

Electrochemical Approach Used For The Potentiometric Determination Of Calcium Ions (Ca^{2+}) In Commercial Mineral Waters

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Abstract:

Background: Calcium (Ca^{2+}) is an essential macroelement involved in critical physiological processes such as bone and teeth development, muscle contraction, blood coagulation, and nerve impulse transmission. A deficiency or excess of calcium in the human diet can result in various health issues, making accurate monitoring of its intake crucial. Mineral waters represent a natural and accessible dietary source of calcium, and their calcium content is often promoted as a measure of quality or health benefit. Therefore, reliable and precise methods are required to determine Ca^{2+} concentrations and verify the accuracy of labeled values on bottled mineral waters.

Materials and Methods: In this study, potentiometric analysis was conducted using a calcium ion-selective electrode (ISE) to determine Ca^{2+} concentrations in several locally available mineral water samples. The method measures the potential difference between a reference electrode and a calcium-sensitive electrode. It was chosen for its simplicity, cost-effectiveness, minimal sample preparation, and ability to produce rapid, reproducible results without the need for complex reagents.

Results: The calcium concentrations obtained through potentiometric measurements were compared with the values indicated on product labels. A strong correlation was observed, demonstrating the accuracy and reliability of the potentiometric method using a calcium-selective electrode.

Conclusion: Potentiometry with a calcium ion-selective electrode is a practical, accurate, and accessible analytical method for determining calcium in mineral waters. Its ease of use and consistency make it particularly suitable for routine applications in quality control laboratories, public health monitoring, and industrial settings, especially where analytical resources may be limited.

Key Word: calcium, ion-selective electrode, potentiometry, mineral water, electrochemical analysis.

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I. Introduction

Calcium (Ca^{2+}) is a multifunctional ion that plays a critical role in both human health and environmental processes. In the human body, it is essential for numerous physiological functions, including bone and tooth mineralization, muscle contraction, nerve signal transmission, blood coagulation, and the regulation of various enzymatic activities^{1,2}. A prolonged deficiency in calcium can result in health issues such as osteoporosis, while excessive intake may lead to pathological calcification in vascular or renal tissues. In this context, drinking water—particularly natural mineral water—serves as an important alternative source of bioavailable calcium, notably for individuals whose diets are deficient in dairy products³.

In the context of drinking water quality, calcium concentration serves as a key indicator of water hardness, which can significantly affect domestic appliances, industrial processes, and ecological systems⁴. Consequently, the availability of reliable, accurate, and accessible analytical methods for determining calcium levels in both natural and treated waters is essential for effective monitoring and management.

Among the available analytical techniques, atomic absorption spectroscopy (AAS), inductively coupled plasma optical emission spectrometry (ICP-OES), and inductively coupled plasma mass spectrometry (ICP-MS) are recognized for their high sensitivity and accuracy in calcium determination^{5,6}. However, these methods involve high operational costs, require sophisticated instrumentation, trained personnel, and often demand extensive sample preparation. Alternatively, colorimetric methods using reagents such as arsenazo or murexide are also employed, but they tend to suffer from interferences and are generally less suitable for rapid or on-site analysis⁷.

In this context, calcium ion-selective electrode (Ca-ISE) potentiometry presents itself as a practical, fast, cost-effective, and portable analytical alternative. This technique relies on measuring the potential difference between a calcium-sensitive electrode and a reference electrode, enabling direct measurement of calcium ions without the need for prior acid digestion and offering satisfactory selectivity^{8,9}. The development of advanced membrane materials—such as nanocomposites and ionophore-based polymers—has further enhanced the sensitivity, selectivity, and long-term stability of modern Ca-ISEs¹⁰.

Accordingly, the objective of this study is to apply the potentiometric method using Ca-ISEs to determine calcium concentrations in various mineral water samples available on the local market. The aim is to assess and compare their mineral content while highlighting the analytical reliability and practical benefits of this technique for routine quality control applications.

II. Material And Methods

Standard reagents and solutions

For the preparation of the calibration curve, a series of standard calcium chloride (CaCl₂) solutions was prepared through successive dilutions using a 0.5 mol/L potassium chloride (KCl) solution, made with ultrapure water (resistivity >18 MΩ·cm). The resulting concentration range extended from 1.0×10^{-5} to 1.0×10^{-1} mol/L. The use of potassium chloride as an ionic strength adjuster (ISA) was intended to maintain a constant ionic strength in all solutions, thereby minimizing the influence of ionic interferences and enhancing the stability and reproducibility of the potentiometric response. According to Bakker and Pretsch (2005)¹¹, the stabilization of ionic strength is essential in potentiometric analysis to ensure a Nernstian response and to minimize signal drift. Bobacka et al. (2008)¹² further emphasized that using an ISA significantly improves the accuracy and consistency of ion-selective electrode (ISE) measurements, especially in complex or variable sample matrices. More recently, Qin et al. (2023)⁹ reaffirmed the importance of this technique in achieving precise and linear calibration in electrochemical ion detection protocols.

Instrumentation

Electrochemical measurements were performed using a high-precision digital laboratory pH meter, model PHENOMENAL 1000L, designed for analytical applications requiring high reliability. This device was coupled to an Orion™ 9720BNWP calcium ion selective electrode (ISE), known for its sensitivity and selectivity for Ca²⁺ ions, and a silver chloride/silver (Ag/AgCl) reference electrode. The ion electrode operates on the principle of the Nernst potential, generated by the specific ionic activity in solution. Before each series of measurements, the electrode was carefully conditioned in a 0.01 mol/L calcium chloride solution for at least 30 minutes, according to the manufacturer's recommendations, to stabilize the membrane and ensure optimal electrochemical response. Electrode calibration was then performed using CaCl₂ standard solutions covering the entire range of concentrations of interest (from 1.0×10^{-5} mol/L to 1.0×10^{-1} mol/L). A KCl-based ionic strength adjuster (ISA) was added to the standards to maintain constant ionic strength and reduce matrix effects.

Experimental Procedure

The mineral water samples were analyzed directly, without any prior pretreatment. For each measurement, 50 mL of the sample was supplemented with 2 g of KCl to maintain a constant ionic strength before the electrochemical potential reading. The Ca²⁺ ion concentration was then determined by interpolation from the established calibration curve.

Statistical analysis

The potential values were recorded and analyzed using Microsoft Excel (Office 2010). Statistical analysis consisted of calculating means and standard deviations for each parameter. The results were presented in tabular form to facilitate interpretation.

III. Result And Discussion

Calibration curve

The electrochemical potential values (in millivolts) obtained for each standard solution of calcium chloride (CaCl₂) are summarized in Table 1. These measurements were carried out using a calcium ion-selective electrode (Ca-ISE) after stabilization of the signal, under controlled ambient temperature conditions. To maintain constant ionic strength and minimize ionic interference, a 0.5 mol/L potassium chloride (KCl) solution was added as an ionic strength adjuster (ISA).

Standard solutions with concentrations ranging from 1.0×10^{-5} M to 1.0×10^{-1} mol/L were analyzed in triplicate to ensure measurement reproducibility and statistical reliability. The corresponding electrode potentials were plotted against the negative logarithm of calcium ion concentration ($-\log[\text{Ca}^{2+}]$) to construct the calibration curve.

This dataset provides the foundation for evaluating the electrode's response behavior according to the Nernstian model. The linearity observed in the calibration curve, with a strong correlation between potential and $-\log[\text{Ca}^{2+}]$, confirms the expected electrochemical behavior of the Ca-ISE. The high repeatability and close alignment of experimental data with the theoretical trendline further validate the reliability of the electrode and the robustness of the analytical protocol. This calibration step is critical to ensure the accuracy of calcium quantification in mineral water samples.

Table 1: values of the potentials of the standard solutions

| $[\text{Ca}^{2+}] (\text{mol/L})$ | 10^{-5} | 5.10^{-5} | 10^{-4} | 5.10^{-4} | 10^{-3} | 5.10^{-3} | 10^{-2} | 5.10^{-2} | 10^{-1} |
|-----------------------------------|-----------|-------------|-----------|-------------|-----------|-------------|-----------|-------------|-----------|
| $-\log[\text{Ca}^{2+}]$ | 5.0 | 4.3 | 4.0 | 3.3 | 3.0 | 2.3 | 2.0 | 1.3 | 1.0 |
| E/ mV | -62.9 | -44.1 | -38.7 | -19.4 | -11.4 | 8.3 | 18.0 | 40.9 | 50.5 |

The resulting curve (**Figure 1**) is a straight line with a coefficient of determination R^2 of 0.9966, indicating excellent linearity of the electrochemical response within the studied concentration range. This linearity confirms the conformity of the electrochemical system to Nernst's laws, thus reinforcing the reliability of the method used.

To verify the accuracy and reproducibility of the calibration curve, two solutions of known concentrations (10^{-3} mol/L and 5×10^{-2} mol/L of CaCl_2) were prepared independently. The potentials measured for these solutions were extrapolated to the calibration curve, yielding calculated concentrations in excellent agreement with the expected values. This agreement validates the calibration curve and confirms the accuracy of the method.

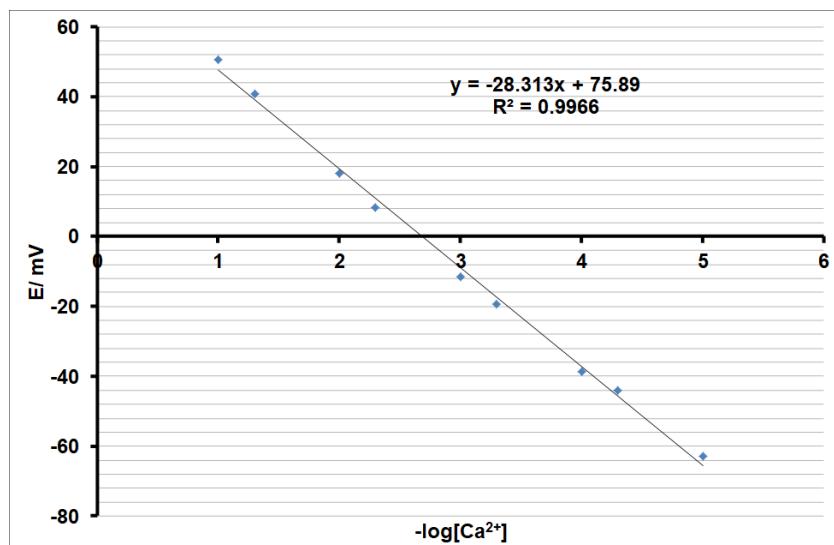


Figure 1: Calibration curve of CaCl_2 solution prepared in KCl solution; electrode Ag/AgCl reference saturated with KCl

Analysis of mineral water samples

Three types of mineral water were used: "Babali water"; "Ideal water" and "Yilemdé water".

The potential values measured for the different mineral water samples, used to determine calcium ion concentrations by extrapolation from the calibration curve, are presented in **Table 2**. These measurements form the basis for calculating the Ca^{2+} content in the analyzed samples.

Table 2: Values of the potentials of the mineral water

| Water Samples | Babali | Idéal | Yilemdé |
|---------------|--------|-------|---------|
| E/ mV | -0.9 | -13.1 | -14.9 |

The calcium concentration values read from the sachet and deduced by extrapolation from the calibration curve are recorded in **Table 2**. The calcium values in mg/L were calculated as follows:

$$[\text{Ca}^{2+}] (\text{mg/L}) = C (\text{mol/L}) \times M_{\text{Ca}} (\text{g/mol}) \times 1000$$

Table 3: Values of the concentrations of the water samples

| Water samples | Babali | Ideal | Yilemdé |
|--------------------------------------|----------------|----------------|----------------|
| Labeled values (mg/L) | 80 | 29.3 | 25.7 |
| Values deduced from the curve (mg/L) | 77.6 ± 0.8 | 28.8 ± 0.5 | 24.9 ± 0.7 |

Advantages of the method

The potentiometric method used in this study demonstrated several significant advantages that make it particularly well-suited for routine analyses. First, it proved to be rapid, providing results in minutes without the need for complex sample pretreatment. Second, it showed good reproducibility, with a standard deviation of less than 2%, indicating stable measurements and reliable results.

Furthermore, the technique requires no sophisticated or expensive equipment: a simple pH meter coupled with a calcium ion-selective electrode is sufficient to perform the analyses. This simplicity of instrumentation makes it an accessible method, even in laboratories with limited technical resources, as is often the case in educational, industrial, or water quality control settings.

Finally, the absence of dangerous or expensive reagents, the low consumption of solvents, and the possibility of directly analyzing real samples (such as mineral waters) without an acid digestion step reinforce the interest of this approach in the context of rapid and effective control of calcium content, particularly for environmental or agri-food applications.

IV. Conclusion

Potentiometry using a calcium ion-selective electrode has emerged as a simple, reliable, and efficient analytical method for quantifying calcium in mineral waters. Its speed, sensitivity, and ease of implementation make it a suitable solution for quality control laboratories. It can also be integrated into nutritional monitoring programs to verify compliance of calcium levels with declared or recommended values, particularly from a public health and food safety perspective.

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