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FLAME ATOMIC EMISSION SPECTROMETRY DETERMINATION OF CESIUM IN MINERAL AND WELL WATERS USING A METHANE-AIR FLAME

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ABSTRACT. Effects of flame composition, the observation height and the spectral bandpass of the monochromator on the emission of Cs in methane-air flame were studied and optimized. The best results were obtained using the 852.19 nm Cs line at the observation height of 11 mm, with the flame composition of 1.12 (relative stoichiometric units) and the slit width of 0.8 mm. The effect of Li, Na, K, Rb, Mg, Ca, Sr, Zn, Al and PO_4^{3-} on the emission of Cs was studied too. The detection limit of 3 ± 1.4 μg.L^{-1} was obtained, in the presence of 200 mg.L^{-1} K, at a significance level of 0.05. The Cs content of mineral and well waters was determined without prior concentration by using both the external calibration and standard addition method. The results of these methods show good agreement implying the use of background correction.

Keywords: Cs, FAES, Water analysis

1. Introduction

Cesium is one of the widespread trace elements of the environment, its relative quantity in the Earth crust being of 7.10^{-5} %. It is distributed unequally in different environmental compartments; the mean Cs content of the rocks is of 0.7 mg.kg^{-1}, of the soils is of 3 mg.kg^{-1}. The seawater contains in average only 50 ng.L^{-1} while the surface waters of 200 ng.L^{-1}, respectively. Higher concentrations of Cs occur in minerals (as pollutite, $CsAlSi_2O_6$), in certain volcanic rocks (in avogadite as $CsBF_4$) or can accompany certain minerals, as biotite and leopoldite, Cs content of which could reach 4.5 % of Cs.

Cs has no special physiological role. Plants (as barley, lichens), wild mushrooms and microorganisms (as *Escherichia coli*, *Anabaena.variabilis, Chlorella salina, Saccaromyces cerevisiae, Streptomyces lividans* etc.*)* accumulate primarily Cs *via* K^+ transport in their organisms [1–6]. More harmful, with high biological risks, are the radioisotopes of Cs (^{134}Cs and ^{137}Cs), the main by-products of nuclear fission, being γ emitters with the half-life of 3 h and 33 years, respectively. Therefore, the main accent falls on the quantification of the Cs radioisotopes, most of the papers in this field workout

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radio-analytical method. Flame atomic absorption spectrometry (FAAS) is the standard method for the determination of the total Cs content of different samples, including natural waters, regardless of their origin. The determinations are carried out at 852.19 nm atomic line; the detection limits are in the order of magnitude of $\mu g.L^{-1}$ [7]. Due to the low Cs content of natural waters, the analyte is usually separated and preconcentrated prior measurements by passing through a Dowex 50–X8 resign column, followed by either an ammonium hexacyanocobalt ferrate or potassium hexanitrocobaltate column [8]. Flame atomic emission spectrometry (FAES) is also used for the quantification of Cs. The determinations are carried out either at the Cs 455.54 or the 852.19 nm atomic line; the detection limits being of order of 0.1 $\mu g.L^{-1}$. The common feature of these methods consists of the use of high temperature C_2H_2–air or C_2H_2–N_2O flames wherein Cs easily excites and ionizes, due to its low excitation and ionization energies, of 1.386 and 3.89 eV, respectively. The ionization is suppressed by adding KCl solution in 1 % final concentration in the sample [8–10]. From this point of view the cooler flames, as H_2–air, propane–butane–air (PB–A), natural gas–air (NG–A) or methane–air (M–A) flames seems to be more advantageous for the direct quantification of Cs in low concentrations. So the lowest detection limits, of 30 $fg.mL^{-1}$, have been obtained in hydrogen and propane flames using the electron avalanche amplification of the laser enhanced two-step ionization of Cs [11].

The PB–A and NG–A flames are used in low performance commercial flame–photometers for the determination of alkaline metals designated for routine analyses. The M–A flame has similar properties (temperature, burning velocity etc) with the former ones [12, 13]. To our best knowledge the behaviour of Cs in the M-A flame has not yet been studied, nor the determination of Cs content of natural waters using this flame. The aim of this work is to study the behaviour of this element in the M–A flame, to optimize instrumental parameters and to determine the Cs content of natural waters, respectively.

2. Experimental

The optimal flame and instrumental parameters were established as follows: first, the emission spectrum of Cs was identified in the M-A flame; then the flame parameters (flame composition, observation height over the burner head (h)) have been optimized. In the following step the detection limit was determined under optimized conditions. Finally, the Cs content of some natural waters was determined.

2.1. Instrumentation

A HEATH–701 (Heath Co., Benton Harbour, MI, USA) spectrophotometer with a HEATH EU–700 scanning monochromator, a HEATH EU–700–30 type photomultiplier module and a M12FC51 (NARVA, Germany) photomultiplier (–1200 V) was used. The photomultiplier signal was introduced via a home made A/V converter/amplifier unit and data acquisition card (Decision–Computer International Co. Ltd., USA) into an IBM Pentium II PC (120 MHz, 32 Mb RAM) and processed using a home written Qbasic software program. The boxcar average technique was used, with data sampling interval of 0.33 ms. One measurement point was the average of 1500 consequent individual readings. The final data represented the mean value of the 50 measurement points. The other instrumental setup was the same as described earlier [14].

2.2. Chemicals

Stock solutions of Cs, Na, K, Li, Rb, Ca, Sr, Zn, Al, Mg and PO_4^{3-} were of 1000 $mg.L^{-1}$, prepared from RbCl, CsCl, Li_2CO_3, H_3PO_4 (Merck, Darmstadt, Germany), NaCl, KCl (Reactivul, Bucuresti, Romania), $CaCO_3$, $SrCO_3$, Mg, Zn and Al (Specpure, Johnson Matthey Chemicals Limited, England), respectively. The calibration solutions were obtained daily by diluting a given volume of stock solution with double distilled water.

2.3. Sampling and Sample Handling

The well water samples were collected in village Săvădisla (county Cluj), located 24 km’s north-west from Cluj-Napoca city. The waters were sampled, handled and conserved in accordance with the EPA-recommendations [7]. The determinations were carried out within 72 hours after sampling. The mineral waters (commercial available, “Harghita”, “Tuşnad”, “Dorna”, “Izvorul Minunilor”) were analyzed after the sealed bottles were opened and degassed by shaking. All water samples were sprayed directly into the flame-photometer without any other treatment.

2.4. Procedure

The behaviour of Cs 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 unit - RSU). 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 too by the F test at the significance level of 0.05. The sensitivity of the amplifier was set properly for each spectral domain, depending on the intensity of the emission lines and the background observed. For a given set of determinations, the sensitivity was kept constant.

3. Results and Discussion

3.1 The Emission Spectrum of Cs, Determination of the Analytical Emission Line

First the emission spectrum of Cs was determined by recording the spectrum of the flame alone, then that of the flame in the presence of Cs by spraying a solution of 100 mg.L^{-1} Cs in the flame. The spectra were recorded in the 300–900 nm domain with a scanning rate of the monochromator of 0.02 nm.sec^{-1}. The composition of the flame was kept constant, of 1.12 RSU. Using spectral tables the emission lines with wavelengths of 455.54 nm, 459.32 nm, 852.19 nm and 894.35 nm were identified [10]. These are all atomic lines, the most intensive ones being of 852.19 nm and 455.54 nm, respectively.

The change of the analytical signal versus h at the formerly detected wavelengths was studied further. The concentrations of the calibration solutions were different, in function of the intensity of Cs emission line under study. The background intensity was measured in all cases in the presence of Cs, at the wavelengths of 457.0 nm, 461.0 nm, 854.0 nm and 896.0 nm, respectively. The variation of the net emission signal of different Cs lines versus h over the burner head is represented in Fig.1.

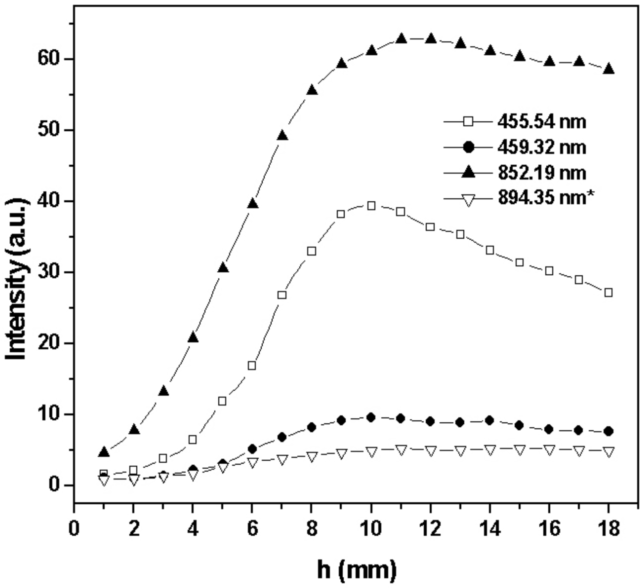

Figure 1. Variation of the net emission signal of the Cs lines vs. h.
* not in scale (5 x magnification)

For the quantitative comparison of the results obtained at different wavelengths only the maximum value of the net analytical signal (I) for each line was selected. The relative intensity (I_{rel}) for each line was calculated too. The reference concentration was of 100 mg.L^{-1}, the sensitivity the highest value used 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 Cs in the M–A flame

Wavelength (nm)	I (a.u.)	h (mm)	I_{rel}	S/N	S/B
455.54	39.4	10	75.76	296.5	6.9
459.32	9.6	10	18.46	72.2	2.0
852.19	62.8	11	120.76	468.7	157.0
894.35	0.52	11	1.00	4.2	2.5

The most intensive Cs line is that of 852.19 nm, superimposed on the low value of the background (high S/B ratio). For analytical purposes the 455.54 nm line could be used too, but in less favorable conditions than the former. The intensity of each Cs line varies in the same manner as the translational temperature of the flame, the maximum intensity being at 10–11 mm over the burner head [15] (see Fig.1.). In conclusion the analytical emission line for Cs in the M-A flame is that of 852.19 nm at h = 11 mm.

3.2. 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 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 slightly 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 Cs in the M–A flame are λ = 852.19 nm, h = 11 mm, flame composition of 1.12.

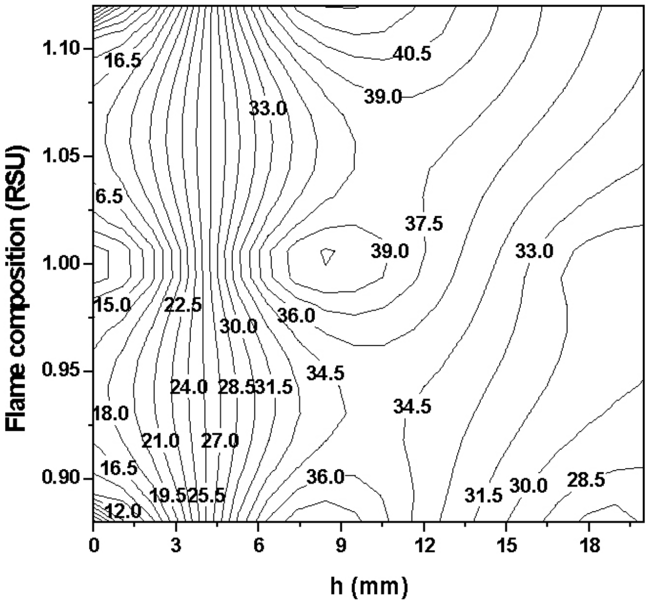

Figure 2. The 2D contour map of the emission of the 852.19 nm Cs line vs. observation height and flame composition. The data labels on the plot indicate the grid matrix values.

3.3. 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 width of the slit (SW), influences in different manner the amplitude and the fluctuations of the emission signal. Therefore the optimal width of the slit 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 width of 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 a linear variation with the slit width up to 1.5 mm, the I–SW relationship could be approximated with a linear function ($I = -43.986 + 0.7608\ SW$, $R^2 = 0.9994$). The standard deviation of the means is homogeneous up to a width of 0.8 mm and then they differ significantly. The highest value for the S/N ratio was found at a value of the width of 0.8 mm. In conclusion, the width of the slit could be increased up to 0.8 mm without decay of the S/N ratio.

3.4. Interferences

The effect of Li, Na, K, Rb, Mg, Ca, Sr, Zn, Al and PO_4^{3-} ions on the emission signal of Cs of 1 mg.L^{-1} was investigated, up to a concentration of the interferent of 500 mg.L^{-1}. Some of these elements are potential inorganic interferents, present in natural waters at higher concentrations. The optimal experimental conditions were described in a previous paragraph. The background signal was measured at 854.0 nm in the presence of the interferent. The variation of the emission signal of Cs versus the concentration of the interferents is represented in Fig. 3.

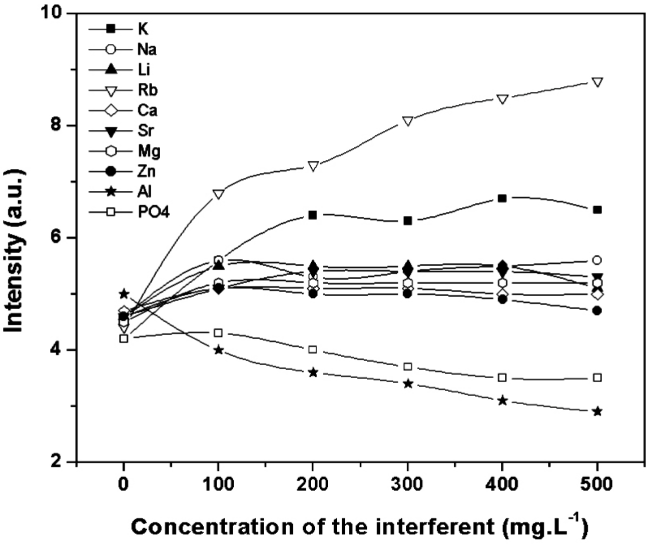

Figure 3. Influence of Li, Na, K, Rb, Ca, Sr, Mg , Zn, Al and PO_4^{3-} on the emission of Cs of 1 mg.L^{-1}

The alkaline metals K and Rb, acting as ionization suppressors, enhance the emission signal of Cs up to an excess of 200 and 100 times, respectively. Both Al and PO_4^{3-} decrease significantly the emission signal of Cs, probably due to a low evaporation rate of Cs from the condensed phase in the M–A flame. The other interferents do not influence the Cs emission, even at higher concentrations.

3.5. Calibration, Determination of the Detection Limit

For the determination of the detection limit the variation of the analytical signal versus concentration was studied. Five calibration curves were plotted, in the 10–10^{-2} mg.L^{-1} Cs concentration range. Each calibration curve was established by using six standard solutions and covers only one order of magnitude of concentration. 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 at the significance level of 0.025 [16,17]. The results are summarized in Table 2.

Table 2. Calibration curves and detection limits (n = 6)

No. eq.	Concentration range Cs ($mg.L^{-1}$)	Slit width (mm)	Equation of the calibration curve	Detection limit ($mg.L^{-1}$)
1	1 – 10	0.1	$I = -1.0407 + 1.7398C$ $R^2 = 0.9991$	0.4 ± 0.14
2*	1 – 10	0.1	$I = 0.6355 + 3.0495C$ $R^2 = 0.9994$	0.2 ± 0.09
3@	1 – 10	0.1	$I = 0.4992 + 2.8415C$ $R^2 = 0.9992$	0.3 ± 0.24
4*	0.1 – 1	0.1	$I = -0.0226 + 3.6297C$ $R^2 = 0.9983$	0.15 ± 0.06
5*	0.01 – 0.1	0.8	$I = 0.0287 + 38.727C$ $R^2 = 0.9964$	0.003 ± 0.0014

* with K added, in final concentration of 200 $mg.L^{-1}$
@ with Rb added, in final concentration of 100 $mg.L^{-1}$

Cs exhibits linear dynamic range in the 1–10 $mg.L^{-1}$ concentration domain in the presence of K of 200 $mg.L^{-1}$, used as ionization suppressor. Rubidium has the same effect (Table 2, Eq.(3)), but in lesser extent. On the other hand the presence of Rb increases the noise level of the determinations, namely the instability of the flame, as compared with K. The increased slit width up to 0.8 mm allows the signal enhancement and the extension of the usable concentration about one order of magnitude. The detection limit obtained for each concentration range is also summarized in Table 2. The lowest detection limit, of 3 ± 1.4 $\mu g.L^{-1}$, obtained with the M–A flame is the same order of magnitude with those obtained with the hotter (C_2H_2–air and C_2H_2–N_2O) flames.

4. Determination of Cs in Water Samples

The Cs content of the water samples was determined by calibration and the standard addition method, the latter being used as reference method for the method validation, in the absence of certified reference material. The determinations were carried out with the SW of 0.8 mm. The other parameters were the optimal ones. Four parallel measurements (n = 4) were made in all cases. Two sets of standard calibration solutions were prepared. One set contained the analyte in the presence of K of 200 mg.L^{-1}. In order to ensure the same evaporation conditions with the well water samples, the other set contained K, Na, Ca, Mg, as matrix, in the same concentration level as the well waters (K, Na of 100 mg.L^{-1} and Ca, Mg of 50 mg.L^{-1}, respectively). The K, Na, Ca, Mg content of these samples has been determined earlier [18, 19]. In the case of standard addition method 100 µL of Cs stock standard was added to the 20 mL of sample. Three additions of standard were made, in 0.025 mg.L^{-1} concentration steps. Using the data set, the reproducibility of the standard addition method was tested first. The recoveries found were within 88.2–132.3%, the slope of regression lines being close to that obtained by standard calibration. The results obtained with the standard calibration using K of 200 mg.L^{-1} are systematically lower with 10–66 % than those obtained with the synthetic well water. This fact suggests the presence of the evaporation interference in the flame due to the high salinity of the well waters. For further considerations only the last case values were taken into account. The results of the two methods (Table 3) agree within the error of determinations for the given water. The confidence limits are wide due to the high noise level of the determinations close to the detection limit. The calibration method using synthetic well water could be used for quantification.

Table 3. Results of analysis of water samples (n = 4)

Sample		Concentration (µg.L^{-1}, by calibration)	Concentration (µg.L^{-1}, by standard addition)
Mineral water	“Harghita”	11 ± 1.6	12 ± 1.5
	“Tuşnad”	8 ± 1.7	7 ± 2.1
	“Dorna”	4 ± 1.6	4 ± 1.9
Well water	no.1	< 3 ± 1.4	< 3 ± 1.4
	no.2	3 ± 1.7	3 ± 1.4
	no.3	5 ± 1.6	6 ± 0.9
	no.4	5 ± 1.6	7 ± 1.1
	no. 5	7 ± 1.7	7 ± 1.4
	no. 6	10 ± 1.5	8 ± 1.9

The mineral water “Harghita” and “Tuşnad” have close Cs content, originating from the same volcanic region of the country (as indicated on the label of the bottles).

The well water samples nos.1–4 have practically the same Cs content, the wells being sunk very close one to the other (about 20 meters).

The other samples (nos.5–6), collected from another site of the village, have significantly higher Cs contents. The potassium and rubidium content of these samples are higher too as well as the K/Rb and K/Cs concentration-ratios [14, 19]. These facts show that the wells from different sites are supplied from other ground water sources, being sunk in rocks with different geological structure and chemical composition. The high alkaline metal content of the waters suggests the presence of rock salt bulbs or layers stratified among the sedimentary structures.

In conclusion, the Cs content of mineral and well waters can be determined directly in the M–A flame with acceptable precision by calibration method using synthetic well waters and background correction.

5. Conclusions

In the M–A flame Cs exhibits only an atomic spectrum. The most intense line is at 852.19 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 to make the detection limit lower, the width of the slit of the monochromator could be increased till 0.8 mm without decay of the S/N ratio. The calibration curves for the 852.19 nm Cs line are linear in the 10–0.001 $mg.L^{-1}$ concentration range; the detection limit obtained is of 3 ± 1.8 $\mu g.L^{-1}$ Cs. The ionization of Cs most efficiently is suppressed with 200 $mg.L^{-1}$ K. The Cs content of mineral and well waters can be determined with acceptable precision using the calibration method and background correction.

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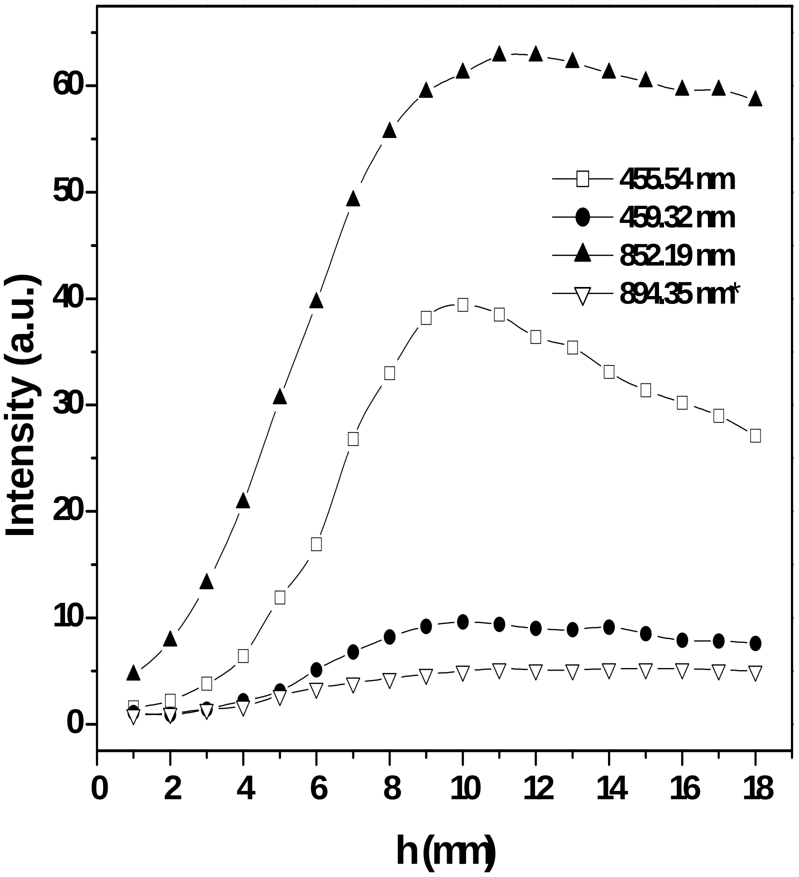
Intensity (a.u.)
0
10
20
30
40
50
60
h (mm)
0
2
4
6
8
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14
16
18
455.54 nm
459.32 nm
852.19 nm
894.35 nm*

Figure 1.

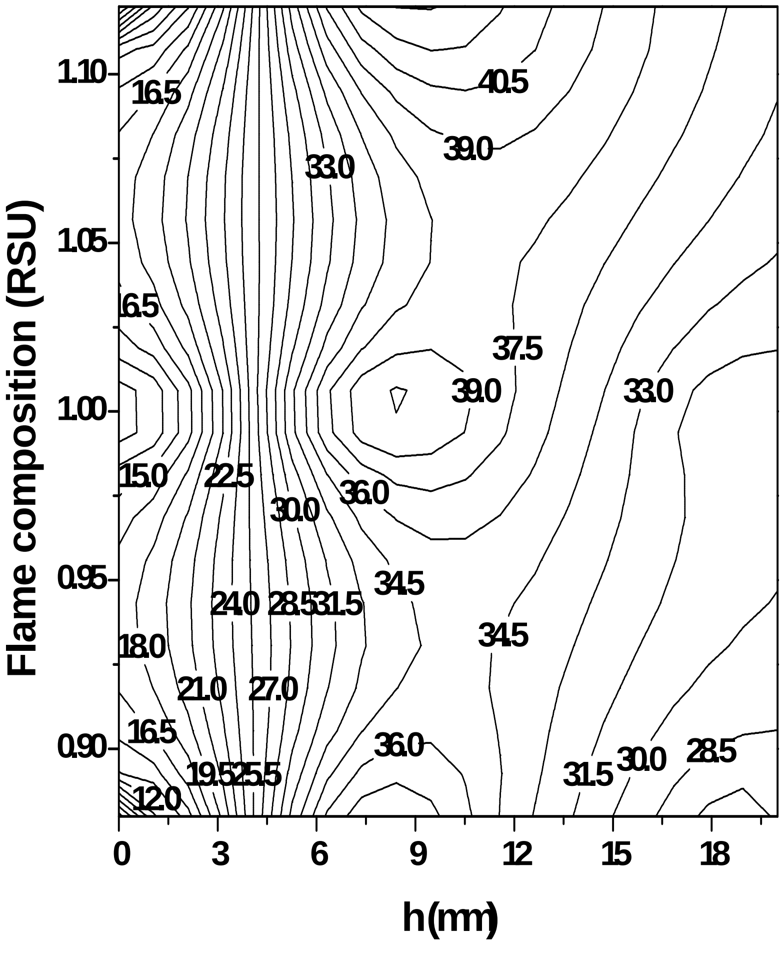
Flame composition (RSU)
1.10
1.05
1.00
0.95
0.90
h(mm)
0
3
6
9
12
15
18
16.5
40.5
39.0
33.0
16.5
37.5
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Figure 2.

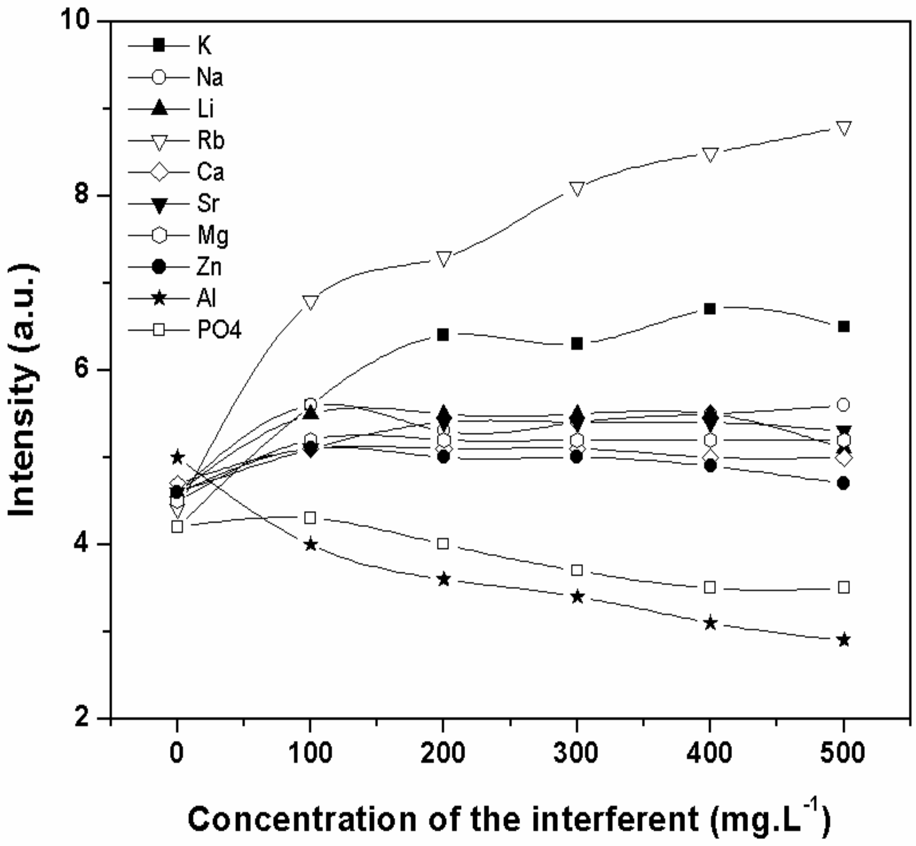
Intensity (a.u.)
Concentration of the interferent (mg.L-1)
10
8
6
4
2
0
100
200
300
400
500
K
Na
Li
Rb
Ca
Sr
Mg
Zn
Al
PO4

Figure 3.