

## Lithium determination in complex ceramic oxides

### $\text{Li}_{5.53}\text{Mg}_{0.97}\text{Zr}_{2.93}\text{O}_{9.43}$ and $\text{Li}_{5.45}\text{Zn}_{0.96}\text{Zr}_{2.94}\text{O}_{9.35}$

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#### Palabras clave:

$\text{Li}_{5.53}\text{Mg}_{0.97}\text{Zr}_{2.93}\text{O}_{9.43}$

$\text{Li}_{5.45}\text{Zn}_{0.96}\text{Zr}_{2.94}\text{O}_{9.35}$

FAAS

#### Keywords:

$\text{Li}_{5.53}\text{Mg}_{0.97}\text{Zr}_{2.93}\text{O}_{9.43}$

$\text{Li}_{5.45}\text{Zn}_{0.96}\text{Zr}_{2.94}\text{O}_{9.35}$

FAAS

#### RESUMEN

Se logró determinar la cantidad de litio en dos nuevos óxidos complejos  $\text{Li}_6\text{MgZr}_3\text{O}_{10}$  y  $\text{Li}_6\text{ZnZr}_3\text{O}_{10}$  por espectrometría de absorción atómica de llama (FAAS). El cálculo estequiométrico para la síntesis de estos dos compuestos cerámicos fue para obtener las formulas nominales, es decir, con números enteros. Pero es posible que a las temperaturas de obtención de 1050°C y 1250°C respectivamente, cierta cantidad de litio se volatilice. Para lograr el refinamiento y determinar la estructura cristalina de ambos compuestos, es necesario conocer la cantidad de átomos de litio. Mediante FAAS se logró determinar la concentración. El cálculo de la cantidad de litio exacta que fue de 5.53 átomos y 5.45 átomos respectivamente. Así las fórmulas determinadas fueron  $\text{Li}_{5.53}\text{Mg}_{0.97}\text{Zr}_{2.93}\text{O}_{9.43}$  y  $\text{Li}_{5.45}\text{Zn}_{0.96}\text{Zr}_{2.94}\text{O}_{9.35}$ .

#### ABSTRACT

It was possible to determine the amount of lithium in two new complex oxides  $\text{Li}_6\text{MgZr}_3\text{O}_{10}$  and  $\text{Li}_6\text{ZnZr}_3\text{O}_{10}$  by flame atomic absorption spectrometry (FAAS). The stoichiometric calculation for the synthesis of these two ceramic compounds was to obtain the nominal formulas, that is, whole numbers. But it is possible that at high temperatures of obtaining 1050°C and 1250°C respectively, a certain amount of lithium volatilizes. To achieve refinement and determine the crystal structure of both compounds, it is necessary to know the amount of lithium atoms. Through FAAS, it was possible to determine the lithium concentration. The calculation of the exact amount of lithium that was 5.53 atoms and 5.45 atoms respectively. Thus the formulas determined were  $\text{Li}_{5.53}\text{Mg}_{0.97}\text{Zr}_{2.93}\text{O}_{9.43}$  and  $\text{Li}_{5.45}\text{Zn}_{0.96}\text{Zr}_{2.94}\text{O}_{9.35}$ .

## Introducción

Lithium is the smallest metal atom in the periodic table of chemical elements, so with certain techniques it is not possible to determine it, for example, with X-ray energy dispersion spectrometry (EDS) is not possible because lithium does not disperse that energy because it has a very small atomic radius of  $1.45 \text{ \AA} \pm 0.12 \text{ \AA}$  (Slater, 1964).

Flame photometry is the most reliable or preferred technique for determining Li, Na, K (Perkin, 2018). What is required is that the chemical compounds containing these metals are solubilized, that is, that these ions are completely dissolved in order to quantify them (Cámara et al., 2004; Das et al., 2011).

Basically there are two optical spectroscopic techniques based on the interaction between electromagnetic radiation and matter that is in the atomic state, which is achieved by a flame that reaches  $2000^\circ\text{C}$ , where the processes of desolvation, vaporization and atomization are (Burguera, 2009; Grunze, 2017). In the atomic cloud are atoms in excited state and atoms in ground state, the relationship between both states is given by the expression:

$$\frac{N_j}{N_0} = \frac{P_j}{P_0} e^{-\frac{E_j}{kT}}$$

$N_j$  = Number of atoms in excited state

$N_0$  = Number of atoms in ground state

$E_j$  = Difference of energy of states

$K$  = Boltzman constant

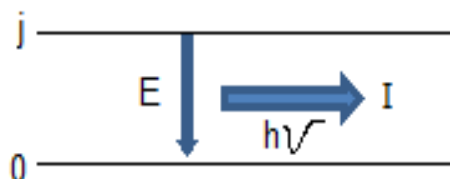
$P_j$  and  $P_0$  statistical factors (number of states with equal energy in each quantum level)

$T$  = Temperature

Atoms that are in an excited state are not in equilibrium, so they tend to emit energy later returning to their fundamental state (Castillo, 2003). The intensity of the emitted energy is proportional to the number of atoms in the excited state and therefore to the concentration of the substance. What constitutes the foundation of Atomic Emission Spectroscopy, which when the atomizer is a flame is called Flame Photometry (Hans, 2012).

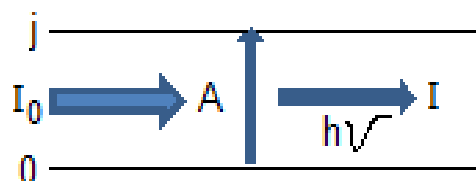
On the other hand, if an appropriate energy radiation is applied to the atoms in the ground state, the absorption of part of this energy by the atoms in the ground state can occur, with which the transmitted energy is lower than the incident energy and is related to the number of atoms in the ground state and therefore the concentration, this is the basis of Atomic Absorption Spectroscopy (Vásquez et al., 2012; Licata, 2004).

The difference between emission and atomic absorption can be explained with simple schemes which are shown in figures 1 and 2 respectively. In figure 1 the atomic emission depends on the excited atoms which emit energy, known as flame emission spectroscopy, called flame photometry. The intensity being a function of  $N_j$ , that is, the number of atoms in the excited state and the intensity is proportional to the concentration (Scoog et al., 2001).



**Figure 1.** Atomic emission spectroscopy (Flame photometry),  $I = f(N_j)$ ;  $I \propto$  concentration.

In figure 2 the atoms in ground state can absorb energy, which is an atomic absorption spectroscopy. Here the intensity is a function of  $N_0$ , that is the number of atoms in the ground state and the absorption is proportional to the concentration (Scoog et al., 2001).



**Figure 2.** Atomic absorption spectroscopy  $I = f(N_0)$ ;  $A \propto$  concentration.

In this paper we describe the optimization of the flame atomic absorption photometry method for the determination of lithium in two new ceramic materials  $\text{Li}_6\text{MgZr}_3\text{O}_{10}$  and  $\text{Li}_6\text{ZnZr}_3\text{O}_{10}$  (Chávez et al., 2015). The interest related to this study was to know the concentration of Lithium in both compounds and in this way it was possible to determine the exact amount of lithium that was 5.53 atoms and 5.45 atoms respectively. Thus the formulas determined were  $\text{Li}_{5.53}\text{Mg}_{0.97}\text{Zr}_{2.93}\text{O}_{9.43}$  y  $\text{Li}_{5.45}\text{Zn}_{0.96}\text{Zr}_{2.94}\text{O}_{9.35}$ .

These formulations differ with the values of the number of atoms in the nominal formula or of subscripts with integers. Obtaining these values will greatly help in the study of the determination of the crystalline structure. In general to greater certainty of the quantity of atoms, greater reliability in the determination of the crystalline structure.

In both compounds what was recorded was the emission that the lithium atoms generated from the ground state to the excited state that occurred at  $\lambda = 660 \text{ nm}$ , whose color of the lithium flame was intense red carmine.

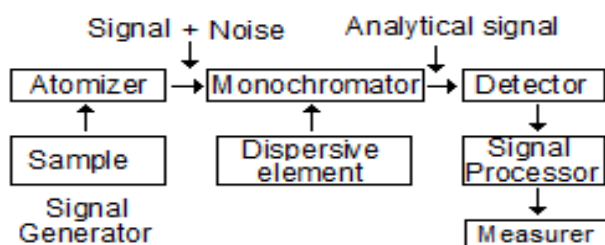
In the present study the calculations of the amount of Lithium atoms from the lithium concentrations determined by FAAS are described in detail.

For the other elements, such as, Mg, Zn and Zr, only the data of the results obtained are shown following the same methodology of the calculations.

### Methodology

As for the equipment Flame Atomic Absorption Spectrometry (FAAS) that was used, it is practically identical to say emission or absorption. Only that for the atomic absorption an external source is required that generates an appropriate radiation, specific to interact with the atoms in fundamental state that will be generated in the atomizer. The signal that leaves the atomizer contains information of the analyte but also other radiations that are produced in the flame that must be eliminated. This is achieved by a monochromator, the signal that leaves the monochromator is the analytical signal and remains an electromagnetic radiation that is transduced into an electrical current in the detector that is a photomultiplier tube or phototube. This electrical current, conveniently processed and amplified, is transformed or transduced into a signal that is registered in the meter (Millán, 2001).

Meanwhile, for a Flame Photometer or atomic emission, the components are practically the same but an external source is not required (Suliburska et al., 2016). This is shown in figure 3.



**Figure 3.** Components of the Flame Photometer used in the determination of lithium of  $\text{Li}_{5.53}\text{Mg}_{0.97}\text{Zr}_{2.93}\text{O}_{9.43}$  and  $\text{Li}_{5.45}\text{Zn}_{0.96}\text{Zr}_{2.94}\text{O}_{9.35}$ .

### Conditions and sample preparation

For the analytical determination of Lithium, an atomic absorption spectrophotometer, PERKIN-ELMER, model 2380, was used in the instrumental mode of flame atomic absorption spectrometry (FAAS). The operational conditions or instrumental parameters were:  $\lambda = 660 \text{ nm}$ ; The slit (called slit) that refers to the width of the spectral band, was  $0.1 \text{ nm}$ , the fuel was acetylene and air support, known as air/acetylene flame type.

The mass of the  $\text{Li}_6\text{MgZr}_3\text{O}_{10}$  and  $\text{Li}_6\text{ZnZr}_3\text{O}_{10}$  compounds was  $1000 \text{ mg/L}$  to prepare the concentrated solutions gravimetrically. The analytes studied were weighed on an OHAUS PIONEER analytical balance with  $0.0001 \text{ g}$  precision and a maximum capacity of  $200 \text{ g}$ . Volumes were measured with GIBSON volumetric pipettes, PIPETMAN P-100, P-200, P-1000 and P-5000 models. The amount used of the samples was dissolved in a mixture of  $3\text{HCl}:\text{HNO}_3$ . The equipment calibration was performed with and without ionization suppressor. Lithium is partially ionized in the flame. To reduce this effect, a KCl ionization suppressant was added, so that its concentration in all standards and samples was  $2000 \mu\text{g mL}^{-1}$ . Data processing was performed by calibration without replicas and calibrated with replicas.

### Results and Discussion

The determination of lithium by flame photometry in the new complex oxides  $\text{Li}_6\text{MgZr}_3\text{O}_{10}$  y  $\text{Li}_6\text{ZnZr}_3\text{O}_{10}$  was carried out in the interest of quantifying the actual amount of lithium. That is, these ceramic materials were obtained at high temperatures and it is possible that a certain amount of lithium has been volatilized. Then, in order to determine the crystalline structure of both compounds, which is carried out by means of a program, for example from Rietveld, an adjustment of the structure is made using a certain known structure model. However, the structural adjustment will be mostly valid and more accurate or accurate if the data or numerical values of the quantities of atoms introduced in the program are the most reliable.

That is, the stoichiometric calculations in obtaining these two complex oxides were to obtain the nominal formula or whole numbers. So with the study by flame photometry, which is the most reliable or preferred technique to determine Li, Na, K, it was possible to know the lithium concentration and therefore calculate the amounts of lithium in each of these new compounds.

### Calibration curve

The lithium concentration was between  $0.0$  and  $1.0, \text{ gL}^{-1}$ . Using a spreadsheet it was shown that these values are randomly distributed, so the residuals  $r$  were  $r = 0.999$  for the analysis of variance. On the other hand the spreadsheet generated the data of the ordinate at the origin, of the slope, as well as the data of the lower interference and the superior interference of the ordinate at the origin include zero and therefore the line was compatible with passing through the origin (Escobedo et al., 2018). When the graphical representation of the measured intensity versus the concentration was made, a straight line was observed, this is observed in figures 4 and 5.

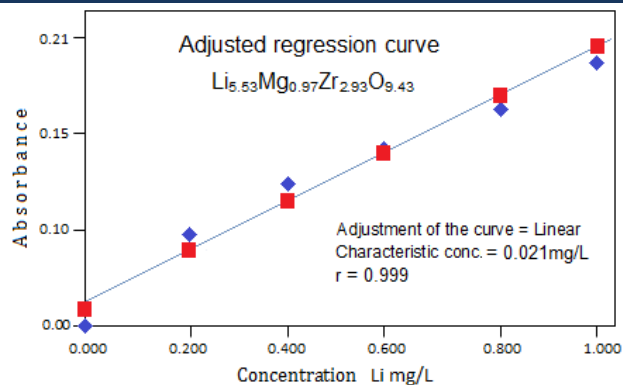


Figure 4. Calibration curve for  $\text{Li}_{5.53}\text{Mg}_{0.97}\text{Zr}_{2.93}\text{O}_{9.43}$ .

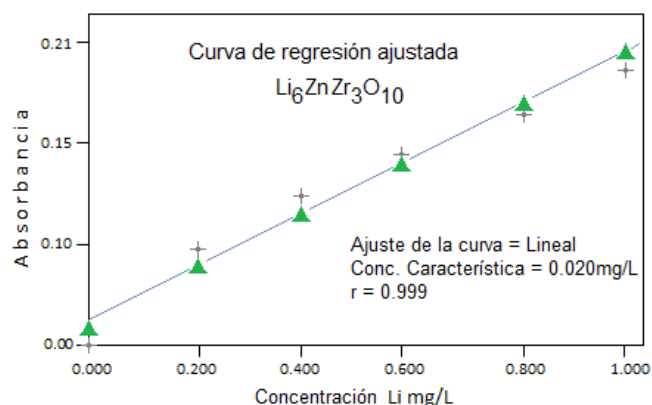


Figure 5. Calibration curve for  $\text{Li}_{5.45}\text{Zn}_{0.96}\text{Zr}_{2.94}\text{O}_{9.35}$ .

### Measurements and results for $\text{Li}_{5.53}\text{Mg}_{0.97}\text{Zr}_{2.93}\text{O}_{9.43}$

Tables 1 and 2 show the measurements obtained, the average absorption and the standard deviation respectively for  $\text{Li}_{5.53}\text{Mg}_{0.97}\text{Zr}_{2.93}\text{O}_{9.43}$ . While table 3 shows the calculated and residual concentrations for  $\text{Li}_{5.53}\text{Mg}_{0.97}\text{Zr}_{2.93}\text{O}_{9.43}$ . Table 4 shows the concentrations compared to the controls for  $\text{Li}_{5.53}\text{Mg}_{0.97}\text{Zr}_{2.93}\text{O}_{9.43}$ .

Table 1. Patterns and readings for obtaining the average Absorption for Lithium in  $\text{Li}_{5.53}\text{Mg}_{0.97}\text{Zr}_{2.93}\text{O}_{9.43}$ .

Sample ID	Li (mg L <sup>-1</sup> )	Measurements		
Pattern	0.0 calibrated	-0.0002	-0.0002	-0.0003
1	0.169	0.1960	0.1660	0.1658
2	0.336	0.1909	0.1709	0.1715
3	0.502	0.1358	0.1058	0.1349
4	0.668	0.1698	0.1408	0.1402
5	0.832	0.1748	0.1748	0.1770
6	1.000	0.4432	0.4131	0.4136

Table 2. Average Absorption and Standard Deviation for Lithium in  $\text{Li}_{5.53}\text{Mg}_{0.97}\text{Zr}_{2.93}\text{O}_{9.43}$ .

Li (mg L <sup>-1</sup> )	Average Absorption	%RSD*
0.0 calibrated	-0.0002	19
0.168	0.0359	0.2
0.334	0.0511	0.3
0.501	0.5055	0.4
0.668	0.5403	0.3
0.834	0.5755	0.6
1.000	0.5132	0.1

%RSD\* Standard deviation

Table 3. Calculated and residual concentrations of Lithium in  $\text{Li}_{5.53}\text{Mg}_{0.97}\text{Zr}_{2.93}\text{O}_{9.43}$ .

-0.001	0.471	0.438	0.499	0.664	0.829	1.008
Residuals:						
0.001	-0.002	-0.002	0.002	0.004	0.004	-0.006

Table 4. Concentrations compared to the controls for Lithium in  $\text{Li}_{5.53}\text{Mg}_{0.97}\text{Zr}_{2.93}\text{O}_{9.43}$ .

	Li (mg L <sup>-1</sup> )		Measurements	
ICB	-0.002	-0.0005	-0.0005	-0.0003
ICV	0.525	0.5076	0.5075	0.5082
Li	0.564	0.0565	0.0566	0.5778
Li	0.564	0.0569	0.0567	0.5763
Control	0.509	0.5071	0.5071	0.5072

To calculate the amount of Lithium atoms in the formula, they were made from the molecular mass of  $\text{Li}_6\text{MgZr}_3\text{O}_{10}$ :

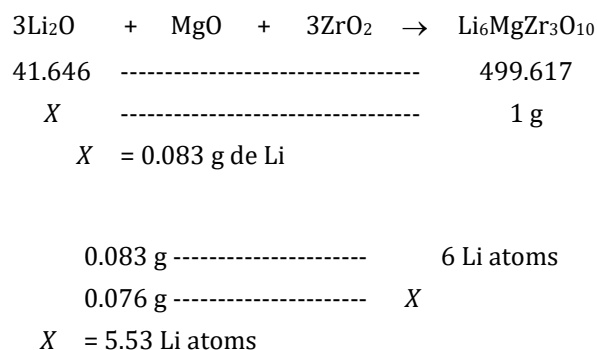
$$\text{Abs} = (0.20079) (C) \times (0.00006)$$

$$= \frac{0.5}{0.525} = 0.953; \quad \frac{100}{0.5} = 200$$

$$\text{Li} = (2.4196\text{mg/Li})(0.953)(200) = 461.18 \text{ mg/L}$$

$$\text{mg/g} = \frac{(461.18\text{mg/L})(0.1\text{L})}{0.1005} = 459.00 \text{ mg/g}$$

For the reaction:



Molecular masses (MM):

MM  $3Li_2 = 41.646$  g/mol

MM  $Li_6MgZr_3O_{10} = 499.617$  g/mol

In each gram of  $Li_6MgZr_3O_{10}$  there is 0.083g of lithium theoretically in six lithium atoms; so at 76.0 mg / g there will be 5.53 lithium atoms. In the same way it was calculated and resolved for Mg and Zr; Table 5 shows the operating parameters, concentration and amount of  $Li_6MgZr_3O_{10}$  atoms.

**Table 5.** Operation parameters and AA results of Mg and Zr for  $Li_{5.53}Mg_{0.97}Zr_{2.93}O_{9.43}$ .

Metal	$\lambda$	Standard solution	Flame	Conc. mg/g	Number of atoms in the formula
Mg	285	200mg/mL $Zn(NO_3)_2$	aire/ $C_2H_2$	46.5	0.97
Zr	360	$ZrCl_4$ 1000 $\mu$ g/mL	$N_2O$ / $C_2H_2$	178	2.93

$\lambda$  = Wavelength

As far as the nominal formula  $Li_6MgZr_3O_{10}$ , it was possible to determine the number of atoms of each of the metal elements by FAAS and EAA, thus obtaining the adjusted formula of  $Li_{5.53}Mg_{0.97}Zr_{2.93}O_{9.43}$ .

### Measurements and results for $Li_{5.45}Zn_{0.96}Zr_{2.94}O_{9.35}$

Tables 6 and 7 show the measurements obtained, the average absorption and the standard deviation respectively for  $Li_{5.45}Zn_{0.96}Zr_{2.94}O_{9.35}$ .

Tables 6 and 7 show the measurements obtained, the average absorption and the standard deviation respectively for  $Li_{5.45}Zn_{0.96}Zr_{2.94}O_{9.35}$ . While table 8 shows the calculated and residual concentrations for  $Li_{5.45}Zn_{0.96}Zr_{2.94}O_{9.35}$ . Table 9 shows the concentrations compared to the controls for  $Li_{5.45}Zn_{0.96}Zr_{2.94}O_{9.35}$ .

**Table 6.** Patterns and readings for obtaining the average Absorption for Lithium in  $Li_{5.45}Zn_{0.96}Zr_{2.94}O_{9.35}$ .

Sample ID	Li (mg L <sup>-1</sup> )	Measurements		
Pattern	0.0 calibrated	-0.0002	-0.0002	-0.0003
1	0.167	0.0359	0.0359	0.0357
2	0.333	0.0708	0.0710	0.0714
3	0.500	0.1057	0.1058	0.1048
4	0.667	0.1397	0.1407	0.1401
5	0.833	0.1747	0.1747	0.1769
6	1.000	0.2131	0.2130	0.2135

**Table 7.** Average Absorption and Standard Deviation for Lithium in  $Li_{5.45}Zn_{0.96}Zr_{2.94}O_{9.35}$ .

Li (mg L <sup>-1</sup> )	Average Absorption	%RSD*
0.0 calibrated	-0.0002	19
0.167	0.0358	0.3
0.333	0.0710	0.4
0.500	0.1054	0.5
0.667	0.1402	0.4
0.833	0.1754	0.7
1.000	0.2132	0.1

%RSD\* Standard deviation

**Table 8.** Calculated and residual concentrations of Lithium in  $Li_{5.45}Zn_{0.96}Zr_{2.94}O_{9.35}$ .

-0.001	0.170	0.336	0.498	0.662	0.828	1.007
Residuals:						
0.001	-0.003	-0.002	0.002	0.005	0.005	-0.007

**Table 9.** Concentrations compared to the controls for Lithium in  $Li_{5.45}Zn_{0.96}Zr_{2.94}O_{9.35}$ .

	Li (mg L <sup>-1</sup> )	Measurements		
ICB	-0.002	-0.0005	-0.0005	-0.0003
ICV	0.509	0.1075	0.1074	0.1081
Li	0.363	0.0764	0.0765	0.0777
Li	0.362	0.0769	0.0766	0.0762
Control	0.506	0.1070	0.1070	0.1071

To calculate the amount of Lithium atoms in the formula, they were made from the molecular mass of  $Li_6ZnZr_3O_{10}$ :

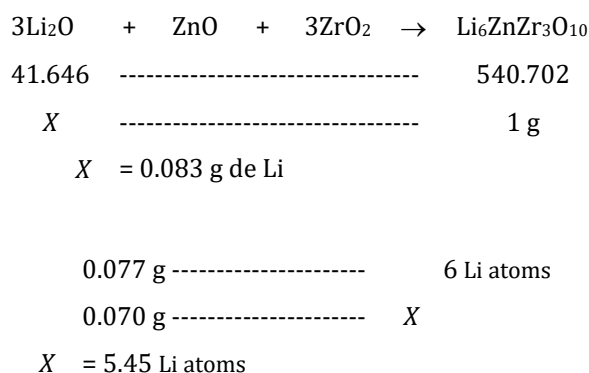
$$Abs = (0.21182) (C) \times (0.00006)$$

$$= \frac{0.5}{0.508} = 0.984; \quad \frac{100}{0.5} = 200$$

$$Li = (0.364 \text{ mg/Li})(0.984)(200) = 71.635 \text{ mg/L}$$

$$\text{mg/g} = \frac{(71635 \text{ mg/L})(0.1L)}{0.1016} = 70.506 \text{ mg/g}$$

For the reaction:



MM  $3\text{Li}_2 = 41.646 \text{ g/mol}$   
MM  $\text{Li}_6\text{ZnZr}_3\text{O}_{10} = 540.702 \text{ g/mol}$

In each gram of  $\text{Li}_6\text{ZnZr}_3\text{O}_{10}$  there is 0.077g of lithium theoretically in six lithium atoms; so at 70.101 mg/g there will be 5.45 lithium atoms. In the same way it was calculated and resolved for Zn and Zr in  $\text{Li}_6\text{ZnZr}_3\text{O}_{10}$ . Table 10 shows the operating parameters, concentration and atoms amount of Zn, Zr in  $\text{Li}_6\text{ZnZr}_3\text{O}_{10}$ .

**Table 10.** Operation parameters and AA results of Zn and Zr in para  $\text{Li}_6\text{ZnZr}_3\text{O}_{10}$ .

Metal	$\lambda$	Standard solution	Flame	Conc. mg/g	Number of atoms in the formula
Zn	214	200 mg/mL $\text{ZnCl}_2$	aire/ $\text{C}_2\text{H}_2$	116.2	0.96
Zr	360	$\text{ZrCl}_4$ 1000 $\mu\text{g/mL}$	$\text{N}_2\text{O}/$ $\text{C}_2\text{H}_2$	166	2.94

$\lambda$  = Wavelength

The accuracy of the spectrometric method used for the analytical determination of lithium was verified by analyzing the standard reference material of  $\text{Li}_2\text{CO}_3$  from Merck with number 4095-1000291. The results obtained in this study are presented in table 11 showing the certified and theoretical values of the average concentration, plus minus the standard deviation in milligrams per liter; as well as relative errors lower than 5% implying accuracy levels of  $100 \pm 5\%$ . In this regard, no statistically significant differences were found between them, evidencing the adequate accuracy in the analytical determinations.

**Studies of accuracy, precision, equation parameters in calibration and sensitivity curves for  $\text{Li}_{5.53}\text{Mg}_{0.97}\text{Zr}_{2.93}\text{O}_{9.43}$  y  $\text{Li}_{5.45}\text{Zn}_{0.96}\text{Zr}_{2.94}\text{O}_{9.35}$**

**Table 11.** Accuracy study for the total determination of lithium in  $\text{Li}_{5.53}\text{Mg}_{0.97}\text{Zr}_{2.93}\text{O}_{9.43}$  and  $\text{Li}_{5.45}\text{Zn}_{0.96}\text{Zr}_{2.94}\text{O}_{9.35}$  by FAAS.

Certified material	Metal	Litio average conc. $\pm$ DE, mg/L		Relative error (%)
$\text{Li}_2\text{CO}_3$ Merck # 4095- 1000291	Li	certified value	Experimental value	(%)
		76.450 + 0.347 -0.277	$76.0 \pm 0.320$ $\text{Li}_{5.53}\text{Mg}_{0.97}\text{Zr}_{2.93}\text{O}_{9.43}$	0.2
		70.0 + 0.752 -0.295	$70.101 \pm 0.551$ $\text{Li}_{5.45}\text{Zn}_{0.96}\text{Zr}_{2.94}\text{O}_{9.35}$	0.195

The precision study in runs for repeatability, expressed by standard deviation (SD, in mg/L) and relative standard deviation (DER in %). The samples were prepared in triplicate and three aliquots of 10 mL. The spectrometric determinations of Li were made by five times. The average DER was 0.54% in the study of analytical repeatability in the two compounds

and  $\text{Li}_{5.53}\text{Mg}_{0.97}\text{Zr}_{2.93}\text{O}_{9.43}$  and  $\text{Li}_{5.45}\text{Zn}_{0.96}\text{Zr}_{2.94}\text{O}_{9.35}$ ; and analytical reproducibility the mean DER for Li was 2.17% in both  $\text{Li}_{5.53}\text{Mg}_{0.97}\text{Zr}_{2.93}\text{O}_{9.43}$  and  $\text{Li}_{5.45}\text{Zn}_{0.96}\text{Zr}_{2.94}\text{O}_{9.35}$ . These results show that the analytical methods used were reproducible and suitable for the determination of lithium in  $\text{Li}_{5.53}\text{Mg}_{0.97}\text{Zr}_{2.93}\text{O}_{9.43}$  and  $\text{Li}_{5.45}\text{Zn}_{0.96}\text{Zr}_{2.94}\text{O}_{9.35}$ . Table 12 shows the precision statistics for the determination of Lithium in  $\text{Li}_{5.53}\text{Mg}_{0.97}\text{Zr}_{2.93}\text{O}_{9.43}$  and  $\text{Li}_{5.45}\text{Zn}_{0.96}\text{Zr}_{2.94}\text{O}_{9.35}$  by FAAS.

**Table 12.** Precision study for the determination of Lithium in  $\text{Li}_{5.53}\text{Mg}_{0.97}\text{Zr}_{2.93}\text{O}_{9.43}$  y  $\text{Li}_{5.45}\text{Zn}_{0.96}\text{Zr}_{2.94}\text{O}_{9.35}$  por FAAS.

Metal	Average con. (mg/L)	In the measurement (Analytical Repetitiveness)		Between measurements (Analytical reproducibility)	
		DE (mg/L)	DER (%)	DE (mg/L)	DER (%)
Li en (a)	0.76	0.0002	0.06	0.009	2.07
	0.72	0.0043	0.78	0.012	2.14
	0.76	0.0071	0.77	0.016	2.38
Li en (b)	0.69	0.0002	0.05	0.008	2.05
	0.701	0.0040	0.77	0.011	2.11
	0.701	0.0070	0.79	0.017	2.36

It is very favorable to show table 13, in which a recovery study is presented for the determination of Lithium in samples of (a)  $\text{Li}_{5.53}\text{Mg}_{0.97}\text{Zr}_{2.93}\text{O}_{9.43}$  and (b)  $\text{Li}_{5.45}\text{Zn}_{0.96}\text{Zr}_{2.94}\text{O}_{9.35}$  by FAAS.

**Table 13.** Recovery study for the determination of Lithium in samples of (a)  $\text{Li}_{5.53}\text{Mg}_{0.97}\text{Zr}_{2.93}\text{O}_{9.43}$  and (b)  $\text{Li}_{5.45}\text{Zn}_{0.96}\text{Zr}_{2.94}\text{O}_{9.35}$  by FAAS.

Metal	Conc. (mg/L)	Adicionado (mg/L)	Expected (mg/L)	Found (mg/L)	Error (%)
Li en (a)	0.76	0.50	1.23	1.24	90.6
		1.52	2.28	2.22	97.4
		2.50	3.28	3.30	97.6
$X \pm \text{DE}: 97.77 \pm 2.35$					
Li en (b)	0.701	0.50	1.25	1.27	85.7
		1.55	2.30	2.24	97.4
		2.55	3.30	3.32	97.6
$X \pm \text{DE}: 98.85 \pm 2.38$					

The analytical quantification of the calibration curve is widely used in the FAAS to know the optimal linear working interval for each chemical element studied. The optimization of the calibration curve for Li, allowed to delimit the optimal linear working interval; in this case it was from 0.0 to 76 mg Li/L.

The linear equation of the calibration curves for Li was:  $A = 0.1528c + 0.0244$  ( $r = 0.9995$ ), thus these values were significant for the coefficient of linear correlation of Pearson ( $r$ ). Table 14 shows the values obtained for the parameters of the equation in the calibration curve and

in the standard addition curve in the total determination of Lithium in (a)  $\text{Li}_{5.53}\text{Mg}_{0.97}\text{Zr}_{2.93}\text{O}_{9.43}$  and (b)  $\text{Li}_{5.45}\text{Zn}_{0.96}\text{Zr}_{2.94}\text{O}_{9.35}$  by FAAS.

**Table 14.** Values obtained for the parameters of the equation in the calibration curve and in the standard addition curve in the total lithium determination in (a)  $\text{Li}_{5.53}\text{Mg}_{0.97}\text{Zr}_{2.93}\text{O}_{9.43}$  and (b)  $\text{Li}_{5.45}\text{Zn}_{0.96}\text{Zr}_{2.94}\text{O}_{9.35}$  by FAAS.

Metal	Calibration Curve Equation	Standard Addition Curve Equation	Error (%)
Li in (a)	$A = 0.1529c + 0.0008$ $r = 0.9998$	$A = 0.0420c + 0.0078$ $r = 0.9997$	0.15
Li in (b)	$A = 0.0419c + 0.0024$ $r = 0.9995$	$A = 0.0426c + 0.0022$ $r = 0.9996$	0.13

The value of the detection limit was expressed three times in the standard deviation of the target, 3s; was 0.01 mg/L for the Li. The value of the limit of quantification was expressed ten times in the standard deviation of the target, 10s; which was 0.0333 mg/L for Li.

The characteristic concentration (Cc) of the lithium required to produce an absorption of 1% which is equivalent to a signal of 0.0044 absorbance units, was 0.021 mg/L for Li. Table 15 indicates the Limits of detection, quantification and instrumental sensitivity for the total determination of Lithium in  $\text{Li}_{5.53}\text{Mg}_{0.97}\text{Zr}_{2.93}\text{O}_{9.43}$  and  $\text{Li}_{5.45}\text{Zn}_{0.96}\text{Zr}_{2.94}\text{O}_{9.35}$  by FAAS.

**Table 15.** Limits of detection, quantification and instrumental sensitivity of Lithium in  $\text{Li}_{5.53}\text{Mg}_{0.97}\text{Zr}_{2.93}\text{O}_{9.43}$  and  $\text{Li}_{5.45}\text{Zn}_{0.96}\text{Zr}_{2.94}\text{O}_{9.35}$  by FAAS.

Limits and conc.	$\text{Li}_{5.53}\text{Mg}_{0.97}\text{Zr}_{2.93}\text{O}_{9.43}$	$\text{Li}_{5.45}\text{Zn}_{0.96}\text{Zr}_{2.94}\text{O}_{9.35}$
Detection limit <sup>a</sup> (mg/L)	0.0002 (0.00001) [Ca.0.00002 (0.00001)] <sup>c</sup>	0.0090(0.00030) [ca.0.00100 (0.00004)] <sup>c</sup>
Limit of quantification (mg/L)	0.0654	0.0333
Characteristic concentration <sup>b</sup> (mg/L)	0.0655 (0.065)	0,0282 (0,031)

<sup>a</sup>The values in parentheses were taken from (Shalbuyeva et al., 2007).

<sup>b</sup>The values in parentheses were taken from (Hyo et al., 2003).

<sup>c</sup>En mEq/L.

## Conclusions

The method developed by flame photometry or FAAS was used to determine the concentration of Li in samples of two new ceramic materials or complex oxides  $\text{Li}_6\text{MgZr}_3\text{O}_{10}$  and  $\text{Li}_6\text{ZnZr}_3\text{O}_{10}$ . By knowing the concentration of Lithium it was possible to determine the correct formula for these two ceramic materials, that is:  $\text{Li}_{5.53}\text{Mg}_{0.97}\text{Zr}_{2.93}\text{O}_{9.43}$  and  $\text{Li}_{5.45}\text{Zn}_{0.96}\text{Zr}_{2.94}\text{O}_{9.35}$ . From these results we will proceed to determine the crystalline structure of both compounds.

It is paper mentioning that ceramic materials are generally obtained at elevated temperatures, above 1000°C. In this particular case, the two compounds contain lithium, which could happen is that at high temperatures the lithium volatilizes, so, when ignoring this loss, the determination of the crystalline structure would not be correct.

The determined values could be expressed in mEq/L units, which is an appropriate concentration. An average value of  $76 \pm 320$  mg Li/L  $\text{Li}_{5.53}\text{Mg}_{0.97}\text{Zr}_{2.93}\text{O}_{9.43}$ ; and  $70.101 \pm 0.551$ mg Li/L for  $\text{Li}_{5.45}\text{Zn}_{0.96}\text{Zr}_{2.94}\text{O}_{9.35}$ . The statistical data determined, such as, mean, standard deviation, coefficient of variation, etc. for the total concentration of Li, they helped the validation of the Atomic flame absorption spectrometry (FAAS) method in these two ceramic materials. So this method could be used to reliably know the concentration of Lithium in other ceramic compounds containing this chemical element.

In addition, the methods used were free of non-spectral interferences, presenting adequate levels of detection, quantification and analytical sensitivity.

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