

NICKEL-63/59 IN WATER

1. SCOPE

- 1.1. This is a method for the separation and measurement of nickel-63/59 in water samples.
- 1.2. This method does not address all aspects of safety, quality control, calibration or instrument set-up. However, enough detail is given for a trained radiochemist to achieve accurate and precise results for the analysis of the analyte(s) from the appropriate matrix, when incorporating the appropriate agency or laboratory safety, quality and laboratory control standards.

2. SUMMARY OF METHOD

- 2.1. Nickel is precipitated as a nickel/dimethylglyoxime complex on the Eichrom Nickel Resin column. The Nickel/dimethylglyoxime complex is then removed with a minimum amount of 3M HNO₃. The strip solution can be measured for ⁶³Ni by LSC and ⁵⁹Ni by X-Ray spectrometry.

3. SIGNIFICANCE OF USE

- 3.1. This is a rapid, reliable method for measurement of ^{63/59}Ni in water samples that is more cost-effective and efficient than traditional DMG precipitation techniques.

4. INTERFERENCES

- 4.1. If ⁵⁵Fe and actinides need to be measured in the sample then they should be separated prior to loading the sample on the nickel column. This can be accomplished using TRU Resin as described in Eichrom Method FEW01.
- 4.2. Other fission products can interfere with determination of ^{63/59}Ni. Adding 1mg of Co and Fe can improve the decontamination factors for these elements during the Ni Resin separation.

- 4.3. The nickel resin column can retain over 6mg of Ni. However, the flow rate of the resin column will slow dramatically if more than 2mg Ni is present in the sample. Therefore, it is recommended to limit the addition of Ni carrier to 2mg or less.
- 4.4. Up to 50mL of solution can be loaded onto the Ni Resin column. Larger volumes of sample will result in significant losses of nickel. Limiting the volume of load solution to 20mL or less is recommended for optimal performance. There are several options for concentrating larger sample volumes to less than 20mL, including ferric hydroxide precipitation and evaporation.

5. APPARATUS

- Analytical balance, 0.0001 g sensitivity
- Cartridge reservoirs, 10mL (Eichrom Part: AR-200-RV10) or 20mL (Eichrom Part: AR-200-RV20)
- Fume hood
- LEPS detector or equivalent if detecting Ni-59 by low energy x-ray emission
- Liquid scintillation counter with alpha/beta discrimination capability
- Liquid scintillation vial
- pH meter
- Stir plate
- Vacuum pump - 115 V, 60 Hz Fisher Part: 01-092-25 (or equivalent) or house vacuum
- Vacuum box system, Eichrom Part: AR-12-BOX or AR-24-BOX
- Vacuum box white inner support tube-PE, Eichrom Part: AR-1000-TUBE-PE
- Vacuum box yellow outer tips- Eichrom Part: AR-1000-OT
- Optional item for collection of load and rinse fractions:
 - Vacuum box inner liner, Eichrom Part: AR-12-LINER or AR-24-LINER
- Optional items for large sample concentration by ferric hydroxide precipitation:
 - Centrifuge, with rotor and carriers for 50mL and 250mL tubes
 - Centrifuge tubes, 50mL and 250mL

6. REAGENTS

Note: Analytical grade or ACS grade reagents are recommended. Evaluation of key reagents, such as aluminum nitrate and ammonium hydrogen phosphate, for contribution to method background levels from naturally occurring radioactive materials is recommended.

<i>Ammonium citrate, (NH₄)₃C₆H₅O₈</i>
<i>Ammonium hydroxide (57%), concentrated NH₄OH</i>
<i>Sodium hydroxide, NaOH</i>
<i>Deionized water, All reagents are prepared using deionized water</i>
<i>Ferric nitrate nonahydrate, Fe(NO₃)₃·9H₂O</i>
<i>Hydrochloric acid (37%), concentrated HCl</i>
<i>Isopropanol, C₃H₇OH</i>
<i>Liquid scintillation cocktail</i>
<i>Nickel nitrate hexahydrate, Ni(NO₃)₂·6H₂O</i>
<i>Nickel resin, 2mL prepacked columns, 100-150µm, Eichrom Part NI-C50-A</i>
<i>Phenolphthalein pH Indicator</i>

- 6.1. *Ammonium citrate (0.2M)* - Dissolve 45.2g of ammonium citrate in 800mL of water. Dilute to 1L water.
- 6.2. *Ammonium citrate (1M)* - Dissolve 226g of ammonium citrate in 800mL of water. Dilute to 1 L water.
- 6.3. *Hydrochloric acid (1M)* - Add 83mL of concentrated HCl to 900mL of water. Dilute to 1L with water.
- 6.4. *Nickel carrier (2mg/ml)* - Dissolve 9.9g of Ni(NO₃)₂·6H₂O in 700mL of water. Dilute the solution to 1L with water.
- 6.5. *Nitric acid (3M)*- Add 188mL of concentrated HNO₃ to 700mL of water. Dilute to 1L with water.
- 6.6. *Phenolphthalein solution*- Dissolve 1g phenolphthalein in 100mL 95% isopropyl alcohol. Dilute with 100mL of water.

- 6.7. *Iron Carrier (5 mg/mL Fe)in 0.1M HNO₃* – To a 500mL volumetric flask, add 18g Fe(NO₃)₃·9H₂O, 400mL of water and 3.1mL of concentrated HNO₃. Swirl to dissolve. Dilute to 500mL with water.
- 6.8. *Sodium Hydroxide (1M)* – Dissolve 40mL of NaOH in 800mL of water. Dilute to 1L with water.

7. PROCEDURE

- 7.1. Water Sample Preparation:
 - 7.1.1. If required, filter the sample through a 0.45 micron filter.
 - 7.1.2. Aliquot 100-500mL of the sample into an appropriately sized beaker. Add 1mL of Ni carrier.
 - 7.1.3. For samples of 100-200mL evaporate to dryness. Continue to step 7.1.5.
 - 7.1.4. For larger samples, add 2mL of iron carrier and 0.05mL of phenolphthalein solution. Mix well. While stirring, slowly add enough 1M NaOH to reach the pink phenolphthalein endpoint (pH 8-9). Iron hydroxide will precipitate carrying Ni.
 - 7.1.5. Transfer to 250mL centrifuge tube. Centrifuge at 2000rpm for 10 minutes. Decant supernate. Add remaining sample, centrifuge, and decant supernate until entire sample has been centrifuged.
 - 7.1.6. Add 5mL of concentrated HCl and evaporate to dryness.
 - 7.1.7. Dissolve residue in 5mL of 1M HCl. If needed, add an additional 5 mL of 1M HCl to dissolve.
 - 7.1.8. Add 1mL of 1M ammonium citrate and 0.1mL of phenolphthalein solution to the sample. Adjust to the pink phenolphthalein endpoint (pH 8-9) with ammonium hydroxide.

Note: Ammonium citrate is used to complex potential interferences and iron in the sample from the preconcentration step. If using the ferric hydroxide precipitation step, 0.25mL additional 1M ammonium citrate may be needed to keep iron in solution during the adjustment to pH 8-9.

- 7.2. Nickel separation using Eichrom Ni Resin column
 - 7.2.1. For each sample, place a Nickel column in the column rack.

- 7.2.2. Place a beaker below each column or use a waste tray to collect the eluate from all of the columns. Remove the cap and bottom plug from each column and allow to drain.
- 7.2.3. Add 5mL of 0.2M ammonium citrate (pH 8-9) to each column reservoir. Allow solution to pass through all columns.
- 7.2.4. Add sample solutions to the appropriate Nickel column reservoirs. A red band will appear on the column. Allow solution to pass through all columns.
- 7.2.5. Add 20mL of 0.2M ammonium citrate (pH 8-9) to each column reservoir. Allow the solution to pass through all columns. Discard solution in beakers or waste tray as waste.
- 7.2.6. Place a clean labeled beaker below each column. Add 15mL of 3M HNO₃ to each column reservoir to strip Ni. Allow solution pass through all columns.
- 7.2.7. Use a portion of the 3M HNO₃ solution to determine Ni yield by by atomic emission spectrometry or perform separation method on a batch recovery sample spiked with stable Ni or Ni-63. The remainder of the sample can be used for counting to determine Ni-63 by liquid scintillation counting (LSC) and Ni-59 by X-Ray spectrometry.

Note: The nickel/dimethylglyoxime complex is difficult to destroy. It is not recommended that the strip solution be evaporated to dryness, as an insoluble black residue will result.

8. CALCULATIONS

Calculate isotope activity:

$$\text{Ni - 63 concentration (pCi/L)} = \frac{S - B}{E \times V \times Y \times 2.22}$$

where:

- S = sample activity, cpm
- B = background, cpm
- E = counting efficiency = measured cpm/dpm of isotopic standard
- V = sample volume, L
- Y = Stable Ni yield

pCi/L = 37 mBq/L

9. REFERENCES

- 1) Strebin, R.S., et al., "Nickel-59 and Nickel-63 Determination in Aqueous Samples," DOE Methods Compendium RP300 (1997).
- 2) Rajkovich, S. et al., "2 Case Studies Using Eichrom's Nickel Resin: A Nuclear Power Plant and a Commercial Laboratory," Eichrom Cincinnati Users' Seminar. Cincinnati, OH(1996).
- 3) "Determination of Nickel-63 in Environmental Samples," Laboratory Procedures Manual, ORISE/IEAV, AP12.