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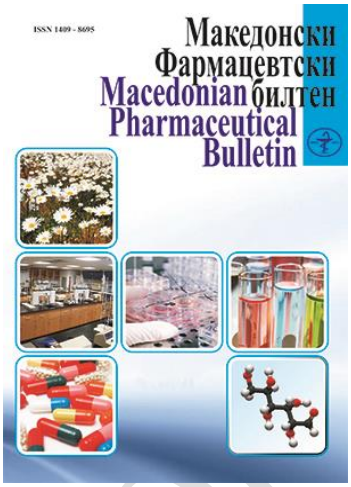

Title: Comparison of titrimetric and ion chromatographic techniques for the determination of calcium and magnesium in raw water

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Comparison of titrimetric and ion chromatographic techniques for the determination of calcium and magnesium in raw water

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Abstract

This research aims to compare the titrimetric method and ion chromatography for determining the concentrations of calcium (Ca^{2+}) and magnesium (Mg^{2+}) in raw water samples collected from the Debar region. The analysis focuses on evaluating the accuracy, sensitivity, cost-effectiveness, and applicability of both methods, considering the local chemical and physical properties of the water. The titrimetric method, which employs complexometric titration with ethylenediaminetetraacetic acid (EDTA), is known for its simplicity and low cost. However, it is susceptible to interference from other ions and has limited sensitivity. In contrast, ion chromatography offers superior precision and sensitivity, enabling the detection of trace levels of calcium and magnesium in complex matrices. However, it requires advanced equipment and additional resources. The findings indicate that ion chromatography is more suitable for detecting low ion concentrations and for analyses intended for research and regulatory purposes. In contrast, the titrimetric method is better suited for routine analyses where moderate accuracy is sufficient. This study offers practical recommendations for selecting the most appropriate methodology based on the specific requirements of the analysis, available resources, and the characteristics of the raw water.

Keywords: titrimetric method, ion chromatography, calcium determination, magnesium determination, raw water analysis, water quality.

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Introduction

Calcium and magnesium are essential elements and among the most abundant alkaline earth metals commonly present in natural water sources. Their concentrations directly affect water hardness, which has significant implications for water quality, industrial operations, and human health. Elevated levels of calcium and magnesium can lead to pipe and boiler scaling, reduce the efficiency of water heating systems, and increase maintenance costs (Sawer et al., 2003). Conversely, low concentrations may adversely affect water treatment processes and biological functions, as both elements are vital for numerous physiological and biochemical reactions (WHO, 2011). Therefore, accurate quantification of calcium and magnesium in raw water is critical for effective water resource management, industrial applications, and compliance with drinking water standards established by organizations such as the World Health Organization (WHO) and the United States Environmental Protection Agency (EPA) (APHA, AWWA, WEF, 2017).

Several methods are available for determining the concentrations of calcium and magnesium, with the titrimetric method and ion chromatography (IC) being the most commonly employed techniques in chemical laboratories. Among these, the titrimetric method specifically, complexometric titration using ethylenediaminetetraacetic acid (EDTA) is a well-established, cost-effective, and straightforward approach (Vogel, 1989). The concentrations of Ca and Mg ions are quantified by titration with disodium dihydrogen ethylenediaminetetraacetate (Na_2-EDTA, also known as complexone III) in the presence of a metallochromic indicator. For calcium determination alone, it is essential to maintain the sample pH between 12 and 13, whereas simultaneous determination of calcium and magnesium requires an optimal pH around 10 (Trajkovic et al., 1983). This method is suitable for analyzing drinking water and mineral waters that are colorless and contain low concentrations of salts and metals. However, it is less applicable for saline waters or those contaminated with elevated levels of salts and metals.

While titration remains a reliable and widely used technique for routine water quality assessments, it has inherent limitations. These include potential interference from other metal ions, subjective determination of the titration endpoint, and lower sensitivity compared to instrumental methods.

Ion chromatography (IC), in contrast, is a highly selective analytical technique employed for the separation and quantitative analysis of ions across diverse sample types, including water, food, biological fluids, and industrial solutions. This method exploits

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differences in ion affinities for the stationary phase, enabling effective separation (Weiss, 2004). During the process, ions are separated through interaction with an ion-exchange resin, and detection is commonly performed via conductivity, UV-Vis spectrometry, or mass spectrometry (Veljanovski, 1994). IC offers several advantages, such as high precision, automation, and the capability to analyze multiple ions simultaneously. However, its high operational costs, requirement for specialized instrumentation, and potential matrix effects in complex water samples pose challenges for routine use (Morris et al., 2018).

Considering the differences between the titrimetric method and ion chromatography, this study aims to compare these two analytical techniques for the determination of calcium and magnesium concentrations in raw water, with the objective of identifying the more accurate and reliable method.

Materials and methods

Sample collection

Raw water samples were collected from a source located in a village within the Debar region, a town in the western part of the Republic of North Macedonia, at various times throughout 2023. The primary objective of collecting these samples was to perform a detailed physico-chemical analysis as part of this study.

Samples were taken directly from the source into clean glass chemical bottles and transported to the laboratory under controlled cold conditions to preserve their integrity. The analysis focused on comparing calcium and magnesium concentrations using two analytical techniques: the titrimetric method and ion chromatography.

Titrimetric method

Standard laboratory equipment was utilized for titrations, including an automatic dark glass burette (25 mL) with a resolution of 0.015 mL to ensure precise titrant delivery. Deionized water was used for preparing and diluting all solutions.

The reagents employed in the titration process included 1 M sodium hydroxide (NaOH), an ammonium buffer solution (pH 10) prepared from ammonium hydroxide (NH_4OH) and ammonium chloride (NH_4Cl; Merck, Germany), and 0.01 M sodium ethylenediaminetetraacetate (Na_2-EDTA, also known as complexone III; analytical grade, Sigma-Aldrich).

For calcium determination, 50 mL of the test water sample and 50 mL of deionized water (used as a blank) were placed separately in Erlenmeyer flasks. Then, 1.5 mL of 1 M

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NaOH and a small amount of murexide indicator (VEB Berlin Chemie, Berlin-Adlershof) were added to each flask. Titration was carried out by gradually adding the EDTA solution until the color changed from red to blue-violet, indicating the endpoint. The calcium concentration was calculated using the following formula:

$$\text{mg CaO/L} = (a \times c \times 56 \times 1000) / p$$

where:

a = volume of complexon III (EDTA) solution consumed during titration (mL)

c = concentration of the complexon III solution (mol/L)

p = volume of the water sample taken for analysis (mL)

Note that 1 mL of a 1 mol/L complexon III solution corresponds to 56 mg CaO (equivalent to 40 mg Ca). According to standards, drinking water can contain calcium concentrations up to 200 mg/L.

To determine the magnesium concentration, the total hardness of the water was first measured. The procedure was as follows: 50 mL of the filtered water sample was placed in a 250 mL Erlenmeyer flask. Then, 1.5 mL of ammonium buffer solution (pH 10) and 1–2 drops of Eriochrome Black T indicator (Merck-Alkaloid) were added. The mixture was titrated with a standard 0.01 M EDTA solution until the endpoint was reached, indicated by a color change from red to blue, which corresponds to the complexation of both calcium and magnesium ions. The total hardness, expressed in German degrees (°dH), was calculated using the following formula:

$$\text{Water hardness (°dH)} = (a \times c \times 5.6 \times 1000) / p$$

where:

a = volume of complexon III solution consumed during titration (mL)

c = concentration of the complexon III solution (mol/L)

p = volume of the water sample analyzed (mL)

Note that 1 mL of 1 mol/L complexon III solution corresponds to 56 mg CaO, which equals 5.6 German degrees (°dH). The magnesium concentration was then determined by subtracting the calcium concentration from the total water hardness (Travis, 1950).

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Ion chromatography

To determine the concentrations of dissolved calcium ions (Ca^{2+}) and magnesium ions (Mg^{2+}) by ion chromatography, optimized analytical conditions were employed to achieve high selectivity and sensitivity. The analysis was performed using a Dionex IonPac™ CS16 cation-exchange column (5 × 250 mm) paired with a CG16 guard column (5 × 50 mm). A 30 mM methanesulfonic acid solution served as the eluent, delivered isocratically at a flow rate of 1.0 mL/min. The column temperature was maintained at 40 °C to enhance separation efficiency and reproducibility.

Detection was carried out by suppressed conductivity using a Dionex Cation Self-Regenerating Suppressor operating at 89 mA. The injection volume was 25 µL. Quantification was based on peak area integration using Chromeleon software version 7.3 (Thermo Fisher Scientific, 2018). The optimized chromatographic conditions are summarized in Table 1. Statistical analysis of the experimental data was performed using Microsoft Excel 2007.

Table 1.

Results and Discussion

This study compares calcium (Ca^{2+}) and magnesium (Mg^{2+}) concentrations in water samples determined by two analytical methods: ion chromatography (IC) and complexometric titration using Na_2-EDTA. Both techniques are commonly employed for quantifying these metal ions, and their accuracy and precision are critical for obtaining reliable results in scientific and industrial applications (Skoog et al., 2018). Table 2 summarizes the Ca^{2+} concentrations, while Table 3 presents the Mg^{2+} concentrations obtained by both IC and titrimetric methods.

Table 2.

Table 3.

The results obtained from the two analytical methods show good agreement, although the titrimetric method consistently produced slightly higher values compared to ion chromatography. To evaluate whether these differences are statistically significant, a *two-*

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sample t-test assuming unequal variances was performed. The outcomes of the t-tests for Ca^{2+} and Mg^{2+} concentrations are presented in Tables 4 and 5, respectively.

Table 4.

Table 5.

Regarding Ca^{2+}, the calculated *t-statistic* (-0.3513) is very close to zero, suggesting minimal difference between the two methods. Moreover, the *p-value* obtained from the two-tailed test is 0.7287, which is considerably higher than the commonly accepted significance level (α = 0.05). This indicates that the observed difference is not statistically significant. Consequently, there is insufficient evidence to reject the null hypothesis, which states that both methods yield equivalent results for calcium determination. Additionally, the magnitude of the t-statistic is smaller than the critical value, further supporting the conclusion that no statistically significant difference exists between the titrimetric method and ion chromatography in measuring Ca^{2+} concentrations.

The analysis of Mg^{2+}resulted in a negative t-statistic, indicating a difference in the mean values obtained by the two methods. To assess the statistical significance of this difference, a two-tailed *p-value* of 0.0605 was calculated. Although this value slightly exceeds the conventional significance level (α = 0.05), it suggests that the observed difference is not statistically significant at the 5% level (Slavica et al., 1979). Therefore, there is insufficient evidence to reject the null hypothesis, which posits that the two methods yield equivalent results for magnesium determination. The fact that the t-statistic falls within the acceptance region and the p-value exceeds the threshold supports this conclusion. It can thus be concluded that no statistically significant difference exists between the titrimetric method and ion chromatography in determining magnesium concentrations. Minor discrepancies observed may be attributed to experimental factors such as laboratory conditions and procedural nuances of the titrimetric method, which can affect its precision. Nonetheless, ion chromatography offers enhanced separation efficiency and greater analytical accuracy for both calcium and magnesium quantification (Kaya et al., 2015).

Observable differences in the results obtained using the two analytical methods underscore the importance of selecting the appropriate technique based on sample characteristics and the specific objectives of the analysis. Ion chromatography demonstrates superior selectivity and accuracy, particularly when analyzing samples containing multiple coexisting ions. In contrast, while the titrimetric method is well-suited for routine

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applications, it may be less accurate in complex matrices due to potential interferences from other metal ions and variations in analytical conditions.

Both methods exhibit good reproducibility, indicating reliable precision. However, ion chromatography holds a clear advantage in the analysis of complex water samples, offering enhanced separation and quantification of individual ions. On the other hand, the titrimetric method remains a valuable tool for routine assessments, owing to its simplicity, cost-effectiveness, and rapid execution.

For samples with higher ionic complexity, ion chromatography is recommended due to its capacity to accurately resolve and quantify metal ions in mixed solutions (Dionex, 2012). A comprehensive comparison of the two methods is presented in Table 6.

Table 6.

Overall, the findings of this study confirm that both the titrimetric method and ion chromatography are suitable for determining calcium and magnesium concentrations in the analyzed raw water samples.

Conclusion

This study underscores the importance of selecting an appropriate analytical technique based on the characteristics of the water sample and the specific objectives of the analysis. The two methods employed, ion chromatography and complexometric titration, yielded comparable results for the determination of calcium and magnesium, with only minor differences observed. These findings confirm that both techniques are suitable for various laboratory applications. Ion chromatography is recommended when high accuracy, sensitivity, and the ability to handle complex matrices are required. In contrast, the titrimetric method remains a reliable, cost-effective, and efficient option for routine analyses where moderate precision is acceptable.

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Резиме

Споредба на титриметрискиот метод и јонската хроматографија за определување на калциум и магнезиум во сурова вода

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Клучни зборови: титриметриски метод, јонска хроматографија, определување калциум, определување магнезиум, анализа на сурова вода, квалитет на вода.

Ова истражување има за цел да ги спореди титриметрискиот метод и јонската хроматографија за определување на концентрациите на калциум (Ca^{2+}) и магнезиум (Mg^{2+}) во сурова вода од Дебарскиот регион. Анализата се фокусира на точноста, чувствителноста, економичноста и применливоста на двата метода во контекст на локалните хемиски својства на водата. Титриметрискиот метод, кој се базира на комплексометриска титрација со EDTA, се одликува со едноставност и ниски трошоци, но е подложен на интерференции и има ограничена чувствителност. Наспроти тоа, јонската хроматографија обезбедува висока прецизност и чувствителност, овозможувајќи детекција на траги на јони, но бара пософистицирана опрема. Резултатите покажуваат дека јонската хроматографија е подобра за анализи кои бараат висока точност, особено во сложени матрици, додека титриметрискиот метод е погоден за рутински анализи со умерени барања. Студијата нуди практични насоки за избор на соодветна методологија според потребите, ресурсите и својствата на водата.

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Table 1. Ion Chromatography Analytical Conditions

Parameter	Value
Column	Dionex IonPac™ CS16 Analytical (5 x 250 mm)
Precolumn	CG16 Guard (5 x 50 mm)
Eluent	30 mM methanesulfonic acid
Eluent flow rate	1.0 mL/min
Elution mode	Isocratic
Column temperature	40 °C
Detection	Suppressed Conductivity
Suppressor	Dionex Cation Self-Regenerating Suppressor
Applied Current	89 Ma
Injection volume	25 µL
Storage solution	eluent
Determination mode	Peak area

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Table 2. Comparison of calcium levels in raw water by ion chromatography and titrimetric method

Place	Ion chromatography Ca^{2+} (mg/L)	Titrimetric method Ca^{2+} (mg/L)	Month
Source 1	32.2	32.86	February
Source 1	34.53	35.18	March
Source 1	37.79	38.21	June
Source 1	42.90	43.53	August
Source 1	46.16	47.04	September
Source 1	34.66	35.12	December
Source 2	31.39	32.36	February
Source 2	33.87	34.60	March
Source 2	38.74	39.23	June
Source 2	40.01	40.98	August
Source 2	42.97	43.35	September
Source 2	38.63	39.49	December

*Source 1 - Soporevo
*Source 2 - Zvoncica

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Table 3. Comparison of magnesium levels in raw water by ion chromatography and titrimetric method

Place	Ion chromatography Mg^{2+} (mg/L)	Titrimetric method Mg^{2+} (mg/L)	Month
Source 1	4.09	4.79	February
Source 1	4.30	4.95	March
Source 1	4.66	5.01	June
Source 1	5.03	5.64	August
Source 1	6.15	6.96	September
Source 1	4.54	5.31	December
Source 2	4.08	4.86	February
Source 2	4.27	5.01	March
Source 2	4.69	5.20	June
Source 2	5.63	5.90	August
Source 2	6.12	6.96	September
Source 2	4.91	5.13	December

*Source 1 - Soporevo
*Source 2 - Zvoncica

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Table 4. Statistical Comparison of calcium determination methods (t-Test Results)

	Variable 1	Variable 2
Mean	37.8300	38.4958
Variance	21.5936	21.5153
Observations	12	12
Pooled Variance	21.5545	
Hypothesized Mean Difference	0	
df	22	
t Stat	-0.3513	
P(T<=t) one-tail	0.3644	
t Critical one-tail	1.7171	
P(T<=t) two-tail	0.7287	
t Critical two-tail	2.0739	

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Table 5. Statistical Comparison of magnesium determination methods (t-Test Results)

	Variable 1	Variable 2
Mean	4.8725	5.4767
Variance	0.5371	0.5814
Observations	12	12
Pooled Variance	0.5593	
Hypothesized Mean Difference	0	
df	22	
t Stat	-1.9789	
P(T<=t) one-tail	0.0302	
t Critical one-tail	1.7171	
P(T<=t) two-tail	0.0605	
t Critical two-tail	2.0739	

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Table 6. Comparative overview of ion chromatography and titrimetric method for calcium and magnesium determination

Criteria	Ion Chromatography	Titrimetric Method
Operating Principle	Separation of ions using a chromatographic column and detection	Titration of a sample with a known solution to the equivalence point
Need for Special Equipment	Specialized chromatographic equipment	Basic laboratory equipment (titrators. pipettes. and buffers)
Precision and Sensitivity	High precision and sensitivity; capable of analyzing low concentrations	Precision depends on performance; may be less sensitive for very low concentrations
Time Efficiency	Efficient for multiple samples. but setup and calibration are time-consuming	Simple and fast procedure. but requires careful execution
Advantages	High precision. trace detection. and analysis of multiple ions	Economical. simple. and requires minimal equipment
Disadvantages	Expensive equipment and operating costs; requires trained operators	Limited sensitivity. susceptible to interferences. and requires skilled operators
Applicability	Suitable for analysis of multiple ions and complex matrices	Suitable for simple samples or specific elements

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