Calcium, Magnesium in Brine

DOC316.53.01562

HNB Method

0 to 100 µg/L as Ca

Scope and application: For ultrapure saturated NaCl feed brine used in the Chlor-alkali industry. Not for water or a non-saturated brine solution.

Test preparation

Before starting

Prepare the calibration curve at the same temperature as the sample temperature (25 ± 5 °C).
This test is for the DR3000 or higher, but can be used with other narrow bandpass spectrophotometers with a sample pathlength of at least 20 mm.
Use plastic ware for this test. Do not use glassware.
Rinse the plastic ware with deionized water after the test. Cover the plastic ware to prevent airborne contamination.
Use the test result (µg/L calcium) to calculate the concentration of magnesium, calcium carbonate or calcium oxide in the brine as necessary. Refer to Table 1 on page 6.
Analyze one purified brine sample and at least one of the calcium brine standards that is prepared in Prepare a calibration curve on page 2 frequently. Use the test results to make sure that the reagents are good and the calibration is satisfactory. The purified brine is controlled at the factory to less than 1.0 µg/L calcium plus magnesium.
Review the Safety Data Sheets (MSDS/SDS) for the chemicals that are used. Use the recommended personal protective equipment.
Dispose of reacted solutions according to local, state and federal regulations. Refer to the Safety Data Sheets for disposal information for unused reagents. Refer to the environmental, health and safety staff for your facility and/or local regulatory agencies for further disposal information.

Items to collect

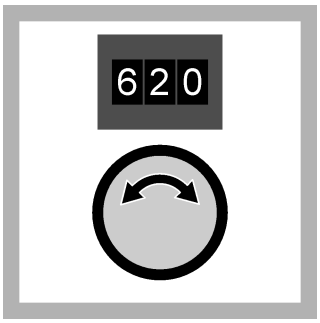
Description	Quantity
HNB Lab Reagent Package	6 mL (mixed solution)
Calcium standard, 10 mg/L	2 mL
Alkali Buffer, 3.0 N	6 mL
EDTA Solution, 1 M	6 drops
Tensette pipet, 0.1 to 1.0 mL	1
Erlenmeyer flask, plastic, 125 mL	5
Graduated cylinder, plastic, 100 mL	1
Sample cells, 1-inch square glass, matched pair, 25 mL	1

Refer to Consumables and replacement items on page 7 for order information.

Prepare a calibration curve

Prepare a new calibration curve for each type of brine analyzed and for each lot of reagents.

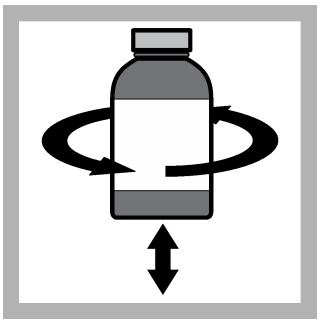
- The mixed HNB dye solution prepared in steps 2 to 5 is stable for 1 month at room temperature. Discard the dye solution after 1 month.
- The calcium brine standards prepared in step 9 are stable for approximately 24 hours. Prepare fresh calcium brine standards daily.



1. On the DR3000 or higher, set the wavelength to 620.0 nm.

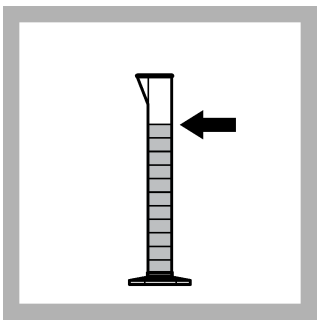
2. HNB dye solution: Add the 6-g bottle of HNB Reagent powder to the 100-mL bottle of HNB Dilution Solvent.

3. Rinse the powder bottle with the HNB Dilution Solvent to remove all of the powder.



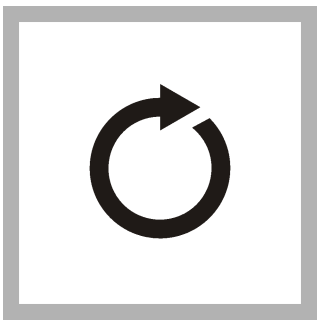
4. Put the cap on the HNB Dilution Solvent bottle. Mix until fully dissolved.

5. Write the mixing date on the bottle.

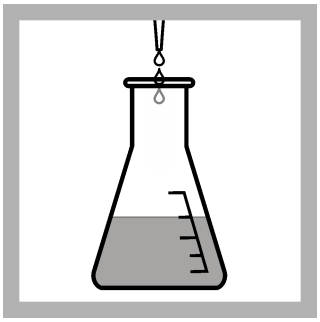


6. Fill a clean, 100-mL plastic graduated cylinder to the 100-mL mark with the brine sample.

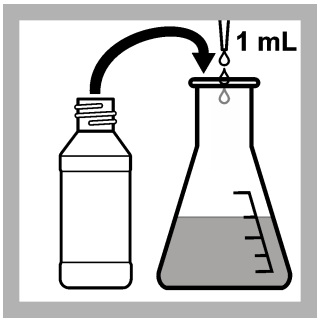
7. Pour the 100-mL brine sample into a 125-mL plastic Erlenmeyer flask.



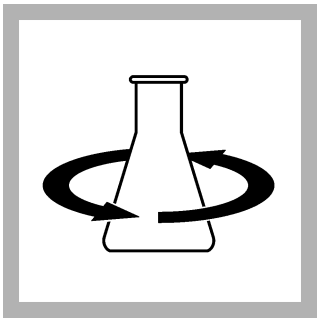
8. Do steps 6 to 7 again four more times.



9. Calcium brine standards (0, 20, 40, 60 and 80 µg/L): Use the Tensette pipet to add 0.0, 0.2, 0.4, 0.6 and 0.8 mL of the 10-mg/L Calcium standard to the five Erlenmeyer flasks.

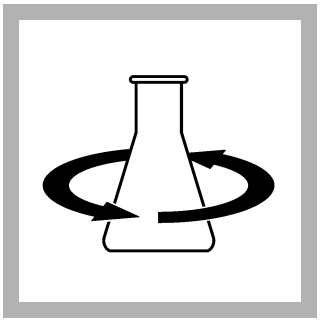


10. 0-µg/L Calcium brine standard: Add 1.0 mL of 3.0 N Alkali Buffer to the 0-µg/L calcium brine standard.



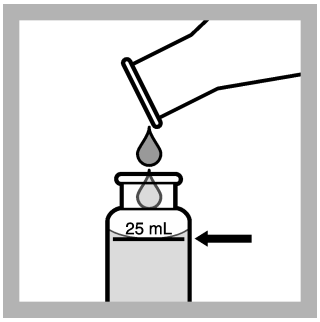
11. Swirl to mix.

12. Add 1.0 mL of the HNB dye solution to the 0-µg/L calcium brine standard.

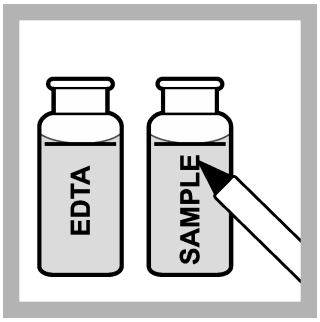


13. Swirl to mix. The dye color is stable for 15 minutes, then decreases.

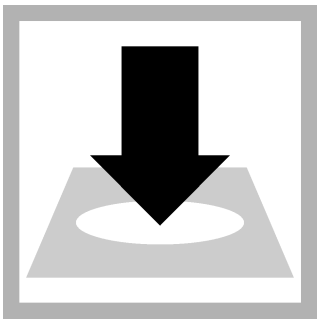
14. Push **2 TIMER** to set a 2-minute timer.



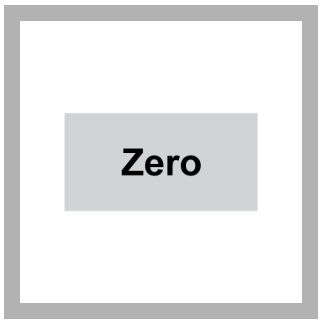
15. After 2 minutes, add approximately 25-mL of the 0-µg/L calcium brine standard to the two matched sample cells.



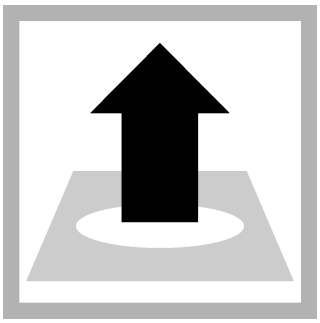
16. Write "EDTA" on one sample cell and "Sample" on the other.



17. Put the "Sample" cell into the cell compartment. Close the sample compartment cover.



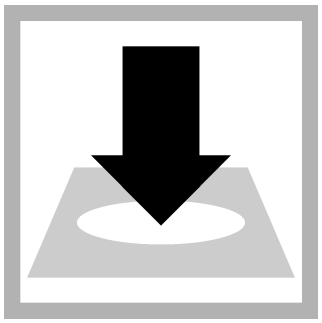
18. Press **ZERO ABS**.



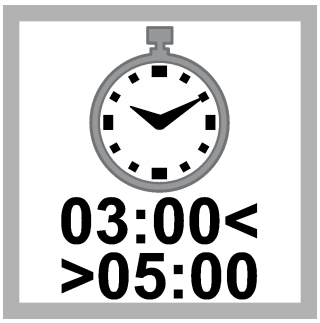
19. Remove the sample cell.

20. Add 1 drop of 1 M EDTA to the "EDTA" cell. Swirl to mix.

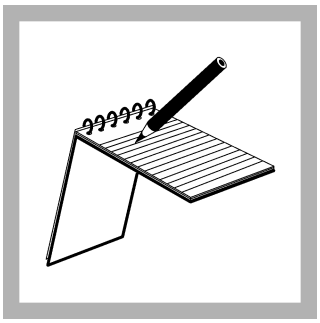
21. Push **3 TIMER** to set a 3-minute timer.



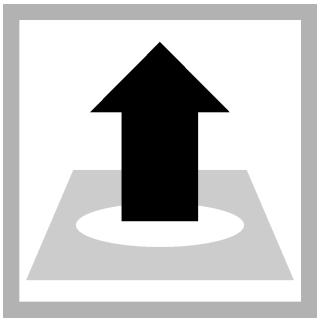
22. Put the "EDTA" cell into the cell compartment. Close the sample compartment cover.



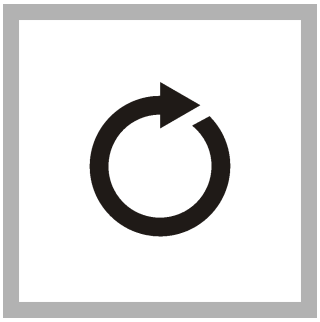
23. After 3 minutes, read the absorbance within 2 minutes.



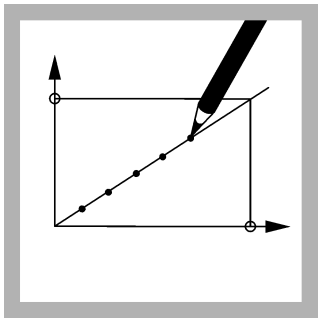
24. Record the absorbance.



25. Remove the sample cell.



26. Do steps 10 to 25 again for each of the calcium brine standards (20, 40, 60 and 80 µg/L).

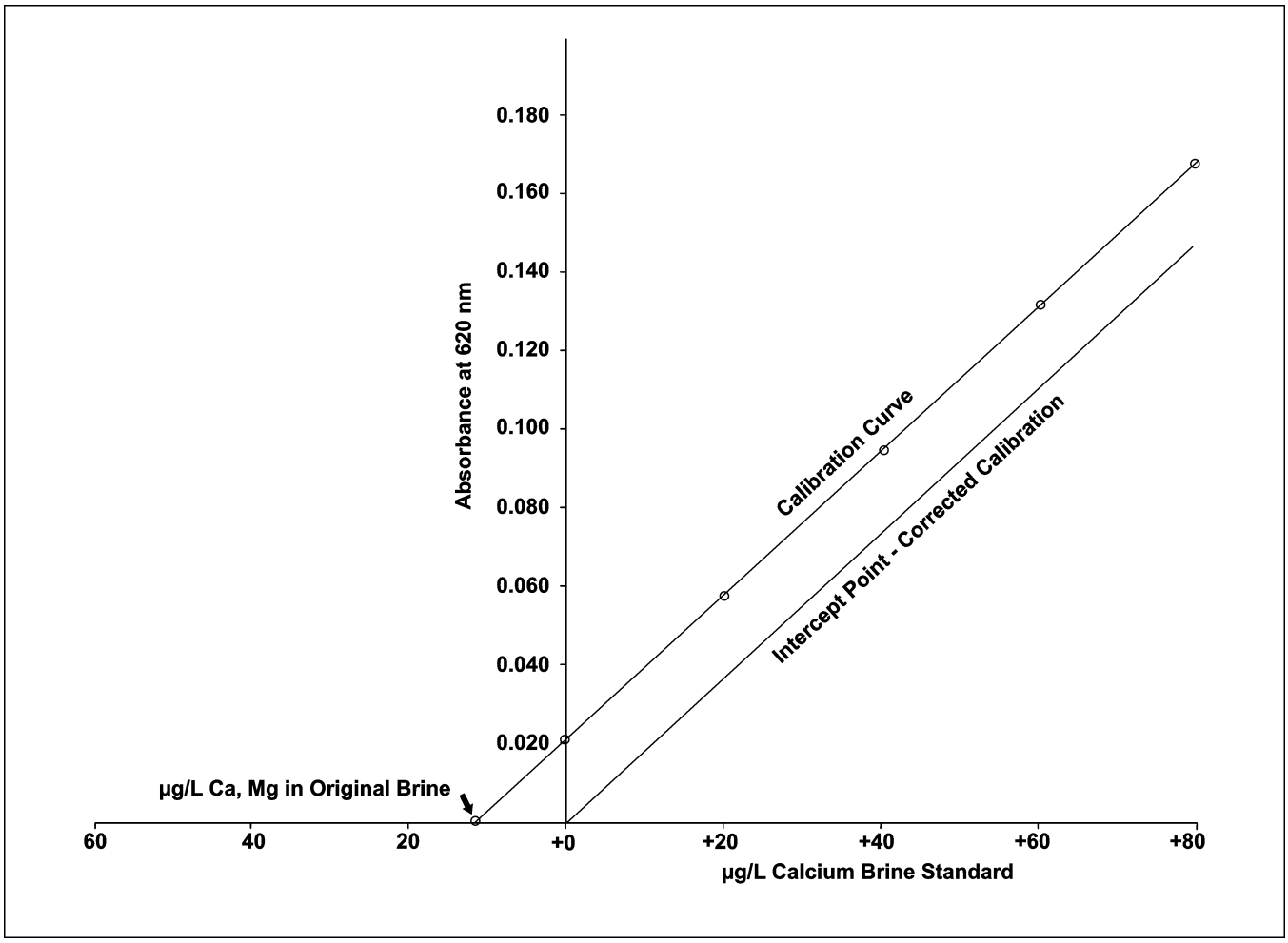


27. Do the steps in Identify the calibration curve on page 4.

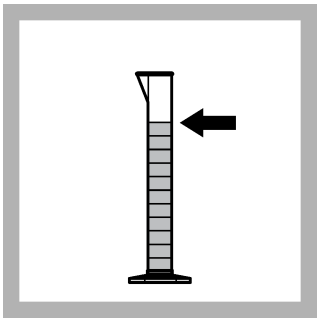
Identify the calibration curve

1. Record the absorbance of each calibration brine standard (0, 20, 40, 60 and 80 µg/L) on a graph similar to Figure 1.
2. Record the combined soluble µg/L Ca, Mg of the original brine on the graph (the negative intercept).
3. Make a line from the negative intercept through the five points on the graph (the calibration curve).
4. Subtract the absorbance of the 0 µg/L calcium brine standard from the absorbance values of the four calcium brine standards (20, 40, 60 and 80 µg/L).
5. Record the adjusted absorbance for each of the four calibration brine standards on the graph.
6. Make a line through the four points on the graph (the intercept point-corrected calibration).
7. Save the four points of the intercept point-corrected calibration as a single wavelength calibration on the DR3000 or higher. Refer to the instrument user manual for instructions.

Figure 1 Example calibration graph

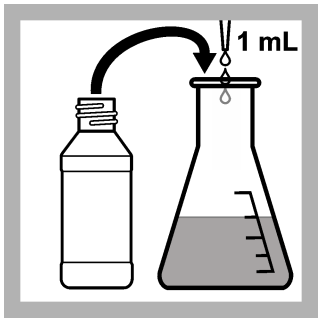


Test procedure

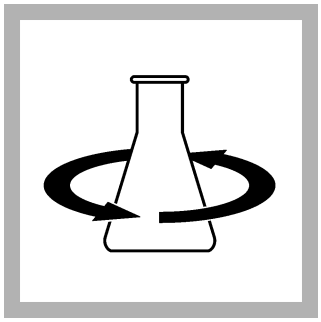


1. Fill a clean, 100-mL plastic graduated cylinder to the 100-mL mark with the brine sample.

2. Pour the 100-mL brine sample into a 125-mL plastic Erlenmeyer flask.

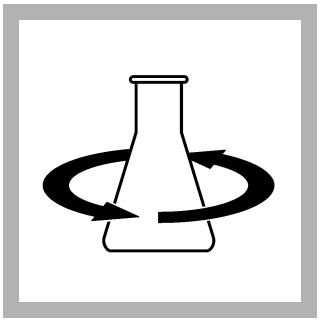


3. Add 1.0 mL of 3.0 N Alkali Buffer to the Erlenmeyer flask.

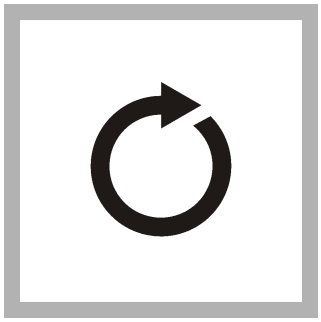


4. Swirl to mix.

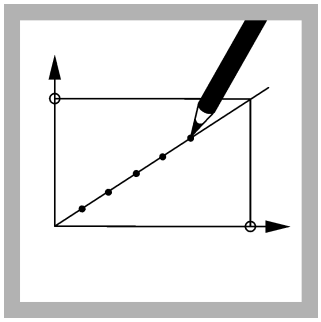
5. Add 1.0 mL of HNB dye solution to the Erlenmeyer flask.



6. Swirl to mix.



7. Do steps 14 to 25 of Prepare a calibration curve on page 2.



8. Record the absorbance on the calibration graph to determine the µg/L calcium, magnesium.

Multiplier factors

Multiply the result (µg/L calcium) by the factor in Table 1 to get the concentration of the chemical compound.

Table 1 Multiplier factors

Chemical compound	multiply by:	Chemical compound	multiply by:
Magnesium (Mg)	0.61	Calcium oxide (CaO)	1.40
Calcium carbonate ($CaCO_3$)	2.50	mg/kg Ca	0.83

Interferences

Chlorine (hypochlorous acid) significantly interferes with this test. Chlorine removes the color of the reagent dye. If chlorine is present, add 5 drops of dechlorinating solution (32332) to each 100 mL of brine before the reagents are added.

Concentration of interferant	Calcium (µg/L) interference			
	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

Summary of Method

The Hydroxy Naphthol Blue (HNB) method uses an dye-indicator that forms a blue color in a strongly alkaline brine. The color changes to red when free calcium and magnesium are present in the brine. EDTA is added to part of the reacted sample. The EDTA combines with the calcium and magnesium to set a reference point. The measurement wavelength is 620 nm.

Consumables and replacement items

Description	Unit	Item no.
Alkali Buffer, 3.0 N	100 mL	2307242
HNB Lab Reagent Package, includes: HNB powder, 6 g and HNB dilution solvent, 100 mL	each	2307300
EDTA Solution, 1 M	50 mL	2241926
Calcium standard, 10.0 mg/L	100 mL	2305442
Graduated cylinder, plastic, 100 mL	each	217242
Erlenmeyer flask with cap, 125 mL	each	—
TenSette pipet, 0.1 to 1.0 mL, includes: 100 pipet tips	each	1970001
Pipet tips for TenSette pipet (1970001)	50/pkg	2185696
Sample cells, 1-inch square glass, matched pair, 25 mL	each	1993500

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