

*Dedicated to Professor Emil Cordoş  
on the occasion of his 80<sup>th</sup> anniversary*

## **SIMULTANEOUS DETERMINATION OF CALCIUM AND MAGNESIUM IN NATURAL WATERS BY METHANE-AIR FLAME EMISSION AND FLAME ATOMIC ABSORPTION SPECTROMETRY USING A MICROSPECTROMETER**

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**ABSTRACT.** The calcium and magnesium content of liquid samples has been determined directly by flame atomic absorption (FAAS) and flame atomic emission (FAES) spectrometry using the methane-air (M-A) flame. We measured simultaneously the intensity of the 554 nm wavelength molecular bands emitted by excited CaOH molecules and the decrease of light intensity of a hollow cathode lamp (HCL) absorbed by ground state Mg atoms. The simultaneous multiwavelength measurements enhanced by a charge-coupled device (CCD) microspectrometer allowed fast background correction for each studied element. The instrumental and flame parameters were optimized; the best results were obtained using a lamp current of 1 mA, and an observation height of 5 mm, in case of a reducing flame. The calcium and magnesium content of bottled water samples and water standard certified reference material (CRM) have been determined with standard addition method. The recovery for CRM was 97.80% for Ca and 98.51% for Mg. Under optimal working conditions the detection limits (according to the 3s criterion) were 25 µg·L<sup>-1</sup> for Ca and 5.4 µg·L<sup>-1</sup> for Mg.

**Keywords:** *methane-air flame, FAES, FAAS, CCD microspectrometer, Ca, Mg, simultaneous determination.*

### **INTRODUCTION**

The most commonly used analytical method for the determination of Ca and Mg is complexometric titration [1], but this technique is time and reagents consuming. A good alternative for Ca and Mg determination in liquid samples is

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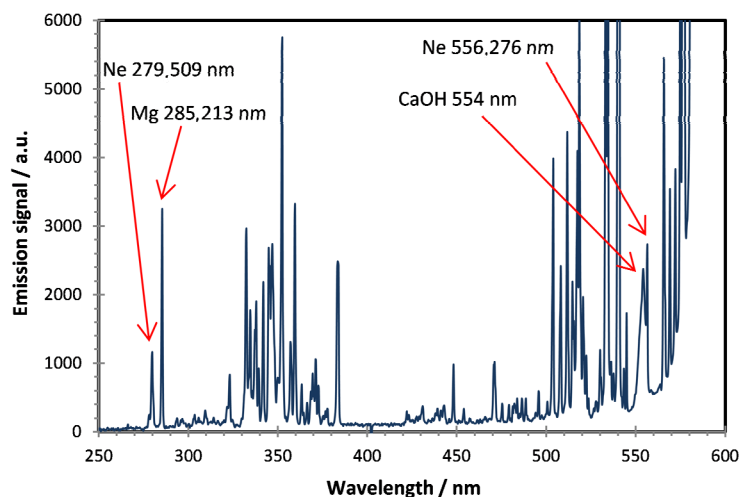
flame atomic absorption (FAAS) [2, 3], flame atomic emission spectrometry (FAES) [4, 5], inductively coupled plasma optical emission spectrometry (ICP-OES) [6], inductively coupled plasma mass spectrometry (ICP-MS) [7], and electrothermal atomization atomic absorption spectrometry (ETAAS) [8]. Actually the trends of Green Analytical Chemistry (GAC) are gaining ground [9, 10]. In concordance with these principles the development of miniaturized instruments and methods are priorities. Using methane gas from the local gas network is economical and the energy consumption of a microspectrometer is very low (450 mA, 5V). The development of CCD microspectrometers allows the use of new signal acquisition and calibration methods in atomic spectrometry [11, 12, 13, 14].

The aim of this study was to attempt a simultaneous use of flame atomic emission and absorption method for Ca and Mg determination in drinking water. In order to achieve this goal we optimized the flame and the instrumental parameters for the simultaneous FAES-FAAS determination in the M-A flame, and applied the results for the quantification of Ca and Mg in different bottled drinking water samples and water standard certified reference material.

## RESULTS AND DISCUSSION

### *Optimization of analytical procedure*

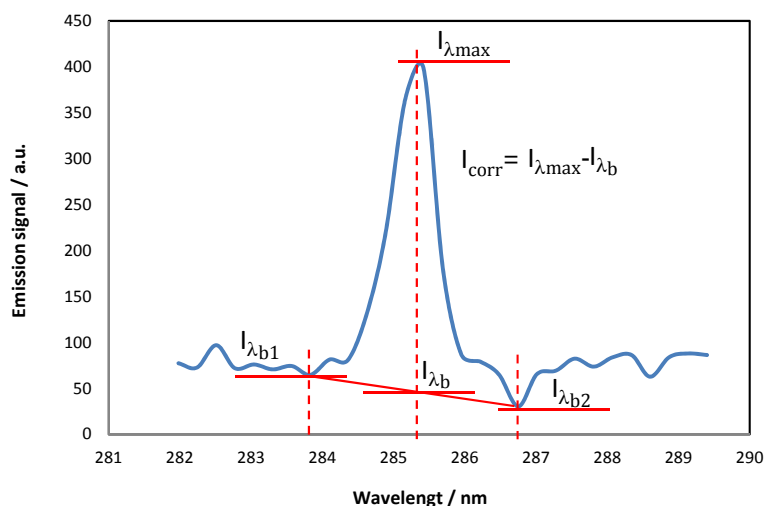
The wavelength selection in the spectral range (250-600 nm) was based on the analysis of the Mg HCL lamp and Ca emission signal (Fig. 1).



**Figure 1.** The Mg HCL lamp and Ca emission signal ( $I_{\text{HCL}}=1$  mA,  $C_{\text{Ca}}=25$  ppm,  $t_{\text{integration}}=5$  s)

For the Mg determination we used the 285.213 nm line, and for Ca the 554 nm CaOH molecular emission band. The 422.672 nm Ca atomic emission line has a low intensity and the 622 nm molecular emission band could not be used because of interference with Ne emission lines.

After the flame and instrumental parameters optimisation, the measurements started with initial background correction. After the selection of integration time and average number, covering the HCL lamp light, we measured the flame background with a blank solution. This background signal was computer-subtracted from each later measured spectrum. The analytical signal was obtained after the second background correction of emission lines based on three wavelength measurements. (Fig. 2.)



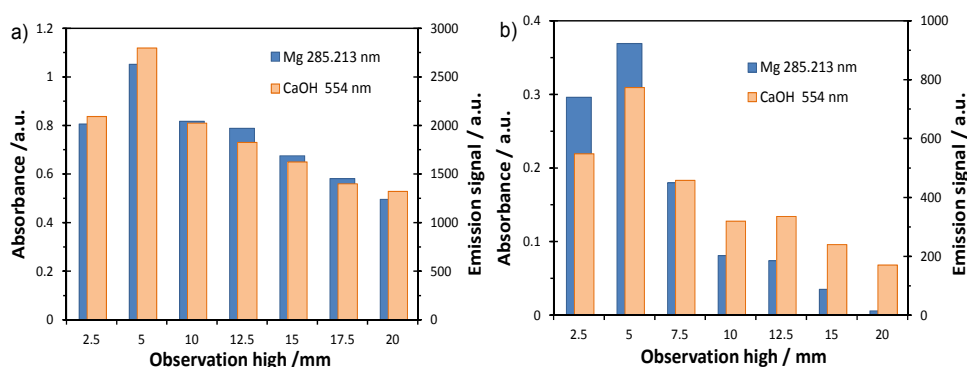
**Figure 2.** The background correction based on three wavelength measurements

### ***Optimization of the flame and observation height***

The flame composition and the observation height were optimised. The concentration of the calibration solution was of 5 mg·L<sup>-1</sup> Mg and 25 mg·L<sup>-1</sup> Ca. Two flame compositions (reducing and oxidizing) were used and measurements were performed at different observation heights. The HCL current was increased in the range 2.5–20 mA in 7 steps. The air flow-rate was kept constant 600 L/h and the flow rate of the methane was fixed at 56 L/h for oxidizing flame, and 66 L/h for reducing flame. The best results were obtained in case of reducing flame (air flow-rate 600 L/h and methane flow rate 66 L/h, at the observation height of 5 mm (Fig. 3).

### Optimization of the hollow-cathode lamp current and integration time

The hollow-cathode lamp current and integration time was optimized by making calibration for each element at different lamp current intensities, between 0.5–2 mA, in 0.5 mA steps and different integration time (3, 4, and 5 s). In each case we followed the coefficient of determination ( $R^2$ ), the sensitivity ( $m$ ) and the detection limit (LOD).



**Figure 3.** Signal at different observation height for (a) reducing (b) oxidizing flame

The results are presented in Fig 4. a), b), c). The measurements demonstrate the increase of calibration sensitivity with integration time, but if an integration time longer than 5 s is used, the time of analyses becomes too long. The detection limit for Mg decreases, and for Ca increases with the increase of lamp current. The 1 mA is an optimal value for both of them. The coefficient of determination ( $R^2$ ) has the best value for 1 mA optimal lamp current for both elements.

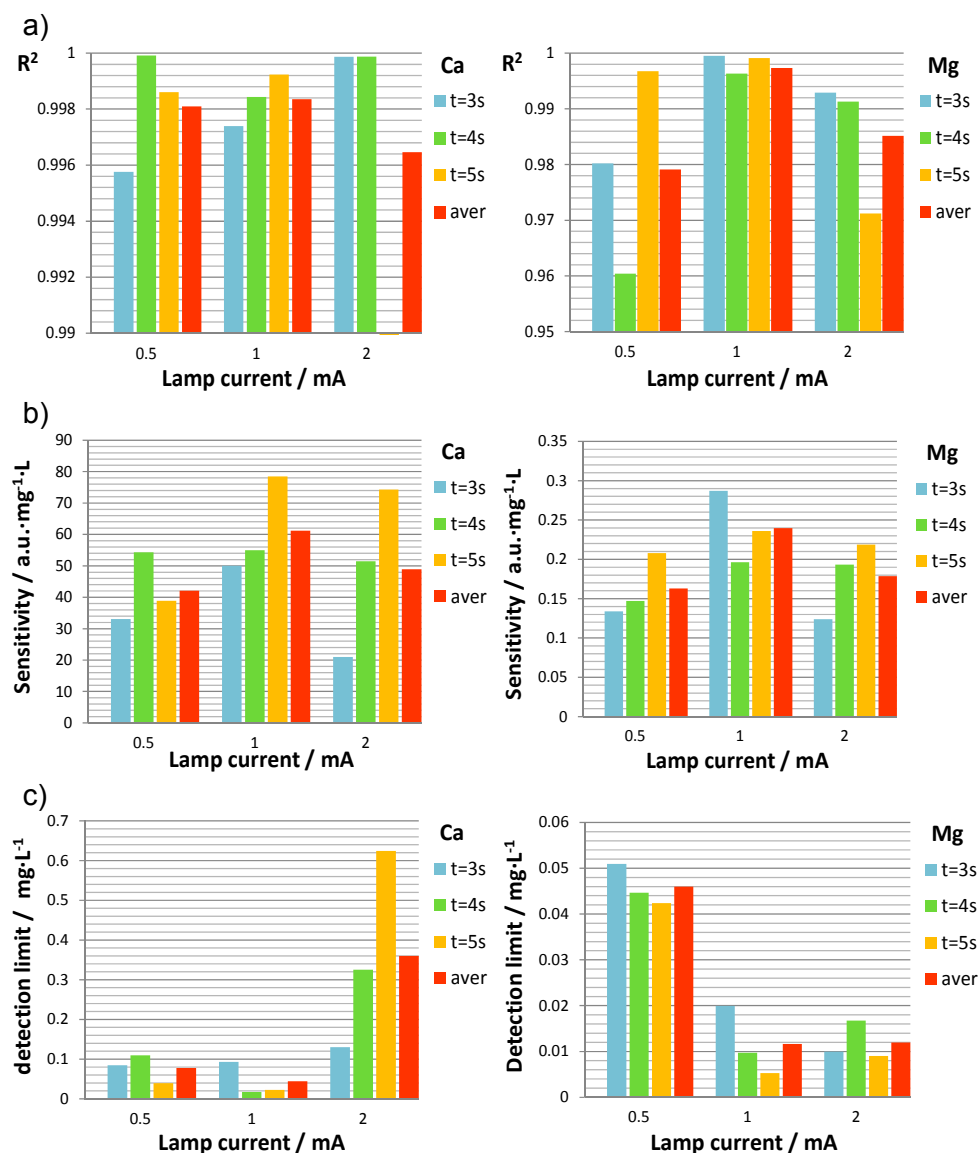
We can consider that the optimal value of the lamp current for the simultaneous determination of Ca and Mg is 1 mA, and the best integrating time is 5 s.

### Figures of merit

For Ca calibration we measured the intensity of CaOH molecular band at 554 nm. The signal and calibration curve are presented in Fig.5.

For Mg calibration the absorbance at 285.213 nm is calculated using the relation  $A = -\lg(p/p_0)$  where  $p_0$  is the radiant power of the lamp in case of background measurement (blank solution) and  $p$  the radiant power of lamp in case of calibration solution measurement. The signal and calibration curve are presented in Fig.6.

The characteristics of calibration curves (coefficient of determination ( $R^2$ ), calibration sensitivity ( $m$ )) and detection limits (LOD) according to the 3 $\sigma$  criterion (3Sb/m) for Ca and Mg are given in Table I. For the determination of the standard deviation of the background (Sb) 10 independent measurements of the blank solution in the proximity of the analytical wavelength were used.



**Figure 4.** a) The coefficient of determination ( $R^2$ ), b) the calibration sensitivity ( $m$ ) c) the detection limit (LOD) for different lamp currents and integration times

As shown in table II. the detection limit in the presented CCD-based FAES-FAAS method is higher than in the case of ICP and Flame AAS, still it is substantially lower than the Ca and Mg concentration of natural waters.

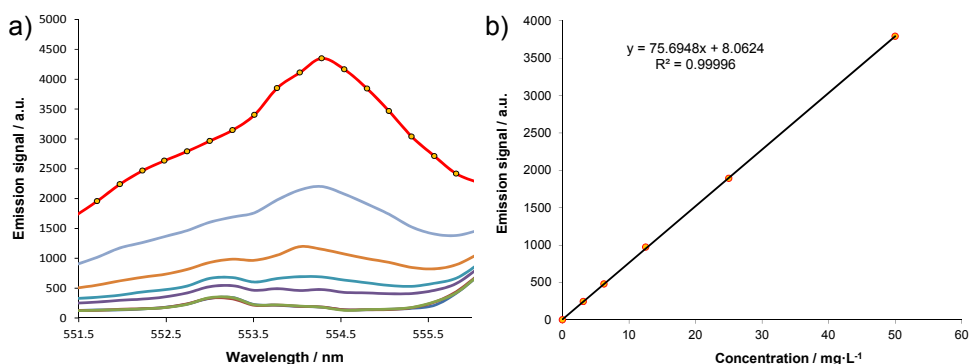


Figure 5. CaOH emission signal and calibration curve (554 nm)

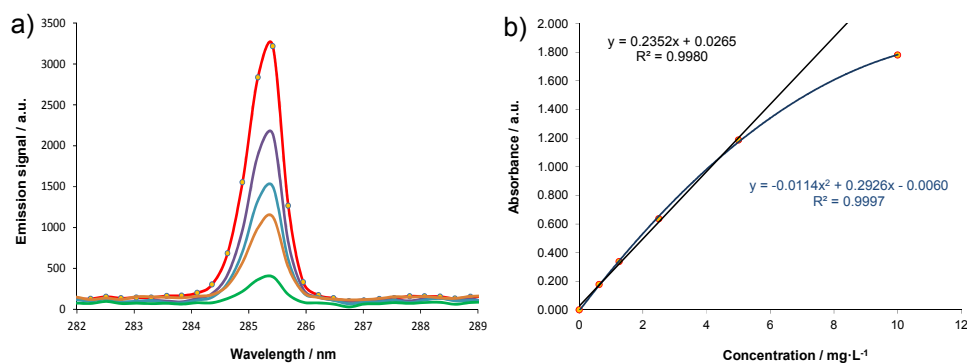


Figure 6. Mg lamp emission signal and calibration curve (285,213 nm)

Table I. Figures of merit for Ca and Mg determination

Element	$\lambda$ (nm)	Dynamic range (mg·L <sup>-1</sup> )	Sensitivity (m) (a.u.·mg <sup>-1</sup> ·L)	RSD slope (%)	Coefficient of determination (R <sup>2</sup> )	LOD (μg·L <sup>-1</sup> )
Ca	554	0.2-50	75.69	0.75	0.9999	25
Mg	285.2	0.05-5	0.235	2.55	0.9980	5.4

**Table II.** Comparison of CCD-based method with ICP and Flame AAS [15]

Element	Method	Wavelength (nm)	LOD ( $\mu\text{g}\cdot\text{L}^{-1}$ )
Ca	CCD-based	554	25
	Flame AAS	422.7	1
	ICP	393.366	0.03
Mg	CCD-based	285.2	5
	Flame AAS	285.2	0.3
	ICP	279.553	0.1

### Sample analysis

The analytical method was tested with different bottled waters (samples 1-5) and water certified reference material.

To minimize the formation of nonvolatile compounds the samples were diluted and treated with perchloric acid (1 mL/500mL). For analysis we applied the standard addition method. The concentration of the standard was  $250 \text{ mg}\cdot\text{L}^{-1}$  Ca and  $50 \text{ mg}\cdot\text{L}^{-1}$  Mg. A volume of 0.2 mL standard was added to 10 mL of diluted sample. Three additions of standard were made. The sample concentration was calculated based on the equation of regression line.

Table III. presents the results obtained for the determination of Ca and Mg in bottled waters. The average recovery was  $101\pm 4\%$  for Ca and  $115\pm 22\%$  for Mg.

The LOD calculated based on standard addition calibration sensitivity was found in the range of  $15\text{--}28 \mu\text{g}\cdot\text{L}^{-1}$  for Ca and  $4,9\text{--}6,3 \mu\text{g}\cdot\text{L}^{-1}$  for Mg. Table IV. presents the results obtained for the water certified reference material.

**Table III.** Bottled water analysis results (n=3)

Sample	Elements	$C_{\text{cert.}} (\text{mg L}^{-1})$	$C (\text{mg L}^{-1})^{\text{a}}$	Recovery (%)
Bottled water 1	Ca	47	$57\pm 1$	$121\pm 2$
Bottled water 2		$17^*$	$18\pm 1$	$106\pm 6$
Bottled water 3		$60^*$	$58\pm 2$	$97\pm 3$
Bottled water 4		$9.5^*$	$8.1\pm 0.5$	$84\pm 6$
Bottled water 5		$113^*$	$112\pm 1$	$99\pm 1$
Bottled water 1	Mg	$6^*$	$9\pm 1$	$150\pm 11$
Bottled water 2		$3^*$	$3\pm 1$	$100\pm 33$
Bottled water 3		$31^*$	$35\pm 2$	$113\pm 6$
Bottled water 4		$3^*$	$3\pm 1$	$100\pm 33$
Bottled water 5		$41^*$	$45\pm 1$	$110\pm 2$

<sup>a</sup> Expanded uncertainty for 95% confidence interval

**Table IV.** Water certified reference material. (n=3)

Sample	Elements	C <sub>cert.</sub> (mg L <sup>-1</sup> )	C (mg L <sup>-1</sup> ) <sup>a</sup>	Recovery (%)
CRM	Ca	73.6±2.7	72.0±1.5	98±2
	Mg	14.78±0.48	14.56±0.51	98±3

<sup>a</sup> Expanded uncertainty for 95% confidence interval

## CONCLUSIONS

In this paper an CCD-based FAES-FAAS original analytical method is presented, which allows the simultaneous determination of Ca and Mg atomised in methane-air flame. Measuring simultaneously the intensity of the 554 nm wavelength molecular bands emitted by excited CaOH molecules and the Mg atomic absorption of a HCL lamp light, we applied the FAES-FAAS methods together. A CCD microspectrometer with UV-VIS-NIR range for detection and background correction having been used, the method is in concordance with the principles of Green Analytical Chemistry (GAC).

The detection limit for Mg are 5.4 µg·L<sup>-1</sup>, the linear measuring range is 0.02–5 µg·L<sup>-1</sup>. The detection limit for Ca are 25 µg·L<sup>-1</sup>, the linear measuring range is 0.1–50 µg·L<sup>-1</sup>. The coefficient of determination  $R^2 > 0.998$  demonstrates a good linearity of the method.

The proposed method was successfully applied to analyse water samples. The recovery for CRM was 98±2 % for Ca and 98±3 % for Mg. The average recovery for bottled water was 101±4 % for Ca and 115±22 % for Mg.

## EXPERIMENTAL SECTION

### *Reagents, Standard Solutions and CRM*

Stock standard solutions of Ca and Mg (1000 mg·L<sup>-1</sup>) and analytical grade perchloric acid purchased from Merck (Darmstadt, Germany) were used. Double distilled water was used for all dilutions. For the CRM ERM CA011b (Hard drinking water) was used.

### *Samples*

The bottled waters were purchased from supermarkets in Cluj-Napoca, Romania.

### *Instrumentation and analytical method*

The FAES-FAAS equipment consisted of a HEATH EU-700-30 type Gas-flow and HCL lamp module, a pneumatic nebulizer chamber and a CCD microspectrometer (Fig. 7)



The pneumatic nebulizer chamber and gas-burner system that was used came from an AAS-1 (Carl Zeiss Jena) atomic absorption spectrometer. The burner-head was Mecker type. The air flow-rate was kept constant, 600 L/h, the flow rate of the methane being varied in 56-66 L/h interval.

The AAS lamp was a max 20 mA Activion Mg HCL lamp (Halstead Essex – England).

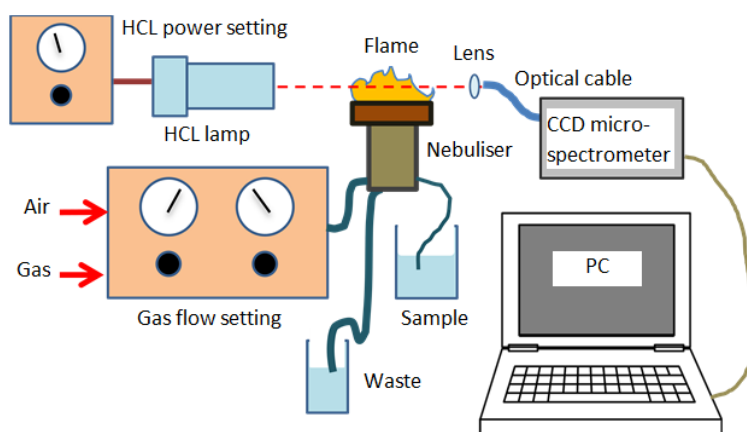
For optical detection a HR4000 Microspectrometer Ocean Optics CG-UV-NIR with the following parameters: 200–1100 nm spectral range, 50  $\mu\text{m}$  entrance slit, Toshiba CCD detector with 3648 pixels, 1304 AP, FWHM: 1.5 nm was used. A collimating fused silica lens (5 mm diameter, 10 mm focal length) and a fibre optic QP 600 Im, 25 cm length (Ocean Optics, Dunedin, USA) assured the transmission of the optical signal.

Data acquisition was performed using Spectrasuite soft (Ocean Optics); 0.1–20 s integration time, and computer-subtracted background correction.

#### **Method validation**

It was plotted the regression line for Ca (0–50  $\text{mg}\cdot\text{L}^{-1}$ ) and Mg (0–10  $\text{mg}\cdot\text{L}^{-1}$ ) standards. The equation of the regression line, the confidence limits and the coefficient of determination,  $R^2$  were calculated with the least squares method.

The limit of detection (LOD) was calculated on the basis of 3 s criterion ( $LOD=3s_B/m$ ), where  $m$  was the slope of calibration curve and  $s_B$  the standard deviation of 10 successive measurements of blank.



**Figure 7.** Schematic diagram of the CCD-based FAES-FAAS equipment

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