STUDIA UNIVERSITATIS BABEŞ-BOLYAI, CHEMIA, XLV, 1-2, 2000

FLAME ATOMIC EMISSION DETERMINATION OF POTASSIUM IN NATURAL WATERS WITH THE METHANE-AIR FLAME AS EXCITATION SOURCE

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 potassium content of some natural (well and mineral) waters and drinking water (tap) has been determined by flame atomic emission spectrometry using the methane-air flame. Effects of the flame and of instrumental parameters (flame composition, the observation height, the spectral bandpass of the monochromator) on the emission of potassium in methane-air flame was studied and optimized. The best results were obtained using the 766.4 nm potassium line at the observation height of 11 mm, with the flame composition of 1.12 (relative stoichiometric units, RSU) and the slit width of 0.7 mm. The effect of Li, Na, Rb, Cs, Mg, Ca, Sr, Al, Cl^-, SO_4^{2-}, PO_4^{3-} and ClO_4^- on the emission of potassium was studied too. The detection limit of 0.3 ± 0.04 $\mu g.l^{-1}$ was obtained, in the presence of 200 $mg.l^{-1}$ Cs, at a significance level of 0.05 using the two-step Neyman-Pearson criterion. The potassium content of waters has been determined directly using both external calibration curve and standard addition method. The results agree between these two methods.

INTRODUCTION

Flame atomic emission spectrometry (FAES) is a fast, simple, recommended method for the determination of potassium content of different waters. Usually as excitation source, the high temperature C_2H_2-air, C_2H_2-O_2, H_2-O_2 flames are used. The optimal flame conditions for the determination of potassium in these flames were established, the detection limits are of order of 0.1 $\mu g.l^{-1}$ [1-13]. Propane-butane-air (PB-A) and the natural gas-air (NG-A) flames are used in low performance commercial flame-photometers. These flames have a lower temperature than the former ones and from this point of view lie between the hot and cool flames. The methane-air (M-A) flame has similar properties (temperature, burning velocity etc) with the PB-A, NG-A flames [14, 15]. To our best knowledge the behaviour of potassium in the M-A flame was not studied and the determination of potassium content of natural waters using the M-A flame was not reported. The aim of this work is to study the behaviour of this element in the M-A flame, to optimize instrumental parameters and the determination of potassium in natural waters, respectively.

EXPERIMENTAL

The optimal flame and instrumental parameters were determined, as follows: 1. Determination of the emission spectrum of potassium in the M-A flame; 2. Determination of the optimal values of flame parameters (flame composition, observation height over the burner head (h)) in the flame; 3. Then, the detection limit was determined under optimized conditions. Finally, the potassium content of some natural waters was determined.

INSTRUMENTATION

The instrumental setup was the same as described earlier [16].

CHEMICALS

Stock solutions of K, Na, Li, Rb, Cs (used as ionization suppressor), Ca, Mg, Sr and Al were of 1000 mg.l^{-1}, prepared from RbCl, CsCl, Li_2CO_3 (Merck, Darmstadt, Germany), NaCl, KCl (Reactivul, Bucuresti, Romania), $CaCO_3$, $SrCO_3$, Al and Mg (Specpure, Johnson Matthey Chemicals Limited, England), HCl, H_2SO_4, $HClO_4$ and H_3PO_4 (analytical grade, Merck, Darmstadt, Germany)), respectively. The calibration solutions were obtained by diluting a given volume of stock solution with double distilled water. The diluted solutions were prepared just before measurements. The natural water samples of 350 ml were conserved with 1 ml of conc. HCl (analytical grade, Merck, Darmstadt, Germany).

SAMPLING AND SAMPLE HANDLING

The well water samples were collected in village Săvădisla (county Cluj), located 24 km far north-west from Cluj-Napoca city. The waters were sampled and handled in accordance with the EPA-recommendations [17]. All determinations were carried out within 72 hours after sampling. The mineral waters (commercial available, “Izvorul Minunilor”, “Anavie”, “Borsec”, “Perla Harghitei”) were analyzed after the sealed bottles were opened and degassed by shaking. All water samples were diluted properly before measurements. The solutions were prepared just before the measurements.

PROCEDURE

The behaviour of potassium in the M-A flame was studied up to h = 18 mm over the burner head in 1 mm steps, at three different flame compositions: 0.88; 1.00; 1.12 (expressed in relative stoichiometric units). Four replicate measurements were made, the mean and the standard deviation, the S/N and the S/B ratios were calculated for each h and flame composition. The homogeneity of the means was tested by the F test at a significance level of 0.05. 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 POTASSIUM, DETERMINATION OF THE ANALYTICAL EMISSION LINE

First the emission spectrum of potassium was determined by recording the spectrum of the flame alone, then that of the flame in the presence of potassium by nebulizing a solution of 100 mg.l^{-1} potassium in the flame. The composition of the flame was kept constant, 1.12. The investigated spectral range was 200 – 800 nm, the scanning rate of the monochromator being 0.02 nm/sec. Comparing the spectrum using spectral tables there were identified the emission lines with wavelengths of 404.4 nm, 404.7 nm, 766.4 nm and 769.9 nm [18]. These are all atomic lines, the most intensive ones being the doublet of 766.4 nm and 769.9 nm, respectively. The first two lines are superimposed on a high background of the flame, the background at the higher wavelengths is insignificant.

The change of the analytical signal versus h at the wavelengths of 404.4 nm, 766.4 nm and 769.9 nm was studied further. The concentration of the calibration solutions was different, in function of the intensity of potassium emission line under the study, and the background intensity at the given wavelength. The background intensity was measured in the presence of potassium only in the case of the shorter wavelength doublet, at 404.0 nm. The variation of the net emission signal of different potassium lines versus h over the burner head is represented in Fig.1.

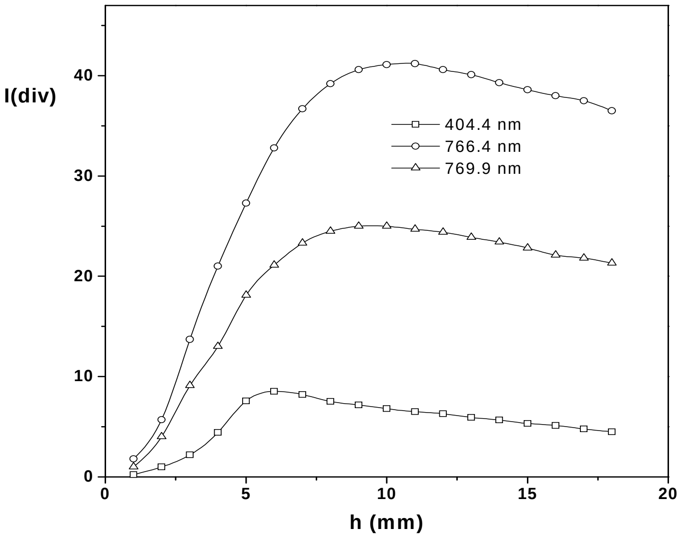

Figure 1. Variation of the net emission signal of different potassium lines versus h.

For the quantitative comparison of the results obtained at different wavelengths only the maximum value of the analytical signal (I) 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, taking account of the concentration of the calibration solution, and the sensitivity of the chart recorder used. The reference concentration was of 100 mg.l^{-1}, the 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 reference concentration being the highest one used. The results are summarized in Table 1.

Table 1

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

Wavelength (nm)	I (div)	h (mm)	I_{corr}	I_{rel}	S/N	S/B
404.4	33.5	10	67.0	1.00	43.5	2.86
766.4	41.7	11	417.0	6.22	426.9	4170.0
769.9	25	11	250.0	3.73	385.7	2500.0

The 404.4 nm line is weak, more intensive lines are at longer wavelength, the most intensive being that of 766.4 nm. The intensity of these lines varies in the same manner as the translational temperature of the flame, the maximum intensity being at 10-11 mm over the burner head [19].

In conclusion the analytical emission line for potassium in the M-A flame is that of 766.4 nm at h = 11 mm. The S/B ratio at this wavelength is high too, due to the low value of the background.

DETERMINATION OF THE OPTIMAL VALUES OF THE FLAME COMPOSITION AND THE HEIGHT OF OBSERVATION OVER THE BURNER HEAD

The influence of the flame composition, on h, on the analytical signal and S/N ratio for the most sensitive line was studied, at the concentration level of 10 mg.l^{-1}. The data were processed by using the MicroCal Origin™ Software package, version 5 (MicroCal Software Inc., MA, USA) and plotted as 2D contour map (Fig.2).

The results show, that the maximum intensity is obtained in all cases at the same h = 11 mm over the burner head, regardless of the flame composition. The analytical signal decreases with the decrease of the methane content in the flame. The standard deviations of all means are homogeneous, therefore the magnitude of the S/N ratio is decided by the magnitude of the mean. In conclusion, the optimal conditions for the quantitative determination of potassium in the M-A flame are λ = 766.4 nm, h = 11 mm, flame composition of 1.12.

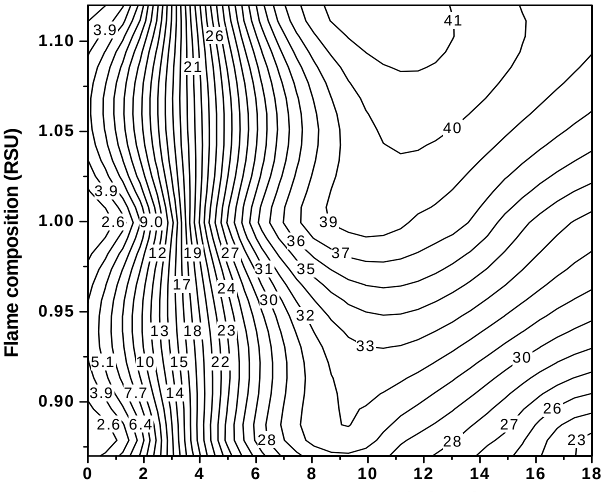

Figure 2. The 2D contour map of the emission of the 766.4 nm potassium line vs. observation height and flame composition. The data labels on the plot indicate the grid matrix values.

THE INFLUENCE OF THE SPECTRAL BANDPASS OF THE MONOCHROMATOR ON THE ANALYTICAL SIGNAL, S/N AND S/B RATIO

The spectral bandwidth of the monochromator, determined by its width of the slit (SW), influences both the amplitude and the fluctuations of the emission signal in different manner. Therefore the optimal slit width 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 slit over I and S/N ratio was studied in the 0.1-1.5 mm domain in steps of 0.1 mm. The analytical signal exhibits almost a linear variation with the slit width up to 1.5 mm, the I-SW relationship could be approximated best with a second order polinomial function ($I = -1,18 + 28,12\ SW + 6,43\ SW^2$, $r^2 = 0.999$). The standard deviation of the means is homogeneous up to a width of 0.7 mm, then they differ significantly. The highest value for the S/N ratio was found at a value of the width of 0.7 mm. In conclusion, the width of the slit could be increased up to 0.7 mm without decay of the S/N ratio.

INTERFERENCES

The effect of Li, Na, Rb, Cs, Ca, Sr, Mg , Al, Cl^-, SO_4^{2-}, PO_4^{3-} and ClO_4^- ions on the emission signal of potassium of 5 mg.l^{-1} was investigated, up to a concentration of the interferent of 500 mg.l^{-1}. Some of these elements and ions are potential inorganic interferents, present in natural waters in higher concentration. The optimal experimental conditions were described in a previous paragraph. The background signal was measured at 767.5 nm in the presence of the interferent. The variation of the emission signal of potassium versus the concentration of the interferents is represented in Fig. 3.

The alkaline metals, possessing a lower excitation and ionization energy than that of potassium (Rb, Cs), enhance the emission signal of potassium up to a concentration of 100 mg.l^{-1}, acting as ionization suppressor. Ca enhances the potassium emission signal too, acting as releasing agent. This effect could be attributed to the shift of the chemical equilibrium concerning formation of the more stable CaOH than that of KOH in the flame. Al and PO_4^{3-} decrease significantly the potassium emission. The other interferents do not influence the potassium emission, even at higher concentrations. ClO_4^- do not influence the emission of potassium, fact which suggests the free evaporation of potassium from the condensed phase in the M-A flame.

CALIBRATION, DETERMINATION OF THE DETECTION LIMIT

For the determination of the detection limit the variation of the analytical signal versus concentration was studied. Seven calibration curves were plotted, in the 10 – 10^{-2} mg.l^{-1} potassium concentration range. One curve covers 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. There were tested the homogeneity of means and the linearity of the calibration curve, the equation of the regression line, the confidence limits and the coefficient of correlation (r^2), with the least squares method were calculated. The detection limit was calculated using the two-step Neyman-Pearson criteria [20,21]. For the fixed values of $(P_{10})_0$ = 0.025 and $(P_{11})_d$ = 0.975 the S/N ratio has the value of 3.92. The results are summarized in Table 2.

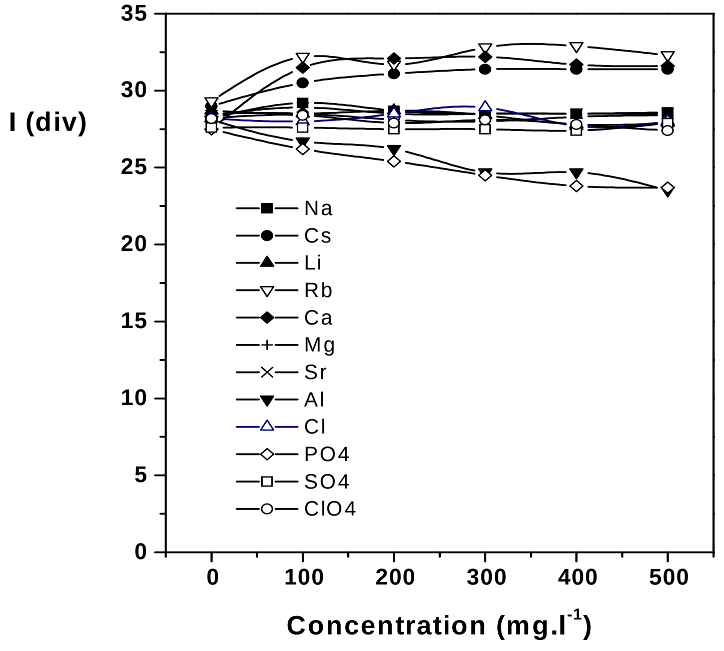

Figure 3. Influence of Li, Na, Rb, Cs, Ca, Sr, Mg , Al, Cl^-, SO_4^{2-}, PO_4^{3-} and ClO_4^- on the emission of potassium of 5 mg.l^{-1}

Table 2

Calibration curves and detection limits

Nr. eq.	Concentration range potassium (mg.l^{-1})	Slit width (mm)	Equation of the calibration curve	Detection limit (mg.l^{-1})
1	1 – 4	0.1	I = 16.03 + 5.20C r^2 = 0.9998	not determined
2	6 - 10	0.1	I = -2.05C + 9.00C r^2 = 0.9994	not determined
3$^{@}$	1 – 10	0.1	I = -1.7 + 2.47C r^2 = 0.9999	0.08 ± 0.05
4	0.1 – 1	0.1	I = -0.5 + 8.56C r^2 = 0.9992	0.025 ± 0.017
5*	0.1 – 1	0.1	I = 0.6 + 12.14C r^2 = 0.9992	0.060 ± 0.033
6*	0.01 – 0. 1	0.1	I = 0.1 + 35.23C r^2 = 0.9907	0.006 ± 0.004
7*	0.01 – 0.1	0.7	I = 0.3 + 467.23C r^2= 0.9997	0.001 ±0.0007
8*	0.001 – 0.01	0.7	I = -0.1 + 645.47C r^2 = 0.9933	0.0003 ± 0.00004

* with Cs added, in final concentration of 200 mg.l^{-1}
$^{@}$ burner held perpendicular to the optical axis, optical path 8 mm through the flame

In the 1 – 10 mg.l^{-1} concentration domain no linear relationship exists between concentration (C) and intensity (I). Linear relationship persists only in the 1- 4 mg.l^{-1} (eq.(1)) and 6-10 mg.l^{-1} domain, respectively (eq.(2)). The calibration equation (3$^{@}$) plotted in the same concentration range (with burner held perpendicular to the optical axis) could be approximated with the straight line at the chosen significance level. In the lower concentration ranges (eq.(4) - (7)) this phenomenon disappears even in long optical path in the flame. This fact suggests the presence of the line reversal phenomenon as main source of the nonlinear relationship between C and I. In order to enhance the potassium emission, a Cs solution was added to each calibration solution, in the concentration of 200 mg.l^{-1}. The increased slit width allows the signal enhancement and the extension of the usable concentration more than one order of magnitude. The detection limit obtained for each concentration range is also summarized in Table 2. The lowest detection limit, of 0.3 ± 0.04 µg.l^{-1}, obtained with the M-A flame is the same order of magnitude with those obtained with the hotter (C_2H_2-air, C_2H_2-O_2, H_2 - O_2) flames.

DETERMINATION OF POTASSIUM IN WATER SAMPLES

The potassium content of the water samples was determined by calibration and the standard addition method, the later being used as reference method for the method validation, due to the absence of certified reference material. The determinations were carried out keeping the burner perpendicular to the optical axis, with the SW of 0.1 mm. The other parameters were the optimal ones. Four parallel measurements (n=4) were made everywhere. 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 potassium standard was added to the 25 ml of diluted sample. Three additions of standard were made, in 1 mg.l^{-1} concentration steps. The potassium content was determined from the intercept with the abscissa of the regression line. Using the data set, the reproducibility of the standard addition method was tested first. The recoveries found were within 83.2 - 105.3%, the slope of regression lines being close to that obtained by calibration. The results of the two methods (Table 3) agree within the error of determinations for the given water, so the calibration method could be used for potassium quantification.

Table 3

Results of analysis of water samples (n=4)

Sample		Dilution	Concentration (mg.l^{-1}, calibration)	Concentration (mg.l^{-1}, standard addition)
Tap water		1:1	2.0 ± 0.6	2.1 ± 0.7
Mineral water	“Anavie”	1:20	21.0 ± 1.8	20.2 ± 2.1
	“Izvorul Minunilor”	1:20	1.4 ± 0.6	1.9 ± 0.8
	“Perla”	1:20	11.8 ± 1.7	11.9 ± 1.6
	“Borsec”	1:20	15.9 ± 1.7	16.0 ± 1.7
Well water	Nr. 1	1:20	3.9 ± 0.9	3.9 ± 0.8
	Nr. 2	1:20	3.0 ± 0.9	2.2 ± 0.8
	Nr. 3	1:20	6.9 ± 1.1	7.4 ± 0.9
	Nr. 4	1:40	36.4 ± 1.7	37.0 ± 1.6
	Nr. 5	1:20	18.1 ± 1.8	18.9 ± 1.8
	Nr.6	1:100	168 ± 4	169.3 ± 5

The mineral water “Perla” and “Anavie” have different potassium content, originating from other region of the country (as indicated on the label of the bottles). The well water samples no.1, 2 have practically the same potassium content, the wells being sunk very close one to the other (about 20 meters). This suggests that the wells are supplied from the same ground water source. The other samples (no.3-6) have significantly higher potassium content (sample no.6 having a fifty-fold higher potassium content).

The rubidium content of these waters has been determined earlier [16]. In the case of mineral and well waters (samples no.1, 2) the potassium and rubidium content varies in the same manner, the K/Rb concentration-ratio being close (2041 and 2951for mineral waters, 684 and 545 for well waters, respectively). The high potassium and rubidium content of sample no.6 (the K/Rb concentration-ratio is also high, being of 12923) clearly shows that the well is supplied from an other ground water source than the others, the wells are sunk in rocks with different geological structure and chemical composition.

In conclusion, the potassium content of natural waters can be determined directly by calibration method in the M-A flame with acceptable precision.

CONCLUSIONS

In the M-A flame potassium exhibits only an atomic spectrum. The most intensive line (the analytical line) is at 766.4 nm. The optimal excitation zone is at 11 mm over the burner head, in fuel rich conditions. 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 width of the slit of the monochromator could be increased till 0.7 mm without decay of the S/N ratio. The calibration curves for the 766.4 nm potassium line are linear in the 4 **-** 0.001 mg.l^{-1} concentration range, the detection limit obtained is of 0.3 ± 0.04 µg.l^{-1} potassium. The ionization of potassium can be suppressed with 200 mg.l^{-1} of Cs. The potassium content of natural waters can be determined directly with acceptable precision using the calibration method.

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