Metrohm

Thermo. Titr. Application Note No. H-108

Title:	**Determination of Ferric Ion in Hydrometallurgical Leach Liquors**

Scope: Determination of the ferric ion content of hydrometallurgical leach liquors

Principle: A measured amount of acidic hydrometallurgical leach liquor is pH modified with a small amount of glacial acetic acid, and the Fe(III) content reduced to Fe(II) with iodide ion. The liberated iodine is titrated with standard thiosulfate solution to an exothermic endpoint.

$[Fe^{3+} + e \leftrightarrow Fe^{2+}] \times 2$
$2I^- \leftrightarrow I_2 + 2e$
$\underline{2S_2O_3^{2-} \leftrightarrow S_4O_6^{2-} + 2e}$
$2Fe^{3+} + 2S_2O_3^{2-} \leftrightarrow 2Fe^{3+} + S_4O_6^{2-}$

Thus, 1 mol $Fe^{3+} \equiv$ 1 mol $S_2O_3^{2-}$

Reagents:
Titrant- Sodium thiosulfate $c(Na_2S_2O_3)$ = 1 mol/L
pH modifier: Glacial acetic acid (HOAc), A.R.
Reducing Agent: Potassium iodide soln. c(KI) = 50% w/v
Standard: Potassium iodate standard solution: $c(KIO_3)$ = 0.04 mol/L

Method:
Basic Experimental Parameters:

Titrant delivery rate (mL/min.)	4
No. of endothermic endpoints	1
Data smoothing factor (DSF)	40
Stirring speed (802 stirrer)	8
Delay before start of titration (secs.)	10

Basic titration procedure.
A 25mL aliquot of acidic process liquor is pipetted by volumetric glass pipette into a PP titration tube, and 2mL glacial HOAc added. The sample solution is swirled to mix prior to being placed in the sample rack. The titration program adds 10mL KI solution 10 seconds prior to commencement of $Na_2S_2O_3$ addition.

	Standardization of $Na_2S_2O_3$ titrant. For this exercise, a 20mL Dosino unit was used to automatically dispense aliquots of 5, 7.5, 10, 12.5, 15, 17.5 and 20mL aliquots into PP titration vessels in the 814 sample rack. Prior to placing in the rack, 2mL of glacial HOAc and sufficient DI water was added to bring the volume of fluid in the vessel to ~30mL after adding the KIO_3 aliquot. The titration program automatically added 10mL KI solution prior to the commencement of $Na_2S_2O_3$ addition. Alternatively, aliquots of KIO_3 may be dispensed using conveniently-sized volumetric bulb pipettes. The molarity was calculated by plotting mmol KIO_3 (x-axis) against mL $Na_2S_2O_3$ titrant (y-axis) and computing the slope by linear regression. This is performed automatically by a prepared *tiamo™* standardization program *Basis for standardization:* $IO_3^- + 5I^- + 6H^+ \leftrightarrow 3I_2 + 3H_2O$ $[I_2 + 2e \leftrightarrow 2I^-] \times 3$ $\underline{[2S_2O_3^{2-} \leftrightarrow S_4O_6^{2-} + 2e] \times 3}$ $IO_3^- + 6S_2O_3^{2-} + 6H^+ \leftrightarrow 3S_4O_6^{2-} + 3H_2O + I^-$ Thus, 1 mol $IO_3^- \equiv$ 6 mol $S_2O_3^{2-}$

Example:	*Acidic hydrometallurgical leach liquor, containing Fe(II), Fe(III)), Mg, Al, Mn, Cr, Cu, Co and Ca.*
	Fe(III) = 9.53±0.01 g/L (n=5)

Calculation:
$\text{Fe(III), g/L} = \dfrac{(\text{(EP vol., mL- Blank, mL)} \times c(Na_2S_2O_3)\ \text{mol/L} \times \text{AW Fe})}{\text{Sample vol., mL}}$

Titration Plots:

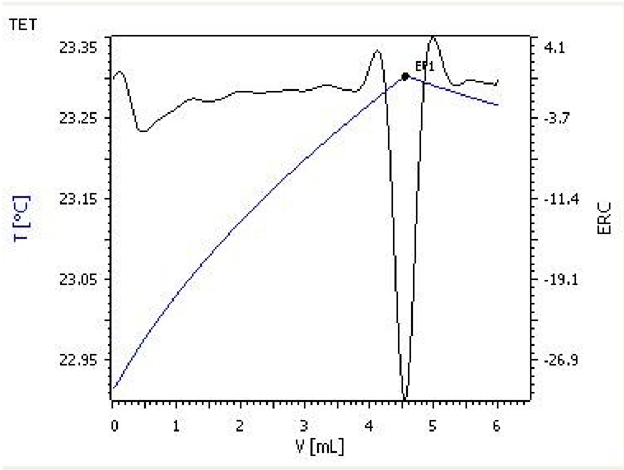

Fig.1. Titration of Fe(III) in test sample with $c(Na_2S_2O_3)$ = 1 mol/L

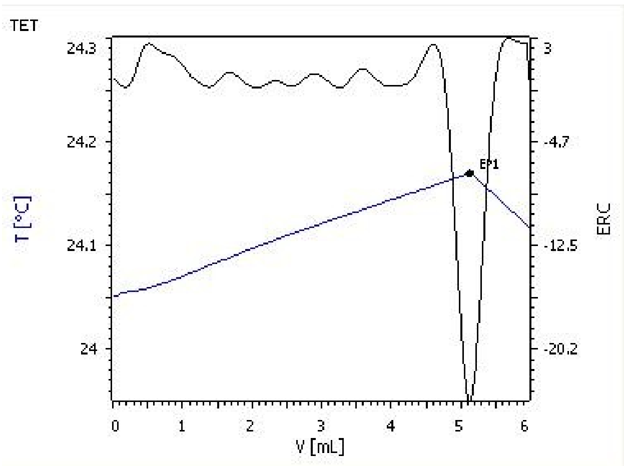

Fig. 2. Standardization of $c(Na_2S_2O_3)$ = 1 mol/L with $c(KIO_3)$ = 0.04 mol/L

Legend:
Blue curve = solution temperature
Black curve = second derivative (ERC)