IRON-55 IN WATER

(WITH VACUUM BOX SYSTEM)

1. SCOPE

1.1. This is a method for the measurement of Iron-55 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. Iron-55 is preconcentrated from water samples using a ferric hydroxide precipitation and separated using Eichrom's TRU Resin column. Up to 2.5mg of stable iron carrier can be added to the sample, as a yield monitor. Once the iron fraction is separated, iron recovery can determined from a batch yield sample, from chemical recovery of stable iron via atomic emission spectrometry or gravimetrically as an iron hydroxide precipitate. Fe-55 is measured by liquid scintillation counting.

3. SIGNIFICANCE OF USE

3.1. This is a rapid, reliable method for measurement of Fe-55 in water samples that is more cost-effective and efficient than traditional techniques.

4. INTERFERENCES

4.1. The maximum amount of iron to be loaded on a 2 mL prepacked TRU column is 2.5mg. Samples with high iron content must be aliquotted appropriately so that the maximum 2.5mg of Fe/sample is not exceeded.

5. APPARATUS

- Analytical balance, 0.0001 g sensitivity
- Beakers, glass

- Cartridge reservoirs, 10mL (Eichrom Part: AR-200-RV10) or 20mL (Eichrom Part: AR-200-RV20)
- Filter, 0.45micron
- Fume hood
- Liquid scintillation counter
- Liquid scintillation vials
- Tweezers
- 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
- Vacuum filter apparatus
- Vacuum pump, 115 V, 60 Hz Fisher Part: 01-092-25 (or equivalent) or house vacuum
- Optional item for collection of load and rinse fractions:
    - Vacuum box inner liner, Eichrom Part: AR-12-LINER or AR-24-LINER

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.

Sodium hydroxide, NaOH
Deionized water, All reagents are prepared using deionized water
Ferric nitrate, $Fe(NO_3)_3 \cdot 9H_2O$
Isopropyl alcohol, C_3H_7OH
Nitric acid (70%), concentrated HNO_3
Phenolphthalein pH Indicator
TRU® resin, 2mL prepacked cartridge, 50-100µm, Eichrom Part TR-R50-S

6.1. *Iron carrier* - (5mg/mL Fe)- Dissolve 3.6g of $Fe(NO_3)_3 \cdot 9H_2O$ in 80mL of water. Dilute to 100mL with water.

6.2. *Phenolphthalein solution*- Dissolve 1g phenolphthalein in 100mL 95% isopropyl alcohol. Dilute with 100mL of water.

6.3. *Nitric acid (2M)*- Add 125mL of concentrated HNO_3 to 700mL of water. Dilute to 1L with water.

6.4. *Nitric acid (8M)* - Add 500mL of concentrated HNO_3 to 400mL of water. Dilute to 1L with water.

6.5. *Nitric acid (0*.5M) – Add 31mL of concentrated HNO_3 to 400mL of water. Dilute to 1L with water.

6.6. *Sodium hydroxide (1M)* - Add 20g of NaOH to 400mL of water. Mix to dissolve. Dilute to 500mL with water.

6.7. *Sodium hydroxide (4M)* – Add 80g of NaOH to 400mL of water. Mix to dissolve. Dilute to 500mL with water.

7. PROCEDURE

7.1. Preconcentration of Fe-55 by ferric hydroxide precipitation

7.1.1. If necessary, filter water sample using 0.45µm filter to remove particulates.

7.1.2. Acidify water samples of up to 1L to pH 2 using concentrated HNO_3.

7.1.3. To each water sample, add 0.75mL of phenolphthalein indicator and 0.5 mL of 5mg/mL Fe carrier.

Note: Fe is added as a yield monitor and to preconcentrate Fe-55 using a ferric hydroxide precipitation.

7.1.4. Mix samples thoroughly and heat to 60-80^{o}C for 15-20 minutes.

7.1.5. Allow samples to cool to room temperature.

7.1.6. While stirring, slowly add enough concentrated 1M NaOH to reach the pink phenolphthalein indicator endpoint.

Note: NaOH should be used to adjust the pH. Adjusting the pH with NH_4OH can lead to lower recoveries of iron during the ferric hydroxide precipitation.

7.1.7. Allow precipitate to settle until supernate can be decanted or proceed to the next step and centrifuge samples for quicker separation.

7.1.8. Transfer samples, including precipitate to 250mL centrifuge tubes. Centrifuge samples at 2000rpm for 10-20 minutes.

Decant supernate. Repeat until entire sample has been transferred to centrifuge tube and centrifuged.

7.1.9. Rinse sample beaker with 10mL of deionized water. Transfer rinse to the appropriate centrifuge tube. Centrifuge samples for 10 minutes at 2000rpm. Decant supernate.

7.1.10. Dissolve precipitate in 5mL of concentrated HNO_3.

7.1.11. Transfer dissolved samples to 15mL centrifuge tubes.

7.1.12. Rinse 250mL centrifuge tubes with 5mL deionized water.

7.1.13. Transfer rinses to the appropriate 15mL centrifuge tubes. Cap 15mL centrifuge tubes and mix.

7.2. Iron separation using Eichrom TRU Resin column

7.2.1. For Place the inner tube rack (supplied with vacuum box system) into the vacuum box with the 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 TRU cartridge on to the inner support tube.

7.2.4. Add syringe barrels (funnels/reservoirs) to the top end of each TRU 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 8M HNO_3 into each TRU cartridge reservoir. Adjust vacuum to achieve a flow rate 1-2mL/min. Allow solution to completely pass through each cartridge.

7.2.7. Load sample in 8M HNO_3 on the TRU cartridge. Allow solution to pass through cartridge at 1-2mL/min.

7.2.8. Rinse sample centrifuge tubes with 5mL 8M HNO_3. Add tube rinse to TRU cartridge reservoir. Allow solution to completely pass through cartridge at 1-2mL/min.

7.2.9. Rinse the TRU cartridge with 10mL of 8M HNO_3. Allow solution to completely pass through cartridge at 1-2mL/min. Disengage vacuum. Dispose of solution as waste.

7.2.10. Place a clean, labeled 50mL centrifuge tube below each TRU cartridge. Add 15mL of 2M HNO_3 to each TRU cartridge reservoir to strip Fe. Engage vacuum. Allow solution to completely pass through cartridges at 1-2mL/min. Turn off vacuum.

7.2.11. Slowly add 4M NaOH to each sample until ferric hydroxide precipitate forms (pH 4-9).

7.2.12. Determine Fe yield using a batch recovery sample, atomic emission spectrometry (Steps in 7.3.) for stable iron or gravimetric recovery of stable iron (Steps in 7.4.).

7.3. Iron recovery by atomic emission spectrometry

7.3.1. Centrifuge at 2000rpm for 5-10 minutes.

7.3.2. Decant supernate.

7.3.3. Dissolve sample in 5mL of 0.5M HNO_3.

7.3.4. Remove a 0.25mL aliquot of each sample from step to a 10mL volumetric flask for stable iron yield analysis by atomic emission spectrometry.

7.3.5. Dilute yield sample aliquot to 10mL with 0.5M HNO_3.

7.3.6. Analyze sample for iron using atomic emission spectrometry.

7.3.7. Transfer remaining sample to a 20mL liquid scintillation vial.

7.3.8. Add 15mL of liquid scintillation cocktail.

7.3.9. Measure Fe-55 using liquid scintillation counting.

7.4. Iron recovery by gravimetric determination of stable iron

7.4.1. Filter the solution from 7.2.7 through a 25mm diameter glass fiber filter using a filter apparatus.

7.4.2. Dry the filter under a heat lamp completely.

7.4.3. Weigh the filter and record the weight.

7.4.4. Place the glass fiber filter in a 20mL liquid scintillation vial.

7.4.5. Add 15mL of liquid scintillation cocktail and count Fe-55 using a liquid scintillation counter.

8. CALCULATIONS

Atomic Emission Spectrometry Recovery of Fe Carrier

$$Yield = \frac{C_{meas}}{7.5\ ppm}$$

where:

C_{meas} = concentration in ppm measured by atomic emission spectrometry

7.5 ppm = Theoretical concentration in ppm for 3 mg stable Fe, 0.25mL aliquot of 5.0mL total, diluted to 10mL.

Gravimetric: Fe carrier

$$\text{Yield} = \frac{(R_w - T_w - B_w)}{C_w}$$

where:

R_w = residue+filter, mg
T_w = tare weight of filter, mg
B_w = blank weight, mg (extractant loss from column)
C_w = Expected FeOH, mg (This is the wt. of Fe carrier added and then converted to FeOH equivalent wt.)

Fe-55 activity

$$A = \frac{(S-B)}{E \times V \times Y \times 60} \times \left(\frac{5}{4.75}\right)$$

where:

A = Fe-55 sample activity (Bq/L)
S = Fe-55 measured activity, cpm
B = blank activity, cpm
E = counting efficiency
V = sample volume, liters

Y = Fe-carrier yield
60 = Conversion from cpm to cps

9. REFERENCES

1) E Philip Horwitz, Renato Chirizia, Mark L. Dietz, Herbert Diamond, and Donald M. Nelson. Separation and Preconcentration of Actinides from Acidic Media be Extraction Chromatography. *Analytica Chimica Acta*, 281 (1993) 361.

2) Pacific Northwest Laboratory Method PNL-ALO-345, Iron-55 Analysis

3) ASTM Method D49922-09, “Standard Test Method for the determination of radioactive iron in water.”

1) Aliquot up to 1000mL of water into glass beaker.

2) Acidify to pH 2 with conc. HNO_3.

3) Add 0.5mL of 5mg/mL Fe yeild tracer (2.5mg Fe).

4) Add 0.75mL of phenolphthalein indicator.

5) Mix thoroughly. Heat at 60-80ºC for 20 minutes.

6) While stirring, slowly add 1M NaOH to phenolphthalein endpoint.

7) Allow ferric hydroxide ppt to settle for 30 minutes to 2 hours.

8) Transfer to 250mL centrifuge tube. Centrifuge at 2000rpm for 10 minutes. Decant supernate. Repeat until entire sample has been centrifuged.

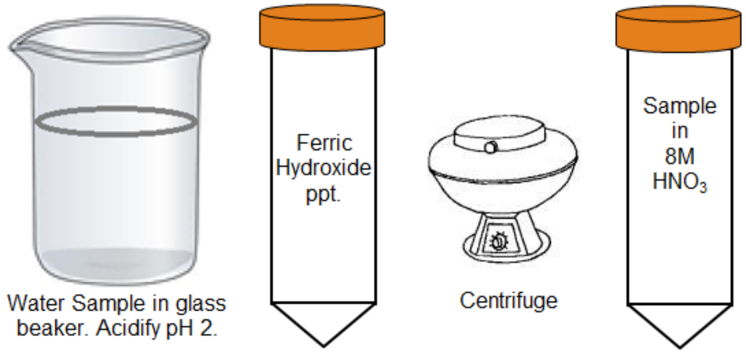
9) Rinse sample beaker with 10mL water. Add to centrifgue tube.

10) Mix rinse/ppt well. Centrifuge at 2000rpm for 10 minutes.

11) Decant supernate. Dissolve precipitate with 5mL conc. HNO_3. Tranfer to 15mL centrifuge tube.

12) Rinse 250mL centrifuge tube with 5mL DI water. Transfer rinse to corresponding 15mL centrifuge tube.

13) Cap 15mL centrifuge tubes and mix.



Water Sample in glass beaker. Acidify pH 2.

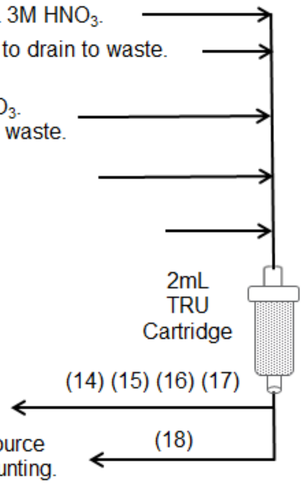
14) Precondition TRU cartridge with 5mL 3M HNO_3.

15) Load sample on to TRU. Allow liquid to drain to waste. Fe is retained.

16) Rinse sample tube with 5mL 8M HNO_3. Add rinse to TRU. Allow liquid to drain to waste.

17) Rinse TRU with 10mL 8M HNO_3. Allow liquid to drain to waste.

18) Strip Fe with 15mL 2M HNO_3.



Fe sample to tracer recovery and source preparation for liquid scintillation counting.