

FLAME ATOMIC EMISSION DETERMINATION OF CALCIUM IN NATURAL WATERS USING THE METHANE-AIR FLAME

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ABSTRACT. The calcium content of some natural waters (lake, river, well, mineral water) and drinking water (tap) has been determined by flame atomic emission spectroscopy using the methane-air flame. It was studied and optimized the flame and instrumental parameters (flame composition, the observation height in the flame) on the emission of calcium. The best results were obtained with the calcium line of 422.67 nm at the observation height of 7 mm, with the flame composition of 1.12 (relative stoichiometric units, (RSU)). The effect of pH, Na, K, Mg, Al, Sr, La, ClO_4^- , SO_4^{2-} , and PO_4^{3-} on the emission of calcium was studied too. The calibration curve was linear in the 0.1-10 mg/L range (long optical path in the flame) and 0.1–100 mg/L range (short optical path), respectively. The detection limit of 0.050 ± 0.022 mg/L was obtained at a significance level of 0.05 using the two-step Neyman-Pearson criterion. The calcium content of waters has been determined after suitable dilution of the sample, in the presence of 0.01 N HClO_4 , using the calibration curve and the standard addition method. In the presence of interferences the best results were obtained with the standard addition method.

INTRODUCTION

Calcium is a common element of all natural waters. The industrial, household, biological etc. applicability of the water, among the other constituents, depends on the calcium content of the water. Flame atomic emission spectrometry (FAES) is a recommended method for the determination of calcium in waters. As excitation source usually C_2H_2 -air, C_2H_2 - O_2 , C_2H_2 - N_2O flames are used. The optimal flame conditions for the determination of calcium in these flames were established, the detection limits being of order of $1 \cdot 10^{-3}$ $\mu\text{g/L}$ [1-7]. The most sensitive is the atomic line of 422.67 nm. Calcium ionises partially in the acetylene flames, this phenomenon can be suppressed by adding K, Cs, Sr salts to the sample in excess [5-7]. Calcium forms the refractory CaO and CaOH in the flame, in the presence of

Al, Mg, Si, etc. the refractory mixed oxides (spinel-type), with well- defined composition [8-12]. Refractory compounds are formed with the SO_4^{2-} and PO_4^{3-} ions too [13-15]. The depletion of the calcium emission signal caused by these interferents can be avoided by using a hotter flame [16,17]; by adding an organic solvent [18-22], or La, Sr salt (releasing agent) [23-26]; EDTA, glycerol, or HClO_4 acid (matrix modifier) to the sample [27-29].

Propane-butane-air (PB-A) and the natural gas-air (NG-A) flames are used in low performance commercial flame-photometers, designated for routine analysis. The methane-air flame (M-A) has similar properties with the PB-A and NG-A flames, exhibiting lower temperature, burning velocity than the C_2H_2 ones. To our best knowledge the behaviour of calcium in the M-A flame was not reported. The aim of this work is to study the behaviour of calcium in the M-A flame, to optimize the flame and instrumental parameters and the determination of calcium in natural waters, respectively.

EXPERIMENTAL

Instrumentation

The measurements were carried out with a HEATH-701 (Heath Co., Benton Harbor, MI, USA) spectrophotometer using a HEATH EU-700 scanning monochromator, a HEATH EU-700-30 type photomultiplier module and a 1P28A (RCA, USA) photomultiplier (-700 V). The photomultiplier signal was recorded with a K-201 (Carl Zeiss Jena) strip chart recorder. The pneumatic nebulizer-spray chamber-burner system was used from an AAS -1 (Carl Zeiss Jena) atomic absorption spectrophotometer. The original 100 mm slot type burner head (for C_2H_2 - air flame) was replaced with a similar, Mecker type, developed by us, for the M-A flame [30,31]. In order to increase the nebulization efficiency the original 8 mm glass ball impactor was replaced with an 1 mm cylindrical one, placed at optimal distance of 5 mm from nebulizer head [32]. The air flow-rate was kept constant, 500 L/h, the flow rate of the methane being varied as a function of the gas mixture wanted. As CH_4 source the city gas of 99 % purity was used, from the pipe.

Reagents

Stock standard solutions (1000 mg/L) were prepared by dissolving the appropriate amounts of metals (La, Mg and Al (Specpure, Johnson Matthey Chemicals Limited, England)) and compounds (CaCO_3 , SrCO_3 (Specpure, Johnson Matthey Chemicals Limited, England) in corresponding acid. KCl, NaCl (analytical grade, Reactivul, Bucuresti, Romania), HCl, H_2SO_4 , HClO_4 and H_3PO_4 (analytical grade, Merck, Darmstadt, Germany)) were dissolved and diluted in double distilled water, respectively. For further dilutions double distilled water was used in all cases.

Sampling and sample handling

The water samples were collected in the Cluj-Napoca city area: from the Someş river, from the central park lake and from some wells outside of the city. The waters were sampled and handled in accordance with the EPA-recommendations [4]. All determinations were carried out within 24 hours after sampling. The drinking water (tap water) from the laboratory was acidified and analysed just after sampling. The mineral waters (commercial available, "Anavie", "Izvorul Minunilor", "Perla") were analysed after the sealed bottles were opened, acidified and degassed by shaking. The samples were diluted properly before measurements. The optimal pH of 1.5-2 of the solutions (in agreement with the literature data) was determined experimentally. The solutions were prepared just before the measurements.

Procedure

The behaviour of calcium in the M-A flame was studied up to $h = 18$ mm over the burner head (1mm steps), at three different flame compositions: 0.88; 1.00; 1.12 (expressed in relative stoichiometric units (RSU)). Four replicate measurements were made. The mean, the standard deviation, the S/N and the signal-to-background (S/B) ratio were calculated for each h and flame composition investigated. The homogeneity of the means was tested by the F test at a significance level of 0.05. The burner was held parallel to the optical axis of the spectrophotometer, unless stated otherwise. The slit width of the monochromator was of 0.1 mm, the sensitivity of the strip chart recorder was different in different spectral domains, in function of the intensity of the emission lines and the background observed. For a given set of determinations the sensitivity was kept constant.

RESULTS AND DISCUSSION

The emission spectrum of calcium, determination of the analytical emission line

The emission spectrum of calcium in the M-A flame was determined first (recording the spectrum of the flame alone, in the 200 - 800 nm spectral range, then that of the flame in the presence of calcium), by nebulizing of a calcium solution of 100 mg/L in the flame. Using spectral Tables [6] it was identified only the atomic line with wavelength of 422.67 nm and two molecular bands in the 420–650 nm spectral domain with the most intensive band heads with wavelength of 555 nm and 623 nm respectively, belonging to refractory CaO and Ca(OH)₂ formed in the flame [1-7].

Optimization of the flame and instrumental parameters

The aim is to obtain those values for the flame composition and observation height h for whose the S/N ratio is maximal. The composition of the flame was kept constant, at 1.12 RSU. The concentration of the calibration solution was of 10 mg/L. The analytical signal, intensity (I), was measured at 422.67 nm, 555 nm, and 623 nm and the background intensity (in the presence of calcium), at the base of the atomic emission line studied, at 423.2 nm. The variation of the line intensities versus observation height over the burner head is represented in Fig.1.

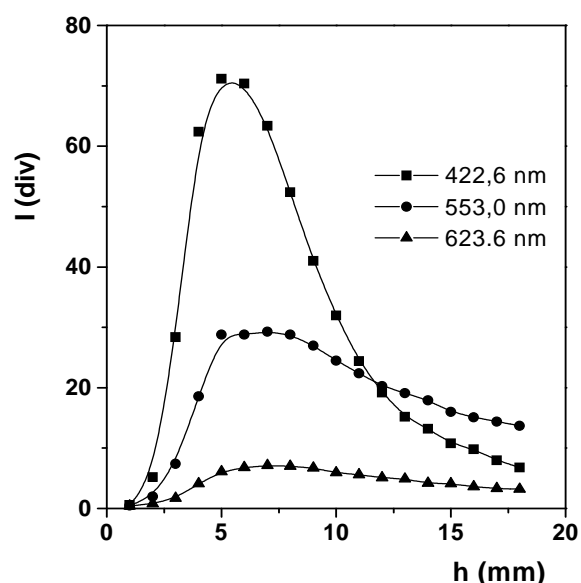


Figure 1. The intensity of different calcium lines versus observation height (h)

For the quantitative estimation of the results at different wavelengths only the maximal value of the analytical signal (I_{max}) for each line was selected. In order to get comparable data it was calculated the corrected intensity (I_{corr}) and the relative intensity (I_{rel}) for each line, considering the sensitivity of the chart recorder. The reference sensitivity of $1 \cdot 10^{-9}$ A/div and the reference line was the weakest one. The S/B ratio was determined in the same way. The results are summarised in Table I.

Table I

The relative intensities of the emission lines of calcium in the M-A flame

Wavelength (nm)	h (mm)	I_{max}	$I_{Corr.}$	I_{rel}	S / B
422.67	7	35.6	71.2	10.20	1.41
555.00	7	29.3	29.3	4.12	7.32
623.00	7	7.1	7.1	1.00	4.73

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The most intensive line is the atomic line of 422.67 nm, being excited in the interconal reaction zone of the flame, observed at 7 mm over the burner head. The S/B ratio is low, due to the high value of the background. The maximum of molecular emission appears at the same height, their emission are less influenced by excitation conditions in the flame. The influence of the flame composition and of observation height on the analytical signal for the most sensitive line was investigated using three flame compositions (0.88, 1.00, 1.12 RSU), at the concentration level of 10 mg/L. The data were processed by using the MicroCal Origin™ Software package, version 5.0 (MicroCal Software Inc., MA, USA) and plotted as 2D contour map (Fig.2).

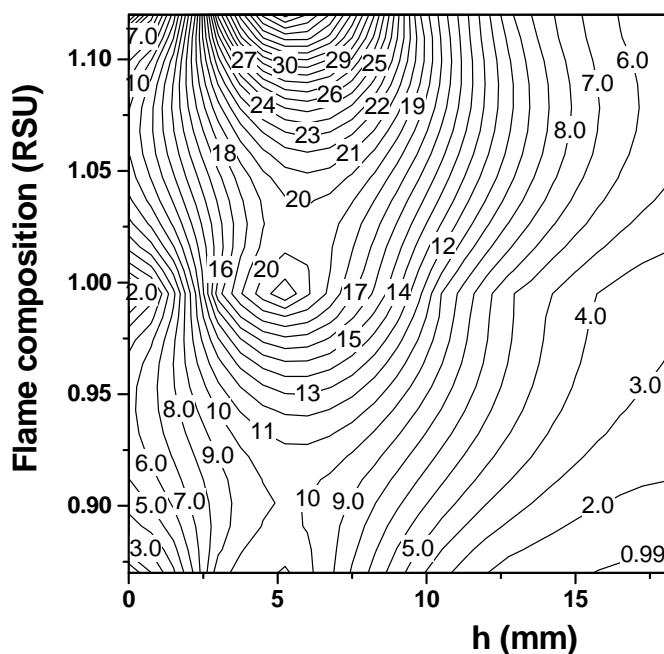


Figure 2. The 2D contour map of the emission of the 422.7 nm calcium-line vs. observation height and flame composition relation. The data labels on the plot indicate the grid matrix values

The results shows, that the analytical signal depends both of observation height and flame composition and increases with the increase of the methane content in the flame. The I-h curves are of Gaussian-shape, with the maximum between $h = 5-7$ mm. The analytical signal varies in the same manner as the concentration of the OH and CN radicals, fact which suggests that excitation of the calcium atoms take place *via* these radicals [33]. The

standard deviation of all means were homogeneous, the magnitude of the S/N ratio being decided by the magnitude of the mean. In conclusion, the optimal conditions for the quantitative determination of calcium in the M-A flame are $\lambda = 422.67$ nm, $h = 7$ mm, flame composition 1.12 RSU.

Interferences

The effect of Na, K, Mg, Al, SO_4^{2-} and PO_4^{3-} on the emission signal of calcium of 10 mg/L was investigated, as possible inorganic interferences, present in natural waters. The effect of Sr, La and HClO_4 were tested too, as releasing agents or as matrix modifier, respectively. The experimental conditions were the optimal ones, determined previously. In the case of Na, K and Sr the background signal was measured at 423,3 nm. The variation of the emission signal versus the concentration of the interferences are represented in Fig 3.

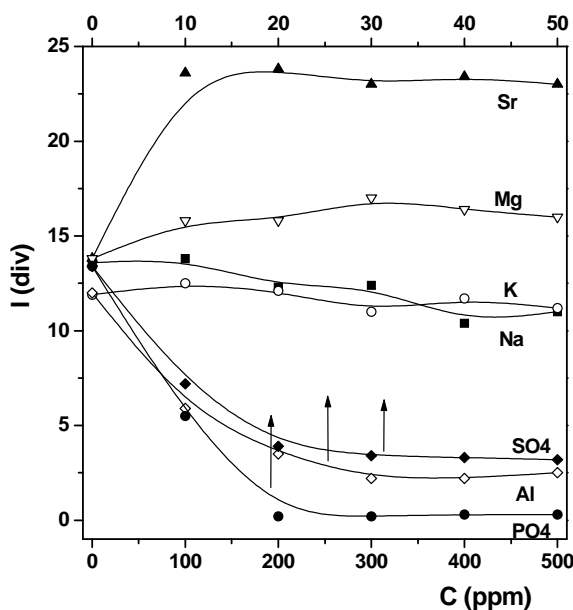


Figure 3. Influence of Na, K, Mg, Al, Sr, SO_4^{2-} , and PO_4^{3-} on the emission signal of calcium of 10 mg/L.

K acts as ionisation suppressor, enhancing simultaneously the calcium and the flame background signal. The influence of Na is lower, and is mainly due to the background enhancement. Surprisingly, Mg increases the calcium emission signal, acting as releasing agent. Al, SO_4^{2-} and PO_4^{3-} ions decrease drastically the calcium emission signal even at low concentrations. In contrast with the acetylene flames, La is not efficient. Sr enhances the flame background and exhibits a good releasing effect (as shown in figure 3), in

accordance with observed in the acetylene flames, acting as ionization suppressor too. It releases the analyte partially only (90% till 40-fold excess of Al, 79% till 10-fold excess of SO_4^{2-} and PO_4^{3-}). The low efficiency of these agents is the consequence of the low temperature of the M-A flame. HClO_4 as matrix modifier, enhances the calcium emission signal with 15.2 %, without enhancing the flame background.

Calibration, determination of the detection limit

For the determination of the detection limit the variation of the analytical signal versus concentration was studied. The calibration curves were plotted in the 0.1-100 mg/L calcium concentration range of. One curve covered only one order of magnitude of concentration. Each calibration curve was established by using six standard solutions. Six replicate measurements were made at each concentration level. The homogeneity of the means and the linearity of the calibration curve was tested, it was calculated the equation of the regression line, the confidence limits, the coefficient of correlation (r), with the least squares method. The detection limit was calculated using the two step Neyman-Pearson model [34,35], for the fixed values of $(P_{10})_0 = 0.025$ and $(P_{11})_d = 0.975$. In order to increase the sensitivity of the determinations, and lower the detection limit the calibrations were carried out in the presence of 100 ppm Sr and 1000 ppm HClO_4 too. The optimal concentrations of these agents were determined experimentally. The results are summarised in Table II.

Table II

The calibration data of calcium determination in the M-A flame

Nr.	Concentration range (mg/L)	Sensitivity (A/div)	Equation of the calibration curve	r
(1)	100 – 10	$10 \cdot 10^{-9}$	$I = -0.022 + 0.788 \cdot C - 0.0027 \cdot C^2$	0.9988
(2) [@]	100 – 10	$2 \cdot 10^{-9}$	$I = 0.22 + 0.472 \cdot C$	0.9999
(3) [@]	100 – 10	$10 \cdot 10^{-9}$	$I = 1.46 + 0.504 \cdot C - 0.0014 \cdot C^2$	0.9972
(4) [*]	10 – 1	$2 \cdot 10^{-9}$	$I = -0.193 + 4.892 \cdot C$	0.9997
(5) [*]	10 – 1	$2 \cdot 10^{-9}$	$I = 1.27 + 7.525 \cdot C$	0.9994
(6) [@]	10 – 1	$1 \cdot 10^{-9}$	$I = -0.78 + 2.695 \cdot C$	0.9999
(7) [#]	10 – 1	$2 \cdot 10^{-9}$	$I = 0.31 + 7.505 \cdot C$	0.9998
(8) [*]	1 – 0.1	$1 \cdot 10^{-9}$	$I = -0.41 + 8.380 \cdot C$	0.9922
(9) [*]	1 – 0.1	$2 \cdot 10^{-9}$	$I = 0.11 + 7.160 \cdot C$	0.9977

[@] burner held perpendicular to the optical axis, optical path 8 mm through the flame

^{*} 100 ppm of Sr added

[#] 1000 ppm of HClO_4 added

In the 10-100 mg/L domain the concentration-intensity relationship is linear only in the case of short optical path through the flame and in the absence of Sr (eq.(2)). Otherwise the relationship could be estimated best with a second order polynomial function. In the lower concentration ranges (eq.(4) - (9)) this phenomenon disappears even in long optical path. The linear correlation can be improved (eq.(6)) by keeping the burner perpendicular to the optical axis. The presence of Sr and HClO₄ enhances simultaneously the sensitivity and the linearity of the calibration curve (higher slope and r values). The detection limit was calculated only in the 0.1 - 1ppm concentration range, in the presence of Sr, being of 0.050 ± 0.022 mg/L.

Determination of calcium in water samples

The calcium content of the water samples was determined by the calibration and the standard addition method, the later being used as reference method due to the absence of certified reference material. The determinations were carried out keeping the burner parallel to the optical axes, the other parameters were the optimal ones. The measurements were carried out in the presence of Sr and HClO₄ too, regardless of method used. Four parallel measurements were made in each case. To minimise the effect of the interferences and to bring the final concentration of the sample within the linear range the samples were properly diluted before measurements. The measuring sample solutions were prepared in 25 mL volumetric flasks. In the case of standard addition method 100 µL of concentrated calcium standard was added to the 25 mL of diluted sample. Three additions of standard were made, in 1 ppm concentration steps. It was calculated the regression line, the calcium content was determined from the intercept with the abscissa of the line. Using the data set, first it was tested the reproducibility of the standard addition method. The recoveries were the closest, within 95-114 %, in the presence of Sr or HClO₄, depending on the salt content of the water. The recovery values are close to 100 %, with most samples within the error of determination, so the standard addition method could be used as reference method.

Comparing the calibration curves, the slope of calibration curves corresponding to the standard additions are significantly lower than of the calibration, fact, which suggests the existence of the chemical interference and the partial release of calcium from its compounds. By using Sr or HClO₄ in the sample, the slopes became higher and closer, they do not differ significantly. The best results were obtained in the presence of HClO₄. The results of the determination of calcium content of waters in the presence of 0.01 N HClO₄ are summarized in Table III.

The results of the two methods agree, they are within the errors of the determinations, for the low salt content waters (tap, lake, river and mineral water). The differences between the two methods are greater for the higher salt content waters. In these cases the standard addition method offers better results, closer to the real calcium content of waters. In conclusion calcium can

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be determined precisely in natural waters in the presence of 0.01 N HClO₄ using the M-A flame. For the low salt content waters the calibration method gives acceptable results, for the higher salt content waters the standard addition method is recommended.

Table III

Results of analysis of water samples

Sample	Dilution	Concentration (ppm, calibration)	Concentration (ppm, standard addition)	
Tap water	1:10	25.8 ± 1.3	27.5 ± 2.1	
Lake water	1:25	16.2 ± 1.9	17.6 ± 2.1	
River water	1:25	21.8 ± 1.8	23.9 ± 2.0	
Mineral water	"Anavie"	1:50	72.4 ± 2.7	77.3 ± 3.0
	"Izvorul Minunilor"	1:10	34.6 ± 2.1	44.3 ± 2.7
	"Perla"	1:50	67.6 ± 4.8	68.0 ± 4.0
Well water	Nr. 1	1:50	108.4 ± 5.6	119.0 ± 6.2
	Nr. 2	1:50	171.5 ± 7.6	180.8 ± 8.1
	Nr. 3	1:50	151.7 ± 6.8	162.5 ± 7.1
	Nr. 4	1:50	122.4 ± 7.4	133.6 ± 7.8

CONCLUSIONS

In the M-A flame calcium exhibits atomic and molecular spectrum, the most intensive is the atomic line of 422.7 nm. The intensity of this line varies with the composition of the flame and observation height, the optimal observation height over the burner head is 7 mm, in fuel rich flame (RSU = 1.12). The presence of Mg, Al, SO₄²⁻, and PO₄³⁻ decreases the emission of calcium. 100 ppm of Sr or 0.01 N HClO₄ exhibits the best releasing effect. This effect is partially, as consequence of the low temperature of the M-A flame. The intensity-concentration relationship is linear in the 0.1-10 ppm range, the detection limit in the presence of 100 ppm Sr is of 0.050 ± 0.022 mg/L. This value is low and lies between the values obtained with cool and hot flames. The calcium content of natural waters can be determined precisely in the presence of HClO₄ using the calibration or the standard addition method. For the higher salt content waters the standard addition method is recommended. In conclusion, M-A flame is a suitable excitation source for precise determination of calcium in natural waters.

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