Thermo. Titr. Application Note No. H-106

Title:	**Determination of Magnesium in Hydrometallurgical Leach Liquors**

***Scope*:**	Determination of magnesium content in hydrometallurgical leach liquors

***Principle*:**	A measured amount of acidic hydrometallurgical leach liquor is treated first with a complexing agent (sodium gluconate). It is then basified to ~pH 10.5 with a NH_3/NH_4Cl buffer, prior to the addition of KCN solution to mask Fe(III). **Caution! Do not add KCN to solutions of pH below 9!** The Fe(III) is then reduced to Fe(II) by additon of ascorbic acid, prior to titrating the Mg content with standard Na_4 EDTA solution.

Reagents:	*Titrant: Tetrasodium EDTA c(Na_4EDTA) = 1mol/L* *Complexing agent: Sodium gluconate solution, 20% w/v in DI water.* *EDTA buffer: NH_3/NH_4Cl buffer. Dissolve 87.5 g NH_4Cl in 568 mL 28% w/v NH_3 solution, and make to 1 L with DI water.* *Masking agent for iron: Potassium cyanide solution, 20% w/v in DI water., stabilized with a few pellets of A.R. NaOH.* *Reducing agent for Fe(III): Ascorbic acid, 5% w/v in DI water. Make up small amounts (~100 mL) and store in a brown glass bottle in a cool place.* *Standard Mg solution, c(Mg) = 0.2 mol/L, prepared from freshly cleaned, bright Mg metal and dilute HNO_3*

Method:

Experimental Parameters:

Titrant delivery rate (mL/min.)	6
No. of endothermic endpoints	1
Data smoothing factor (DSF)	45
Stirring speed (802 stirrer)	8
Delay before start of titration (secs.)	10

Basic titration procedure.

A 5 mL aliquot of acidic process liquor is pipetted into a PP titration tube, and 1 mL 5% w/v ascorbic acid and 5 mL DI water added.

The automation program adds successively (with stirring):

- 5mL 20% w/v sodium gluconate solution
- 10mL NH_3/NH_4Cl buffer solution
- 5mL 20% w/v KCN solution, with the KCN solution being added just 5 seconds prior to the commencement of the titration.

Standardization of EDTA.

Aliquots of standard Mg solution of volumes 5, 10, 15, 20, 25 and 30 mL were pipetted into individual PP titration tubes. DI water was added to bring the titration volume to at least 20 mL where needed.

The samples were placed in the rack of the 814 Sample Processor, and an automation program was devised which automatically added 10 mL NH_3/NH_4Cl buffer prior to the commencement of the titration.

The automated standardization program computes the titrant molarity from a regression analysis, and determines the coefficient of correlation for the linear regression

Example:	Acidic hydrometallurgical leach liquor, containing Fe(II), Fe(III), Mg, Al, Mn, Cr, Cu, Co and Ca.
	Mg = 20.35 ± 0.05 g/L (n=6), compared with a value of 21.5 g/L obtained by AAS, and ~20 g/L by manual titration.

Calculations:

$$\text{Mg, g/L} = \frac{((\text{EP vol., mL} - \text{Blank, mL}) \times c(Na_{4EDTA}) \text{ mol/L} \times \text{AW Mg})}{\text{Sample vol., mL}}$$

Determination of EDTA molarity:

c(Na4EDTA) = 1.03984 mol/L,

coefficient of correlation (R2) = 1.0000

blank = 0.0547 mL

Titration Plots:

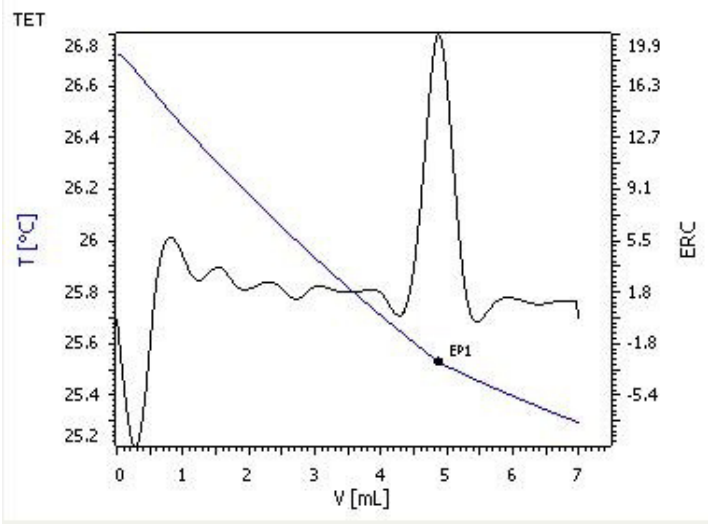

Fig. 1. Titration of Mg standard with 1 mol/L Na_4EDTA

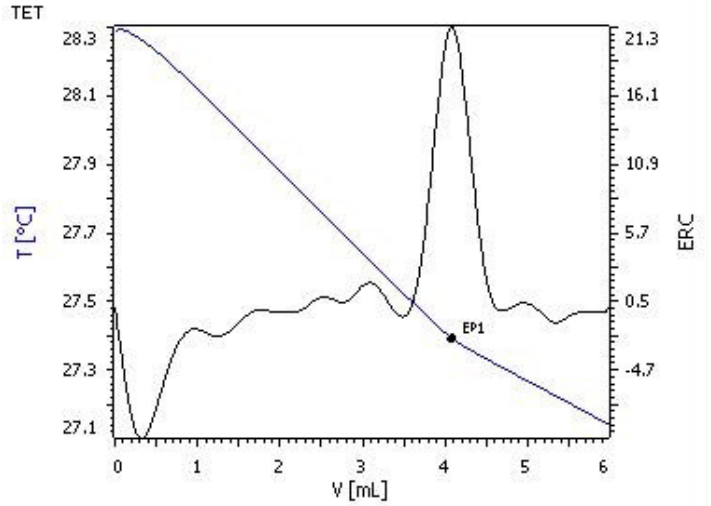

Fig.2. Titration of Mg in test sample with 1 mol/L Na_4EDTA.
Legend:
Blue curve = solution temperature
Black curve = second derivative (ERC)

Note on handling potassium cyanide:
Extreme caution must be exercised when handling potassium cyanide or its solutions. The pH of any cyanide solution should not be allowed to fall below pH 9. Protective clothing including disposable gloves and safety glasses with side shields or goggles should be worn at all times. Amyl nitrate antidote should be at hand, and analysts should be trained in first aid procedures involving cyanide poisoning.

Note on disposal of titration residues:
Titration residues contain cyanide, ammonia and ammonium salts. Normally, adding a solution of sodium hypochlorite is a cheap and efficient method of decomposing cyanide, however hypochlorite reacts very exothermically (sometimes violently) with ammonia solutions. It is therefore recommended to use 30% w/v hydrogen peroxide solution to destroy cyanide prior to disposal.