Thermo. Titr. Application Note No. H-097

Title:	**Determination of Calcium and Magnesium in Harvested Salt**

***Scope*:**	Determination of calcium and magnesium in raw or harvested salt.

***Principle*:**	A measured amount of salt 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.* **Stability Constants of EDTA complexes (as log K):** Ca^{2+} = 10.7, Mg^{2+} = 8.7

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 according to AN H-075. 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) 65
	Stirring speed (802 stirrer) 15
	Delay before start of titration (secs.) 10
	Weigh accurately approximately 10g of raw salt into a titration vessel. Add 50mL DI water, 5mL buffer solution and 200µL acetylacetone accurately by air pipette. Titrate to a second, endothermic endpoint. Raw salt of coarse crystal size can be slow and difficult to dissolve, and may foul the stirrer. Further, some samples might be quite heterogeneous. In such cases, it is advisable to make a serial dilution. Weigh 50g of salt and dissolve and make to volume with DI water in a 250mL volumetric flask (or dilute 100g to 500mL). Take a 50mL aliquot for analysis. Solutions from samples containing considerable amounts of dirt should be allowed to settle or filtered through a Whatman no. 4 filter paper prior to analysis.

Examples:

Results were not corrected for the moisture content of the samples	*Sample type*	*Ca % w/w*	*Mg % w/w*
	„Celtic Sea Salt“ – Brittany, France	0.28±0.012 (n=8)	0.46±0.014 (n=8)
	„Himalayan Crystal Salt“ - Pakistan	0.22±0.002 (n=8)	0.20±0.004 (n=8)

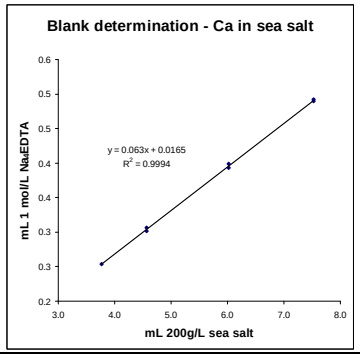
Calculations:

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

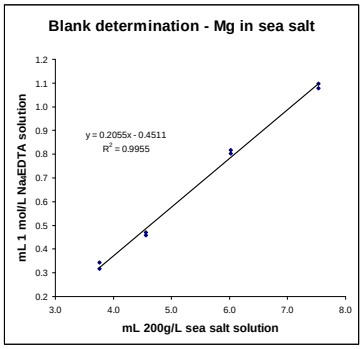
$$\text{Mg g/L} = \frac{((\text{EP2 mL} - \text{EP1 mL} - \text{Mg blank mL}) \times \text{M EDTA} \times \text{FW Mg})}{\text{sample volume, mL}}$$

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 200g/L sea salt solutions 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).



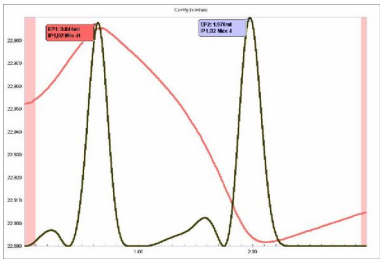
Blank determination – Ca titration.
Blank = +0.0165mL



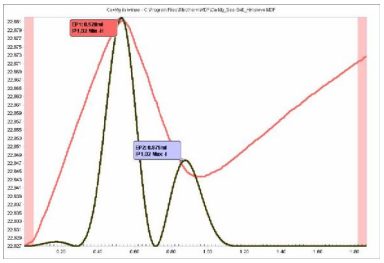
Blank determination – Mg titration.
Blank = -0.451mL

Thermometric Titration Plots:

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



Ca & Mg in “Celtic Sea Salt”



Ca & Mg in “Himalayan Crystal Salt”