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SAVANNAH RIVER LABORATORY DIVISION
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Category 2 Procedure

DETERMINATION OF Fe(II)/Fe(III) RATIO IN GLASS (U)

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Fe (II) / Fe (III)

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DETERMINATION OF Fe(II)/ Fe(III) RATIO IN GLASS (U)

I. SCOPE

The procedure is designed for the simple, rapid determination of the Fe(II)/Fe(III) ratio in glass samples. Directions for the preparation of glass from non-radioactive sludge sample are presented. The range of the method, as written, is 1- 3 mg of total iron.

II. GENERAL LIMITATIONS AND INTERFERENCES

No interfering elements or compounds are expected to be found in the samples.

III. QUALITY OF DATA/DATA VALIDATION

A. Quality of Data

Data proving the method were developed and are recorded in DPST-87-304, Feb. - 20, 1987, Ref. 1. Calibration curves were prepared, demonstrating that the developed ferrous Ferrozone complex follows Beer's Law. A "Verification Procedure" for the method was developed to be used as a check on the system and reagents to assure that they were operational. Known synthetic mixtures of ferric and ferrous ions were analyzed to demonstrate the accuracy of the method.

The estimated relative standard deviation is $\pm 5\%$ of the ratio value.

B. Data Validation

All reagents used in the analysis or for the preparation of QC or calibration standards shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society (ACS), where such specifications are available.

Analytical balances shall have a current QC calibration for the balance/balance weight combination.

Calibrated pipets shall be used in the preparation of reagent solutions and bench standards and for all standard/sample aliquots. Calibration is every six months.

Class B volumetric flasks are adequate for this method.

Liquid QC standards for Fe(II)/Fe(III) are not available for the method due to the difficulty in preparing and preserving a true Fe(II)/Fe(III) standard. This is due to the oxidation of Fe(II).

QC glass samples have been carefully characterized for use with this method. A QC sample shall be run prior to the analysis of samples and after each 10 samples in a group. Results must be within $\pm 10\%$ of the standard value listed on the QC chart. Submit the QC chart after task supervisor's signature to the QC Coordinator on a monthly basis. Consult the task supervisor if the result is not within the limits. Included under Section X, Calibration and Standardization, is a "Verification of Fe(II)/Fe(III) Method" which is designed as a quick way to establish that the Fe(II)/Fe(III) method is working, but it does not provide a standard. This method is available when desired.

IV. TRAINING

On-the-job training is sufficient for certification for the use of this method.

To be considered qualified, the trainee must be capable of the following:

- Preparing glass from sludge samples,
- Performing the "verification" of the Fe(II)/Fe(III) method, and
- Analyzing five glass standard samples for Fe(II)/Fe(III) to the satisfaction of the task supervisor.

The task supervisor will decide when the training is complete and enter this on the training record.

V. DESCRIPTION

The procedure was designed for the simple, rapid determination of the Fe(II)/Fe(III) ratio in glass samples. The procedure consists of the following steps:

- dissolution of the pulverized glass sample in a sulfuric-hydrofluoric acid mixture, containing ammonium vanadate, which preserves the Fe(II) content;
- addition of boric acid to destroy iron-fluoride complexes, making the iron available for color formation with Ferrozine;
- addition of pH 5 buffer and Ferrozine reagent to form the magenta-colored ferrous-Ferrozine complex, with measurement of the absorbance for the determination of Fe(II) content; and,
- addition of ascorbic acid to reduce Fe(III) to Fe(II), with a second absorbance measurement that determines total Fe.

When only the ratio is required, the quantitative measure of sample and reagents is unnecessary as long as Steps 9-12 of Section XI are carried out on the same solution and the final absorbance values fall within the range of the method.

Directions for the preparation of glass from non-radioactive sludge samples are provided. The analysis of this prepared glass for the Fe (II) / Fe (III) ratio is an indication of the ratio that would be in a plant batch of glass if made from this sludge.

VI. EQUIPMENT

Alumina crucibles - Coors, with fitted lids, 100-mL, or equivalent.

Aluminum weighing pans.

Analytical balance - Sensitive to 0.1 mg.

Brinkmann Vibratory Mill - Or the equivalent, to pulverize glass samples. The sample container and pulverizer must be of agate

Crucible tongs.

Cuvette - 10 x 10 x 4.5 mm, 4.5 mL capacity.

Graduated cylinder - 25-mL.

Hammer

Magnetic stirrer with Teflon covered stirring bars.

Micropipets with tips - Assorted, including 100-, 500- and 1000- μ L.

Muffle furnace - Thermolyne, or equivalent.

Polystyrene vials - 1" in diameter by 3" high, with caps.

Spalula.

Spectrophotometer/colorimeter -

Any one of the following instruments can be used:

- Brinkmann PC 800 Probe Colorimeter with a 570 nm filter, and 1-cm path length probe,
- grating spectrophotometer or Model 8451-A Hewlett-Packard photodiode array spectrophotometer (HP-8451-A) with 1- cm cuvettes, at 562 nm,

- Model 8451 Hewlett-Packard photodiode array spectrophotometer modified with fiber optics (2A) for measurements within radioactive containment, at 562 nm.

NOTE: Section XI, Analysis, is written for the HP-8451-A and for the Brinkmann PC 800.

Timer.

Transfer pipets - 20-mL.

Volumetric flasks - 100-mL. Class B flasks are suitable.

VII. REAGENTS

Purity of reagents - Unless otherwise stated, reagent grade chemicals shall be used, where available. All reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society (ACS), where such specifications are available.

Purity of water - Unless otherwise indicated, reference to water shall be understood to mean distilled or deionized water, which meets the ASTM Standard Specification for Type II Reagent Water as defined in ASTM D1193-77.

Ammonium vanadate, meta - (NH_4VO_3) - Crystal. This chemical is not available as Reagent ACS. It is available as a purified grade from Fisher Scientific as Cat. No. A714I-500, or from other vendors.

Ascorbic acid - ($\text{C}_6\text{H}_8\text{O}_6$) - Crystal.

Boric acid - (H_3BO_3) - Saturated solution - Prepare as follows: Add 6.5 g of H_3BO_3 to 100 mL of water in a 250-mL beaker and stir to dissolve. Some undissolved crystals should remain.

Buffered Ferrozine solution - Prepare as follows: Dilute 50 mL of buffer solution and 50 mL of Ferrozine, 1% solution, to one liter with water. Mix well.

Buffer solution, pH 5 - Prepare as follows: Dissolve 270 g of sodium acetate, trihydrate, ($\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$) in about 800 mL of water and add 60 mL of glacial acetic acid (CH_3COOH). Dilute to one liter. Mix well.

Fe(III) Test Solution (FTS) - [$\text{FeNH}_4(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$] - 0.0100M - Prepare as follows: Weigh exactly 0.482 g of ferric ammonium sulfate, dodecahydrate [$\text{FeNH}_4(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$], and quantitatively transfer to a 100-mL volumetric flask and dilute to volume with 0.1M H_2SO_4 . Replace the solution at least every three months.

The FTS is used in Section X. A, Verification of Fe(II)/Fe(III) Method. This solution contains 560 μg Fe(III) per mL, or 28 μg Fe(III) per 50- μL aliquot.

Ferrozine solution - 1% - Prepare as follows: Dissolve 1.00 g of Ferrozine Iron Reagent (Hach Chemical Company) in 100 mL of water.

Hydrofluoric acid - (HF) - Concentrated, 48-51%.

Sulfuric acid - (H_2SO_4) - Concentrated, 95-98%.

Sulfuric acid - (H_2SO_4) - 0.1M - Prepare as follows: Add 1.1 mL of sulfuric acid, concentrated, to 200 mL of water. Mix well.

VIII. SAFETY PRECAUTIONS

FOLLOW THE ADS RADIATION SAFETY GUIDELINES
FOLLOW THE ADS LABORATORY SAFETY GUIDELINES

SPECIAL

- Hydrofluoric acid, liquid or vapor, is dangerous when in contact with the eyes, skin, or respiratory system. The liquid or vapor in contact with any part of the body may immediately cause serious and extremely painful burns. Very often, contact with dilute hydrofluoric acid causes no immediate reactions, but can cause severe injury and pain some hours later. When handling hydrofluoric acid, work in a hood and wear rubber gloves, safety glasses, and lab coat. If hydrofluoric acid contacts the skin, flush the affected area immediately with copious quantities of running water for 2-4 hours. Contact supervision and get medical attention immediately.
- Exercise care in handling ammonium vanadate as it is a poison on inhalation or ingestion.

REMEMBER: always

1. Use a fume hood.
2. Add acid to water.
3. Wear plastic gloves when handling chemicals.
4. Avoid contact with skin and breathing of vapors.
5. Voice contact or supervision present off shift.
6. Supervision present for high activity work.
7. Do not exceed:
 - hood and radiobench activity limits
 - self-monitoring limits
 - unsupervised off-shift limits.

IX. CALIBRATION FREQUENCY

No calibrations are required.

X. CALIBRATION AND STANDARDIZATION

Calibration: No calibration is performed.

A method is provided to verify that the system and the reagents are operational. It does not provide a known standard. It can be used to test the system when desired. Glass QC standards are analyzed prior to the analysis of samples.

A. Verification of Fe(II)/Fe(III) Method

For verification of the method, analyze iron test solution, FTS, by this procedure, using 50 μ L of FTS to 20 mL of buffered Ferrozine solution in the vial. Continue the analysis from Steps 10-12 of Section XI.

NOTE: The absorbance before the addition of ascorbic acid will be very low. After the ascorbic acid addition, the expected absorbance will be in the range of 0.6 absorbance units.

XI. ANALYSIS

A. Glassmaking Procedure for Non-Radioactive Sludge Samples

1. Preheat the muffle furnace to 1150°C.

NOTE: Avoid exceeding 1150°C, as this can shorten the life of the furnace.

2. Mix the sample thoroughly and add 40-60 mL of the sample to a 100-ML alumina crucible.
3. Place the lid on the crucible and using crucible tongs, place the crucible in the furnace and close the door.
4. Note the time the crucible is placed in the furnace. Heat the crucible for 4 hours at 1150°C.
5. Remove the crucible from the furnace, place on a clean metal or ceramic tile surface, and allow to cool for 1 hour.

B. Glass Crushing Procedure

1. Place the cooled crucible containing the prepared glass in double plastic bags, approximately 10 in. x 8 in. size.

NOTE: The plastic bags will help contain the pieces of glass when the crucible is broken.

2. Strike the crucible repeatedly with a hammer to shatter the glass into pieces small enough to fit easily in the agate crushing mortar.

NOTE: Wear goggles and leather gloves for protection in the event that broken glass escapes from the plastic bags.

3. Pick out the smaller pieces of glass with tongs or forceps and add to the agate grinding mortar. Approximately 200 mg are sufficient for duplicate analysis and rechecks if necessary.

NOTE: Avoid glass with pieces of crucible attached.

4. Place two agate crushing balls in the mortar and replace the top.
5. Secure the mortar in the clamp on the mixer mill and grind for 15 minutes at maximum speed.
6. After the mixer mill stops, remove the mortar from the clamps.
7. Remove the top from the mortar and carefully empty the powdered glass into an aluminum weighing dish. Use a clean spatula to loosen the glass powder that sticks to the mortar and cap.
8. Carefully tap as much of the powder as possible into the weighing pan.
9. Remove the agate balls from the weighing pan, using a clean pair of tongs, and transfer the powdered glass to a labeled plastic vial.

C. Measurement of the Fe (II) / Fe (III) Ratio

C.1 Measurement Using the HP-8451-A

1. Turn on the power to the HP-8451-A photodiode array spectrophotometer and allow it to warm up. After the diagnostic program has run, the diagnostic light will go out and the instrument is ready for use.
2. Place 10 to 30 mg of the finely ground glass in a polystyrene vial.

NOTE: This quantity of glass should give a total absorbance reading, for total iron, at 562 nm of less than 1.0. It is important not to exceed an absorbance reading of 1.0 because the absorbance versus concentration may not be linear above this value. If the absorbance does exceed 1.0, either reduce the glass sample size, increase the volume of the buffered Ferrozine solution used in XI. C.1, Step 9, or reduce the sample solution aliquot in XI. C.1, Step 8.

3. Add about 10 mg of solid ammonium vanadate to the vial.

NOTE: Steps 4 through 7 following must be performed in a hood; gloves required.

4. Add 500 μ L of concentrated sulfuric acid. Gently swirl the vial to wet the glass.
5. Cautiously add 1500 μ L of hydrofluoric acid to the vial containing the glass.

HAZARD: Wear gloves; solution becomes hot; follow the instructions in the safety section AT ONCE if hydrofluoric acids contacts skin.

NOTE: Do not use glass equipment with hydrofluoric acid.

6. Swirl the vial to aid in dissolving the glass.

NOTE: The glass should dissolve almost immediately. If not, allow to stand until dissolution is obtained.

7. Add 20 mL of saturated boric acid solution and mix thoroughly by using a plastic dropper to draw up and expel the solution back into the vial several times.

NOTE: Make sure the solution is well mixed before proceeding.

8. Transfer a 200 μ L-aliquot of the solution from Step 7 to a second plastic vial.

NOTE: The aliquot size can be varied to obtain a suitable absorbance range of less than 1.0. See NOTE under Step 2 just above.

9. Place 20 mL of the buffered Ferrozine solution to this second vial. Mix with a clean plastic dropper. Allow the purple color to develop for exactly 10 minutes before reading the absorbance.

10. While the purple color is developing, complete the set-up of the HP-8451-A and the blank measurement of the buffered Ferrozine solution as directed in Steps 11-15 following.
11. Press STOP-ERASE STATUS EXECUTE as directed in the "Getting Started" card in the front of the instrument.
12. Press λ 562 EXECUTE to enter the wavelength.
13. Fill a clean, dry cuvette with the buffered Ferrozine solution and place it in the measuring position.
14. Press REFERENCE EXECUTE to read the absorbance of the reagent blank solution. The reading of the absorbance of the sample solution will be corrected by this value.

NOTE: The reference reading should be taken near the time of the measure reading.
15. Remove the cuvette and rinse with water.
16. Fill a clean dry cuvette with the sample solution from Step 9 just above.
17. Place the cuvette in the measuring position.
18. Press MEASURE - EXECUTE when the purple color has developed for 10 minutes. The printout will be in absorbance units corresponding to Fe (II). Call this absorbance A.
19. Add about 5 mg of solid ascorbic acid to the solution in the vial and mix thoroughly.

NOTE: This addition can be conveniently done with two or three squeezes from a small squeeze bottle containing finely powdered ascorbic acid. This reduces Fe (III) to Fe (II) and allows measurement of total Fe.
20. Fill a clean dry cuvette with the sample solution from Step 19.
21. Place the cuvette in the measuring position. Be sure solution is clear and there are no bubbles.

22. After 1-2 minutes development time, press MEASURE - EXECUTE. The printout will be in absorbance units corresponding to the total Fe measured as Fe (II). Call this absorbance B.

23. Remove the cuvette and rinse with water.

C.2 Measurement Using the Brinkmann PC 800

1. Grind a portion of the sample in the Brinkmann mill using an agate container and pulverizer as described in XI. B, Glass Crushing Procedure.
2. Place 10 to 30 mg of this finely ground glass in a polystyrene vial.

NOTE: This quantity of glass should give a total absorbance reading, for total iron, at 570 nm of less than 1.0. It is important not to exceed an absorbance reading of 1.0 because the absorbance versus concentration may not be linear above this value. If the absorbance does exceed 1.0, either reduce the glass sample size, increase the volume of the buffered Ferrozine solution used in XI. C.2, Step 8, or reduce the sample solution aliquot in XI. C.2, Step 9.

3. Add about 10 mg of solid ammonium vanadate to the vial.

NOTE: Steps 4 through 7 must be performed in a hood; gloves required.

4. Add 500 μ L of concentrated sulfuric acid. Gently swirl the vial to wet the glass.
5. Cautiously add 1500 μ L of hydrofluoric acid to the vial containing the glass.

HAZARD: Wear gloves; solution becomes hot; follow the instructions in the safety section AT ONCE if hydrofluoric acid contacts skin.

NOTE: Do not use glass equipment with hydrofluoric acid.

6. Swirl the vial to aid in dissolving the glass.

NOTE: The glass should dissolve almost immediately. If not, allow to stand until dissolution is obtained.

7. Add 20 mL of saturated boric acid solution and mix thoroughly by using a plastic dropper to draw up and then expel the solution back into the vial several times..

NOTE: Make sure the solution is well mixed before proceeding.

8. Place 20 mL of buffered Ferrozine solution in a separate vial and, with the 570 nm filter in place, zero the probe colorimeter, while stirring.

NOTE: The absorbance should be adjusted to 0.000; make sure the probe is free of air bubbles.

9. Transfer a 200 μ L-aliquot of the solution from Step 7 to the vial containing the Ferrozine.

NOTE: The aliquot size can be varied as needed to obtain a suitable absorbance range of less than 1.0. See NOTE under Step 2 just above.

10. Allow the purple color to develop for exactly 10 minutes.

11. Read the absorbance of the solution; call this A.

NOTE: This determines Fe(II).

12. Add about 10-20 mg of solid ascorbic acid to the solution and mix thoroughly - with a clean plastic dropper.

NOTE: This addition can be conveniently done with two or three squeezes from a small squeeze bottle containing the finely powdered ascorbic acid.

13. Allow the color to develop for 10 minutes.

14. Read the absorbance of the solution; call this B.

NOTE: This determines total Fe.

XII. CALCULATIONS

Calculate the Fe(II)/Fe(III) ratio as follows for measurements made with either the HP-8451-A or the Brinkmann PC 800.

$$\text{Fe(II)/Fe(III)} = \frac{A}{B-A}$$

where:

A = absorbance due to Fe(II),

B = absorbance due to Fe(II) + Fe(III), or total Fe, and

B-A = absorbance due to Fe(III).

Typical Calculation

A = 0.17

$$B = 0.50$$

$$B-A = 0.33$$

$$\text{Fe(II)/Fe(III)} = \frac{A}{B-A} = \frac{0.17}{0.33} = 0.52$$

XIII. REFERENCES

1. Baumann, E. W., Colorimetric Determination of Ferrous-Ferric Ratio in Glass, DPST-87-304 (February 20, 1987).
2. Van Hare, D. R., Prather, W. S., Fiber Optic Modification of a Diode Array Spectrophotometer, DP-1714 (January 1986).

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