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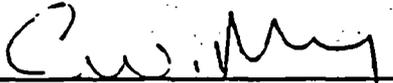
WEST VALLEY NUCLEAR SERVICES CO., INC.

ANALYTICAL CHEMISTRY METHOD
ANALYTICAL AND PROCESS CHEMISTRY

ACM-FE-2201, Rev. 3
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DETERMINATION OF THE FERROUS-FERRIC RATIO IN GLASS

Approved by:



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Part I

1.0 PURPOSE

This method provides a simple method to determine the amount of reduced and total iron in glass.

2.0 APPLICATION

This method, which has been developed and used at PNL, [2] is applicable for the determination of Fe^{+2}/Fe^{+3} over a range of 0.01 to values exceeding 1.0 for glasses containing total iron of about five percent or higher. If the iron concentration is lower, the range may be extended by taking a larger aliquot.

3.0 DISCUSSION

- 3.1 Empirical interpretation of Ferrous-Ferric ratio gives redox information, important for successful glass production. It has been shown that a ratio of 0.1 to 0.5 is an ideal range for melting conditions. [1]
- 3.2 Redox control of glass is important. If the melt is too oxidizing, foaming occurs, which impedes the melting processing and feed rates become prohibitively slow. When the conditions of the melt become too reducing, metallic phases will form. These will drop to the bottom of the melter and could cause a short circuit of the electrode. Work done at PNL [3] has demonstrated that by careful monitoring of the Ferrous-Ferric ratio, it is possible to achieve the optimum balance.

3.3 Possible sources of error would include:

3.3.1 If the pH is not adjusted correctly it is possible that the results will be low.

3.3.2 Insufficient heating will result in low total iron values.

4.0 REFERENCES

- [1] Bickford, D. F. and Diemer, Jr., R. B. July 1985. "Redox Control of Electric Melters with Complex Feed Compositions Part 1: Analytical Methods and Models" in proceedings of Physics and Chemistry of Glass and Glass making, New York State College of Ceramics, Alfred University.
- [2] Jones IV, D. R., Jansheski, W. C., Goldman, D. S., Analytical Chemistry 1981, 53, 923-924.
- [3] Goldman, D. S., Bewley, D. E., J. Am. Ceramic Society, 68[12] 691-95 (1985).

Part II

5.0 EQUIPMENT

- 5.1 Plastic beakers, 100 mL.
- 5.2 Plastic watch glasses.
- 5.3 Pipet 1.0 mL delivery with plastic tips.
- 5.4 pH meter.
- 5.5 Spectrophotometer with 1 cm cells. (Acrylic, disposable cells may be used.)

6.0 REAGENTS AND STANDARDS

- 6.1 Prepare standards according to ACP 8.1 The solutions have a shelf life of one year if kept in a tightly closed container. All reagents should be reagent grade unless otherwise specified.
- 6.2 Hydroxylamine hydrochloride.
- 6.3 Ammonium acetate buffer solution. Dissolve 250 g $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ in 150 mL distilled water. Add 700 mL glacial acetic acid and stir.
- 6.4 1, 10 - phenanthroline solution at least 99.9 percent pure: Dissolve 100 mg of 1, 10 - phenanthroline monohydrate in 100 mL distilled water. Add a couple drops of HCl to hasten dissolution.

- 6.5 Iron stock solution (1000 $\mu\text{g}/\text{mL}$): Either prepared from high purity iron or as a purchased solution.
- 6.6 Iron standard solution (100 $\mu\text{g}/\text{mL}$): Dilute 10.0 mL of the iron stock solution (6.5) to 100 mL in a volumetric flask with distilled water.
- 6.7 Hydrofluoric Acid (48-51 percent)
- 6.8 Sulfuric Acid (Sp. Gr. 1.84)

7.0 SAFETY PRECAUTIONS

- 7.1 Extra care should be taken when handling hydrofluoric acid including the wearing of disposable skindex gloves and eye protection. Any contact with the skin should be given immediate attention, washing the area well with water, and if necessary seek medical aid.
- 7.2 The dissolution must be done in a fume hood.
- 7.3 Follow standard laboratory safety procedures (ACP 7.2).

8.0 RECORDS

- 8.1 All measurement data and sample identification shall be recorded on the worksheet (Attachment A). The final result shall be recorded on the analytical request sheet.

9.0 CALIBRATION AND CONTROL

- > 9.1 Calibration Curve - Place 0, 0.5 mL, 1.0 mL, 1.5 mL of the standard iron solution (6.6) into 100 mL beakers. To make 0 μg , 50 μg , 100 μg and 150 μg standard respectively, add 25 mL H_2O and 2 drops H_2SO_4 (0.1 mL). Adjust the pH to 3.4 \pm 0.1 with ammonium acetate buffer. Add 5 mL 1, 10 - phenanthroline solution and a small scoop of hydroxylamine HCl (20 - 30 mg). Heat to boiling and allow to cool. Dilute to 50.0 mL with distilled water and read at 520 nm. Plot μg Fe vs percent transmittance (T) on semilog graph paper.
- 9.2 The calibration curve shall be determined at a frequency of every 12 months.
- 9.3 Alternatively, the data may be entered into a programmable calculator or into a computer program. Using a linear regression equation*, the iron values may be obtained.

* See operating instructions for the calculator on how this is done.

- 9.4 A sample of known $\text{Fe}^{+2}/\text{Fe}^{+3}$ ratio, or alternatively a solution of known iron concentration within the calibration range of the instrument is carried along with each set of samples as a QC with the QC repeated every 20 samples in the set. Results are kept in a quality control log book per ACP 8.2. A confidence interval of $\pm 3 \sigma$ (sigma) is established and individual tests are plotted to observe any long term trends.
- 9.5 A reagent blank is carried through with every set of samples and used to zero the spectrophotometer prior to sample reading.
- 9.6 If the deviation exceeds 3σ from the mean, the known will be re-analyzed. If the standard is still out of control after three trials, notify the laboratory manager. The manager will decide if the test must be repeated. Document in the Q.C. Log Book that the method is out of control.

10.0 PROCEDURE

- > 10.1 Place a few pieces of glass (approximately 1/4-inch diameter) in a mortar and pestle. Carefully grind the glass to a fine powder, about 100 mesh or finer. If the glass is not ground fine enough it may be difficult to dissolve. If available a ball mill may be used. If ground glass is not totally dissolved but 1st addition of the acids then heat on hot plate if necessary to assist dissolution.
- > 10.2 Transfer approximately 50 mg of the finely ground glass to a 100 mL plastic beaker. Add 1.0 mL H_2SO_4 and 1.0 mL HF.
- > 10.3 Dilute to the mark with distilled water and mix.
- 10.4 Standardize pH meter using the usual calibration standards per ACM-pH-1-1017, Rev. 0.
- 10.5 Using a plastic tipped pipet, transfer 2.0 mL to a plastic beaker. Add approximately 25 mL H_2O . Adjust the pH to 3.4 ± 0.1 with the ammonium acetate buffer solution. Add 5 mL of 1, 10 - phenanthroline solution (with large tip eppendorf) and dilute to 50 mL in a graduated beaker with distilled water.
- 10.6 After waiting about ten minutes, but no more than 20 minutes, transfer a portion of the test solution to a one cm cell and measure percent transmittance (T) at 520 nm on the spectrophotometer. Referring to the calibration curve or equation (9.0), determine the concentration of ferrous ions in the test solution. This value is the Fe^{+2} in Section 11.

10.7 Add a small scoop of hydroxylamine HCl crystals to the remainder of the sample. Place it on a hot plate at less than 150°C (or a microwave oven may be used**) and heat. Remove from the heat and allow to cool. Measure the percent transmittance (T) at 520 nm to obtain the concentration of total iron in the test solution.

11.0 CALCULATION

To obtain the ferric ion concentration:

$$\text{Fe}^{+3} = \text{Fe (total)} - \text{Fe}^{+2} \text{ (in } \mu\text{g)}$$

The iron ratio is then obtained by dividing the ferrous ion concentration by the ferric ion concentration.

$$\frac{\text{Fe}^{+2}}{\text{Fe}^{+3}} = \text{Ferrous Ferric Ratio}$$

12.0 ATTACHMENTS

12.1 Attachment A - Ferrous-Ferric Ratio Work Sheet

** Typically use 80 percent power at 30 sec. for 2 beakers 1-1/2 min total @ 80 percent power if you have more than 2 beakers. Cover beakers with plastic watch glasses before heating.

ATTACHMENT A

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Fe+2/Fe+3 WORK SHEET

SAMPLE NAME _____ LOG NUMBER _____

SPECIAL INSTRUCTIONS _____

UV SPEC. SERIAL # _____

> Sample ID							QC
% T Fe++							
µg Fe++ (B)							
% T Total Fe							
µg Total Fe (A)							
µg Fe+3 (A-B)-(C)							
Fe+2/Fe+3 $\frac{(B)}{C}$							

Analyst _____ Date _____

Approved _____ Date _____