AP12

DETERMINATION OF NICKEL-63 IN ENVIRONMENTAL SAMPLES

PART A

PRINCIPLE

Nickel-63 (Ni-63) in environmental samples is precipitated as a nickel/dimethylglyoxime precipitate on an extraction chromatographic resin (Ni Resin from Eichrom Technologies, Darien, IL). Iron is removed from soil, sediment, and smear samples prior to the nickel separation using anion exchange chromatography. Samples that contain sufficient amounts of radioactive cobalt are processed through an anion exchange column prior to passing the samples through the Ni resin. Other potential interfering elements are removed from the Ni column with a buffered ammonium citrate solution. Nickel is eluted off the column with dilute nitric acid. The Ni-63 activity is determined via liquid scintillation counting. A batch yield is used to determine chemical recovery.

REFERENCES

1. Bhat, I. S., Iyer, R. S., and Chandramonli, S., Anal. Chem., 48, pp 224, 1976.

2. Hillebrand, Lundell, Bright, and Hoffman, App. Inorg. Anal., John Wiley and Sons, New York, 2nd Ed., 1953.

3. Krieger, H. L., Gold, S., Procedures for the Radiochemical analysis of Nuclear Reactor Aqueous Solutions, U. S. EPA Publ., EPA-R4-73-014, 1973.

4. Annual Book of ASTM, Standards Vol. 11.02, p. 379.

5. Eichrom Technologies, Inc., Analytical Procedures, "Nickel 63/59 in Water", February 13, 2002.

Certification Record for

AP12
DETERMINATION OF NICKEL-63 IN ENVIRONMENTAL SAMPLES

CHECKPOINTS

1.	**JOB HAZARD ANALYSIS (JHA)**	_____
2.	**MSDS/HAZARDS DISCUSSED**	_____
3.	**SAMPLE DIGESTION**	_____
4.	**COLUMN SEPARATION**	_____
5.	**COUNTING PREPARATION**	_____
6.	**FINAL CALCULATIONS**	_____

ANALYST'S SIGNATURE: _____

CERTIFIED BY: _____

DATE: _____

ANALYSIS VALUE: _____

KNOWN VALUE: _____

MEASURED/KNOWN: _____

See Task _____, Batch_____ for the original data.

COMMENTS:_____
_____
_____
_____

PART B

1.0 PURPOSE AND SCOPE

This procedure provides the analytical method for the determination of Nickel-63 in environmental samples.

2.0 REAGENTS

All chemicals are hazardous. See MSDS for specific precautions. **See step 2.0 of AP12 JHA.** Unless otherwise indicated, all references to water should be understood to mean reagent grade water.

Ammonium citrate, reagent grade, crystalline.

Ammonium citrate, 1 M: Dissolve 22.6 g of ammonium citrate in 80 mL of water and dilute to 100 mL. Store in a dark bottle.

Ammonium citrate, 0.2 M: Dissolve 45.2 g of ammonium citrate in 800 mL of water and dilute to 1 L.

Ammonium hydroxide, NH_4OH, concentrated, reagent grade.

Anion exchange resin, BioRad 1 X 8, chloride form, 100-200 mesh, or equivalent.

Cobalt carrier (1 mg/mL): AA quality Co solution of 1000 µg/mL.

Hydrochloric acid, HCl, concentrated, 12 M.

Hydrochloric acid, 10 M: Add 833 mL of concentrated HCl to 150 mL water and dilute to 1 L with water.

Hydrochloric acid, 1 M: Add 83 mL of concentrated HCl to 900 mL water and dilute to 1 L with water.

Liquid scintillation cocktail – Perkin Elmer Ultima Gold-LLT, or equivalent.

Nickel-63, NIST traceable standardized solution.

Nickel carrier (1 mg/mL): AA quality Ni solution of 1000 µg/mL.

Nickel resin, pre-packed 2 mL cartridges, 100-150 µm particle size resin.

Nitric acid, HNO_3, concentrated, 16 M.

Nitric acid, HNO_3, 3 M: Add 191 mL of concentrated HNO_3 to 700 mL water and dilute to 1 L with water.

3.0 APPARATUS

Analytical balance
Anion exchange column and frits
Beakers, various sizes
Centrifuge tubes
Extension funnels
Filtering flask
Filters, Supor-450, 47 mm, or equivalent
Fume hood
Glass filtering assembly
Hot plate
Liquid scintillation analyzer (LSA)
Liquid scintillation vials
pH paper
Stir bar
Stir rod
Transfer pipette
Vacuum box assembly
Vacuum pump

4.0 PROCEDURE

4.1 General Requirements

Before proceeding, you must be certified as indicated in QCP1 of this manual and Section 3 of the Quality Program (QP) Manual. See page two for a copy of the certification record.

A batch yield sample must be run with each batch to determine chemical recovery for the batch (see below for calculations). This is not a QC sample; two QC samples must be run with each batch.

4.2 Water Samples

NOTE: Prior to beginning this analysis, ensure the sample has been counted for gamma emitting isotopes, in particular radioactive isotopes of cobalt.

4.2.1 Filter the sample through a 0.45 μm filter unless otherwise stated in the Laboratory Work Request (LWR). Measure 0.025 to 0.25 L into an appropriate size beaker. Add 1 mL Ni carrier to each sample, blank, Laboratory Control Standard (LCS), and batch yield. Add a known amount of Ni-63 to the LCS and the batch yield sample. For samples containing an appreciable amount of radioactive cobalt, add 1 mL Co carrier to each sample. **See step 4.2.1 of AP12 JHA**.

4.2.2 Add 10 mL 12 M HCl and gently heat to ~1 to 2 mL. DO NOT BAKE. For samples that have an appreciable amount of radioactive cobalt, proceed to Cobalt Separation, section 4.3. For samples that do not have an appreciable amount of radioactive cobalt proceed to Nickel Separation, section 4.6. **See step 4.2.2 of AP12 JHA**.

4.3 Cobalt Separation

4.3.1 Dissolve residue in 20 mL 10 M HCl. **See step 4.3.1 of AP12 JHA**.

4.3.2 Prepare the anion exchange columns by adding approximately 10 g (preconditioned with 10 M HCl) of the anion exchange resin to each column. Allow the resin to settle and place a frit on top of the resin.

4.3.3 Place a waste beaker under each column and pour 50 mL 10 M HCl into each column. Allow the solution to drain by gravity into the waste beakers. **See step 4.3.3 of AP12 JHA**.

4.3.4 Place a labeled 250 mL beaker under each column and pour the samples through the column.

4.3.5 Rinse the columns with 100 mL 10 M HCl and collect in the same beaker as in step 4.3.4. **See step 4.3.5 of AP12 JHA**.

4.3.6 Place the beakers on a hot plate and gently bring each solution down to 1-2 mL. **See step 4.3.6 of AP12 JHA**.

4.3.7 Proceed to Nickel Separation, section 4.6.

4.4 Soil, Sediment, and Smear Samples

NOTE: Prior to beginning this analysis, ensure the sample has been counted for gamma emitting isotopes, in particular radioactive isotopes of cobalt.

4.4.1 Weigh up to 2 g of ground dry soil, sediment, or solid material into an appropriate size beaker. Use soil with no Ni-63 present and/or a clean smear for the blank. Add a known amount of Ni-63 to the LCS and batch yield sample. **See step 4.4.1 of AP12 JHA**.

4.4.2 Add 1 mL Ni carrier to each sample, blank, LCS, and batch yield. For samples containing an appreciable amount of radioactive cobalt, add 1 mL Co carrier to each sample. **See step 4.4.2 of AP12 JHA**.

4.4.3 Add 25 mL of 16 M HNO_3 and 25 mL 12 M HCl to each beaker. **See step 4.4.3 of AP12 JHA**.

4.4.4 Place a watch glass on each beaker on a hot plate and heat at 80°C for 2 hours while stirring. Carefully, add 16 M HNO_3 and 12 M HCl in a one to one ratio as needed to prevent evaporation. **See step 4.4.4 of AP12 JHA**.

NOTE: Be very careful when adding HCl after adding HNO_3 because there will be a vigorous reaction.

4.4.5 Remove each beaker from the hotplate and allow samples to cool.

4.4.6 Filter samples through a Supor-450, 47 mm filter (or equivalent) using a glass filtering assembly. Transfer the solution to an appropriate size beaker. Dispose of the solids into the appropriate waste stream. **See step 4.4.6 of AP12 JHA**.

4.4.7 Evaporate the samples to near dryness (~1 mL).

4.4.8 Add 20 mL of 10 M HCl and set samples aside to prepare anion exchange columns. Proceed to Anion Exchange Chromatography, section 4.5. **See step 4.4.8 of AP12 JHA**.

4.5 Anion Exchange Chromatography

NOTE: This section will remove any iron and/or cobalt they may be present in the samples.

4.5.1 For each column, slurry ~10 g anion exchange resin in a beaker with 10 M HCl. Let set a minimum of 30 minutes before proceeding with step 4.4.2 to allow for the swelling of the resin. **See steps 4.5.1-4.5.3 of AP12 JHA**.

4.5.2 Add ~10 g of the slurry to each column and allow resin to settle. Rinse the resin beads that stick on the column with 10 M HCl. Place a frit on top of the resin bed using a glass rod.

4.5.3 Pour 50 mL 10 M HCl through each column to pre-condition it. Collect in a waste beaker for disposal in the dilute acid waste.

4.5.4 Place a labeled 250 mL beaker under each column. Pour the sample (from step 4.4.8) through each column and collect eluent.

4.5.5 Add 50 mL 10 M HCl to each column and collect in the same beaker. Repeat one more 50 mL 10 M HCl addition and collect. **See step 4.4.5 of AP12 JHA**.

4.5.6 Place a waste beaker under each column and pour water through column until the pH is at least 5. Discard rinse into an appropriate waste stream.

4.5.7 Slowly evaporate the samples to 1-2 mL. DO NOT BAKE. **See step 4.5.7 of AP12 JHA**.

4.5.8 Proceed to Nickel Separation, section 4.6.

4.6 Nickel Separation

4.6.1 Dissolve residue with 10-20 mL 1 M HCl. Heat gently if needed. **See step 4.6.1 of AP12 JHA**.

4.6.2 Add 1 mL 1 M ammonium citrate per 10 mL 1 M HCl used to the sample and adjust to pH 10-11 with concentrated NH_4OH (it usually takes 30-70 drops). **See step 4.6.2 of AP12 JHA.**

NOTE: For soil samples, add the NH_4OH very slowly with stirring so that hydroxides do not form quickly. If too many hydroxides form the flow rate for the columns may stop. If hydroxides do form, use dilute HCl to dissolve them.

4.6.3 For each sample, place a nickel cartridge in the vacuum box assembly.

4.6.4 Put a 10 mL syringe on each cartridge.

4.6.5 Condition each column by pipetting 5 mL 0.2 M ammonium citrate, buffered to pH 10, and allow solution to drain into a waste container. **See step 4.6.5 of AP12 JHA.**

4.6.6 Load sample from steps 4.2.2, 4.3.7 or 4.4.9 onto cartridge and allow solution to drain into a waste container at 1 to 2 drops per second. A red band will appear on the column. **See step 4.6.6 of AP12 JHA.**

4.6.7 Rinse beaker with 5 mL 0.2 M ammonium citrate, buffered to pH 10, and pour onto column. Allow rinse to drain into a waste container. **See step 4.6.7 of AP12 JHA**.

4.6.8 Rinse the column with 25 mL 0.2 M ammonium citrate, buffered to pH 10, and allow to drain into a waste container. **See step 4.6.8 of AP12 JHA.**

4.6.9 Place a labeled centrifuge tube under each column.

4.6.10 Strip Ni with three 2 mL additions of 3 M HNO_3. **See step 4.6.10 of AP12 JHA.**

4.6.11 Pour solution into a 50 mL beaker. Rinse centrifuge tube with water and add to the beaker. **See step 4.6.11 of AP12 JHA.**

4.6.12 Heat each sample to near dryness (~1 mL). Add 5 mL water. Repeat. **See step 4.6.12 of AP12 JHA.**

4.6.13 Heat each sample to near dryness (~1 mL). **See steps 4.6.13 – 4.6.14 of AP12 JHA.**

4.6.14 Transfer solution to a scintillation vial using a plastic transfer pipette.

4.6.15 Rinse beaker in very small increments with water and transfer to vial. Bring final volume in vial to 3 mL. **See step 4.6.15 of AP12 JHA.**

4.6.16 Add 17 mL of scintillation cocktail and shake well. **See step 4.6.16 of AP12 JHA.**

4.6.17 Submit samples for scintillation counting.

5.0 CALIBRATIONS

5.1 Instrument Background Preparation

5.1.1 Add 1 mL Ni carrier and 2 mL water to a scintillation vial. **See step 5.1.1 of AP12 JHA.**

5.1.2 Add 17 mL of scintillation cocktail and shake well. **See step 5.1.2 of AP12 JHA.**

5.2 Instrument Efficiency Standard Preparation

5.2.1 Add 1 mL Ni carrier to a scintillation vial. **See step 5.2.1 of AP12 JHA.**

5.2.2 Add Ni-63 standard to the vial. **See step 5.2.2 of AP12 JHA.**

5.2.3 Bring total volume to 3 mL with water.

5.2.4 Add 17 mL of scintillation cocktail, shake well, and submit for counting. **See step 5.2.4 of AP12 JHA.**

5.2.5 The Laboratory Manager must review and approve the counting efficiency.

6.0 CALCULATIONS

Critical data values will be documented on standard forms maintained as critical records. The following equations define the critical data values. All data will be recorded and reduced according to these calculations.

$$Concentration = \frac{G - B}{E \cdot Y \cdot Q} = pCi / unit$$

$$2\sigma\ Error = \frac{1.96\sqrt{(G + B) \cdot T}}{T \cdot E \cdot Y \cdot Q} = pCi / unit$$

$$2\sigma\, TPU = C \cdot 1.96\sqrt{\frac{(G+B)\cdot T}{((G-B)\cdot T)^2} + RE^2 + RY^2 + RQ^2} = pCi/unit$$

$$MDC = \frac{3 + 4.65\sqrt{B \cdot T}}{T \cdot E \cdot Y \cdot Q} = pCi/unit$$

To calculate efficiency:

$$E = \frac{G_E - B}{A} = cpm/\ pCi$$

To calculate chemical yield:

$$Y = \frac{G_{BY} - G}{E \cdot AY} = no\ units$$

where:	A	=	activity in pCi for efficiency determination
	AY	=	activity in pCi for yield determination
	B	=	background cpm beta
	C	=	concentration in pCi/unit
	E	=	counting efficiency (cpm/pCi)
	G	=	sample gross cpm beta
	G_{BY}	=	batch yield gross cpm beta
	G_E	=	efficiency gross cpm beta
	MDC	=	minimum detectable concentration
	Q	=	quantity
	RE	=	1σ relative uncertainty of the efficiency
	RQ	=	1σ relative uncertainty of the quantity
	RY	=	1σ relative uncertainty of the yield
	T	=	time minutes
	TPU	=	total propagated uncertainty
	Y	=	chemical yield

7.0 RECORDS

7.1 Reference QP Manual for general record requirements.

7.2 The raw count data is saved during the weekly backup of the LSA to the ORISE network disks.

7.3 Hard copies of assignment and calculation sheets are maintained in the archived site file. Electronic copies of assignment and calculation sheets are saved during the daily incremental backup of the network system. The following data sheets show the required data and information. These forms or the equivalent should be completed and retained:

- Ni Analysis Assignment Form
- Ni Lab Data Sheet
- Ni Concentration and Uncertainty Report (This report may be generated using approved Excel spreadsheets or from the database, if available.)

AP12 (Rev 6) - Ni-63 ANALYSIS ASSIGNMENT FORM

Assigned To: _____ Date: _____ Batch: _____

Task #: _____ LWR #: _____ Activity Level*: _____

Sample #s: _____

_____

_____

Analysis Required:

Batch Yield ☐ Sample # _____
Initial below sample

Ni-63 STD # _____ Quantity: _____
Units: _____

Eff. Spike ☐ Ni-63 STD # _____ Quantity: _____
(see Special Instructions, if any) Units: _____

QC Required:

Blank ☐

LCS ☐ Ni-63 STD # _____ Quantity: _____ Initials ☐
Units: _____

Pipette # _____ Volume (mL) _____ Weight (g) _____

Replicate ☐ Sample # _____ # Replicates: _____

Matrix Spike ☐ Sample # _____

Ni-63 STD # _____ Quantity: _____ Initials ☐
Units: _____

1 mg Ni CARRIER ADDED? Initials ☐

SPECIAL INSTRUCTIONS: _____

_____

_____

_____

* If Activity Level is indicated as Moderate or High, perform area survey.

COMMENTS: _____

_____

_____

_____

AP12 (Rev 6) - Ni-63 LAB DATA SHEET

			BATCH YIELD	SAMPLE			
Sample #							
Quantity							
Units							

Sample #							
Quantity							
Units							

Sample #							
Quantity							
Units							

Sample #			
Quantity			
Units			

AP12(Rev 6) - Nickel-63 (by batch yield) Concentration and Uncertainty Report

INPUT BY:

DATE:

TASK#

BATCH#

Batch Yield (BY) Calculation	
BY sample ID	
BY sample cpm	
BY Sample Quantity (SQ)	
BY SQ error	
Sample cpm	
SQ	
SQ error	
BY pCi added	
BY pCi added error	
BY	
BY Error	
BY Relative Error	

Efficiency (Eff) Calculation	
Eff spike cpm	
Background cpm	
pCi added	
pCi added error	
Eff (cpm/pCi)	
Eff Error (cpm/pCi)	
Eff Relative Error	

Counting time for Eff and BYcalculations (min)	

Position #	SAMPLE ID	GROSS cpm	SQ	SQ ERROR	UNITS	TIME (min)	CONC.	TPU	4.65 sigma MDC
1									
2									
3									
4									
BY									
BY Sample									
7									
8									
9									
10									
11									
12									
13									
14									
15									
16									
17									
18									
19									
20									

Ni-63 Known Activity	Unc.	Meas./ Known	Unc.

BLANK CORRECT? YES[ ] NO[ ] INIT_____

LCS CORRECT? YES[ ] NO[ ] INIT_____

BATCH YIELD CORRECT? YES[ ] NO[ ] INIT_____

IF NO, SPECIFY REASON:

ANALYST REVIEW:_____ DATE:_____

REVIEWED BY:_____ DATE:_____

GIVEN TO:_____ DATE:_____

QC ENTERED BY:_____ DATE:_____