

## FLAME ATOMIC EMISSION QUANTIFICATION OF LITHIUM IN NATURAL WATERS USING THE METHANE–AIR FLAME AS AN ALTERNATIVE EXCITATION SOURCE

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**ABSTRACT.** The lithium content of some natural waters has been determined by flame atomic emission spectroscopy using the methane-air flame. It was studied the effect of Na, K, Rb, Cs, Mg, Ca, Sr and Ba on the emission of lithium in the conditions of earlier optimized flame and instrumental parameters. The lithium content of some mineral -, well - and seawaters has been quantified using the standard calibration and the standard addition method. The results agree between these two methods.

### INTRODUCTION

Lithium is a physiologically important trace element for human, animal and plant life. It is the 27<sup>th</sup> in the rank of the element-abundance in the Earth crust, the mean Li-content of the soils being of 32 mg kg<sup>-1</sup>, that of surface waters of tens of µg L<sup>-1</sup>, respectively [1]. The peat, moorland and alluvial soils have low lithium content, whereas the calcareous soils as well as the soils in contact with high-salinity mineralized waters could contain with one order of magnitude higher quantities of Li, exhibiting phytotoxic effects. Lithium has a large mobility in the environment being retained by soils and by biosorption, primarily by plants (the mean Li-content of plants being between 20 – 200 mg kg<sup>-1</sup>, species dependent). Usually, for most plant-species there is a direct relationship between the soil and the built in Li-content [2]. For human and animal life lithium is considered at present as an essential element, with multiple physiological effects: the lithium deficiency can cause for domestic animals and pets loss of gain in weight, increase of juvenile and dam mortality, decrease of milk production of goats [3]. These symptoms can occur for the humans too. In human medicine Li-salts are used in the therapy of psychic depression, its overdoses can produce different side effects, as: decrease of insulin and zinc [4], the vanadium and manganese [5] concentration in the blood plasma with the increase of the aluminum content in the same time, renal insufficiency [6]. The daily human lithium intake is attained with vegetables, dairy products and drinking water. The knowledge of lithium content of different natural waters is important regarding to health protection aspect as well as to hydro-geochemical one concerning his origin.

Flame atomic emission spectrometry (FAES) is the standard method for the quantification of lithium in natural waters of different origin [7, 8, 9 and 10]. As excitation sources the use of C<sub>2</sub>H<sub>2</sub>-air, propane-butane-air (PB-A) flames are recommended, the optimal flame, instrumental and experimental conditions for the

quantification of lithium in waters are well known. The methane-air flame (M-A) has similar properties with the PB-A and natural gas-air (NG-A) flames, exhibiting lower temperature and burning velocity than the  $C_2H_2$  ones. To our best knowledge the quantification of lithium in natural waters using the M-A flame was not reported. The aim of this work is to study the effect of different elements, existing in waters (as possible interferents) on the emission of lithium in the M-A flame and the quantification of lithium in natural waters of different origin, respectively.

## **EXPERIMENTAL INSTRUMENTATION**

The instrumental setup and operation conditions were the same as described earlier [11].

## **REAGENTS**

Stock standard solutions of  $1000 \text{ mg L}^{-1}$  were prepared by dissolving the appropriate amounts of metals (Mg (Specpure, Johnson Matthey Chemicals Limited, England)) and compounds ( $Li_2CO_3$ ,  $CaCO_3$ ,  $SrCO_3$  (Specpure, Johnson Matthey Chemicals Limited, England) in corresponding acid. KCl, NaCl (analytical grade, Reactivul, București, Romania), CsCl, RbCl (used as ionization suppressors), HCl (analytical grade, Merck, Darmstadt, Germany)) were dissolved and diluted with double distilled water, respectively. For further dilutions double distilled water was used in all cases. 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 sea water sample arose from the Black Sea coast, Constanța zone. All waters were sampled and handled in accordance with the EPA-recommendations [7]. The mineral waters (commercial available, "Izvorul Minunilor", "Anavie", "Borsec", "Perla Harghitei", "Bona Aqua") were analyzed after the sealed bottles were opened and degassed by shaking and acidified with 2 ml of conc. HCl (analytical grade, Merck, Darmstadt, Germany). The determinations were carried out within 72 hours after sampling, the water samples were diluted properly before measurements.

## **PROCEDURE**

The determinations have been carried out in the M-A flame at  $\mu = 670.78 \text{ nm}$ , at observation height over the burner head of 7 mm in fuel rich conditions, established earlier [12]. Six replicate measurements were made in each case. The mean, the standard deviation were calculated, it was tested the homogeneity of the means (at a significance level of 0.05) too [13,14]. The burner was held parallel to 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, considering the size of the measured signal intensity. For a given set of determinations the sensitivity was kept constant.

### RESULTS AND DISCUSSION

First the effect of Na, K, Mg, Ca, Sr and Ba on the emission signal of lithium of  $1 \text{ mg L}^{-1}$  was investigated, till to five hundred-fold concentration excesses, as possible inorganic interferences in the samples. The effect of Rb, Cs was tested too, as ionization suppressors. The analytical signal, intensity ( $I$ , in a.u.), was measured at  $670.78 \text{ nm}$  and the background intensity (in the presence of interferent), at the base of the atomic emission, at  $672 \text{ nm}$ . The variation of the emission signal of lithium versus the concentration of the interferents is represented in Fig. 1 (The experimental data series for different elements are slightly shifted for better visibility).

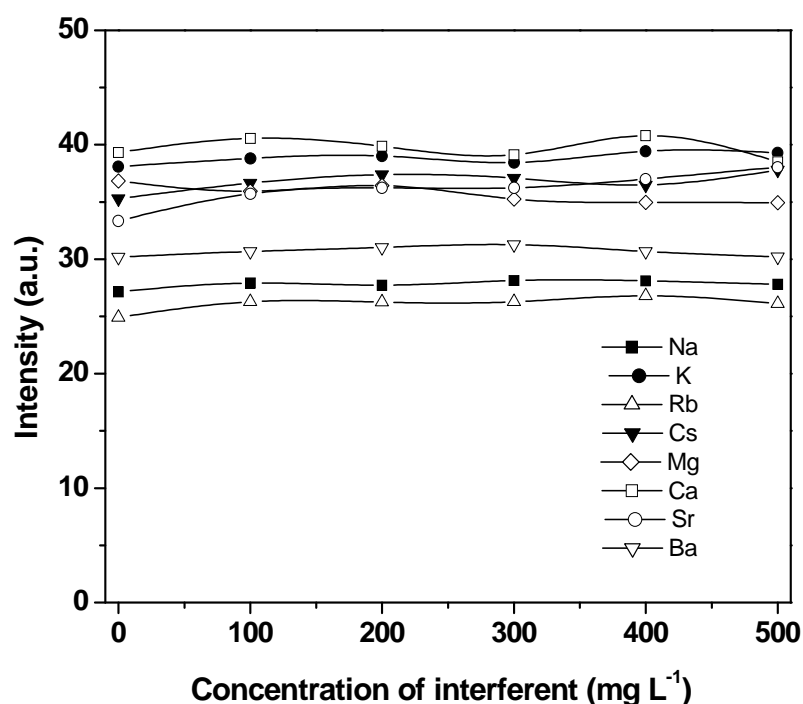


Fig. 1. Influence of Na, K, Rb, Cs, Mg, Ca, Sr and Ba on the emission of lithium of  $1 \text{ mg L}^{-1}$

As expected, Rb, Cs acts as ionization suppressors due to slight ionization of lithium in the M-A flame. Sr and Ca enhances the analyte signal too, acting as releasing agent by binding the free OH radicals of the flame and hindering the formation of the low stability LiOH. Sr increases the flame background emission too by superimposing the SrOH molecular band over the flame spectrum. Na and Ba have no influence. Mg decreases gradually the lithium emission signal.

### QUANTIFICATION OF LITHIUM IN WATER SAMPLES

The standard calibration and the standard addition method were carried out for the lithium quantification in natural waters, the later being used as reference one (absence of certified reference material) for validation. The determinations were performed with optimal instrumental parameters. Four parallel measurements ( $n=4$ ) were made everywhere. To minimise the effect of the interferences the samples were diluted 1:1 before measurements. The linear regression calibration curve was established using six standards in the  $0,1 - 1 \mu\text{g L}^{-1}$  concentration domain ( $I = 1.7037 + 45.647C$  and  $r^2 = 0.998$ ). In case of standard addition method  $100 \mu\text{L}$  of concentrated lithium standard was added (three additions in  $1\text{-mg L}^{-1}$  concentration steps) to the  $25 \text{ ml}$  of diluted sample. The analyte content was determined from the intercept of the regression line. Comparing the calibration curves, the slope of calibration curves corresponding to the standard additions are close to that obtained by calibration, which suggests the absence of any interference. The results of the two methods (Table 1) agree within the error of determinations for the given water (except of mineral water "Borsec"), so the calibration method could be used for lithium quantification.

**Table 1**

Results of analysis of water samples ( $n = 4$ )

Sample		Concentration ( $\mu\text{g L}^{-1}$ , calibration)	Concentration ( $\mu\text{g L}^{-1}$ , standard addition)
Sea water		$78 \pm 6.6$	$76 \pm 10.1$
Mineral water	"Anavie"	$636 \pm 27$	$620 \pm 45$
	"Bona Aqua"	$6.2 \pm 3.8$	$8.1 \pm 4.2$
	"Izvorul Minunilor"	$5.6 \pm 3.8$	$6.1 \pm 4.2$
	"Perla Harghitei"	$185 \pm 7.6$	$164 \pm 12.6$
	"Borsec"	$256 \pm 6.6$	$218 \pm 14.4$
Well water	Nr. 1	$60 \pm 3.8$	$63 \pm 4.2$
	Nr. 2	$43 \pm 3.8$	$43 \pm 4.2$
	Nr. 3	$82 \pm 3.8$	$93 \pm 4.2$
	Nr. 4	$60 \pm 3.8$	$58 \pm 4.2$
	Nr. 5	$54 \pm 3.8$	$50 \pm 4.2$
	Nr.6	$35 \pm 3.8$	$32 \pm 4.2$
	Nr.7	$13 \pm 3.8$	$13 \pm 4.2$
	Nr.8	$13 \pm 3.8$	$13 \pm 4.2$
	Nr.9	$15 \pm 4.1$	$15 \pm 4.2$

The Li content of the seawater obtained with both methods is very close to each other although it exhibits high salinity, the highest of all waters studied. The mineral waters "Anavie", "Perla Harghitei" and "Borsec" have high lithium content suggesting (among the other dissolved alkaline- and earth metal ions) a deep groundwater origin, while "Bona Aqua" and "Izvorul Minunilor" could be considered mostly as surface spring waters. The well waters (samples Nr.1 – Nr.5) collected from the center area of the village has significantly higher Li-concentration as those ones collected from the side area (samples Nr.6 – Nr.9). This suggests the different origin of the ground waters feeding the wells and dissimilar geochemical composition of the rocks through the ground waters flow.

## FLAME AES DETERMINATION OF LITHIUM IN NATURAL WATERS

In conclusion we can consider that both methods give acceptable results, the lithium content of sea-, mineral- and well waters can be quantified with acceptable precision using atomic emission spectrometry with the M-A flame and the standard calibration. For the corroboration of the results the standard addition method is recommended.

### CONCLUSIONS

Lithium exhibits slight ionization in the M-A flame, the phenomenon could be overcome by use Rb, Cs or K in 200 mg L<sup>-1</sup> concentration, adding to the sample. The Ca and Sr salts act as releasing agents, increasing the emission of lithium, while Mg exhibits adverse effect. The lithium content of sea-, mineral- and well waters can be determined precisely with the standard calibration or the standard addition method. The former method is faster and easier, but for the corroboration of the results the standard addition method is recommended.

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