Metrohm

Thermo. Titr. Application Note No. H-070

Title:	**Determination of Ferric and Cupric Ions in Copper Refining Solutions**

Scope:	Determination of Fe^{3+} and Cu^{2+} in copper refining solutions by thermometric titration. It was found that the conventional approach of masking Fe^{3+} to permit the iodometric determination of Cu^{2+} is not possible in some copper refining solutions.

Principle:	Fe^{3+} content is determined by titration with fluoride (refer to AN H-069). The combined Fe^{3+} and Cu^{2+} content is determined by iodometric titration. The Cu^{2+} content is computed by subtraction.

Reagents:

1. Fe^{3+} determination.

Titrant: 1mol/L standard NaF solution
Combined acetate buffer: Dissolve 130.9g anhydrous potassium acetate and 54.7g anhydrous sodium acetate in 500mL DI water. Add 115mL glacial acetic acid, and make to 1L with DI water. Alternatively, dissolve 164g anhydrous sodium acetate and 75g potassium chloride in 700mL DI water, add 115mL glacial acetic acid and make to 1L with DI water.

2. Fe^{3+} + Cu^{2+} determination.

Titrant: 1mol/L standard $Na_2S_2O_3$ solution
- Glacial acetic acid
- 50% w/v KI solution (store in amber bottle in a cool place).
- 0.04mol/L KIO_3 solution (for standardizing $Na_2S_2O_3$ titrant)

Method:

Basic Experimental Parameters:

1. Fe^{3+} determination.

Titrant delivery rate (mL/min.)	4
No. of exothermic endpoints	1
Data smoothing factor (DSF)	70
Stirring speed (802 stirrer)	10

Iron must be in Fe^{3+} form, and sufficiently acidic to prevent hydrolysis of the $Fe(H_2O)_6{}^{3+}$ aquo ion. Dispense aliquot into titration vessel. Add 10mL combined acetate buffer and make to approximately 30mL with DI water. Titrate to an exothermic endpoint with 1mol/L NaF solution.
Standardization of NaF titrant. This may be standardized against standard Al solution prepared from high purity Al metal.

2. Fe^{3+} + Cu^{2+} determination.
Basic Experimental Parameters:

Titrant delivery rate (mL/min.)	4
No. of exothermic endpoints	1
Delay start of titration (secs.)	20
Data smoothing factor (DSF)	60
Stirring speed (802 stirrer)	10

Iron must be in Fe^{3+} form, and sufficiently acidic to prevent hydrolysis of the $Fe(H_2O)_6{}^{3+}$ aquo ion. Dispense aliquot into titration vessel. Add 2mL glacial acetic acid. Fit titration vessel to titration head and start the analysis sequence. Add 10mL KI solution through a port in the titration head imediately after clicking the “Start” button.

Standardization of $Na_2S_2O_3$ titrant. Pipette aliquots of 5, 10, 15, 20 and 25mL KIO3 solution into titration vessels. Add 2mL glacial acetic acid, and make to ~30mL with DI water. Start the titration, and add 10mL KI solution through a port in the titration head imediately after clicking the “Start” button. Plot mmole of KIO_3 (x-axis) against mL $Na_2S_2O_3$ titrant (y-axis) and compute the titrant molarity.

Examples: Solutions from copper refinery operation, containing Fe^{3+}, Fe^{2+} and Cu^{2+}

Sample no.	Cu^{2+} g/L	Fe^{3+} g/L
1	7.50, 7.48	4.89, 4.91
2	24.35, 24.29	6.44, 6.45
3	3.35, 3.31	6.23, 6.22
4	61.23, 61.68	11.55, 11.50
5	3.46, 3.54	2.43, 2.37

Calculation Procedure:	
1. *From fluoride titration, calculate Fe^{3+} g/L*	(1) $$Fe^{3+} g/L = \frac{((Titre, mL - blank, mL) \times NaF\ mol/L \times 55.845)}{(sample\ vol, mL \times 6)}$$
2. *From iodometric titration, calculate (Cu^{2+}+Fe^{3+}), expressed as Fe^{3+} g/L*	(2) $$(Cu^{2+} + Fe^{3+}) g/L = \frac{((Titre, mL - blank, mL) \times Na_2S_2O_3 \times 55.845)}{(sample\ vol, mL)}$$
3. *Subtract (2) from (1)*	
4. *Convert (3) to Cu^{2+} g/L*	Cu^{2+} g/L =(2) - (1) x 63.546/55.845