

Analytical Determination of Magnesium and Calcium in Diverse Matrices from Cyclopentane Hydrate Desalination.

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History

- Received: 19-05-2026
- Revised: 24-06-2026
- Accepted: 25-06-2026
- Published Online: 17-10-2026

DOI : 10.32508/vnuhcmj-std.v29i4.4722



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ABSTRACT

Cyclopentane hydrate desalination has emerged as a promising low-energy alternative to conventional desalination because water forms hydrate lattices that encapsulate cyclopentane while excluding dissolved salts. In addition to producing fresh water, the proposed process analyzes streams such as seawater, hydrate-concentrated brine, and post-recovery process solutions that require accurate Ca^{2+} and Mg^{2+} determination for process monitoring, mass balance calculations, and resource recovery optimization. These ions are also precursors for high-value products such as struvite fertilizers, magnesium oxide nanoparticles, and hydroxyapatite materials.

The process centers on an inexpensive ethylenediaminetetraacetic acid (EDTA) complexometric titration for Mg^{2+} and Ca^{2+} determination in diverse matrices associated with cyclopentane hydrate desalination. It is compared for performance with flame atomic absorption spectroscopy (AAS). Total ($\text{Ca}^{2+} + \text{Mg}^{2+}$) concentration was determined via titration with standardized EDTA at pH 10 using Eriochrome black T. Ca^{2+} concentration was determined at pH 12 using calcon after Mg^{2+} precipitation as magnesium hydroxide, and Mg^{2+} concentration was calculated as the difference between the total and Ca^{2+} concentrations. Analytical conditions were optimized with respect to sample dilution factor, sodium chloride concentration, pH, indicator dosage, and potential Sr^{2+} and boron species interferences. The proposed method demonstrated excellent linearity ($R^2 > 0.999$), limits of detection (4.5 mg L^{-1} and 5.5 mg L^{-1} for Ca^{2+} and Mg^{2+} , respectively), recoveries (98%–103%), and relative standard deviations (below 3.5%). Statistical comparison with flame AAS showed excellent agreement without significant differences in precision or mean values based on *F* tests and Student's *t* tests at the 95% confidence level. The proposed method provides an accurate and economical analytical tool for Mg^{2+} and Ca^{2+} determination across multiple matrices and supports sustainable resource recovery.

Key words: Cyclopentane hydrate desalination, brine valorization, complexometric titration

INTRODUCTION

Demand for freshwater resources has risen with increasing global population, rapid industrialization, and climate change, especially in coastal and arid regions with limited conventional water supplies. More than two billion people currently reside in water-stressed areas, and this number is expected to significantly increase in coming decades^{1,2}. Therefore, desalination has emerged as an essential technology for converting seawater into potable and industrial water. Commercial desalination is dominated by thermal processes and membrane-based systems such as reverse osmosis (RO). Although RO is energy-efficient, its widespread implementation remains limited due to membrane fouling, concentrating disposal, and significant operational costs^{3,4}. Such limitations motivate the development of alternative desalination processes that combine low energy consumption with opportunities for resource recovery.

Clathrate hydrates are nonstoichiometric crystalline inclusion compounds formed when guest molecules of suitable size and geometry, such as methane (CH_4), carbon dioxide (CO_2), cyclopentane (C_5H_{10}), and tetrahydrofuran ($\text{C}_4\text{H}_8\text{O}$), are trapped within cage-like structures comprising hydrogen-bonded water molecules under specific temperature and pressure conditions. Although clathrate hydrates are not true chemical compounds, the guest molecules stabilize within the water cages through van der Waals interactions rather than covalent bonding. This is exploited by hydrate-based desalination, emerging as a promising low-energy technology because water molecules form the hydrate lattice while excluding dissolved salts^{5,6}. Among the available guest molecules, cyclopentane is particularly attractive because it forms structure II hydrates at atmospheric pressure and temperatures close to 8°C , thereby reducing equipment complexity and energy demand^{7,8}. During hydrate

Cite this article : Duong N H, Nguyen D A, Tran Q N, Lam H S T. **Analytical Determination of Magnesium and Calcium in Diverse Matrices from Cyclopentane Hydrate Desalination.** *VNUHCM J. Sci. Technol. Dev.* 2026; 29(4):4303-4311.

crystallization, water forms the hydrate lattice, leaving dissolved ions in the residual liquid phase. Dissociating the hydrate crystals produces low-salinity water together with a concentrated brine of dissolved minerals⁹. This brine can be considered a valuable secondary resource for mineral recovery. Seawater contains substantial quantities of magnesium (Mg^{2+}) and calcium (Ca^{2+}) ions, with ion concentrations increasing during desalination¹⁰. Mg^{2+} can be recovered to produce struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$), magnesium sulfate (MgSO_4), and magnesium oxide (MgO) nanoparticles used in agriculture, pharmaceuticals, catalysis, and environmental remediation¹¹⁻¹³. Ca^{2+} can be transformed into hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$), a high-value biomaterial widely employed in biomedical coatings, adsorbents, and bone tissue engineering^{14,15}. Ion recovery aligns with circular economy principles by reducing saline discharge and generating marketable products. Accurate Mg^{2+} and Ca^{2+} determination is essential for process monitoring and optimizing their selective precipitation and purification. However, the analysis of seawater, hydrate-concentrated brine, and post-recovery process solutions is challenging because of their high sodium chloride (NaCl) content, elevated ionic strength, and variable composition. Additionally, trace species such as strontium (Sr^{2+}), iron (Fe^{3+}), and boron species may interfere with complexation reactions and instrumental measurements⁷.

Flame atomic absorption spectroscopy (F-AAS) is well-established for Mg^{2+} and Ca^{2+} determination with excellent selectivity and sensitivity⁷. However, its implementation requires dedicated instrumentation, fuel gases, and trained personnel, which may limit accessibility in small laboratories and pilot-scale desalination facilities. By contrast, ethylenediaminetetraacetic acid (EDTA) complexometric titration is inexpensive, simple, and suitable for samples containing relatively high concentrations of divalent cations¹⁶. By controlling pH and employing appropriate metallochromic indicators such as Eriochrome black T (EBT) and calcon, the total ($\text{Ca}^{2+} + \text{Mg}^{2+}$) and Ca^{2+} concentrations can be determined, allowing Mg^{2+} concentration to be calculated as the difference between the concentration values. Although EDTA titration is routinely used for water hardness analysis, most published procedures are intended for drinking water and natural waters with moderate salinity. Few studies have systematically optimized this technique for highly saline and compositionally diverse matrices encountered in cyclopentane hydrate desalination^{8,17}. This presents a significant analytical

gap, especially for laboratories seeking cost-effective methods for process monitoring and resource recovery. To address this gap, we propose an analytical method for Mg^{2+} and Ca^{2+} determination in diverse matrices generated during cyclopentane hydrate desalination, including seawater, hydrate-concentrated brine, and post-recovery process solutions. EDTA complexometric titration was optimized with respect to sample dilution factor, matrix effects, pH, indicator dosage, and potential interferences. The proposed method's analytical performance was evaluated and compared with F-AAS. The proposed method provides a robust, accurate, and economical tool for monitoring desalination processes and supporting the sustainable recovery of magnesium- and calcium-based products. The objectives of this study were as follows: (i) develop an EDTA complexometric titration for Mg^{2+} and Ca^{2+} determination; (ii) optimize analytical conditions for highly saline matrices; (iii) evaluate analytical performance and compare results with F-AAS; and (iv) demonstrate the proposed method's applicability to seawater, hydrate-concentrated brine, and post-recovery process solutions.

MATERIALS AND METHODS

Reagents and chemicals

The experiments within this study employed analytical-grade reagents and deionized water. A $0.0100 \pm 0.0002 \text{ mol L}^{-1}$ EDTA solution was prepared by dissolving 3.7220 g of $\text{Na}_2\text{H}_2\text{Y} \cdot 2\text{H}_2\text{O}$ previously dried at 80°C , transferred to a 1000 mL volumetric flask, and diluted to the mark with distilled water. The EDTA solution was then standardized against a $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ standard solution ($0.010000 \pm 0.000015 \text{ mol L}^{-1}$). An ammonia/ammonium chloride ($\text{NH}_3/\text{NH}_4\text{Cl}$) buffer (pH 10.0 ± 0.1) and EBT were used to determine the total concentration, while calcon and 4 mol L^{-1} sodium hydroxide (NaOH , pH 12–13) were used for selective Ca^{2+} titration after Mg^{2+} precipitated as magnesium hydroxide. Certified Mg^{2+} and Ca^{2+} standard solutions (1000 mg L^{-1}) were used for calibration and recovery studies. Concentrated nitric acid (HNO_3 , 65 wt.%) was used for sample preservation. For Flame AAS analysis, lanthanum chloride (LaCl_3 , 1% as La^{3+}) was added as a releasing agent to minimize phosphate and sulfate interferences.

Instrumentation

Complexometric titrations were performed using Class A burettes (25 mL), volumetric flasks, and pipettes. Sample pH was monitored using a calibrated digital pH meter equipped with a combined

glass electrode (Mettler Toledo, Switzerland). Comparative measurements were conducted using F-AAS equipped with air-acetylene flame and hollow cathode lamps for Ca^{2+} and Mg^{2+} determination (AAS 6300, Shimadzu, Japan). The F-AAS signals of Ca^{2+} and Mg^{2+} were measured at 422.7 and 285.2 nm, respectively.

Method development and optimization

Method development focused on the accurate determination of Mg^{2+} and Ca^{2+} in high-salinity matrices. Dilution factors (5–100 $\times$), sodium chloride concentrations (0–14%, w/v), pH, indicator dosage, and potential interferences were systematically evaluated. A 100 $\times$ dilution minimized matrix effects while maintaining suitable titration volumes. Optimal conditions were pH 10 for total $\text{Ca}^{2+} + \text{Mg}^{2+}$ determination and pH 12.5 for selective Ca^{2+} titration after precipitation of magnesium hydroxide. Three drops each of EBT and calcon provided distinct endpoints.

Samples and analytical procedures

Four sample types were analyzed: raw seawater, hydrate-concentrated brine obtained from cyclopentane hydrate desalination, post-magnesium recovery solution, and post-calcium recovery solution. Samples were filtered through 0.45 μm membrane filters and diluted to bring analyte concentrations into the working range. The EDTA titrant was standardized via titration against a Ca^{2+} standard solution under the same conditions used for analysis. Total concentration was determined by transferring an aliquot of the sample into a conical flask and adding pH 10 buffer along with three drops of EBT. The solution was titrated with standardized EDTA until the color changed from wine red to pure blue. Ca^{2+} was determined in a separate aliquot by adjusting the pH to 12 with sodium hydroxide. After adding three drops of calcon, the sample was titrated with EDTA to a red/pink-to-blue endpoint. The Mg^{2+} concentration was calculated according to the following equation: $[\text{Mg}^{2+}] = [(\text{Ca}^{2+} + \text{Mg}^{2+})] - [\text{Ca}^{2+}]$ where $[(\text{Ca}^{2+} + \text{Mg}^{2+})]$ is the total hardness determined by EDTA titration, and $[\text{Ca}^{2+}]$ is the calcium concentration determined separately.

For F-AAS, samples were appropriately diluted with 1% (v/v) nitric acid and supplemented with lanthanum chloride to minimize chemical interferences. Calibration curves were prepared using certified Ca^{2+} and Mg^{2+} standard solutions covering the expected concentration ranges in the diluted samples. The F-AAS results were compared with those from the pro-

posed method using linear regression, relative difference calculations, paired Student's t tests, and correlation analysis. The overall analytical workflow for Mg^{2+} and Ca^{2+} determination in raw seawater, hydrate-concentrated brine, and post-recovery process solutions is illustrated in Figure 1.

Method validation and comparison with F-AAS

The method was validated according to the AOAC International guidelines¹⁸ by evaluating linearity, precision, accuracy, limits of detection (LOD) and quantification (LOQ), and robustness. Precision was assessed in terms of repeatability ($n = 6$) and intermediate precision over three days, while accuracy was determined via spike recovery at 80%–120% of the nominal concentration. The LOD and LOQ were estimated using the 3σ and 10σ criteria, respectively. Robustness was examined by introducing small variations in pH, indicator volume, and EDTA concentration. At least ten samples were analyzed using EDTA titration and F-AAS, and the results were compared using paired t tests, linear regression, and relative difference analysis. Agreement between the two methods was considered acceptable when $r > 0.99$, $p > 0.05$, and relative differences were below 5%. The F test and paired Student's t test were performed using the equations and statistical procedures reported by Westgard and Hunt and Feng et al., respectively. Statistical significance was evaluated at the 95% confidence level ($= 0.05$).

RESULTS

Composition of raw seawater and hydrate-concentrated brine

Figure 2 outlines the cyclopentane hydrate desalination and subsequent brine valorization. Raw seawater is introduced into a stirred reactor together with cyclopentane. Under cooling conditions, cyclopentane forms hydrate crystals that exclude the dissolved salts. The hydrates are separated and dissociated to produce low-salinity fresh water. The brine left behind can be further processed to recover valuable products. Mg^{2+} can be converted into struvite, magnesium sulfate, and magnesium oxide, while Ca^{2+} can be used to synthesize hydroxyapatite and other calcium-based compounds. The figure demonstrates the dual benefit of the process: freshwater production and sustainable mineral recovery from concentrated brine.

The chemical compositions of the raw seawater used and the concentrated brine produced via cyclopentane hydrate desalination are summarized in Table 1.

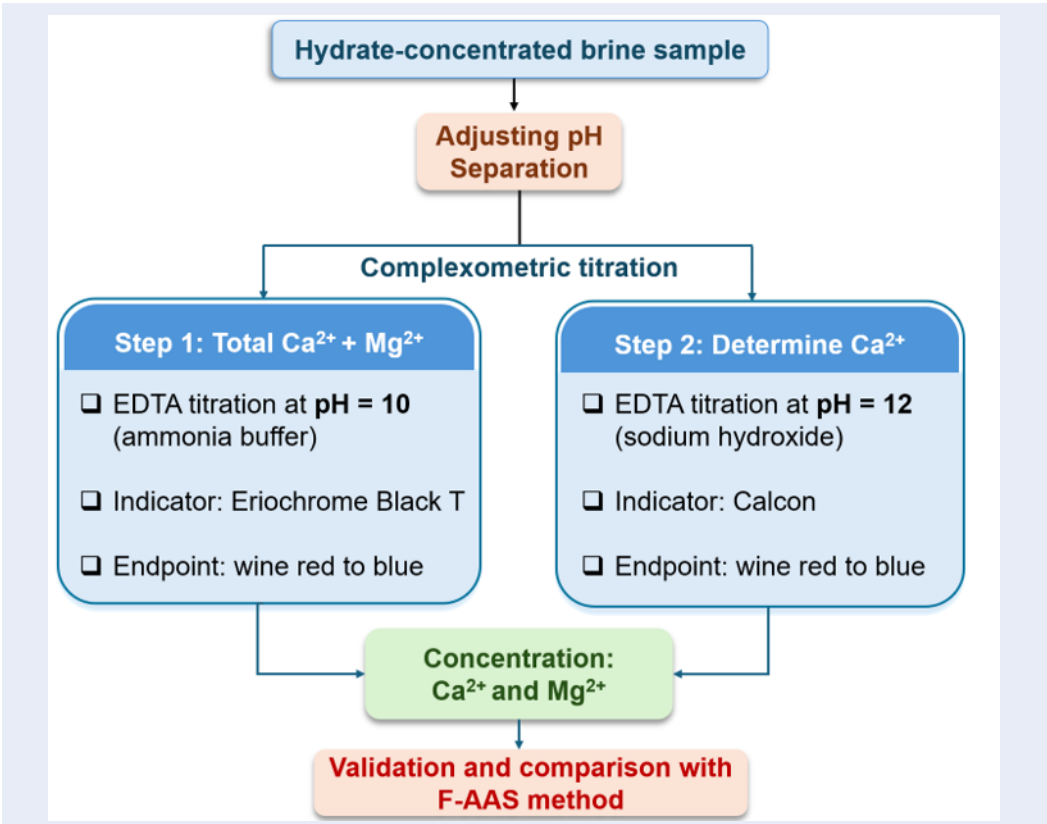


Figure 1: Flowchart of the analytical procedure for the determination of magnesium and calcium in seawater, hydrate-concentrated brine, and post-recovery solutions.

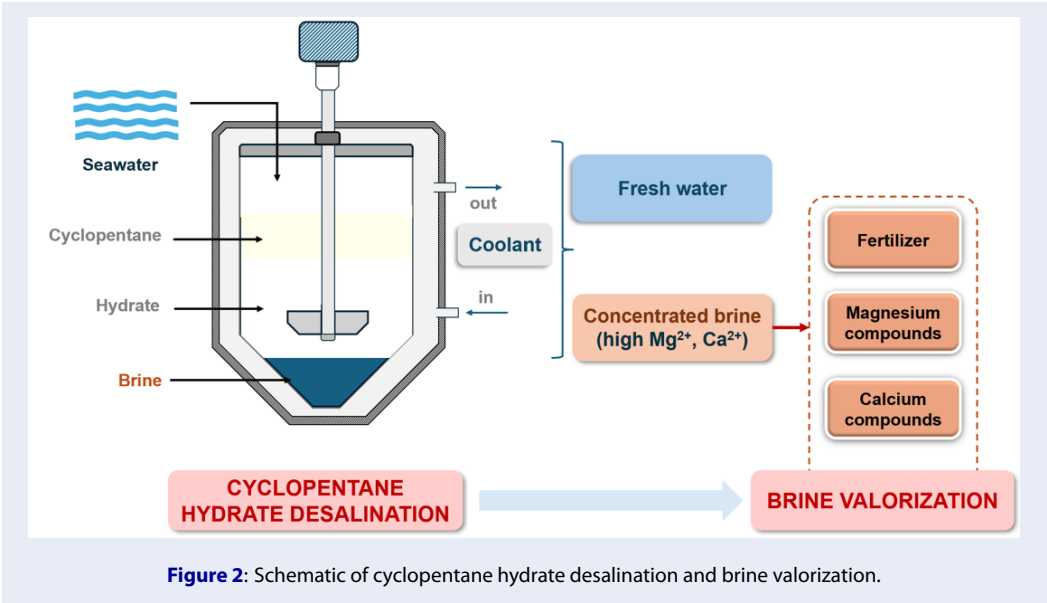


Figure 2: Schematic of cyclopentane hydrate desalination and brine valorization.

Table 1: Compositions of input seawater and resultant brine

Parameter	Seawater (gL ⁻¹)	Brine (gL ⁻¹)	Concentration factor
Na ⁺	19.05	114.30	6.0
Ca ²⁺	0.35	2.15	6.2
Mg ²⁺	1.07	6.80	6.2
K ⁺	0.67	4.02	6.0
Cl ⁻	30.92	188.61	6.1
SO ₄ ²⁻	3.94	23.64	6.0
HCO ₃ ³⁻	0.12	0.74	6.2
Salinity	32.0	192.0	6.0

Optimization

Method optimization focused on improving endpoint clarity and minimizing matrix effects associated with the high salinity of the concentrated brine. Dilution factors of 5×, 25×, 50×, and 100× were evaluated. At the lowest dilution (5×), the solution exhibited strong ionic strength, resulting in sluggish color transitions and slight overestimation of analyte concentrations. At the highest dilution (100×), titration volumes were too small, increasing relative uncertainty. Dilution factors of 25× and 50× were selected as compromises, yielding titration volumes of 8–20 mL and well-defined endpoints. The influence of solution pH and sample dilution on the accuracy and endpoint sharpness of EDTA complexometric titrations has been well documented in analytical chemistry and standard water analysis method.

The pH of the titration medium played a decisive role in achieving selective determination of Ca²⁺ in the presence of Mg²⁺. For total concentration determination, the most stable endpoint with EBT was obtained at pH 10.0 ± 0.1, which is the recommended condition for EDTA complexometric titration because it provides optimal complex stability while preventing metal hydroxide precipitation.⁽²⁵⁾ At lower pH values, incomplete deprotonation of EDTA reduced complexation efficiency, whereas at higher pH values, magnesium hydroxide precipitation could occur. For selective Ca²⁺ determination, pH values between 11 and 13 were investigated. At pH 12, Mg²⁺ precipitated quantitatively as magnesium hydroxide, and calcon produced a distinct red-to-blue endpoint. Below pH 12, incomplete magnesium precipitation caused a positive bias in Ca²⁺ determination. The optimized analytical conditions are summarized in Table 2.

Figure 3 illustrates the effect of sample salinity, corresponding to brine concentrations after 2–6 concentration cycles relative to seawater, on the analytical recovery of Ca²⁺ and Mg²⁺ using the proposed EDTA complexometric titration method. Salinity varied from approximately 3.5 to 13.5 wt.% sodium chloride to simulate raw seawater and hydrate-concentrated brine matrices. The dashed horizontal lines indicate the acceptable Ca²⁺ and Mg²⁺ recovery range of 95%–105%. For Ca²⁺, recoveries remained highly stable, ranging from approximately 98% to 100%, with relatively small error bars, indicating excellent precision and minimal matrix interference across the investigated salinity range. Mg²⁺ recoveries were slightly higher at lower salinity, reaching approximately 102%–103%, but gradually approached 100% as salinity increased.

Validation Performance

Table 3 summarizes the key validation parameters of the proposed method for the determination of Ca²⁺ and Mg²⁺ in hydrate-concentrated brine. The LOD values were 4.5 mg L⁻¹ for Ca²⁺ and 5.5 mg L⁻¹ for Mg²⁺, while the corresponding LOQ values were 15 and 17 mg L⁻¹ for Ca²⁺ and Mg²⁺, respectively. These values are sufficiently low for the intended application because the ion concentrations in the seawater and concentrated brine are several orders of magnitude higher, allowing their accurate determination after appropriate dilution of the samples into the method's working range.

Comparison between EDTA titration and F-AAS

Table 4 presents the Ca²⁺ and Mg²⁺ concentrations for representative samples analyzed using the proposed method and F-AAS. The concentrations,

Table 2: Optimization of analytical conditions

Experimental parameter	Investigated range	List of abbreviations	Rationale
Buffer pH for determining total ($\text{Ca}^{2+} + \text{Mg}^{2+}$)	8.0–10.5 (0.5 pH unit intervals)	10.0	Stable endpoint with EBT
pH for determining Ca^{2+}	11.0–13.0 (0.5 pH unit intervals)	12.0–12.5	Quantitative $\text{Mg}(\text{OH})_2$ precipitation
EBT indicator	100 – 250 μL (2 – 5 drops)	150 μL (3 drops)	Sharp color transition
Calcon indicator	100 – 250 μL (2 – 5 drops)	150 μL (3 drops)	Stable pink-to-blue endpoint
EDTA concentration	0.005–0.02 M	0.010 M	Suitable titration volume

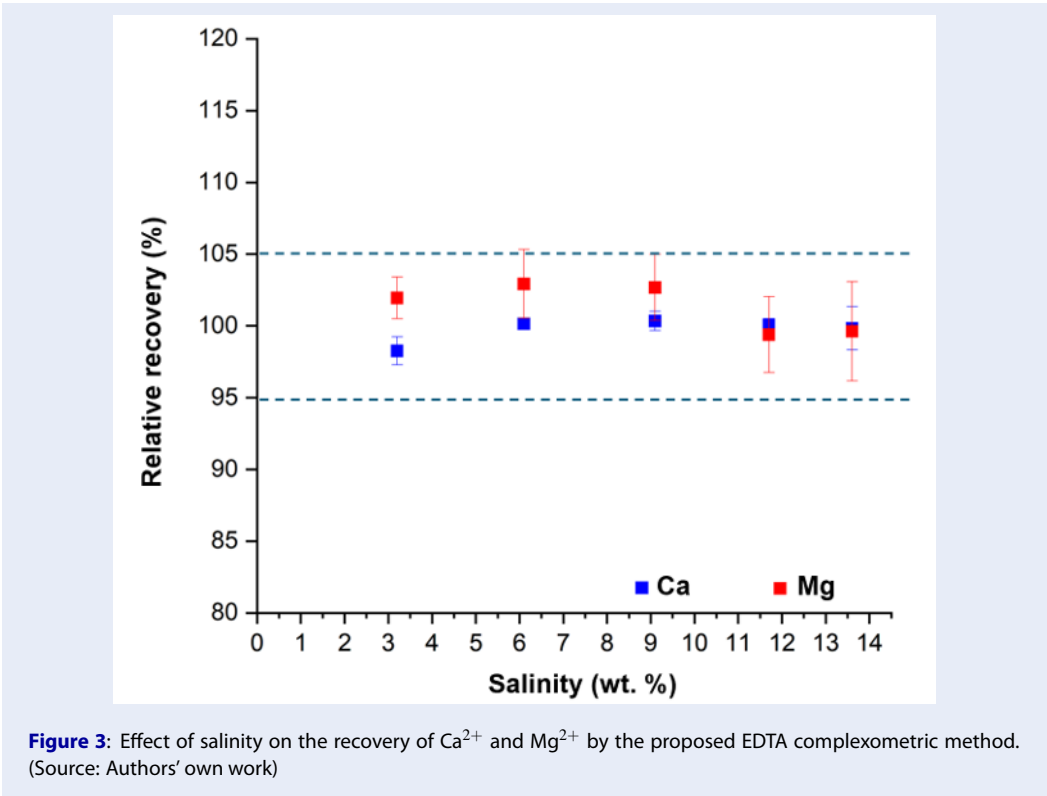


Table 3: Analytical performance characteristics of the validated EDTA complexometric method for determination of Ca^{2+} and Mg^{2+} (Source: Authors' own work)

Validation Parameter	Ca^{2+}	Mg^{2+}	Acceptance Criteria
LOD (mg L^{-1})	4.5	5.5	-
LOQ (mg L^{-1})	15	17	-
Precision (RSD, %)	2.1	2.7	< 3.0
Recovery (%)	98.6–103.2	97.9–103.1	95–105
Robustness	Pass	Pass	No significant change

Table 4: Statistical comparison of Ca^{2+} and Mg^{2+} concentrations determined via the proposed EDTA complexometric and F-AAS.

Analyte	EDTA (mg L^{-1})	Flame AAS (mg L^{-1})	F test	t test	Conclusion
Ca^{2+}	393 ± 4	402 ± 2	$F_{TN} < F_{0.95}$	$t_{TN} < t_{0.95}$	No significant difference
Mg^{2+}	1360 ± 6	1257 ± 11	$F_{TN} < F_{0.95}$	$t_{TN} < t_{0.95}$	No significant difference
Ca^{2+} (brine)	2148 ± 18	2111 ± 31	$F_{TN} < F_{0.95}$	$t_{TN} < t_{0.95}$	No significant difference
Mg^{2+} (brine)	6804 ± 17	7082 ± 21	$F_{TN} < F_{0.95}$	$t_{TN} < t_{0.95}$	No significant difference

reported as mean $\pm$ standard deviation, demonstrate closely comparable values at various concentration levels, including in raw seawater and hydrate-concentrated brine samples.

DISCUSSION

As documented in Table 1, the hydrate formation selectively excludes dissolved salts, leaving a residual brine substantially enriched in all major ions. Sodium and chloride remained the dominant constituents, with salinity increasing from approximately 32 g L^{-1} in raw seawater to approximately 192 g L^{-1} in the concentrated brine. This corresponds to an overall concentration factor of approximately 6.0–6.2. Mg^{2+} and Ca^{2+} exhibited similar enrichment behavior. Mg^{2+} concentration increased from approximately 1.07 g L^{-1} to 6.8 g L^{-1} in raw seawater and hydrate-concentrated brine, respectively. While Ca^{2+} concentration increased from 0.35 to 2.15 g L^{-1} in raw seawater and hydrate-concentrated brine, respectively. These results confirm that hydrate-concentrated brine is a significant secondary source of alkaline earth metals. The Mg/Ca mass ratio remained close to that of seawater, indicating that the hydrate desalination process proportionally concentrated both ions without significant selectivity. This observation is consistent with the nonstoichiometric and largely nonselective salt exclusion behavior reported for cyclopentane hydrate-based desalination systems^{6,8,18}. The elevated ion concentrations are advantageous for resource recovery because they reduce reagent consumption and reactor volume requirements during downstream precipitation processes. Magnesium can be recovered as struvite, magnesium sulfate, magnesium hydroxide, or magnesium oxide nanoparticles, while calcium can be converted into hydroxyapatite or calcium carbonate products. Accurate Mg^{2+} and Ca^{2+} determination is essential for optimization extraction, subsequent processes, and product quality control.

All measured recovery levels for the analytes remained within the predefined acceptance limits,

demonstrating satisfactory accuracy under all tested conditions. The slightly larger variances observed for Mg^{2+} at higher salinity suggest an increase in experimental variability associated with the indirect Mg^{2+} determination by calculating the difference between total and Ca^{2+} concentrations. Nevertheless, this effect was not large enough to compromise the analytical performance of the method, and no systematic bias was observed. Overall, the results confirm that sodium chloride concentrations up to at least 13.5 wt.% do not significantly affect Ca^{2+} and Mg^{2+} determination after appropriate dilution. These findings demonstrate the strong matrix tolerance and robustness of the proposed method and support its applicability for routine analysis of seawater and highly saline hydrate-concentrated brines.

The method exhibited good precision, with relative standard deviations of 2.1% for Ca^{2+} and 2.7% for Mg^{2+} , both meeting the predefined acceptance criterion of less than 3.0%. Recovery experiments yielded Ca^{2+} and Mg^{2+} recoveries of 98.6%–103.2% and 97.9%–103.1%, respectively, which fall well within the acceptable range of 95%–105%, confirming satisfactory accuracy and negligible matrix effects. Robustness testing showed that small deliberate variations in pH, indicator volume, and titrant concentration did not significantly affect the analytical results, and both analytes met the predefined robustness criterion. Overall, the results demonstrate that the proposed method provides adequate sensitivity, precision, accuracy, and robustness for the routine Ca^{2+} and Mg^{2+} determination in high-salinity brines generated from cyclopentane hydrate desalination. These performance characteristics confirm the suitability of the method for process monitoring and mineral recovery during brine valorization.

To assess method equivalence, the variances and mean values obtained via the two methods were compared using the F test and Student's t test, respectively. In all cases, the calculated F values fell below the 95% confidence threshold ($F_{\text{calculated}} < F_{0.95}$), indicating no significant difference in precision between the two

analytical methods. Similarly, the calculated t values fell below 95% confidence threshold ($t_{\text{calculated}} < t_{0.95}$), confirming that the differences between mean concentrations were not statistically significant at this level. For Ca^{2+} , the EDTA and F-AAS results agreed closely despite slight variations attributable to sample heterogeneity and experimental uncertainty. A similar trend was observed for Mg^{2+} , even at concentrations exceeding several grams per liter in the concentrated brine. The consistency of the statistical outcomes across all samples demonstrates that the proposed method provides results equivalent to those obtained by F-AAS. These findings confirm the accuracy and reliability of the proposed method for Ca^{2+} and Mg^{2+} determination in highly saline matrices. Given its low cost, simplicity, and minimal instrumentation requirements, the method represents a practical alternative to F-AAS for routine analysis and process monitoring during brine valorization.

The validated method was applied to monitor Ca^{2+} and Mg^{2+} concentrations throughout the brine valorization process. During Mg^{2+} precipitation, Mg^{2+} concentrations in solution decreased by approximately 84%, while Ca^{2+} remained largely in solution, confirming effective selective recovery of Mg^{2+} . Subsequently, the resulting precipitate was converted into products such as struvite, magnesium hydroxide, and magnesium oxide nanoparticles. In the Ca^{2+} recovery stage, Ca^{2+} concentrations decreased by approximately 63%, enabling the synthesis of hydroxyapatite and related calcium-based materials. These findings demonstrate that the proposed method is a practical analytical tool for real-time process control, enabling rapid assessment of product removal efficiencies and optimization of reagent consumption. Its low cost and analytical reliability make the method particularly suitable for supporting integrated freshwater production and mineral recovery in cyclopentane hydrate desalination systems.

CONCLUSIONS

This study demonstrates successful selective EDTA complexometric titration and validated Mg^{2+} and Ca^{2+} determination in high-salinity brines generated from cyclopentane hydrate desalination. The analytical approach, based on total concentration titration at pH 10 and selective calcium determination at pH 12, enabled reliable differentiation of Ca^{2+} and Mg^{2+} despite the elevated sodium chloride content of the matrix. Method validation demonstrated excellent linearity, satisfactory precision and accuracy, recoveries within 98%–103%, and robust performance under

minor variations in analytical conditions. Comparative analysis with F-AAS did not show statistically significant differences between the two methods, confirming that the proposed method provides analytical performance comparable to that of an established instrumental technique. Because the method requires only common laboratory glassware and inexpensive reagents, it offers a practical and cost-effective alternative for laboratories without access to advanced instrumentation. The validated method was successfully applied to raw seawater, hydrate-concentrated brine, and post-recovery process solutions, enabling accurate monitoring of Mg^{2+} and Ca^{2+} removal during the production of struvite, magnesium oxide, and hydroxyapatite. This study provides a robust analytical tool to support routine process control and sustainable brine valorization in hydrate-based desalination systems.

LIST OF ABBREVIATIONS

EBT: Eriochrome black T
EDTA: Ethylenediaminetetraacetic acid
F – AAS: Flame atomic absorption spectroscopy
RO: Reverse osmosis
w/v: Weight/volume
RSD: Relative Standard Deviation

COMPETING INTERESTS

The authors declare that there are no conflicts of interest related to this study. All figures, tables, and data presented in this manuscript are original and were generated by the authors.

AUTHORS' CONTRIBUTIONS

Ninh Hoai Duong, Dat Anh Nguyen: Methodology, Seawater analysis, Investigation, Writing - Original Draft, Writing - Review & Editing. **Ninh Hoai Duong and Dat Anh Nguyen contributed equally to this work.**

Quang Nhat Tran: Seawater analysis, Methodology, Investigation, Writing - Review & Editing.

Hai Son Truong-Lam: Develop apparatus, Conceptualization, Funding acquisition, Methodology, Writing - Original Draft, Writing - Review & Editing.

ACKNOWLEDGEMENTS

This research is funded by Vietnam National University Ho Chi Minh City (VNUHCM) under grant number B2026-18-14, to Truong Lam Son Hai.

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