

Determination of calcium in mineral waters by flame atomic absorption spectrometry

Diana Uždavinienė* and

Stasys Tautkus

*Faculty of Chemistry, Vilnius
University, Naugarduko 24,
LT-03225 Vilnius, Lithuania*

A method for the determination of calcium in mineral waters by flame atomic absorption spectrometry (FAAS) has been suggested. The main characteristics for the determination of Ca have been optimized and investigated: optimum air and gas pressure and the influence of hydrochloric acid and the effect of time on the absorbance of Ca. The selectivity of the determination of calcium was also investigated. The limiting interfering Ca / M ratios (the determination error $\pm 10\%$) have been estimated. The suggested technique is simple, fast, accurate and sufficiently selective.

Key words: calcium, mineral water, flame atomic absorption spectrometry

INTRODUCTION

Calcium is an element that a human body needs for numerous functions, such as building and maintaining the bones and teeth, blood clotting, transmitting of the nerve impulses and regulating heart's rhythm. Ninety nine percent of calcium in a human body is stored in bones and teeth. The remaining one percent is found in the blood and other tissues. The body gets calcium by pulling it from the bones when blood levels of calcium drop too low, usually when quite a long time passes since having taken calcium with meal.

Ideally, the calcium "borrowed" from the bones is replaced at a later point. However, this does not always take place, and calcium deficiency can increase the risk of bone disorders, such as osteoporosis [1]. One of the ways to prevent osteoporosis is to consume enough calcium in order to reduce the amount the body is made to "borrow" from the bones [2].

Milk and dairy products are a convenient source of calcium for many people. For individuals, who have some degree of lactose intolerance or dislike dairy products, other options are available. Calcium can also be found in dark green leafy vegetables, dried beans and legumes, calcium-fortified juice [3–5]. Calcium (and vitamin D) can also be ingested as a supplement [6]. A good way to improve calcium intake is to drink enriched mineral water [7, 8].

There is a number of methods for analyzing calcium in water. A traditional method in the quality control of calcium is titrimetry [9, 10]. The concentration of calcium in natural waters is determined by spectrophotometric method [11], indirect potentiometric method using a metallic cobalt wire electrode [12], single-use optical sensor [13], capillary electrophoresis [14–15] and ion chromatography [16–18]. However, flame atomic absorption spectrometry (FAAS) is one of the most extensively used techniques for the determination of various elements with

significant precision and accuracy. This analytical technique is remarkable for its selectivity, speed and fairly low operational cost [19]. However, in some cases, chemical interferences pose a serious problem – some components accompanying the analyte in the sample assayed affect the analytical signal. If this effect is not adequately taken into account during the analysis, it should be expected that the analytical results will be inaccurate to a certain extent [20].

The aim of the present study was to investigate the experimental parameters, the effect of a source of potential interference on the development of a simple method for the determination of calcium in mineral water samples of high saline content.

EXPERIMENTAL

Double-distilled water and analytical-grade reagents were used in all the experiments. Standard stock solution of calcium, 1.0 mg ml^{-1} , was prepared by dissolving an appropriate amount of CaO in diluted hydrochloric acid (1 : 1). Calcium ion standard solution was diluted daily in order to obtain a working standard solution of calcium ($100 \text{ } \mu\text{g ml}^{-1}$). Standard solutions of other metals, $2 \cdot 10^4 \text{ } \mu\text{g ml}^{-1}$, were prepared by dissolving appropriate amounts of: (i) metallic Pb, Cu, Mn, Fe and Co or $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{Sr}(\text{NO}_3)_2$, $\text{Ba Cl}_2 \cdot 2\text{H}_2\text{O}$ and Ni_2O_3 in diluted nitric acid (1 : 1), (ii) metallic Mg in diluted hydrochloric acid (1 : 1), (iii) metallic Cr in diluted sulfuric acid (1 : 4), (iv) metallic Bi in aqua regia, (v) salts KCl and NaCl in double-distilled water.

The solutions of calcium, $1.0 \text{ } \mu\text{g ml}^{-1}$, along with appropriate amounts of interfering ions, were prepared for the evaluation of selectivity. Solutions of calcium of the same concentration without additives were used as reference solutions. In order to determine the influence of the concentration of hydrochloric acid, appropriate amounts of 0.02 mol l^{-1} HCl were added to the solutions to be analysed. Equally concentrated calcium solution without an acid was used as a reference solution.

* Corresponding author. E-mail: u.diana@vv.lt

The model types of mineral water were prepared by dissolving an appropriate amount of metal sulfuric or chloride salts subject to their qualitative and quantitative composition.

The calibration curve used for the determination of calcium in mineral water samples by FAAS was drawn using the following procedure: an appropriate amount of the working standard solution of calcium and 5 ml of 0.02 mol l^{-1} HCl were transferred to a 100 ml volumetric flask and diluted with double-distilled water. The calibration solutions were prepared over the concentration range of $0.1\text{--}12.0 \text{ }\mu\text{g ml}^{-1}$ of Ca.

For the determination of calcium in mineral waters, the test portion of the sample was placed into a 100 ml one-mark volumetric flask containing 0.2 to 8.0 mg l^{-1} of calcium, 5 ml of 0.02 mol l^{-1} HCl and diluted with double-distilled water up to the mark.

A Hitachi 170-50 (Japan) flame atomic absorption spectrometer equipped with hollow cathode lamps was used for the analysis. The instrumental parameters were adjusted according to the manufacturer's recommendations. A Ca hollow cathode lamp operating at 240.7 nm was used as the radiation source. The lamp current was set at 10 mA . The flame composition was acetylene (gas pressure $2.94 \cdot 10^4 \text{ Pa}$) and air (gas pressure $1.28 \cdot 10^5 \text{ Pa}$).

RESULTS AND DISCUSSION

The influence of hydrochloric acid used in the analytical procedure on the absorbance of calcium was estimated. It was determined that the analytical signal of calcium increases by about 14% after the addition of HCl up to 1 mmol l^{-1} (Fig. 1). The influence of acetylene and air gas pressure on the Ca signals was studied systematically and optimum values were estimated. It was determined that the atomic absorption depended on the acetylene gas pressure and was stable in a narrow acetylene gas pressure interval $(2.45\text{--}3.43) \cdot 10^4 \text{ Pa}$ (Fig. 2). The optimum air pressure interval for Ca was from 1.08 to $1.47 \cdot 10^5 \text{ Pa}$ (Fig. 3). The calibration curve obtained under the best conditions showed a linear correlation within the concentration range of $0.2\text{--}8.0 \text{ }\mu\text{g ml}^{-1}$. The detection limit was $0.05 \text{ }\mu\text{g ml}^{-1}$ Ca.

The effect of time on absorbance of calcium was also studied. The adsorption of calcium on the vessel walls was assessed with reference to the absorbance of calcium solutions. It was determined that the absorbance of the calcium solutions after three months remained without any changes.

The selectivity of the determination of calcium was investigated. The limiting interfering Ca / M ratios were considered as limiting when the error of the determination did not exceed $\pm 10\%$. The selectivity studies are summarized in Figs. 4–6.

Evidently, Zn, Mn, Co and Sr have the lowest influence on the absorbance of calcium (Fig. 4). These metals did not interfere with the determination of calcium by FAAS even when their concentrations were by 20 000 times higher than that of calcium. Secondly, about 5 000 times higher concentrations of Fe and Cr had no influence on the absorbance of calcium either. Ni did not interfere with the determination of calcium when its concentration was 4 000 times higher than that of calcium. The concentrations of K, Pb and Na that were two times lower did not influence the determination of calcium (Fig. 5). Figure 6 im-

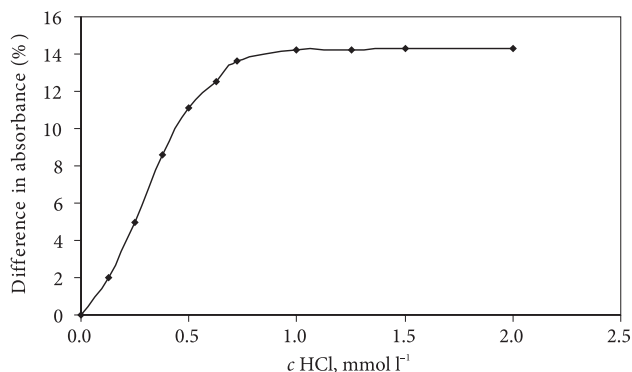


Fig. 1. Correlation between the absorption signal and hydrochloric acid ($p_{\text{C}_2\text{H}_2} = 2.94 \cdot 10^4 \text{ Pa}$, $p_{\text{air}} = 1.28 \cdot 10^5 \text{ Pa}$, $c_{\text{Ca}} = 2 \text{ }\mu\text{g ml}^{-1}$)

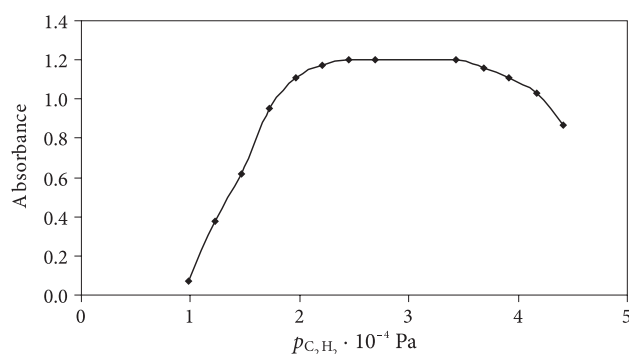


Fig. 2. Correlation between the absorbance of calcium and the pressure of acetylene ($p_{\text{air}} = 1.28 \cdot 10^5 \text{ Pa}$, $c_{\text{Ca}} = 2 \text{ }\mu\text{g ml}^{-1}$)

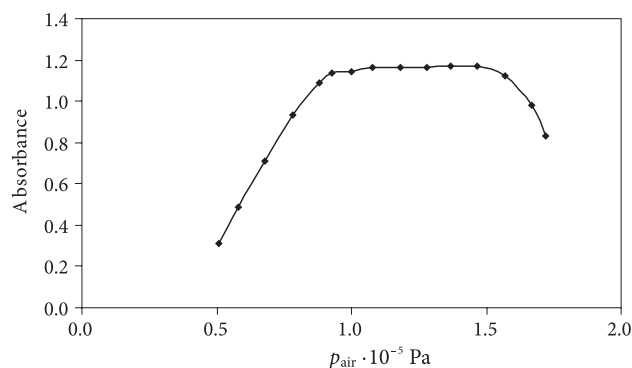


Fig. 3. Correlation between the absorbance of calcium and the pressure of air ($p_{\text{C}_2\text{H}_2} = 2.94 \cdot 10^4 \text{ Pa}$, $c_{\text{Ca}} = 2 \text{ }\mu\text{g ml}^{-1}$)

plies that Ba, Mg, Bi and Cu had the highest interfering effects on calcium determination. Ba and Mg could be tolerated up to their concentrations at least 1 000 times higher than those of calcium; the concentration of Bi was 800 times higher. The concentration of Cu had to be lower more than 200 times. Therefore, according to the interfering effect, the examined metals can be placed in the following order: $\text{Cu} > \text{Bi} > \text{Mg}$, $\text{Ba} > \text{Na}$, Pb , $\text{K} > \text{Ni} > \text{Cr}$, $\text{Fe} > \text{Zn}$, Sr , Co and Mn .

The determination of calcium by FAAS method was investigated and optimized. The analysis of different commercially available mineral water samples was performed. The quantities of calcium are presented in Table 1. It can be seen that the concentration of Ca in the tested water samples ranges from

Table 1. FAAS results for the determination of calcium in the model types of mineral water

Type of mineral water	Amount of calcium, mg l ⁻¹			Abstraction, %
	Specified in the labels	Enclosed	Measured	
"Tichė"	220	220	220	100
"Žalia giria"	62	62	65	105
"Montavit"	5–30	5	4.8	96
		30	30	100
"Cristaline"	106	106	110	104
"Spa"	4.5	4.5	4.2	93

Table 2. FAAS results for the determination of calcium in mineral waters

Mineral water	Specified in the labels	Amount of calcium, mg l ⁻¹ (n = 5, P = 0.95)	
		$\bar{X} \pm \delta_{0.95}$	S _r , %
"Tichė"	220	205	1.5
"Žalia giria"	62	55	2.2
"Montavit"	5–30	5.8	3.5
"Cristaline"	106	118	1.5
"Spa"	4.5	2.4	4.0

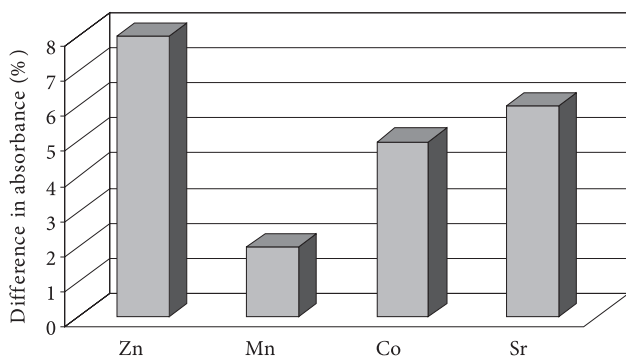


Fig. 4. Effect of the concentration of Zn, Mn, Co and Sr ions on the analytical signal of Ca (Ca : M = 1 : 20 000)

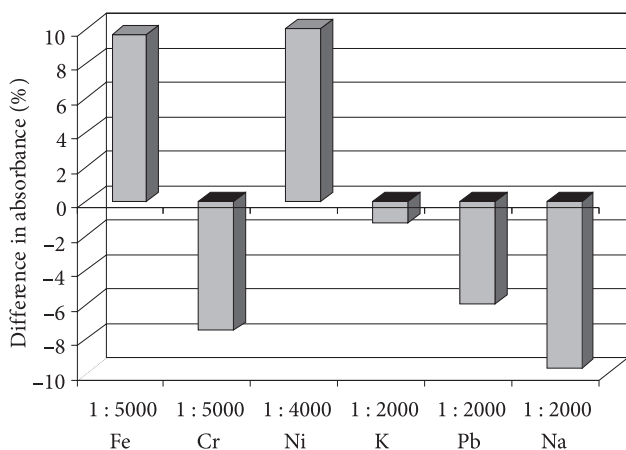


Fig. 5. Effect of the concentration of Fe, Cr, Ni, K, Pb and Na ions on the analytical signal of Ca

4.5 to 220 mg l⁻¹. It is quite a wide range of Ca concentration, thus, the accuracy and reliability of the results were assessed by analysing the model types of mineral water. The findings of the analysis presented in Table 1 show that the suggested Ca determination method provides quite reliable results (abstraction 93–105%).

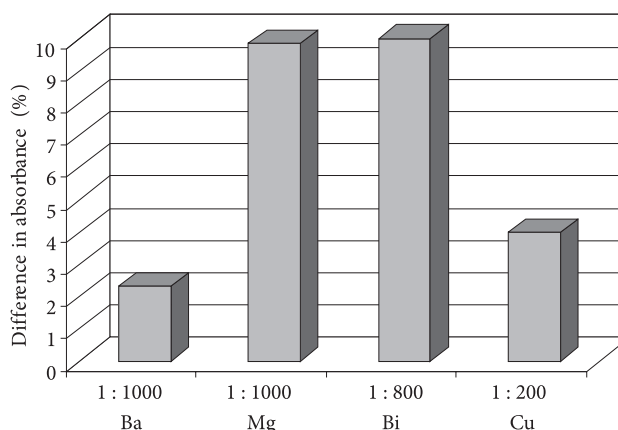


Fig. 6. Effect of the concentration of Ba, Mg, Bi and Cu ions on the analytical signal of Ca

Afterwards, real mineral water samples were analysed in accordance with the methodology described in section "Experimental". The findings show (Table 2) that in some sorts of the mineral water samples tested ("Montavit", "Cristaline", "Tichė" and "Žalia giria"), the amount of Ca was exactly as specified on the labels, but in one sort ("Spa") it was different. In mineral water the amount of Ca ranges from 2.4 to 205 mg l⁻¹, and the standard deviation ranges from 1.5 to 4.0%.

CONCLUSIONS

1. The influence of different parameters on calcium atomic absorption was systematically studied. The influence of hydrochloric acid used in the analytical procedure on the absorbance of calcium was estimated. It was determined that the analytical signal of calcium increases by about 14% after the addition of HCl up to 1 mmol l⁻¹. The influence of acetylene and air gas pressure on the Ca signals was systematically studied and optimum values were estimated. The absorbance of calcium is stable in a narrow acetylene gas pressure interval $(2.45\text{--}3.43) \cdot 10^4$ Pa. The effect of time on the absorbance of calcium was also studied. It

was determined that the absorbance of calcium solutions after three months remained without any changes.

2. The selectivity of the determination of calcium was investigated. The limiting interfering Ca / M ratios (the determination error $\pm 10\%$) have been estimated. All the metals studied can be placed in the following order of obstruction characteristics: Cu > Bi > Mg, Ba > Na, Pb, K > Ni > Cr, Fe > Zn, Sr, Co and Mn.

3. A simple method for the determination of calcium in mineral water by flame atomic absorption spectrometry has been suggested. The methodological approach is fast and not labour consuming. Besides, this method showed an excellent reproducibility, sufficient accuracy (S_r 1.5 to 4.0%) and high selectivity.

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Diana Uždavinienė, Stasys Tautkus

KALCIO NUSTATYMAS MINERALINIULOSE VANDENYSE ATOMINĖS ABSORBCINĖS SPEKTROMETRIJOS METODU

Santrauka

Pasiūlyta metodika kalcio kiekiui mineraliniuose vandenyse nustatyti liepsnos atominės absorbcinės spektrometrijos metodu. Tirta įvairių veiksnių įtaka kalcio atominei absorbcijai. Iš kalibravimo kreivės nustatyta, kad tiesinė priklausomybė yra nuo 0,2 iki 8,0 $\mu\text{g/ml}$, radimo riba 0,05 $\mu\text{g/ml}$. Parinkti optimalūs acetileno dujų ir oro slėgiai. Kalcio atominė absorbcija yra pastovi siaurame acetileno dujų slėgio intervale (2,45–3,43) $\cdot 10^4$ Pa, kai oro srauto slėgis yra 1,28 $\cdot 10^5$ Pa. Įvertintas šios metodikos atrankumas ir nustatyti leidžiamieji ribiniai Ca/Me, kai nustatymo paklaida neviršija $\pm 10\%$. Tirtus metalų jonų pagal trukdantį poveikį galima surašyti tokia tvarka: Cu > Bi > Mg, Ba > Na, Pb, K > Ni > Cr, Fe > Zn, Sr, Co ir Mn. Parengta ir pritaikyta LAAS metodika kalciumi nustatyti mineraliniuose vandenyse yra paprasta, greita, atranki ir tiksli (S_r reikšmės 1,5–4,0%).