NICKEL - 63/59 IN WATER

(WITH VACUUM BOX SYSTEM)

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 HNO_3. The strip solution can be measured for ^{63}Ni by LSC and ^{59}Ni 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 ^{55}Fe 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 for contribution to method background levels from naturally occurring radioactive materials is recommended.

Ammonium Citrate, $(NH_4)_3C_6H_5O_8$
Ammonium hydroxide (57% NH_4OH or 28% NH_3), concentrated NH_4OH
Sodium Hydroxide, NaOH
Deionized water, All reagents are prepared using deionized water
Ferric Nitrate Nonahydrate, $Fe(NO_3)_3{\cdot}9H_2O$
Hydrochloric acid (37%), concentrated HCl
Isopropanol, C_3H_7OH
Liquid Scintillation Cocktail
Nickel Nitrate Hexahydrate, $Ni(NO_3)_2{\cdot}6H_2O$
Nickel Resin, 2mL prepacked cartridge, 50-100µm, Eichrom Part NI-R50-S
Phenolphthalein pH Indicator

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 $Ni(NO_3)_2{\cdot}6H_2O$ in 700mL of water. Dilute the solution to 1L with water.

6.5. *Nitric acid (3M)*- Add 188mL of concentrated HNO_3 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 HNO_3* – To a 500mL volumetric flask, add 18g $Fe(NO_3)_3 \cdot 9H_2O$, 400mL of water and 3.1mL of concentrated HNO_3. 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 cartridge

7.2.1. Place the inner tube rack (supplied with vacuum box system) into the vacuum box. Place centrifuge tubes in the rack. Fit the lid to the vacuum system box. Alternatively, a vacuum box inner liner may be used.

7.2.2. Place yellow outer tips into all 12 or 24 openings in the lid of the vacuum box. Fit a white inner support tube into each yellow tip.

7.2.3. For each sample solution, fit a Nickel cartridge on to the inner support tube.

7.2.4. Add syringe barrels (funnels/reservoirs) to the top end of each Nickel cartridge.

7.2.5. Connect the vacuum pump to the box. Turn the vacuum pump on and ensure proper fitting of the lid.

Note: The unused openings on the vacuum box should be sealed. Vacuum manifold plugs can be used to plug unused white tips to achieve good seal during the separation. Alternatively, unused vacuum box holes can be sealed with scotch tape.

7.2.6. Add 5mL of 0.2M ammonium citrate (pH 8-9) to each Nickel cartridge reservoir. Adjust vacuum to achieve a flow rate of 1mL/min. Allow solution to completely pass through each cartridge.

7.2.7. Add sample solutions to the appropriate Nickel cartridge reservoirs. A red band will appear on the column. Allow solution to completely pass through all cartridges at 1mL/min.

7.2.8. Place a clean reservoir above each Nickel cartridge.

7.2.9. Add 20mL of 0.2M ammonium citrate (pH 8-9) to each Nickel cartridge reservoir. Allow the solution to pass through all cartridges at 1mL/min. Disengage vacuum. Discard eluate to this point as waste.

7.2.10. Place a clean labeled centrifuge tube below each Nickel cartridge. Replacing yellow outer tips and inner support tubes at this point can help ensure clean nickel fractions in the following steps.

7.2.11. Add 15mL of 3M HNO_3 to each Nickel cartridge reservoir to strip Ni. Engage vacuum. Strip Ni at 1mL/min.

7.2.12. Use a portion of the 3M HNO3 solution to determine Ni yield 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:

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

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.