Thermo. Titr. Application Note No. H-034

Title:	**Determination of Calcium and Magnesium in Process Samples**

***Scope*:**	Determination of calcium and magnesium in process solutions.

***Principle*:**	A weighed aliquot of solution is titrated directly with a solution of 1mol/L tetra-sodium EDTA to thermometrically determined endpoints for Ca and Mg. Acetylacetone is added to alter the Ca- and Mg-EDTA stability constants for better endpoint sharpness. $Ca^{2+} + Y^{4-} \leftrightarrow CaY^{2-}$ (Y = EDTA) $Mg^{2+} + Y^{4-} \leftrightarrow MgY^{2-}$ **Thermodynamic Constants:** Heat of chelation, Ca^{2+} with EDTA: $\Delta H_r \approx$ -23.4 KJ/mol Heat of chelation, Mg^{2+} with EDTA: $\Delta H_r \approx$ +20.1 KJ/mol *The reaction with Ca^{2+} is thus exothermic, and that of Mg^{2+} endothermic.*

Reagents:	3.1. 1.000mol/L Na_4EDTA. 372.24g A.R. Na_2H_2EDTA is quantitatively transferred to a 1000mL volumetric flask. 80g A.R. NaOH is carefully dissolved in 500mL D.I. water, cooled, and added to the same flask. When all solids have dissolved (with the addition of more water), make to volume and mix well 3.2. NH_3/NH_4Cl buffer. Dissolve 17.5 g A.R. NH_4Cl in 172 mL A.R. conc. (28%) NH_3 soln. and make to 250 mL with deionised water 3.3. Acetylacetone (2,4-Pentanedione). CAS 123-54-6, Aldrich cat. no. P7754

Method:	Basic Experimental Parameters:	
	Titrant delivery rate (mL/min.)	2
	No. of exothermic endpoints	2
	Data smoothing factor (DSF)	*50, 75
	Stirring speed (802 stirrer)	6
	**Use a DSF of 50 for samples similar type B, and a DSF of 75 for samples similar to type A*	
	Using a disposable plastic syringe, weigh accurately ~4g of sample (~3.5mL) into a clean dry 140mL polypropylene titration vessel. *For Ca only samples use ~8g (~7mL).* Add 5mL. NH_3/NH_4Cl buffer and 25mL DI water (this may be done using Dosinos in pre-dose mode). For viscous samples, program the stirrer to start 120 seconds prior to the start of the titration ***If Ca or Mg are present together in the sample***, add 200µL acetylacetone accurately with an air pipette (Eppendorf type) prior to commencement of the titration - ***otherwise, titrate without addition of acetylacetone.*** Titrate past second (Mg) endpoint.	
	Note: This method was originally developed for the analysis of Ca and Mg carboxylates. Easily dispersed samples containing Ca and Mg do not required an extensive pre-mixing period. A typical total titre (Ca+Mg) of approximately 4 – 5mL is satisfactory.	

Examples:

	Sample type	Ca %	Mg %
	Mg only	-	2.09±0.006 (n=5)
	Ca only	1.94±0.0006 (n=5)	-
	Ca+Mg	1.24±0.008 (n=6)	0.76±0.008 (n=6)

Calculations:

$$\%Ca = \frac{((EP, mL - Ca\ blank, mL) \times M\ Na_4EDTA \times FW\ Ca \times 100)}{(Sample\ mass, g \times 1000)}$$

WHERE Mg IS PRESENT IN THE PRODUCT WITH Ca :

$$\%Mg = \frac{((EP2 - EP1, mL - Mg\ blank, mL) \times M\ Na_4EDTA \times FW\ Mg \times 100)}{(Sample\ mass, g \times 1000)}$$

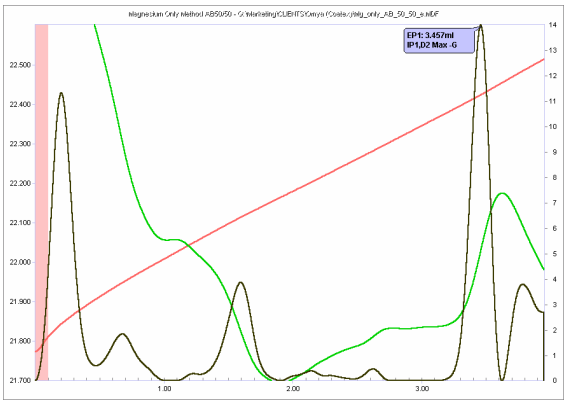
WHERE Mg IS ONLY PRESENT IN THE PRODUCT :

$$\%Mg = \frac{((EP\ mL - Mg\ blank, mL) \times M\ Na_4EDTA \times FW\ Mg \times 100)}{(Sample\ mass, g \times 1000)}$$

Determination of Ca and Mg blanks:

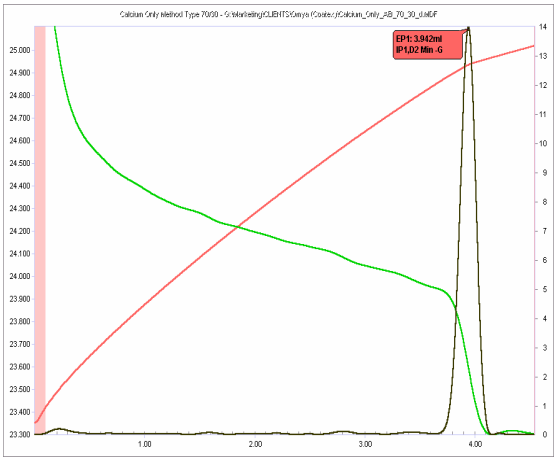
It is necessary to determine blank factors for Ca and Mg for different sample types. The complexation coefficients with EDTA for Ca and Mg are similar, and this can cause mutual interference when both are present in solution. Blank factors are determined by titrating a range of masses or volumes of each sample type for Ca and/or Mg. Regression analysis is performed on a plot of sample mass or volume (x-axis) and endpoint volumes of EDTA (y-axis). The y-axis intercept is the blank volume for the particular anion and sample type. The blank, whether positive or negative, is subtracted from the respective endpoint titre.

Thermometric Titration Plots:

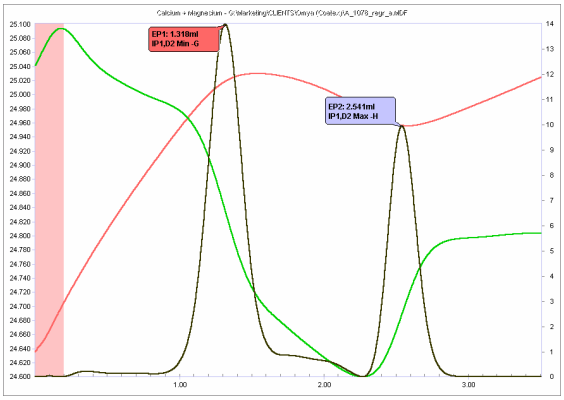


Mg only – no acetylacetone added

Legend:
Red = solution temperature curve
Green=first derivative curve
Black =second derivative curve (for endpoints)



Ca only – no acetylacetone added



Ca and Mg – acetylacetone added to enhance Ca endpoint