Thermo. Titr. Application Note No. H-074

Title:	**Determination of Calcium and Magnesium in Marine Brines**

***Scope*:**	Determination of calcium and magnesium in marine brines. The method is suitable for determining the effect of caustic soda and alumina refinery aluminate solutions on the calcium and magnesium content of sea water.

***Principle*:**	A measured 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. 1mol/L Na_4EDTA. Prepare from A.R. tetrasodium EDTA. Alternatively, weigh 372.24g A.R. Na_2H_2EDTA and quantitatively transfer 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. The EDTA solution may be standardized against a 0.2mol/L Mg^{2+} solution, prepared from Mg metal. 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.)	4
	No. of exothermic endpoints	1
	No. of endothermic endpoints	1
	Data smoothing factor (DSF)	80
	Stirring speed (802 stirrer)	15
	Delay before start of titration (secs.)	10
	Pipette 50mL of marine brine into a titration vessel. Add 5mL buffer solution and 200µL acetylacetone by air pipette. Titrate to a second, endothermic endpoint.	

Examples:

(sea water collected from Moreton Bay, Queensland Australia, 25/06/2008)	Sample type	Ca g/L	Mg g/L
	Sea water	0.517±0.008 (n=11)	1.237±0.007 (n=11)
	Sea water contaminated by 2dm^3 spent aluminate liquor per m^3	0.496	1.018
	Sea water contaminated by 4dm^3 spent aluminate liquor per m^3	0.472	0.789
	Sea water contaminated by 10dm^3 spent aluminate liquor per m^3	0.282	0.223

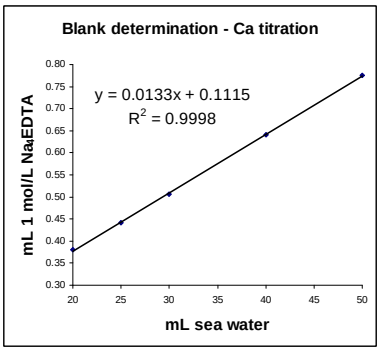
Calculations:

$$\text{Ca g/L} = \frac{((\text{EP1 mL} - \text{Ca blank mL}) \times \text{M EDTA} \times \text{FW Ca})}{\text{sample volume, mL}}$$

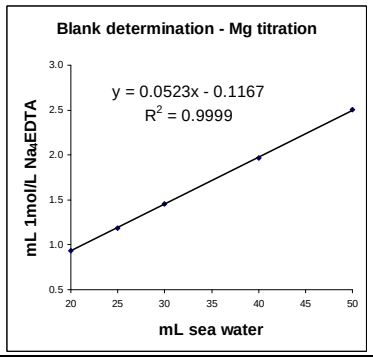
$$\text{Mg g/L} = \frac{((\text{EP2 mL} - \text{EP1 mL} - \text{Mg blank mL}) \times \text{M EDTA} \times \text{FW Mg})}{\text{sample volume, mL}}$$

Determination of Ca and Mg blanks:	It is necessary to determine blank factors for Ca and Mg. The complexation coefficients for Ca and Mg with EDTA are similar, and this can cause mutual interference when

both are present in solution. Blank factors are determined by titrating a range of volumes of sea water from 20 – 50mL for Ca and Mg. Regression analysis is performed on a plot of aliquot volume (x-axis) and endpoint volumes of EDTA (y-axis). The y-axis intercept is the blank volume for the particular anion. The blank, whether positive or negative, is subtracted from the respective endpoint volumes. Thus in the case of the Ca titration, the endpoint volume is reduced by the amount of the blank; and in the case of the Mg titration, the endpoint volume is increased by the amount of the blank (since this has a negative value).



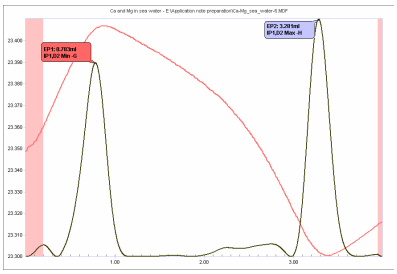
Blank determination – Ca titration.
Blank = +0.1115mL



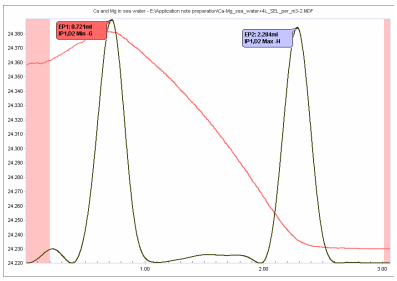
Blank determination – Mg titration.
Blank = -0.1167

Thermometric Titration Plots:

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



Ca & Mg in sea water



Ca & Mg in sea water contaminated with 4dm^3 spent aluminate liquor per m^3