on aluminum hydroxide to remove sulfate interferences prior to the color development of the thorium-arsenazo complex. After the colorimetric assay, the thorium is coprecipitated on lanthanum fluoride for radiometric measurement.

3. Sample Handling and Preservation

- 3.1 Samples should be analyzed as soon as possible after collection.
- 3.2 For storage, samples should be acidified with 5 mL of concentrated hydrochloric acid.

4. Interference

- 4.1 Lanthanum carrier contains interfering alpha activity to varying degrees. This activity should be determined and the carrier rejected if the associated alpha activity exceeds 0.2 alpha cpm per milligram of lanthanum.
- 4.2 Measurement for the isotope 234 should be made as soon as possible after the colorimetric analysis as beta activity associated in the decay of thorium 228 will cause high results.
- 4.3 Sulfates and nitrate reduce the intensity of the thorium-arsenazo color and should be removed.

5. Apparatus

- 5.1 Gas flow proportional counting system, low background beta counting system, or scintillation detection system.
- 5.2 Spectrophotometer operating at 665 m μ and having a near infrared filter (NIR).

5.3 Hot plates

5.4 Separatory funnels, 60 mL

5.5 Large millipore glass filtering apparatus and 47 mm 0.45 μ polyvinyl chloride (PVC) membrane filters.

5.6 Stainless steel planchets, 2 inch diameter

5.7 Aluminum foil for absorber material.

5.8 Glassware and drying ovens.

5.9 Centrifuge

5.10 Microliter pipet, adjustable 100-1000 μ L.

6. Reagents

6.1 Acetone-alcohol solution - Mix equal volume of acetone and 95% ethanol.

6.2 Aluminum carrier, 5 mg/mL. Dissolve 2.5g aluminum metal in 380 mL of 6N HCl in a 500 mL volumetric flask. Cool and dilute to volume with water. Mix thoroughly and filter.

6.3 Arsenazo III reagent, 0.02%. Dissolve 20 \pm 1 mg arsenazo III reagent in 100 mL of water.

6.4 Cyclohexane, reagent grade.

6.5 Ferric chloride, 20 mg/mL. Dissolve 9.6 g of FeCl₃ · 6H₂O into 75 mL of 0.1N HCl in a 100 mL volumetric flask. Dilute to volume with 0.1N HCl.

6.6 Hydrochloric acid, 8N Add 670 mL concentrated HCl to 300 mL water, cool and dilute to 1000 mL with water.
- 7N Dilute 350 mL of 8N HCl to 400 mL with water.
6N Dilute 150 mL of 8N HCl to 200 mL with water.
4N Dilute 200 mL of 8N HCl to 400 mL with water.
0.5N Dilute 25 mL of 4N HCl to 200 mL with water.
0.1N Dilute 5 mL of 4N HCl to 200 mL with water.

6.7 Hydrofluoric acid, 48%.

6.8 Lanthanum carrier - 5 mg/mL. Dissolve 1.272 LaCl₃ · 6H₂O in 100 mL of 0.5N HCl.

- 6.9 Sodium hydroxide, 6N. Dissolve 120 grams of NaOH in 300 mL of water. Cool and dilute to 500 mL with water.
- 6.10 Sodium nitrite, 1N. Dissolve 6.9g of NaNO₂ in 75 mL of water in a 100 mL volumetric flask. Dilute to volume.
- 6.11 Sulfuric acid, 0.3M. Add 17 mL of concentrated sulfuric to 700 mL water in a 1-L volumetric flask and dilute to volume. Mix thoroughly.
- 6.12 Standard thorium solution, 10 mg/mL. Dry approximately 5-10 grams Th(NO₃)₂ · 4H₂O in a drying oven at 107°C for 4 hours. Remove and cool in a desiccator. Transfer 3-500 mg aliquots to three previously fired, cooled and tared platinum or porcelain crucibles. Place in a muffle furnace and slowly increase heat for 1 hour and then to 650°C for 1 hour. Remove, cool in a desiccator and reweigh. Determine the % thorium in the thorium nitrate. Weigh out sufficient dried Th(NO₃)₂ · 4H₂O equivalent to 1000 mg thorium and dissolve in 50 ml 0.5N HCl in a 100 mL volumetric flask. Dilute to volume and mix thoroughly.
- 10 µg/mL. Transfer 1.0 mL of the 10 mg/mL standard thorium solution to 900 mL 4N HCl in a 1-liter volumetric flask, dilute to volume with 4N HCl and mix thoroughly.
- 6.13 Tri-isooctyl amine, 10%. Dilute 50 mL of tri-isooctyl amine with xylene in a 500 mL volumetric flask.
- 6.14 Trioctyl phosphine oxide, 0.1 M. Dissolve 19.3g TOPO in 400 mL of cyclohexane in a 500 mL volumetric flask. Dilute to volume with cyclohexane.
- 6.15 Zylene, reagent grade

7. Calibration

- 7.1 Thorium-230. Determine the counter efficiency for the alpha emitting Th-230 by transferring a known quantity of a Th-230 standard to a beaker containing 50 ml of 0.5M HCl and 1 mL of lanthanum carrier. With constant stirring add 2 mL of 48% HF, and allow to stand for 20 minutes with occasional stirring. Filter through a 47 mm diameter 0.45 µ metricel filter, wash one time each with 10 mL of water and ethanol. Transfer the filter to a 2-inch stainless steel planchet previously coated with rubber cement and containing 5 drops of 1:1 acetone:alcohol mixture. Dry at 70°C for 3-5 minutes. Count for sufficient time to collect 10000 counts.

$$\text{Thorium-230 Counting Efficiency, } E = \frac{A - B}{C}$$

where: A = Gross cpm of Th-230 standard
B = Alpha Reagent Blank of Lanthanum Carrier, cpm
C = dpm of Th-230 standard.

- 7.2 Thorium-234. Transfer approximately 250 dpm of NBS Uranium-238 standard to a beaker containing 50 mL 0.5M HCl and 1 mL of lanthanum carrier and add approximately 100 mg ascorbic acid. Warm to dissolve. Cool and add 0.1 mL of 20% $TiCl_3$ and mix. Add 2 mL 48% HF with stirring and allow to stand for 20 minutes, stirring occasionally. Filter through a 47 mm diameter 0.45 μ metricel filter, wash one time each with 10 mL of water and ethanol. Transfer the filter to a 2-inch stainless steel planchet previously coated with rubber cement and containing 5 drops of 1:1 acetone: alcohol mixture. Dry at 80°C for 3-5 minutes. Cover the filter with a circle of aluminum foil (4.5 mg/cm²) and beta count. Count for sufficient time to accumulate 10000 counts.

$$\text{Thorium-234 Counting Efficiency, } E = \frac{A - B}{C}$$

where: A = Gross Th-234 + Pa 234^m cpm
B = Beta Reagent Blank of lanthanum carrier, cpm
C = dpm Uranium-238 standard

7.3 Thorium-232 (Natural Thorium)

- 7.3.1 Transfer 0, 100, 400, 700, and 1000 μ L of the standard 10 μ g/mL thorium solution to each of five 10 mL volumetric flasks.
- 7.3.2 Add 1.0 mL of the aluminum carrier solution and 5 mL of 4N HCl, stopper, and shake to mix thoroughly.
- 7.3.3 To each standard and to each sample from step 8.31, add 1.0 mL of the arsenazo III reagent solution.
- 7.3.4 Dilute to mark with 4N HCl, stopper, and shake to mix thoroughly.
- 7.3.5 Read each sample and standard at 665 m μ using a near infrared filter and a 2 cm light path cell.
- 7.3.6 Using the standard sample readings, plot a curve using absorbancy readings as the ordinate versus the μ g of thorium as the abscissa, or compute the equation for a straight line by least squares analysis using the absorbancy as the dependent variable.

8.0 Procedure

- 8.1 Acidify a 1-liter sample of tap water with 10 mL of 6N HCl. (If sample was acidified for storage as in 3.2., omit 8.1.)

- 8.2 Add 1 mL of the FeCl_3 carrier solution and 10 mL of 1N NaNO_2 and heat to boiling.
- 8.3 With continuous stirring, add sufficient 6N NaOH to make alkaline to pH 10 and continue heating for 5 minutes.
- 8.4 Remove from heat, cool and settle in a cold water bath.
- 8.5 Filter through a 47 mm 0.45 μ membrane filter, discarding the filtrate.
- 8.6 Place a 40 mL cone bottom centrifuge tube in a Fisher filtrator and attach the filtering apparatus to the filtrator.
- 8.7 Add 10 mL of 8N HCl to the filter to dissolve the precipitate.
- 8.8 With vacuum, filter the solution into the centrifuge tube.
- 8.9 Repeat steps 8.7 and 8.8 one more time.
- 8.10 Rinse the filtering apparatus twice using 5 mL of 8N HCl , filtering between each addition.
- 8.11 Transfer the solution to a 60 mL separatory funnel, rinsing the tube twice with 5 mL portions of 8N HCl .
- 8.12 Add 20 mL of a 10% tri-isooctyl amine/xylene solution and shake for two minutes.
- 8.13 Allow the two phases to separate for 5 minutes, draining the bottom layer into a second 60 mL separatory funnel. (Note time of separation if Th-234 is being determined.)
- 8.14 Wash the organic phase once with 5 mL of 8N HCl by shaking for 1 minute.
- 8.15 Allow the wash to separate and combine it with the acid phase in the second funnel.
- 8.16 Add 6 mL of water to the second separatory funnel to reduce the acid concentration to 7N and add 10 mL of 0.1M trioctyl phosphine oxide/cyclohexane (TOPO) solution.
- 8.17 Extract for two minutes, allow to separate, and drain the acid phase into a third 60 mL separatory funnel.
- 8.18 Add 10 mL of the TOPO solution to the acid phase and extract a second time for two minutes.
- 8.19 Allow the phases to separate completely, drain and discard the acid phase.

- 8.20 Combine the second TOPO phase with the first extraction, and wash the combined phases with 10 mL of 7N HCl by shaking for 1 minute.
- 8.21 Allow the phases to separate, drain and discard the wash.
- 8.22 Add 10 mL of 0.3M H₂SO₄ to the separatory funnel and shake for two minutes.
- 8.23 Allow the phases to separate and drain the acid layer (bottom) into a 40 mL cone bottom centrifuge tube.
- 8.24 Repeat steps 8.22 and 8.23 two more times.
- 8.25 Add 1 mL of the aluminum carrier solution and warm in a hot water bath.
- 8.26 While stirring, add concentrated NH₄OH dropwise until alkaline.
- 8.27 Centrifuge for five minutes and discard the supernate.
- 8.28 Wash the precipitate with 20 mL of water, centrifuge, and discard the wash.
- 8.29 Dissolve the precipitate in 2 mL of 4N HCl and transfer the solution to a 10 mL volumetric flask, using a Pasteur transfer pipet.
- 8.30 Rinse the centrifuge tube twice with 1 mL portions of 4N HCl adding the rinsings to the volumetric flask. (Be careful not to exceed 8 mL.)
- 8.31 Save the solution for colorimetric analysis as in 7.3.3 to 7.3.5.
- 8.32 After the colorimetric analysis, transfer the solution to a 100 mL beaker and wash cuvette and volumetric flask thoroughly with water, adding the washes to the beaker.
- 8.33 Add 1 mL of the lanthanum carrier and 1 mL of concentrated HNO₃ and heat to destroy the color complex.
- 8.34 Dilute to 60 mL with water, remove from heat, and add 2 mL of 48% HF with stirring.
- 8.35 Allow the precipitate to develop for ten minutes, stirring occasionally.
- 8.36 Filter through a 47 mm PVC membrane filter, washing once with water and once with 95% ethanol.
- 8.37 Transfer the filter to a stainless steel planchet previously coated with rubber cement and containing 3-5 drops of a 1:1 solution of ethanol and acetone.

8.38 Place in a drying oven at 80°C for 5 minutes to dry.

8.39 Cool and alpha count in an internal proportional counter or store in a dessicator for later counting.

9. Calculations

9.1 Total Alpha Thorium

$$\text{pCi/l} = \frac{S - B}{2.22 EV}$$

where: S = gross alpha cpm
B = alpha reagent blank, cpm
E = Thorium-230 counting efficiency, cpm/dpm
V = volume of sample, liters

9.2 Thorium-234 (Cover filter with aluminum foil)

$$\text{pCi/l} = \frac{S - B}{2.22 E V e^{-\lambda t}}$$

where: S = gross beta cpm
B = beta reagent blank, cpm
E = Th-234 + Pa 234^m counter efficiency, cpm/dpm
V = volume of sample, liters
 $e^{-\lambda t}$ = decay correction from step 8.13 to time of count
= 0.0012 hr⁻¹

9.3 Thorium-232 (Natural Thorium)

9.3.1 Using the plot determined from 7.3.6, determine the µg thorium content of each sample by interpolation using the absorbancy reading for each sample.

9.3.2 Using the linear equation of best fit as determined from 7.3.6, calculate the µg thorium for each sample (X-value) by placing the y-value equal to the absorbancy of each sample.

9.3.3 From the µg thorium found from either step 9.3.1 or 9.3.2, calculate the thorium concentration by dividing the mass thorium found by the volume of the sample aliquot in liters.

10. Accuracy and Precision

10.1 A stock thorium test solution was prepared containing nominally 1 µg thorium-232 and nominally 2 pCi thorium-230 per mL of solution. Five 5-mL aliquots were assayed by spectrophotometry to determine the thorium-232 content and five 5 mL aliquot were assayed by alpha counting to determine the total alpha activity content.

Thorium-232 content was determined to be 4.76 ± 0.16 $\mu\text{g}/5$ mL and total alpha thorium was determined to be 11.25 ± 0.52 pCi/5mL.

Eight 1-liter tap water samples were each spiked with 5.0 mL of the stock thorium test solution and analyzed by the prescribed method.

The mean thorium-232 recovery was found to be 4.52 ± 0.3 $\mu\text{g}/\text{L}$ for an average recovery of $94.9\% \pm 7\%$.

The mean total alpha thorium recovery was found to be 11.43 ± 1.24 pCi/L for an average recovery of $101.6 \pm 12\%$.

A Student-t test comparing the two thorium recoveries using a pooled estimate of the standard deviation of the means indicated that the means were not different at the 95% confidence level.

The average recovery for the method is thus estimated to be 98%.

10.2 Precision

Since precision is a function of analyte concentration and instrument measurement technique, it may vary.

Since instrumental errors for both the spectrophotometric and radiometric determination are not related to the concentration by the same magnitude, their variance cannot be compared and thus they cannot be pooled.

However, it can be stated that the precision of method for thorium-232 at the 5 $\mu\text{g}/\text{L}$ concentration level is $\pm 7.5\%$ and that the precision of method for total alpha thorium at the 11 pCi/L concentration level is $\pm 12\%$.

11. References

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