Soluble Calcium, Magnesium in Brine*

*This procedure was developed for ultrapure saturated NaCl feed brine used in the chloro-alkali industry. It will not work in water or a non-saturated brine solution. The calibration curve must be done at the same temperature (25 ±5 °C) as the sample temperature.

Range: 0-100 µg/L as Calcium
Hydroxy Naphthol Blue (HNB) Method

Introduction

Calcium and other polyvalent cations can foul ion-exchange membranes used in electrolytic manufacture of chlorine and alkali from brine solutions. These cations must be minimized and closely monitored to prevent membrane plugging.

The HNB Method incorporates an indicator dye which forms a blue color in a strongly alkaline brine and changes to red when complexing free calcium and magnesium. EDTA, which is added to a portion of the reacted sample, complexes the calcium and magnesium, and sets a reference point.

Because metal standards are not very stable in saturated alkaline brines and each brine matrix may be variable, use the standard additions method to establish the calibration curve for each type of brine analyzed and with each new lot of reagents.

The following procedure is written for the DR/3000 Spectrophotometer, but may be used with any suitable narrow bandpass spectrophotometer with a sample pathlength of at least 20 mm.

Procedure for Preparing a Calibration Curve

1. Turn on the DR/3000 Spectrophotometer and set the wavelength to 620.0 nm.

2. Prepare the HNB dye solution by adding the contents of one bottle of HNB Reagent powder to one bottle of HNB Dilution Solvent. If necessary, rinse the powder bottle with HNB Dilution Solvent to ensure all powder has been transferred. Cap and mix well until all dye particles are dissolved completely . Label the mixing date on the bottle *(see Note A).*

3. Using a 100-mL plastic graduated cylinder, add 100 mL of purified brine to each of five 125-mL plastic erlenmeyer flasks *(see Note B).*

4. Using the TenSette pipet, add aliquots of 0.0, 0.2, 0.4, 0.6 and 0.8 mL of 10.0 mg/L Calcium Standard Solution to the five flasks to make a set of + 0, + 20, + 40, + 60 and + 80 µg/L calcium standards. Fresh brine standards should be prepared before each run if brine type or reagent lot changes *(see Note C).*

5. Add 1.0 mL of 3.0 N Alkali Buffer to the 0.0 µg/L brine. Swirl to mix.

6. Add 1.0 mL of the prepared HNB dye solution. Swirl to mix well *(see Note D).*

7. Time a reaction period of 2 minutes. Start the timer as follows:

Press: **2 TIMER**

8. Pour approximately 25 mL of the prepared brine into each of two matched sample cells.

9. Label one cell "EDTA" and the other "Sample."

10. Place the "Sample" cell into the cell compartment and close the sample compartment cover. After the timer beeps, zero the instrument as follows:

Press: **ZERO ABS**

11. To the cell labeled "EDTA" add 1 drop of 1 M EDTA solution. Swirl to mix.

12. Time a 3-minute reaction period after the addition of EDTA.

Press: **3 TIMER**

13. Place the "EDTA" cell into the cell compartment and close the sample compartment door.

14. When the timer beeps, read the absorbance *(see Note E).*

15. Repeat Steps 5-14 for each of the spiked brine standards (+ 20, + 40, + 60 and + 80 µg/L Ca).

16. Plot the absorbance versus spiked concentration similar to the graph in *Figure 1.* The negative intercept is the combined soluble calcium, magnesium concentration (µg/L) in the original brine *(see Note F).*

Analysis of a Brine Sample

1. Fill a clean 100-mL plastic graduated cylinder to the 100-mL mark with brine sample. Transfer to a clean 125-mL plastic erlenmeyer flask.

2. Add 1.0 mL of 3.0 N Alkali Buffer. Swirl to mix.

3. Add 1.0 mL of prepared HNB dye solution. Swirl to mix completely.

4. Continue as in Steps 7 to 14 above.

5. Determine the µg/L calcium, magnesium from the intercept-corrected calibration curve *(see Note F).*

Notes

A. The mixed dye-indicator solution is stable for at least one month at room temperature. Discard any unused dye solution older than 1 month.

B. The use of glass in trace calcium analysis is discouraged. Use plastic ware for trace calcium, magnesium analyses. Rinse with deionized water after use and covered to prevent airborne contamination.

C. Spiked calcium brine standards are stable for approximately 24 hours. Prepare fresh standard spikes daily.

D. The dye solution is stable for approximately 15 minutes before the dye color begins to fade.

E. The color peaks between 3-5 minutes after addition of the EDTA. The color begins to fade after 5 minutes.

F. The calibration line can be corrected for the original concentration and stored into the DR/3000 memory. Refer to *Section 3.3 Operating Modes* of the DR/3000 Spectrophotometer Manual.

G.The reagent blank contribution is controlled at the factory to less than 1.0 µg/L calcium plus magnesium. It is advisable to analyze one purified brine and at least one standard calcium addition frequently to ensure the reagents are good and the calibration is acceptable. The intercept point-corrected calibration is made by subtracting the absorbance of the + 0 µg/L brine from the absorbance values of the spiked brines *(see Figure 2).*

H. The following cations also will register in the test at the indicated concentration:

Concentration	Equivalent µg/L Ca:			
of Interferant	Sr	Ba	Al	Fe^{3+}
100 µg/L	0	0	1.5	0
500 µg/L	1	0	4	14
1000 µg/L	4	0	9	33
2000 µg/L	8	0	13	43

Chlorine (hypochlorous acid), present in some recirculated brines, interferes significantly by bleaching the reagent dye color. In this case, add 5 drops of Dechlorinating Solution, Cat. No. 323-32, per 100 mL of brine prior to addition of the reagents.

I. The results are expressed as µg/L calcium but may be expressed as either magnesium, calcium carbonate or calcium oxide by multiplying by the appropriate factor.

To express results as:	**multiply by:**
Magnesium (Mg)	0.61
Calcium Carbonate ($CaCO_3$)	2.50
Calcium Oxide (CaO)	1.40
mg/kg Ca	0.83

Required Reagents and Apparatus

Cat. No.	**Description (Unit)**
23072-42	Alkali Buffer, 3.0 N (100 mL) ~ 0.25 HNB
23073-00	HNB Lab Reagent Package (each) (contains one unit #23073-55 HNB powder and one unit #23050-14 HNB Dilution Solvent) ~ 10mL 30% EG
22419-26	EDTA Solution, 1 M (59 mL)
23054-42	10.0 mg/L Calcium Standard (100 mL)
19600-00	DR/3000 Spectrophotometer (each)
2172-42	Graduated Cylinder, plastic, 100 mL (each)
20897-43	Plastic Erlenmeyer Flasks w/screw enclosures, 125 mL (each)
19700-01	TenSette Pipet, 0.1 to 1.0 mL, with 100 tips (each)
21856-96	Pipet Tips for Cat. No. 19700-01 (pkg/50)
19935-00	Sample cells, 1-inch, matched pair DR/3000 (each)

1.1 gm → 957mL

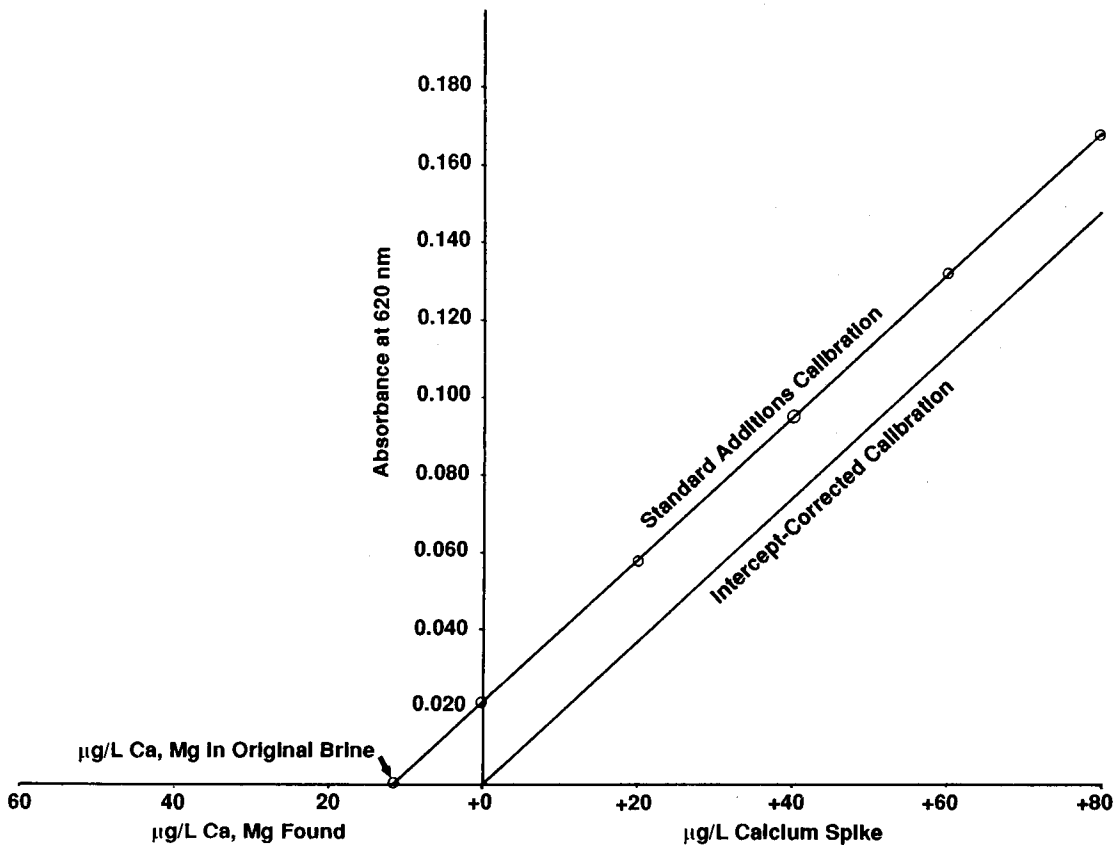

FIGURE 2 Standard Additions for Calcium & Magnesium in Brine