Ferrous Iron Analysis

Meta-Vanadate Method *after Von Arnd Peters (1968): Ein neues Verfahren zur Bestimmung von Eisen (II) oxid in Mineralen und Gesteinen. N. Jb. Miner. Mh. ¾, 119-125*

Standard Solution Preparation

A. Vanadate Solution (AMV)

Weigh out 3.2565g ammonium meta-vanadate (NH_4VO_3).
Slowly add 25 ml conc. sulfuric acid (H_2SO_4) to 125 ml fresh deionized H_2O.
Don't add additional water at this point or the NH_4VO_3 will not dissolve.
Stir the H_2SO_4 solution with a magnetic stirrer then add the NH_4VO_3.
Transfer the above mixture quantitatively to a 1000 ml volumetric flask.
Fill the flask to the 1000 ml mark with fresh deionized H_2O.

B. Fe (II) Solution (FAS)

Weigh out 12.0 g of ferrous ammonium sulfate ($Fe(NH_4)2(SO4)_2\ 6H_2O$).
Add 10 ml conc.H_2SO_4 to 500 ml fresh deionized H_2O.
Transfer the above mixture to a 1000 ml volumetric flask.
Add the $Fe(NH_4)2(SO_4)_2\ 6H_20$ to the volumetric flask.
Dissolve by shaking.
Fill the flaks to the 1000 ml mark with fresh deionized H_2O.

C. Indicator Solution

Weigh out 0.1 g of barium diphenylamine-sulfonate.
Dissolve the above in 10 ml of conc. H_2SO_4.
Add to approximately 50-100 ml deionized H_2O.

D. Acid Solutions

1. 1:3 H_2SO_4 - mix 1 part 18 molar H_2SO_4 with 3 parts fresh deionized H_2O.
   Caution Very Exothermic Process.
   Add Sulfuric acid slowly to magnetically stirred beaker.
   Add half the acid let cool then add the rest.
2. 48% hydrofluoric acid (HF)- use as is from the bottle.
3. 1:3 phosphoric acid - mix 1 part 85% phosphoric acid with 3 parts fresh deionized H_2O.

Sample Preparation and Analysis

A. Clean some 250 ml wide-mouth polyethylene beakers. Rinse with nitric acid followed by fresh deionized H_2O.
B. Weigh a sufficient amount of sample (rock powder) to provide 20-50 mg of FeO for analysis. This will usually require 100-500 mg of sample (rock powder (mg) = 20 mg / (%FeO/100). For example - a sample with 10% FeO would require a sample weight of 200 mg to provide 20 mg of FeO for analysis. Note: include two blanks and at least one in-house or USGS standard with each batch of samples.
C. Place weighed sample into polyethylene beaker. Add 20.0 ml of vanadate solution by burette and 20.0 ml 1:3 H_2SO_4 solution by burette or pipette. Swirl the beaker to wet the powder before you add the HF. Take the container to the fume hood and add 5 ml of 48% HF using the automatic pipetter. Swirl the mixture, cover with a watchglass and set it overnight on the hot plate in the fume hood. (A shaking hot plate is a must). The hot plate should be set at about 65 degrees C (50-80 degrees C).
D. The next day, add 10 ml of 1:3 phosphoric acid (by pipette) to the solution. Then add 3-5 drops of indicator solution. Titrate the excess NH_4VO_3 with the Fe(II) solution (i.e. titrate the sample solution until it turns green). After passing the endpoint (the sample solution has turned green), back titrate with the NH_4VO_3 solution to the **exact** endpoint (the sample solution has turned blue). Let the solution sit for about a minute to make sure the reaction is complete. Back titrate with more NH_4VO_3, if necessary. Be sure to use 2-3 blank solutions with each batch of samples to obtain a standardization factor.

Additional guidelines for iron titrations:

- For samples with incomplete dissolution -

Following the standard Fe-titration method (using 20 ml H_2SO_4 and 5 ml HF and overnight on the hot plate),some samples may have incomplete dissolution. Residues noted include fine-grained black or brown particles and/or a coarser-looking residue which sticks to the bottom of the beaker when swirling the solution. These types of residue appear different from undissolved sample powder, which usually forms a thin film or a hard concrete-like mass on the bottom of the beakers. (Note: undissolved sample powder will result in an incorrect analysis.) Adding 5ml more of HF for a total of 10 ml may increase or complete the dissolution of the samples. However, the additional HF may result in the solution developing a white cloud of suspended particles which settle over time and indicate some type of insoluble fluorite due to excess HF. Duplicate and triplicate analyses

demonstrate that these residues (dark-colored or white-colored) do not affect the final results. Duplicate dissolutions are recommended in order to demonstrate the lack of effect on the Fe-titration results by a residue.

- *For over-evaporated samples (those with less than one-third the original volume)*-

Some samples may be over-evaporated due to watchglass covers slipping sideways uncovering the beakers, sample beakers being left too long (greater than 24 hours) on the hot plate, or hot plate temperature above 80^{o}C. Although duplicate samples (normal- and over-evaporated pairs) did not show a noticeable difference in %FeO values, over-evaporation may cause problems if complete drying of the sample or precipitation of a solid occurs.

- *Missing the H_3PO_4 acid addition step*-

No difference for the %FeO values was observed in samples missing the H_3PO_4 acid. However titrations were preformed immediately upon removal of the samples from the hot plate. As a check at least 1 sample (preferably 2) should be run in the next batch for confirmation of no effect.

- *Effect of old standard solutions*-

Using old AMV and FAS solutions for titration is fine as long as two blanks are analyzed and they give consistent F values. If new solutions made part way through analyzing a group of samples it is recommended that at least 1 sample is run as a duplicate in the first batch using the new solutions.

Calculations

A. Standardization Factor (F)

The standardization factor (F) is calculated using values obtained when titrating the blanks.

The blanks will typically titrate 18-19 ml of FAS solution.

$$F = \frac{\text{(total } NH_4VO_3 \text{ used (20.0ml + back titration(ml))}}{\text{total Fe(II) solution used(ml)}}$$

B. Weight Percent FeO

$$\text{wt\% FeO} = \frac{[(\text{total } NH_4VO_3 \text{ ml}) - (\text{total Fe (II) ml})(F)] \times 200}{\text{weight of sample (mg)}}$$