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FLAME ATOMIC EMISSION SPECTROMETRIC DETERMINATION OF BARIUM USING THE METHANE - AIR FLAME. OPTIMIZATION OF THE FLAME AND INSTRUMENTAL PARAMETERS

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ABSTRACT. The effect of the flame composition, the observation height in the flame and the bandpass of the monochromator on the emission of barium in the methane-air flame were studied. The effect of Na, K, Mg, Sr, SO_4^{2-}, and PO_4^{3-} on the emission of barium was studied too. The best results were obtained with the barium line of 553.5 nm at the observation height of 5 mm, with the fuel rich flame and the slitwidth of 1.5 mm. The detection limit of 0.2 ± 0.1 mg/L was obtained at a significance level of 0.05, using the two step Neyman-Pearson criterion.

INTRODUCTION

Barium, as an alkali-earth metal, exhibits a low excitation and ionization energy (2.23 eV and 5.21eV, respectively), which makes suitable its determination by atomic emission spectrometry. Flame atomic emission spectrometry (FAES) is a simple, sensitive method for the determination of barium 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 barium in these flames were established, the detection limits are of order of 10^{-1}-10^{-3} mg/L [1-8].

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 [9]. To our best knowledge the behaviour of barium 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 barium 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 experimental setup used was the same as described earlier [10,11].

Chemicals

The stock standard solution of barium (1000 mg/L) was prepared by dissolving 1.436 g of $BaCO_3$ (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 other stock standard solutions (1000 mg/L) were prepared by dissolving the appropriate amounts of metals (Mg (Specpure, Johson Matthey Chemicals Limited, England)) and compounds ($SrCO_3$ (Specpure, Johnson Matthey Chemicals Limited, England) in corresponding acid. KCl, NaCl (analytical grade, Reactivul, Bucuresti, Romania), HCl, H_2SO_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.

Procedure

The behaviour of barium 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 in each case. The mean, the standard deviation, the S/N and the signal-to-background ratio (S/B) 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 with the optical axis of the spectrophotometer. 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 barium

The emission spectrum of barium in the M-A flame was determined in the 200 – 800 nm spectral domain. The spectrum of the flame alone was recorded first, then that of the flame in the presence of 1000 mg/L barium solution in the flame. Using spectral tables only the resonance atomic line with λ = 553.5 nm was identified. Barium emits a broad molecular spectrum too, in the spectral domain of 450.0 – 580.0 nm. The molecular emission band belongs to BaO with the band-heads at λ = 496.5 nm, 503.0 nm, 508.6 nm, 549.2 nm, 571.8 nm and to BaOH with the band-heads at λ = 487.0 nm, 512.0 nm, 520.3 nm, respectively [12]. Intensive band-heads lines are those of 487.0 nm, 508.6 nm, 520.3 nm, 549.2 nm in the M-A

flame. The emission atomic line is superimposed on the molecular band spectrum, which make difficult the precise quantitative determination of barium.

Optimization of the flame 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 composition of the flame was kept constant, at 1.12 RSU. The concentration of the calibration solution was of 100 mg/L. The analytical signal, intensity (I), was measured for the most intensive lines selected, at 487.0 nm, 520.3 nm and 553.5 nm, respectively. The variation of the line intensities versus observation height over the burner head is represented in Fig.1.

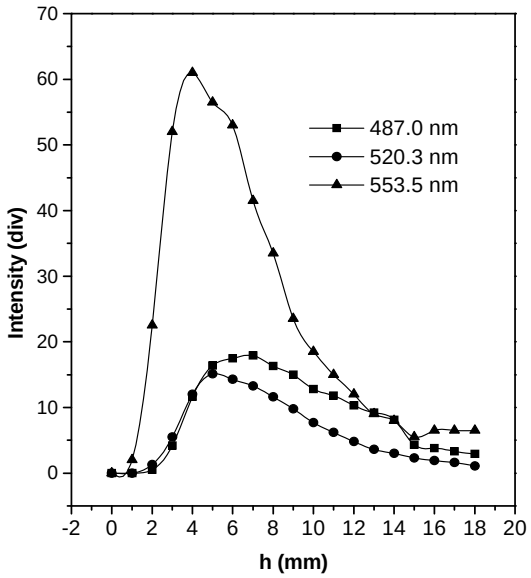

Figure 1**.** The intensity of different barium lines versus observation height (h)

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 were 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 barium in the M-A flame

Wavelength (nm)	Emittent	h(mm)	I_{max} (div)	$I_{Corr.}$ (div)	I_{rel}	S / B
487.0	BaOH	6-7	17.9	17.9	1.18	1.72
520.3	BaOH	5	15.1	15.1	1.00	1.98
553.5	Ba I	4-5	12.2	122.0	8.07	17.40

The intensity of the molecular emission lines is the same order of magnitude, the most intensive being the resonance atomic emission line at 553.5 nm. This line is excited in the primary reaction zone in the flame, at 4-5 mm over the burner head. The molecular species, BaOH, is excited in the interconal zone in the flame, where the OH radicals reach its maximum concentration. This fact suggests that the formation and the excitation of BaOH take place *via* these radicals [13]. The S/B ratio is low, due to the high value of the flame background in relation to the line intensity.

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

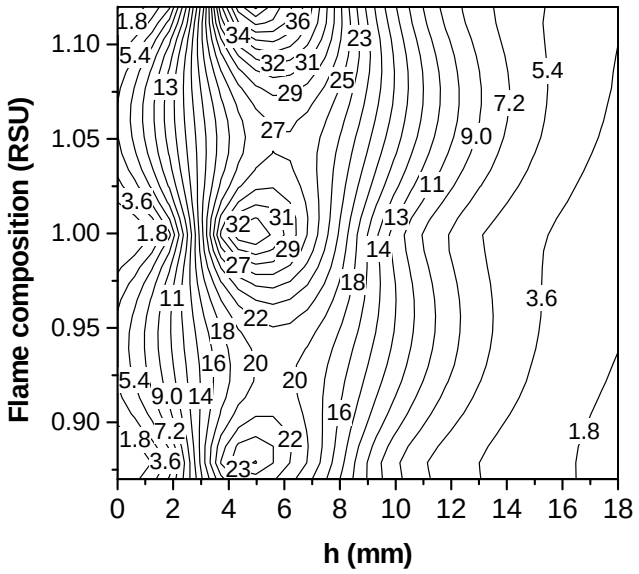

Figure 2. The 2D contour map of the emission of the 553.5 nm barium-line vs. observation height and flame composition. The labels on the plot indicate the grid matrix values.

The analytical signal depends both on observation height and flame composition. The emission increases slowly with the increase of the methane content of the flame, being the highest in fuel-rich conditions. The maximum emission intensity was observed at the same height of 5 mm over the burner head, regardless of flame composition. 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 barium in the M-A flame are λ = 553.5 nm, h = 5 mm and flame composition 1.12 RSU.

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, determined by its slitwidth (SW), influences in different manner the amplitude and the fluctuations of the emission signal. Therefore the optimal value of SW can be determined for which the S/N ratio is maximum. 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 – 1.5 mm domain, in steps of 0.1 mm, using a 100 mg/L barium solution. The results show that the emission signal increases linearly with the spectral bandpass of the monochromator ($I = -2.798 + 18.664SW$, $r = 0.9930$). The standard deviation of the means increases slowly with the increase of SW but remains homogeneous in the entire SW domain. The maximum value of S/N was of 187.5 at the SW of 1.4 mm. The S/N ratio decreases uniformly, its variation could be approximated with a third order polinomial function ($S/B = 2.348 - 2.130SW + 0.931SW^2 - 0.140SW^3$, $r = 0.9949$). This is the consequence of the fact that the 553.5 nm barium line is superimposed on the BaOH emission molecular band and the flame background.

In conclusion, the slitwidth could be increased up to 1.5 mm without a significant decay of the S/N ratio, but the broader SW diminishes seriously the S/B ratio.

Interferences

The effect of Na, K, Mg, Sr, SO_4^{2-} and PO_4^{3-} on the emission signal of barium of 10 mg/L was investigated. The experimental conditions were the optimal ones, determined previously. In the presence of Na, K, Mg and Sr the background signal was measured at 552.0 nm. The variation of the barium emission signal versus the concentration of the interferents are represented in Fig 3.

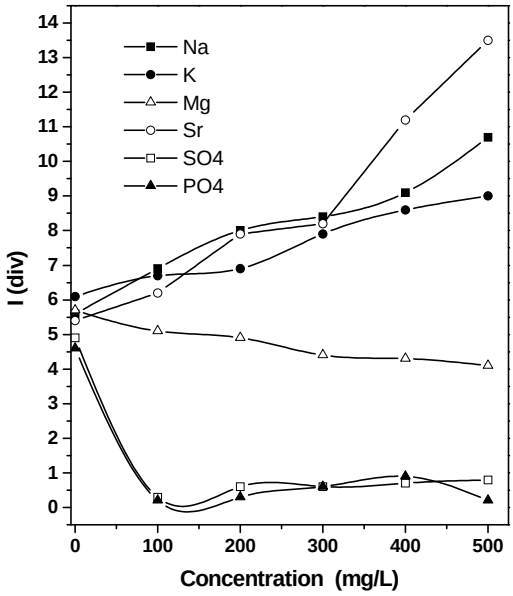

Figure 3. Influence of Na, K, Mg, Sr, SO_4^{2-}, and PO_4^{3-} on the emission signal of barium of 10 mg/L.

The barium emission signal increases in the presence of Na, K and Sr as the result of the flame background signal enhancement. Sr and K over the concentration of 300 mg/L exhibit a releasing effect, increasing efficiently the net barium emission signal too. Mg, SO_4^{2-} and PO_4^{3-} ions decrease the barium emission signal, due to formation of stable, refractory compounds in the flame.

Calibration, determination of the detection limit

For the determination of the detection limit the variation of the analytical signal versus concentration was studied in the 1-1000 mg/L barium concentration range. Four calibration curves were plotted; 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 measurements were carried out at two wavelengths: at 553.5 nm and, for background correction, at 552.0 nm. 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 [14,15], 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 barium determination in the M-A flame

Concentration range (mg/L)	Sensitivity (A/div)	Slit width (mm)	Equation of the calibration curve	Detection limit (ppm)
1000 - 100	$20*10^{-9}$	0.1	I = -0.0032 + 0.0679*C r = 0.9999	7 ± 3
100 – 10	$5*10^{-9}$	0.1	I = -0.385 + 0.316*C r = 0.9998	2 ± 1
10 – 1	$1*10^{-9}$	0.1	I = -0.348 + 1.267*C r = 0.9992	0.2 ± 0.1
10 – 1	$50*10^{-9}$	1.5	I = -0.456 + 0.969*C r = 0.9993	0.2 ± 0.1

The concentration-intensity relationship is linear over three orders of concentration domain (1 – 1000 mg/L), regardless of the barium concentration. The sensitivity of the determinations can be enhanced, by using a broader slitwidth. The detection limits obtained for each concentration range are also summarized in Table II. These values are low but they are about one order of magnitude higher than those obtained with acetylene flames. The broader slit width does not allow attaining a lower the detection limit.

CONCLUSIONS

In the M-A flame barium exhibits an atomic and molecular spectrum. The most intensive line (the analytical line) is the atomic line at 553.5 nm. The intensity of the barium lines vary with the composition of the flame and observation height over the burner head. In the fuel rich flame the optimal excitation zone is at 5 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 the slitwidth of the monochromator could be increased till 1.5 mm without decay of the S/N ratio and attaining a lower detection limit. Mg, SO_4^{2-} and PO_4^{3-} ions decrease the barium emission signal. The calibration curves (in optimal experimental conditions) are linear in the 1 - 1000 mg/L concentration range, the detection limit obtained being of 0.2 ± 0.1 mg/L.

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