SECTION 12
URANIUM IN DRINKING WATER - RADIOCHEMICAL METHOD
METHOD 908.0

1. Scope and Application

1.2 This method covers the measurement of total uranium alpha particle activity in drinking water. Most drinking water sources, especially ground water sources, contain soluble carbonates and bicarbonates which complex and keep uranium in the water in solution.

1.2 Uranium isotopic abundances in drinking water sources are apt to be present in ratios different from the ratios in the deposits from which the uranium entered the water sources. The two predominant natural alpha emitting isotopes of uranium are uranium-234 and uranium-238. Uranium-238 is the predominant mass abundant isotope; greater than 99% compared to about 0.OO6% for uranium-234. However, uranium-234 has a specific activity for alpha particle emission that is 1.8 x 10^4 times greater than that of uranium-238. For an equilibrium condition, the activity of the uranium-234 is equal to that of the uranium-238. Therefore, the uranium mass concentration in water is not related to the alpha particle activity of the water.

1.3 The Drinking Water Regulations under the Safe Drinking Water Act, PL 93-523, require a measurement of uranium for drinking water samples that have a gross alpha activity greater than 15 pCi/l. A mass uranium concentration measurement of a water sample cannot be converted to uranium alpha activity without first analyzing for isotopic abundances. Therefore, a method such as this one is needed to determine the total uranium alpha activity of the sample, without doing an isotopic uranium analysis.

2. Summary of Method

2.1 The water sample is made acid by adding HC1 and the sample is boiled to eliminate carbonate and bicarbonate ions. Uranium is coprecipitated with ferric hydroxide and separated from the sample. The uranium is then separated from other radionuclides which were carried down with the ferric hydroxide by dissolving the hydroxide precipitate in 8N HC1, putting the solution through an anion exchange column, washing the column with 8N HC1, and finally eluting the uranium with 0.1N HC1. The uranium eluate is evaporated and the uranium chemical form is converted to nitrate. The residue is transferred to a stainless steel planchet, dried, flamed, and counted for alpha particle activity.

2.2 Uranium recovery is determined with blank samples spiked with known amounts of uranium and taken through the procedure as a regular sample.

2.3 Counting efficiency is determined by transferring measured aliquots of an uranium standard to a planchet, diluting with 6-8 ml of a 1 mg/ml HIO_3 solution in 4N $HN0_3$, evaporating to dryness, flaming the planchet, and counting in an alpha counter.

3. Sample Handling and Preservation.

3.1 Although carbonate ions in a water sample will help to keep uranium in solution, the addition of extra carbonate or bicarbonate ions to the sample as a preservative is not recommended because an increased carbonate concentration in the sample may cause some precipitation. Therefore, it is recommended that samples be preserved with HCl to pH 2 at the time of collection.

3.2 A sample size of at least 1 liter should be collected for uranium analysis.

4. Interferences

4.1 The only alpha-emitting radionuclide that may come through the chemistry and cause interference would be protactinium-231, However, protactinium-231 results from the decay of uranium-235, a low abundance natural isotope of uranium, and would therefore cause only a very small interference.

4.2 Since uranium is a naturally occurring radionuclide, reagents must be checked for uranium contamination by analyzing a complete reagent blank by the same procedure as used for the samples.

5. Apparatus - See Appendix D for details and specifications

5.1 Gas-flow proportional counting system or

5.2 Scintillation detection system

5.3 Glassware

5.4 Electric hot plate

5.5 Ion exchange column: approximately 13 ma (i.d.) x 150 mm long with a 100 ml reservoir.

5.6 Stainless steel counting planchets, 2 inch diameter by 1/4 inch deep.

5.7 Millipore filter apparatus, 47 mm.

6. Reagents

6.1 All chemicals should be of reagent grade or equivalent whenever they are commercially available.

6.2 Ammonium hydroxide, 6N: Mix 2 volumes 15N NH_40H (cone.) with 3 volumes of water (carbonate-free.)

6.3 Anion exchange resin - Strongly basic, styrene, quaternary amnonium salt, 4% crosslinked, 100-200 mesh, chloride form (such as Dowex 1x4, or equivalent).

6.4 Ferric chloride carrier, 20 mg Fe^{+3}/ml: Dissolve 9.6g of $FeC1_3.6H_20$ in 100 ml of 0.5 N HC1.

6.5 Hydriodic acid: HI (conc.), sp. gr. 1.5, 47%.

6.6 Hydrochloric acid, 12N: HC1 (cone.), sp. gr. 1.19, 37.2%.

6.7 Hydrochloric acid, 8N: Mix 2 volumes 12N HCI (conc.) with 1 volume of water.

6.8 Hydrochloric acid, 6N: Mix 1 volume 12N HC1 (conc.) with 1 volume of water.

6.9 Hydrochloric acid, 0.1N: - Mix 1 volume O.5N HC1 with 4 volumes of water.

6.10 Iodic acid, 1 mg/ml: Dissolve 100 mg $HI0_3$ in 100 ml 4N $HN0_3$.

6.11 Nitric acid, 16N: $HN0_3$ (conc.), sp. gr. 1.42, 70.4%:

6.12 Nltric acid, 4N: Mix 1 volume 16N HNO_3 (conc.) with 3 volumes of water.

6.13 Sodium hydrogen sulfite, $NaHS0_3$.

6.14 Sodium hydrogen sulfite, 1% in HC1: Dissolve lg $NaHS0_3$ in 100 ml 6N HC1.

7. Calibrations

7.1 Determine a counting efficiency (E), for a known amount of standard uranium (about 1000 dpm) evaporated from a 6-8 ml volume of a 1 mg/ml $HI0_3$ solution in a 2 inch diameter stainless steel planchet. If the standard solution is an HCI solution, then aliquot portions of that solution must be converted to nitrate/ $HN0_3$ solutions, eliminating all chloride ions from the solutions. This can be done by three successive evaporations after adding 5 ml portions of 16N $HN0_3$ to aliquot portions of the standard in small beakers (avoiding dry baking of the evaporated residue). The final solutions of the standard aliquots are made by adding 2 ml 4N HNO_3 solution to the third evaporated residues. Transfer the uranium standard aliquot solutions to 2 inch diameter stainless steel planchets.

Complete the transfer by rinsing the beakers two times with 2 ml portions of 4N HN03 and evaporate to dryness. Flame the planchets and count for at least 50 minutes for alpha particle activity. A reagent blank should be run along with the standard aliquots and should be alpha counted.

$$\text{Efficiency, cpm/dpm,(E)} = \frac{A - B}{C}$$

where:

A = gross cpm for standard
B = cpm for instrument background
C = dpm of standard used.

7.2 A uranium recovery factor R, is determined by the following procedure: Spike one liter tap water samples with aliquots of uranium standard solution (500-1000 dpm per sample). Take these spiked samples and a tap water blank through the entire procedure and count the separated and evaporated uranium for alpha particle activity.

$$\text{Recovery factor, (R)} = \frac{(F - B)}{CE}$$

where:

C = dpm of uranium standard added
F = gross cpm of spiked sample
B = cpm of reagent blank
E = efficiency factor, cpm/dpm

8. Procedure

8.1 Measure the volume of approximately one liter of the water sample to be analyzed.

8.1.2 If the sample has not been acidified, add 5 ml 12N HCl. and 1 ml ferric chloride carrier.

8.1.3 Mix the sample completely and use pH paper to check the hydrogen-ion concentration. If the pH is > 1, add 12N HCl until it reaches this value.

8.1.4 Cover with a watch glass and heat the water sample to boiling for 20 minutes.

8.1.5 The pH must be checked again after boiling and if it is > 1, 12N HCl must be added to bring the pH back to 1.

8.1.6 While the sample is still boiling gently add 6N NH_4OH to the sample from a polyethylene squeeze bottle with the bottle delivery tube inserted between the watch glass and the pouring lip of the beaker. The boiling action of the sample provides sufficient stirring action. Add 6N NH_4OH until turbidity persists while boiling continues; then add an additional 10 ml, (estimated addition from the squeeze bottle).

8.1.7 Continue to boil the sample for 10 minutes more; then set it aside for 30 minutes to cool and settle.

8.1.8 After the sample has settled sufficiently, decant and filter the supernate through a 47 mm 0.45 micron membrane filter, using the larger millipore filtering apparatus.

8.1.9 Slurry the remaining precipitate, transfer to the filtering apparatus and filter with suction.

8.1.10 Place the filtering apparatus over a clean250 ml filtering flask, add 25 ml 8N HCl to dissolve precipitate, and filter the solution.

8.1.11 Add another 25 ml 8N HC1 to wash the filter, and then filter.

8.1.12 Transfer solution to the 100 ml reservoir of the ion exchange column.

8.1.13 Rinse the side arm filtering flask twice with 25 ml portions of 8N HCl. Combine in the ion exchange reservoir.

8.2 Anion Exchange Separation

8.2.1 Prepare the column by slurrying the anion exchange resin with 8N HCl and pouring it onto a column of about 13 mm inside diameter. The height of the resin bed should be about 80 mm.

8.2.2 Pass the sample solution through the anion exchange resin column at a flow rate not to exceed 5 ml/min.

8.2.3 After the sample has passed through the column, elute the iron (and plutonium if present) with 6 column volumes of 8N HCl containing 1 ml 47% HI per 9 ml of 8N HCI (freshly prepared).

8.2.4 Wash the column with an additional two column volumes of 8N HC1.

8.2.5 Elute the uranium with six column volumes of 0.1N HCl.

8.2.6 Evaporate the acid eluate to near dryness and convert the residue salts to nitrates by three successive treatments with 5 ml portions of 16N HNO_3, evaporating to near dryness each time.

8.2.7 Dissolve the residue (may be very little visible residue) in 2 ml 4N HNO_3.

8.2.8 Transfer the residue solution, using a Pasteur pipet, to a marked planchet, and complete the transfer by rinsing the sample beaker three times with 2 ml portions of 4N HNO_3.

8.2.9 Evaporate the contents in the planchet to dryness, flame to remove traces of HIO_3, cool, and count for alpha particle activity.

8.3 Column Regeneration

8.3.1 Pass three column volumes of 1% $NaHSO_3$ in 6N HCl through the column.

8.3.2 Pass six column volumes of 6N HCl through the column.

8.3.3 Pass three column volumes of water through the column.

8.3.4 Pass six column volumes of 8N HCl through the column to equilibrate and ready the resin for the next set of samples.

9. Calculations

$$\text{Uranium alpha activity, pCi/l} = \frac{(S-B)*1000}{2.22*ERV}$$

where:

S = gross cpm for sample
B = cpm of reagent blank
V = volume of sample used, mi
E = efficiency, cpm/dpm
R = recovery factor
2.22 = conversion factor for dpm/pCi

10. Precision and Accuracy

In a single laboratory test of this method, a stock uranium solution was prepared using tap water and spiked with an NBS uranium standard. The calculated concentration was 26.7 pCi/l. This stock solution was acidified with HCl as a preservative. Nine 1-liter aliquots were withdrawn and the procedure tested. Individual results were 22.4, 22.5, 24.0, 25.9, 26.9, 26.5, 24.6, 25.7 and 23.9 pCi/l. The average concentration was 24.7 pCi/l with a standard deviation of 1.7 pCi/l. From these data, the method shows a negative 7.4% bias and a precision of + 6.7% without the correction of the recovery factor.

References

1. Bishop, C. T., et.al. "Radiometric Method for the Determination of Uranium in Water," EPA 600/7-79-093, EMSL-LV, April 1979.

2. Edwards, K. W. "Isotopic Analysis of Uranium in Natural Waters by Alpha Spectrometry, "Radiochemical Analysis of Water, Geological Survey Water-Supply Paper 1696-F, U.S. Government Printing Office, Washington, D.C., 1968.