STUDIA UNIVERSITATIS BABEŞ-BOLYAI, CHEMIA, XLIV, 1-2, 1999

OPTIMIZATION OF THE FLAME ATOMIC EMISSION DETERMINATION OF MAGNESIUM IN THE METHANE - AIR FLAME

LADISLAU KÉKEDY-NAGY and EMIL A. CORDOŞ

Universitatea "Babeş-Bolyai" Facultatea de Chimie şi Inginerie Chimică
3400 Cluj-Napoca, Arany J. 11, România

ABSTRACT. The effect of the flame composition, the observation height in the flame and the bandpass of the monochromator on the emission of magnesium in the methane-air flame were studied. These parameters were optimized in order to achieve the highest signal-to-noise ratio and the lowest detection limit. The best results were obtained with the magnesium line of 371.9 nm at the observation height of 6 mm over the burner head, with the stoichiometric flame and the slitwidth of 0.34 mm. The detection limit of 0.3 ± 0.1 mg/L was obtained at a significance level of 0.05, using the two step Neyman-Pearson criterion.

INTRODUCTION

Magnesium ranks eighth among the elements in order of abundance and is a common constituent of different samples. Flame atomic emission spectrometry (FAES) is a simple, precise method for the determination of magnesium in low concentrations. As excitation source usually the high temperature C_2H_2-air, C_2H_2-O_2, C_2H_2–N_2O, H_2-air flames are used. The optimal conditions for the determination of magnesium in these flames were established, the detection limits are of order of 10^{-1}-10^{-2} mg/L [1-6].

The low temperature flames (~ 2000 K), as propane-butane-air (PB-A), are used in low performance commercial flame-photometers, designated for routine analysis. The methane-air (M-A) flame has similar properties (temperature, burning velocity etc) with the PB-A flame [7]. To our best knowledge the behaviour of magnesium in the M-A flame was not studied, and the detection limits are not known. The aim of this work is to study the behaviour of magnesium in the M-A flame, to optimize the flame and instrumental parameters in order to obtain the highest signal-to-noise ratio (S/N) and the lowest detection limit.

EXPERIMENTAL

Instrumentation

The measurements were carried out with a HEATH-701 (Heath Co., Benton Harbor, MI, USA) spectrophotometer, 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 [8,9]. The burner was held parallel to the optical axis of the spectrophotometer. For higher 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 [10]. The air flow-rate was kept constant at 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.

Chemicals

Stock standard solution of magnesium (1000 mg/L) was prepared by dissolving 1g of magnesium metal (Specpure, Johnson Matthey Chemicals Limited, England) in 10 mL HCl 1:1 (analytical grade, Merck, Darmstadt, Germany) and diluted with double distilled water to 1 L. The pH of the stock standard solution as well as of the diluted measuring standard solutions was kept constant, at the value of 2 [1]. For further dilutions double distilled water was used in all cases.

Procedure

The behaviour of magnesium in the M-A flame was observed in the flame up to h = 18 mm over the burner head (in1mm 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 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 magnesium

The emission spectrum of magnesium in the M-A flame was determined first by nebulizing a magnesium solution of 1000 mg/L in the flame, recording the spectrum of the flame alone, in the 200 - 800 nm spectral range, then that of the flame in the presence of magnesium. Using spectral tables there were identified atomic lines with λ = 277.98 nm, 285.27 nm, 382.94 nm, 383.23 nm, 383.83 nm, 457.11 nm, 516.73 nm, 517.27 nm and 518.36 nm, respectively. Magnesium emits two ionic lines with λ = 279.55 nm, 280.27 nm and an intense molecular emission band in the spectral domain of 370-400 nm. The molecular band, with the most intensive band-heads at 371.9 nm and 382.2 nm, respectively belongs to MgO and MgOH formed in the flame [11].

Optimization of the flame composition and instrumental parameters, determination of the analytical emission line

The aim is to obtain those values for the flame composition and observation height h for whose the S/N ratio is maximal. The concentration of the calibration solution was 100 mg/L. The analytical signal, intensity (I), was measured for the most intensive lines selected, at 277.98 nm, 279.55 nm, 285.27 nm, 371.9 nm, 382.2 nm, 516.73 nm, 517.27 nm and 518.36 nm, respectively. The composition of the flame in this step was kept constant, at 1.12 RSU. The variation of the line intensities versus observation height over the burner head is represented in Fig.1.

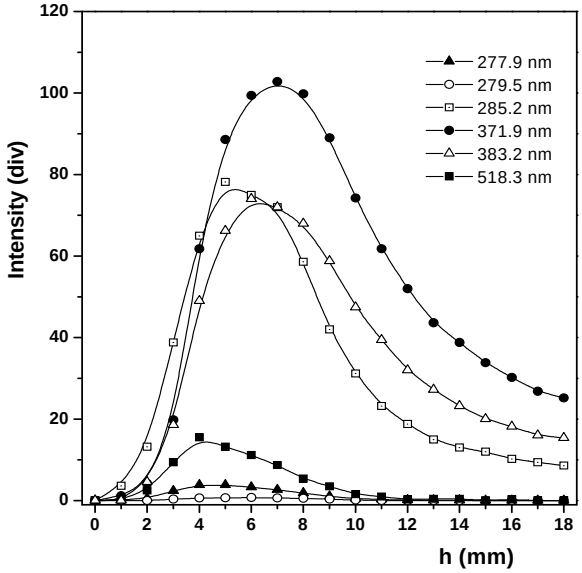

Figure 1**.** The intensity of different magnesium lines versus observation height (h)

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 the corrected intensity (I_{cor}) and the relative intensity (I_{rel}) for each line was calculated, considering the sensitivity of the chart recorder. The reference sensitivity of 1.10^{-9} A/div and the reference line was the weakest one. The S/B ratio was determined in the same way. The results are summarized in Table I.

Table I

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

Wavelength (nm)	Emittent	h (mm)	I_{max} (div)	$I_{Corr.}$ (div)	I_{rel}	S / B
277.98	Mg I	4-5	38.6	38.6	5.21	0.81
279.55	Mg II	6	7.4	7.4	1.00	0.17
285.27	Mg I	5	39.5	790.0	106.75	7.60
371.9	MgO, MgOH	7	51.4	1028.0	138.91	21.80
382.2	MgO, MgOH	6	37.0	740.0	100.00	13.80
516.73	Mg I	7	3.1	62.0	8.37	1.40
517.27	Mg I	3-4	12.6	126.0	17.02	11.60
518.36	Mg I	4	15.5	155.0	20.94	13.80

The most intensive line is the molecular emission band head at 371.9 nm, observed at 7 mm over the burner head, being excited in the interconal reaction zone of the flame. The S/B ratio is low, due to the high value of the background. The atomic lines are less intensive, only the resonance atomic emission line of λ = 285.27 nm has comparable intensity to the molecular band head lines. The intensity of the lines varies in the same manner as the concentration of different radicals in the flame, fact which suggests that the excitation process takes place *via* these radicals [12].

The influence of the flame composition and of the observation height on the emission signal for the most sensitive line was investigated (the analytical line) using three flame compositions (0.88, 1.00, 1.12 RSU) and at the concentration level of 100 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).

The emission signal depends both on observation height and flame composition. The I-h curves are of Gaussian-shape, with the maximum between h = 5-7 mm. The emission increases with the increase of the methane content in the flame, being the highest in the stoichiometric flame. In the fuel rich flame the emission decreases slowly. The standard deviation of all means was 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 magnesium in the M-A flame are λ = 371.9 nm (the analytical line), h = 6 mm and flame composition 1.00 RSU.

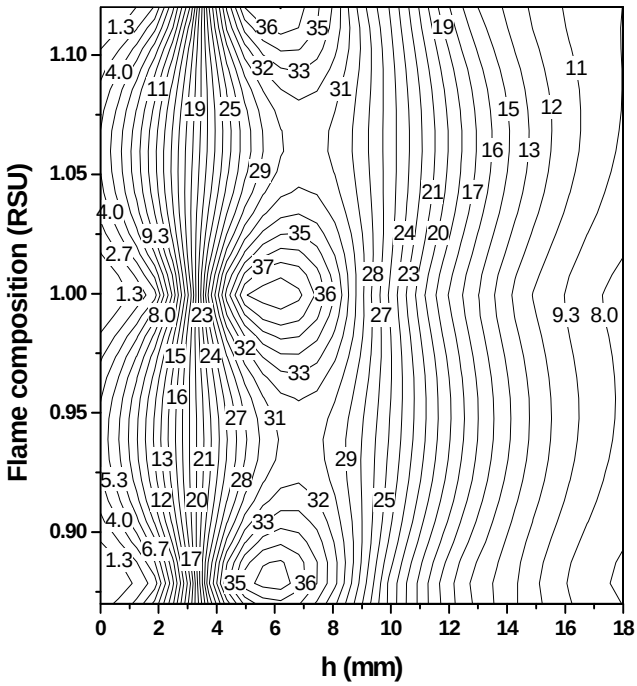

Figure 2. The 2D contour map of the emission of the 371.9 nm magnesium-line vs. observation height and flame composition. The labels on the plot indicate the grid matrix values.

The influence of the spectral bandpass of the monochromator on the Analytical signal, S/N and S/B ratio

The spectral bandpass of the monochromator is determined by its slitwidth (SW). The SW influences both the amplitude and the fluctuations of the emission signal, but not in the same manner. Therefore the optimal slitwidth for which the S/N ratio is maximum can be determined. The flame and instrumental parameters used were the optimal ones, determined earlier. The influence of the slitwidth on I, the S/N and S/B ratio was studied in the 0.1 - 0.7 mm domain in steps of 0.1 mm, using a 100 mg/L magnesium solution.The results are shown in Figure 3.

The results show that the emission signal increases with the spectral bandpass of the monochromator, it varies according to a second order polinomial function ($I = -0.47143-7.42857\ SW+290\ SW^2$, $r = 0.9999$). The S/N ratio increases too, up to a SW of 0.55 mm, then decreases. The standard deviation of the means increases suddenly at SW value of 0.6 mm, but remains homogeneous in the entire SW domain. The S/B ratio is practically constant regardless of the SW value. This is the consequence of the fact that the 371.9 nm magnesium line is a molecular band-head line.

In conclusion, the slitwidth could be increased up to 0.7 mm without a significant decay of the S/N ratio.

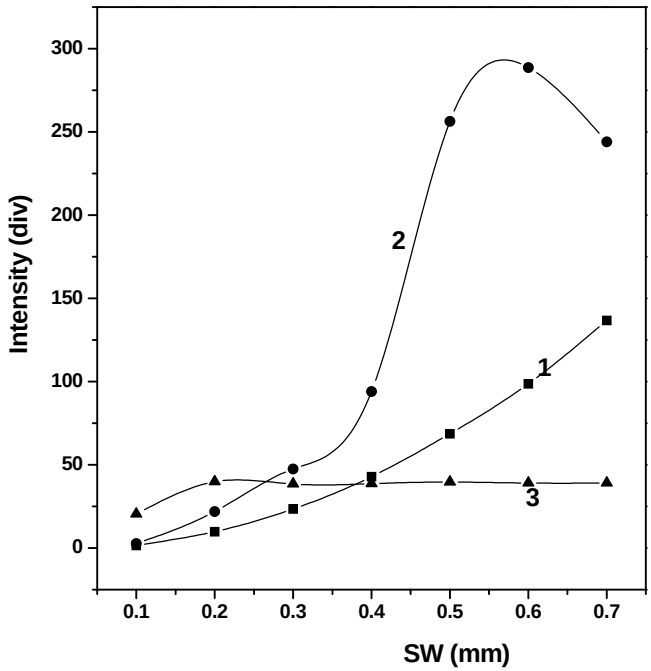

Figure 3. Variation of the intensity of 371.9 nm magnesium line (100 mg/L) versus the slitwidth (SW) of the monochromator: 1 – line intensity, 2 – S/N ratio, 3 – S/B ratio.

Interferences

The effect of Na, K, Mg, Sr, SO_4^{2-} and PO_4^{3-} on the emission signal of magnesium of 10 mg/L was investigated. The experimental conditions were the optimal ones, determined previously. The variation of the magnesium emission signal versus the concentration of the interferents is represented in Fig 4.

Na, K, Ca and Sr influence simultaneously the emission of magnesium and that of the flame. The alkaline metals depletes slowly the magnesium emission, whilst Ca and Sr increase it. These interferents exhibit the greatest influence on emission of the flame, increasing linearly the flame background with the concentration of the interferent. This effect varies for the studied elements in order of Sr > K > Ca > Na. The SO_4^{2-} and PO_4^{3-} ions decrease drastically the magnesium emission signal, due to formation of stable, refractory compounds in the flame.

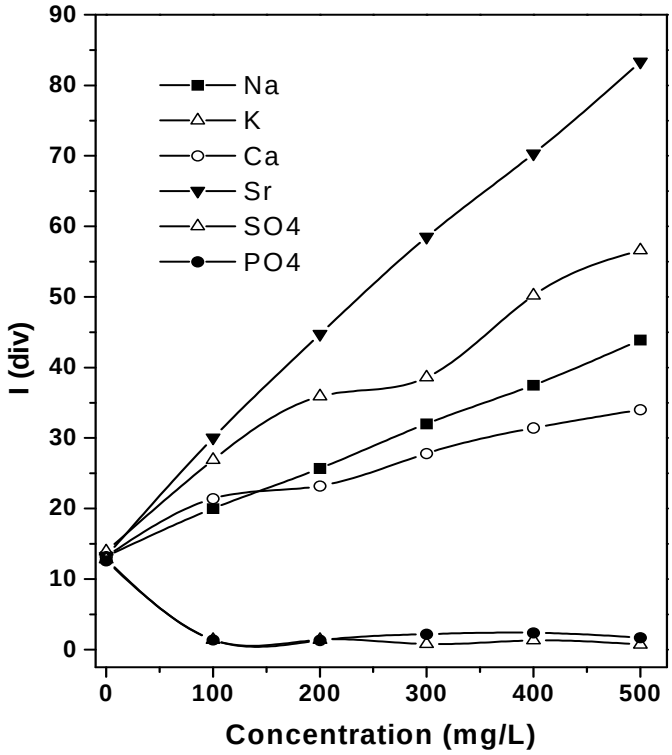

Figure 4. Influence of Na, K, Ca, Sr, SO_4^{2-}, and PO_4^{3-} on the emission signal of magnesium of 10 mg/L.

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 1-100 mg/L magnesium concentration range. 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 were tested. The equation of the regression line, the confidence limits and the coefficient of correlation (r) were calculated with the least squares method. The detection limit was calculated using the two step Neyman-Pearson model [13,14], for the fixed values of $(P_{10})_0 = 0.025$ and $(P_{11})_d = 0.975$. The results are summarized in Table II.

Table II

Calibration data of magnesium determination in the M-A flame

Concentration range (mg/L)	Sensitivity (A/div)	Slit width (mm)	Equation of the calibration curve	Detection limit (ppm)
100 – 10	$2*10^{-9}$	0.10	I = -1.65 + 0.502*C r = 0.9996	0.8 ± 0.6
10 – 1	$1*10^{-9}$	0.10	I = -1.32 + 0.982*C r = 0.9897	0.7 ± 0.5
10 – 1	$5*10^{-9}$	0.34	I = -3.77 + 2.483*C r = 0.9987	0.3 ± 0.1

The concentration-intensity relationship is linear in the 1 – 100 mg/L domain, regardless of the magnesium concentration. The sensitivity of the determinations can be enhanced, by using a broader slitwidth. The slitwidth could be increased only till 0.34 mm because the flame photometer does not afford to compensate the high flame emission background signal, which overlaps the low analytical signal. The detection limits obtained for each concentration range are also summarized in Table II. These values are low being comparable with those obtained with other types of flames. The increased slit width does not improve significantly the detection limit.

CONCLUSIONS

In the M-A flame magnesium exhibits a complex spectrum (atomic, ionic and molecular). The most intensive line (the analytical line) is the molecular band-head line at 371.9 nm. The intensity of the magnesium lines vary with the composition of the flame and observation height over the burner head. In the stoichiometric flame the optimal excitation zone is at 6 mm over the burner head. The observation height for the maximum intensity is independent of the flame composition. In order to increase the S/N ratio, and lower the detection limit, the slitwidth of the monochromator could be increased till 0.7 mm without decay of the S/N ratio. Na, K, Ca and Sr increase significantly the emission of magnesium by a linear increase of the flame background with their concentrations. The calibration curves (in optimal experimental conditions) are linear in the 100 -1 mg/L concentration range, the detection limit obtained is of 0.3 ± 0.1 mg/L.

REFERENCES

[1] J.D. Winefordner, *Spectrochemical methods of analysis*, New York., Wiley Interscience, 1971, p.130.
[2] D.A. Hickman, G. Harbottle, E.V. Sayre, *Forensic.Sci.Int.*, 1983, **23**,189
[3] H. Matusiewicz, *J.Anal.At.Spectrom*., 1989, 4, 265
[4] G.E. Roscoe,R. Miles, C.G. Taylor, *Anal.Chim.Acta*, 1990, **234**, 439
[5] F. Hu, Z. Wang, Q. Liu, *Chin.Sci.Bull*., 1991, **36**, 560
[6] I.B. Razagui, P.J. Barlow, *Food.Chem*., 1992, **44**, 309
[7] A.G. Gaydon, H.G. Wolfhardt, *Flames, their Structure, Radiation and Temperature*, Chapman and Hill, New York, 1970.
[8] E. Cordoş, L.N. Kékedy, R. Hui, Patent RSR, nr. 67867 / 1977.
[9] E. Cordoş, L. Kékedy-Nagy, *Studia*, 1992, **37**, 61.
[10] L. Kékedy-Nagy, *Talanta*, 1997, **44**, 1919.
[11] R. Mavrodineanu, H. Boiteux, *Flame spectroscopy*, John Wiley, New York, 1965, p.326.
[12] L. Kékedy Nagy, *Studia*, 1992, **37**, 109.
[13] C. LIteanu, I. Rîcă, *Statistical Theory and Methodology of Trace Analysis,* John Wiley, New York, 1980.
[14] D.L. Massart, B.G.M. Vandeginste, S.N. Deming, Y. Michotte, L. Kaufman, *Chemometrics: a textbook,* Elsevier, New York, 1988.