

# Speciation of calcium in ternary mixtures of calcium compounds by flame atomic absorption spectrometry and slurry atomization

*Adela R. Mauri, R. Martínez-Avila, Amparo Salvador and Miguel de la Guardia\**  
Department of Analytical Chemistry, University of Valencia 50 Dr. Moliner St. E46100  
Burjassot (Valencia), Spain

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## Abstract

A method for the determination of Ca in ternary mixtures of dissolved calcium and undissolved  $\text{Ca}(\text{OH})_2$  and  $\text{Ca}_3(\text{PO}_4)_2$  by flame atomic absorption spectrometry and slurry atomization has been developed. This method is based on the different behaviour of Ca slurries and aqueous solutions of Ca. The speciation of calcium is carried out from the determination of the total content of Ca and the use of the absorbance values at two burner heights. Accuracy, relative errors found, using an air/ $\text{C}_2\text{H}_2$  flame, are lower than 10 per cent.

**Key words:** Calcium hydroxide; calcium phosphate; calcium speciation; flame atomic absorption analysis; slurry atomization.

## Especiación del calcio en mezclas ternarias de componentes de calcio por espectrometría de absorción atómica con llama y atomización de suspensión

### Resumen

Se presenta el desarrollo de un método para la determinación de Ca en mezclas ternarias de calcio disuelto y de  $\text{Ca}(\text{OH})_2$  y  $\text{Ca}_3(\text{PO}_4)_2$  sin disolver, usando espectrometría de absorción atómica con llama y atomización de la suspensión. El método se fundamenta en el comportamiento diferente de las suspensiones de Ca con respecto a las soluciones acuosas de Ca. La especiación del Ca se realizó a partir de la determinación del contenido total de Ca y del uso de los valores de absorbancia a dos alturas del quemador. La exactitud y los errores relativos encontrados, usando una llama de aire/ $\text{C}_2\text{H}_2$ , son menores al 10%.

**Palabras claves:** Análisis por absorción atómica con llama; atomización de suspensión; especiación del calcio; fosfato de calcio; hidróxido de calcio.

### Introduction

It is well known that the slurry introduction of solids in atomic spectrometry provides a direct analysis of samples without prior matrix decomposition (1-3). However, small particle size dispersed solids are necessary in order to obtain atomization

yields of the elements to be determined comparable to those found for dissolved ones (4-6).

Studies carried out on the atomization of slurries have demonstrated that the absorbance measurements obtained of large size dispersed solids depend more on the

\* Corresponding author.

nature of the compounds dispersed than on the sample size (7). This fact could be employed for the speciation of different compounds present in the same sample in dissolved and undissolved forms.

In this paper the speciation of calcium in mixtures of ionic calcium, and undissolved  $\text{Ca}(\text{OH})_2$  and  $\text{Ca}_3(\text{PO}_4)_2$  has been carried out after a prior determination of the total content of calcium in the sample, and using calibration curves corresponding to each one of the compounds considered. The absorbance of samples and standards is measured in two different experimental conditions, in order to obtain a system of three equations with three unknowns which provides the determination of the concentration of each one of the components of the sample. This is similar to the methods employed in other cases for the speciation of lead additives (8,9) and the multicomponent analysis of lanthanides (10).

The ternary system studied in the present paper is very important from an environmental point of view, because the presence of ionic calcium in natural waters acts as a protective agent against the increase of phosphates by means of the precipitation of  $\text{Ca}_3(\text{PO}_4)_2$  and, the presence of  $\text{Ca}(\text{OH})_2$  is a consequence of the alkaline pH of a series of natural waters.

## Experimental

### Apparatus

A Shimadzu Model AA-660 atomic absorption spectrometer equipped with a multi-element hollow cathode lamp of Al, Ca, Mg, Fe, Cu and Si, and two conventional burners for air/ $\text{C}_2\text{H}_2$  and  $\text{N}_2\text{O}/\text{C}_2\text{H}_2$  flame was employed to carry out the absorbance measurements.

The instrumental conditions used are shown in Table 1. The burner heights and flow rates of air/ $\text{C}_2\text{H}_2$  and  $\text{N}_2\text{O}/\text{C}_2\text{H}_2$  were optimized in each case in order to obtain experimental conditions at which the cal-

Table 1  
Instrumental conditions for flame atomic absorption spectrometric determination of calcium

Instrumental conditions	Air/ $\text{C}_2\text{H}_2$	$\text{N}_2\text{O}/\text{C}_2\text{H}_2$
l/nm	422.7	422.7
i/mA	12	12
Slit/nm	0.5	0.5
Aspiration flow/mL/min	5.8	3.0

cium compounds considered provided different sensitivities.

### Reagents

The stock solution of 100 mg/L of calcium was prepared from 2.4973 g of  $\text{CaCO}_3$  (Probus), dissolved in 25 mL of 1M HCl and diluted with distilled water to 1 L.

Stock slurries of 100 mg/L of calcium as  $\text{Ca}_3(\text{PO}_4)_2$  and 100 mg/L of calcium as  $\text{Ca}(\text{OH})_2$  were prepared from  $\text{Ca}_3(\text{PO}_4)_2$  (Rhône-Poulenc) and  $\text{Ca}(\text{OH})_2$  (Merck), respectively, by dispersion in water of a fixed quantity of each compound (with an average particle size of 200  $\mu\text{m}$ ) using an ultrasound bath to obtain a good dispersion.

Stock solution of 10% of lanthanum was prepared from  $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$  (Panreac), dissolved in distilled water, and used to avoid the calcium ionization in hot flames. 10 g/L of lanthanum was added to the diluted standards of each of the three calcium compounds.

### General Procedure

Flame profiles were obtained for both types of flame (air/ $\text{C}_2\text{H}_2$  and  $\text{N}_2\text{O}/\text{C}_2\text{H}_2$ ) and for all species of calcium studied. The calibration curves were prepared in the

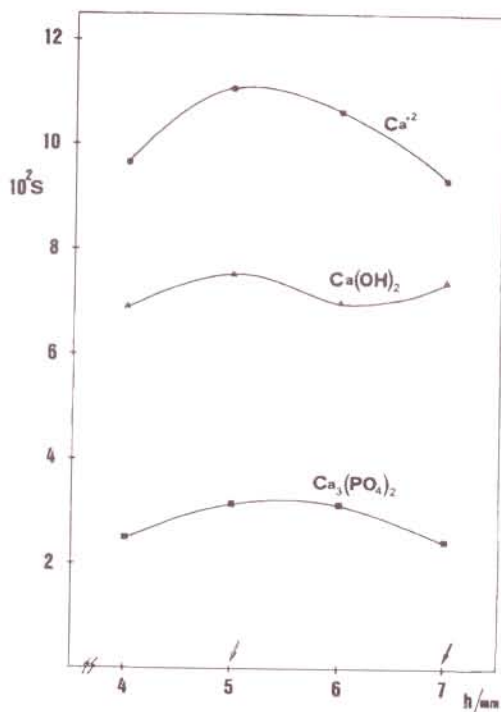


Figure 1. Flame profiles for the atomization of calcium compounds in an air-acetylene flame.  $S$ =sensitivity expressed as the quotient between absorbance and calcium concentration in mg/L. Concentration of  $\text{Ca}^{2+}$  2 mg/L,  $\text{Ca}_3(\text{PO}_4)_2$  1.9 mg/L and  $\text{Ca}(\text{OH})_2$  1.8 mg/L. Acetylene flow rate 2 L/min and air flow rate 10 L/min.

range from 0 to 4 mg/L, by dilution of the corresponding stock solutions. Synthetic samples, containing different amounts of dissolved calcium, and dispersed  $\text{Ca}_3(\text{PO}_4)_2$ , and  $\text{Ca}(\text{OH})_2$ , were analyzed.

The absorbance measurements were obtained for samples and standards in two experimental conditions, previously selected from the flame profiles. The concentration of each species of calcium was determined by using the corresponding equations, in which the regression parameters correspond to those found for pure stand-

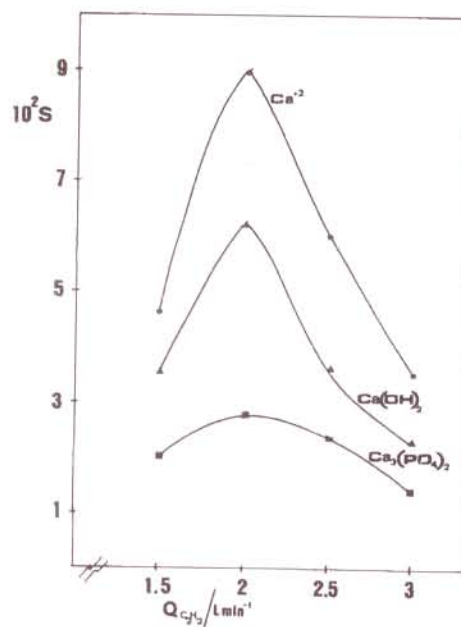


Figure 2. Effect of the acetylene flow on the absorbance of calcium compounds in an air-acetylene flame.  $S$ =sensitivity expressed as the quotient between absorbance and calcium concentration in mg/L. Concentration of  $\text{Ca}^{2+}$  2 mg/L,  $\text{Ca}_3(\text{PO}_4)_2$  1.9 mg/L and  $\text{Ca}(\text{OH})_2$  1.8 mg/L. Air flow rate 10 L/min and burner height 6 mm.

ards of each one of the species considered. A third equation was obtained from the independent determination of the total content of calcium in the sample considered, which corresponds to the sum of the three species concentrations.

## Results and discussion

### Flame Profile

As it can be seen in Figures 1 and 2, a burner height of 5 mm and a flow rate of 2 L/min of  $\text{C}_2\text{H}_2$  provide the maximum sensitivity for all three species of calcium considered in the air/ $\text{C}_2\text{H}_2$  flame.



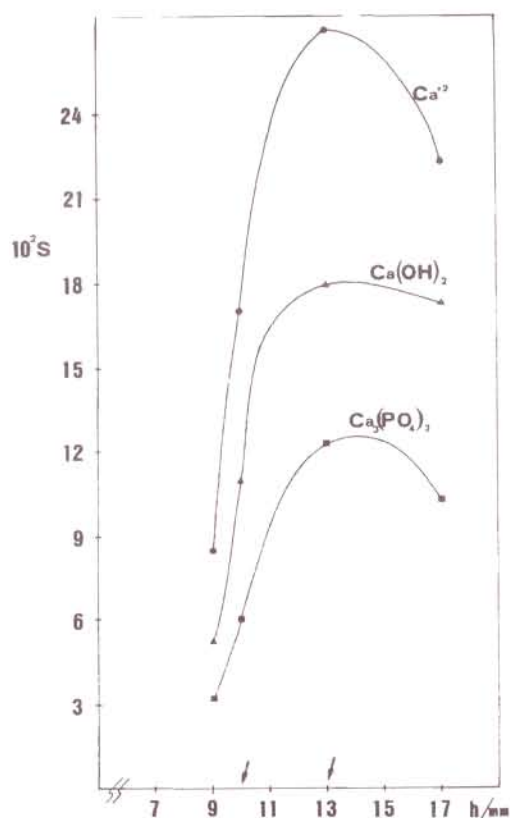


Figure 3. Flame profiles for the atomization of calcium compounds in a nitrous oxide-acetylene flame.  $S$ =sensitivity expressed as the quotient between absorbance and calcium concentration in mg/L. Concentration of  $\text{Ca}^{2+}$  2 mg/L,  $\text{Ca}_3(\text{PO}_4)_2$  1.9 mg/L and  $\text{Ca}(\text{OH})_2$  1.8 mg/L. Acetylene flow rate 6 L/min and nitrous oxide flow rate 7.5 L/min.

Figure 3 shows that a burner height of 13 mm provides the maximum sensitivity for all species in an  $\text{N}_2\text{O}/\text{C}_2\text{H}_2$  flame. However the best  $\text{N}_2\text{O}$  flow rate is different for ionic calcium than that for slurries. A flow rate of 7.85 L/min provides the best sensitivity for dissolved calcium whereas a flow rate of 8.2 L/min of  $\text{N}_2\text{O}$  seems to be optimum for slurries of  $\text{Ca}_3(\text{PO}_4)_2$  and  $\text{Ca}(\text{OH})_2$  (Figure 4).

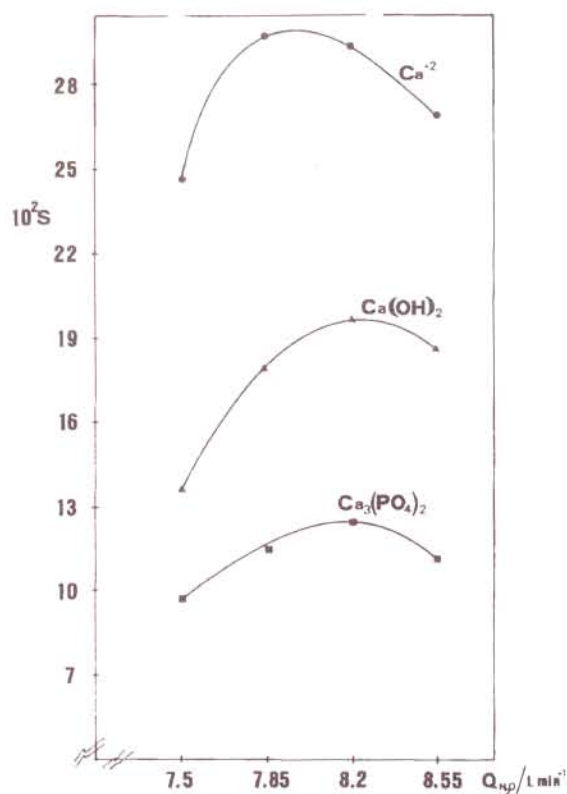


Figure 4. Effect of the acetylene flow on the absorbance of calcium compounds in a nitrous oxide-acetylene flame.  $S$ =sensitivity expressed as the quotient between absorbance and calcium concentration in mg/L. Concentration of  $\text{Ca}^{2+}$  2 mg/L,  $\text{Ca}_3(\text{PO}_4)_2$  1.9 mg/L and  $\text{Ca}(\text{OH})_2$  1.8 mg/L. Acetylene flow rate 6 L/min and burner height 13 mm.

### Analysis of ternary mixtures

To obtain accurate results in the analysis of ternary mixtures it is necessary to have three independent equations which relate experimental data with the concentration of the three species considered in the same sample. However, it is not easy to find three experimental conditions at which the behavior of the three compounds is different

Table 2  
Conditions selected for the speciation of calcium

Condition	Flame	Burner height (mm)	Fuel flow (L/min)	Oxidant flow (L/min)	$\alpha$
A	Air/C <sub>2</sub> H <sub>2</sub>	5	2	10	0
B	Air/C <sub>2</sub> H <sub>2</sub>	7	2	10	0
C	N <sub>2</sub> O-C <sub>2</sub> H <sub>2</sub>	10	6	7.85	0
D	N <sub>2</sub> O-C <sub>2</sub> H <sub>2</sub>	13	6	8.2	15

$\alpha$  = burner angles

and thus it is better to use the total concentration of calcium in the samples and two absorbance values obtained at different conditions.

One of the possibilities offered by the use of two flames, in the determination of calcium by flame atomic absorption spectrometry, is to determine the absorbance of samples and standards at the best experimental conditions by using both flames. The concentration of Ca<sup>2+</sup>, Ca(OH)<sub>2</sub> and Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> can be evaluated from the total concentration of calcium and the two equations obtained, which relate the absorbance of the sample with the concentration of each compound and the relative sensitivity corresponding to each one in the working conditions.

However, it is well known that the major problem in speciation studies in flame atomic absorption spectrometry is the stability of the experimental measurements (8, 10).

As a result, it could be preferable to use different parameters with the same flame than to use different flames, in order to avoid the burner change. However, the use of the air/C<sub>2</sub>H<sub>2</sub> flame could be more interesting than that of N<sub>2</sub>O/C<sub>2</sub>H<sub>2</sub> due to the higher stability of cooler flames. An additional aspect, to take into account, in order to select the appropriate conditions, is that more reproducible experimental values

were obtained in the determination of the burner height than for the measurement of the acetylene flow, because the exact position of the burners is easily determined being the control of the flow in our instrument less precise (a simple rotameter was used).

In Figures 1 and 3 the values of the burner height selected for each flame are indicated and in Table 2 the values of the experimental parameters employed in each case are summarized.

When absorbance measurements were obtained using conditions D, it was necessary to rotate the burner 15° in order to work in a linear range.

As seen in Table 3, the sensitivities obtained for the determination of each compound in the four conditions employed were sufficiently different to carry out speciation studies.

In this way, two equations were obtained:

$$A_s = a_{Ca^{2+}} \cdot C_{Ca^{2+}} + b_{Ca(OH)_2} \cdot C_{Ca(OH)_2} + c_{Ca_3(PO_4)_2} \cdot C_{Ca_3(PO_4)_2} \quad [1]$$

working with one set of the experimental conditions selected and

$$A'_s = a'_{Ca^{2+}} \cdot C_{Ca^{2+}} + b'_{Ca(OH)_2} \cdot C_{Ca(OH)_2} + c'_{Ca_3(PO_4)_2} \cdot C_{Ca_3(PO_4)_2} \quad [2]$$

Table 3  
Analytical parameters of the developed procedure

Atomization system (condition)	Calibration line								
	Ca <sup>2+</sup>			Ca(OH) <sub>2</sub>			Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>		
	Equation and regression coefficient	LOD (mg/L)	C.V. (%)	Equation and regression coefficient	LOD (mg/L)	C.V. (%)	Equation and regression coefficient	LOD (mg/L)	C.V. (%)
Air-C <sub>2</sub> H <sub>2</sub> (A)	A=0.14+0.1300 C r = 0.9998	0.06	1	A=0.013+0.0951 C r = 0.9991	0.04	0.7	A=0.006+0.0357 C r = 0.9991	0.3	6
Air-C <sub>2</sub> H <sub>2</sub> (B)	A=0.20+0.0971 C r = 0.9996	0.1	1.8	A=0.014+0.0683 C r = 0.998	0.2	2.9	A=0.002+0.0267 C r = 0.991	0.3	6
N <sub>2</sub> O-C <sub>2</sub> H <sub>2</sub> (C)	A=0.032+0.1177 C r = 0.9992	0.07	1	A=0.003+0.1000 C r = 0.997	0.06	1	A=-0.004+0.0364 C r = 0.996	0.2	3
N <sub>2</sub> O-C <sub>2</sub> H <sub>2</sub> (D)	A=-0.004+0.0817 C r = 0.997	0.06	1	A=-0.003+0.0497 C r = 0.998	0.05	1	A=-0.002+0.0269 C r = 0.998	0.22	3

Note:

LOD: Limit of detection

C.V. : Coefficient of variation of 10 independent measurements of a standard solution containing 2 mg/L



working in another set of conditions;  $A_S$  and  $A'_S$  being the experimental absorbance values obtained for the same sample in both conditions considered, and  $a, b, c$  and  $a', b', c'$  the slopes of the calibration lines corresponding to each compound considered, measured in each one of the conditions selected.

The total concentration of calcium could be expressed as:

$$C_T = C_{Ca^{2+}} + C_{Ca(OH)_2} + C_{Ca_3(PO_4)_2} \quad [3]$$

and so a system with three equations and three unknowns can be written as follows:

$$\begin{pmatrix} A_S \\ A'_S \\ C_T \end{pmatrix} = \begin{pmatrix} a_{Ca^{2+}} & b_{Ca(OH)_2} & c_{Ca_3(PO_4)_2} \\ a'_{Ca^{2+}} & b'_{Ca(OH)_2} & c'_{Ca_3(PO_4)_2} \\ 1 & 1 & 1 \end{pmatrix} \begin{pmatrix} C_{Ca^{2+}} \\ C_{Ca(OH)_2} \\ C_{Ca_3(PO_4)_2} \end{pmatrix} \quad [4]$$

In previous works (8-9), we considered a weighted contribution of the intercepts of the calibration lines. In this case, best results were obtained without considering the intercepts, as observed in the multicomponent analysis of lanthanide elements (10).

### Analytical parameters of the developed procedure

The figures of merit of the proposed method are shown in Table 3; the sensitivity, limit of detection and precision of the determination of the different calcium compounds in each one of the experimental conditions assayed are given. The analytical sensitivity obtained for the flame atomic absorption spectrometric determination of dissolved calcium is better than that found for the  $Ca(OH)_2$  slurries and the sensitivity found for  $Ca(OH)_2$  slurries is three-times higher than that obtained for  $Ca_3(PO_4)_2$ .

### Analysis of synthetic samples

A series of samples were analyzed using different conditions and results obtained are summarized in Table 4. As it can

be seen when only an air/ $C_2H_2$  flame is employed results obtained are more accurate, being the relative errors found lower than 10% in all cases.

The use of absorbance values obtained in an air/ $C_2H_2$  and an  $N_2O/C_2H_2$ , or the use of absorbance readings obtained in only  $N_2O/C_2H_2$  flame, provide less accurate results as a consequence of the lower stability and the higher background observed in hot flames.

From results obtained it can be concluded that the speciation of ionic calcium, and  $Ca(OH)_2$  and  $Ca_3(PO_4)_2$  is possible if the absorbance measurements obtained in two experimental conditions provide sensitivity values for these three species which are sufficiently different.

On the other hand it is necessary to have a good stability of the absorbance readings in order to obtain experimental values for samples and standards in comparable conditions.

### Explanation of the mechanism involved

The fact that aqueous solutions of  $Ca^{2+}$  provide higher sensitivity than slurries of calcium hydroxide and calcium phosphate is due to the bad atomization, into the flame, of dispersed solid particles with a size higher than  $1 \mu m$  and, because of that, the absorbance values found in the latter case are really due to the residual solubility of  $Ca(OH)_2$  and  $Ca_3(PO_4)_2$ , which is a function of their respective solubility products.

The leaching of  $Ca^{2+}$  from slurries of  $Ca(OH)_2$  corresponds to 75% of the total calcium concentration and the leaching from slurries of  $Ca_3(PO_4)_2$  corresponds to 30% of the total calcium concentration. These values are independent of the temperature of the flame, as shown by comparing the data obtained for regression lines found for the different chemical forms of calcium considered by using different con-

Table 4  
Analysis of synthetic samples of  $\text{Ca}^{2+}$ ,  $\text{Ca}(\text{OH})_2$  y  $\text{Ca}_3(\text{PO}_4)_2$

Conditions Sample	Concentration (mg/L)											
	Total			$\text{Ca}_3(\text{PO}_4)_2$			$\text{Ca}(\text{OH})_2$			$\text{Ca}^{2+}$		
	Added	Found	$\epsilon_r$ (%)	Added	Found	$\epsilon_r$ (%)	Added	Found	$\epsilon_r$ (%)	Added	Found	$\epsilon_r$ (%)
A and B 1	4.7	1.9	2.0	5.3	1.8	1.7	-5.5	1	1	0		
A and B 2	3.8	0.9	0.8	-11	0.9	0.8	-11.1	2	2.3	15		
A and B 3	3.7	0.9	0.9	0	1.8	1.7	-5.5	1	1.1	10		
A and B 4	4.8	1.9	1.9	0	0.9	0.8	-11.1	2	2	0		
A and B 5	2.8	0.9	0.9	0	0.9	0.8	-11.1	1	1.1	10		
A and B 6	5.7	1.9	1.9	0	1.8	1.6	-11.1	2	2.2	10		
A and B 7	4.7	0.9	0.9	0	1.8	2.0	11.1	2	1.9	-5		
A and C 3	3.7	0.9	0.9	0	1.8	1.9	5.5	1	1.9	-10		
A and C 7	4.7	0.9	1.0	11	1.8	1.6	-11.1	2	2.2	10		
B and C 1	4.7	1.9	1.9	0	1.8	2.0	11.1	1	0.8	-20		
B and D 1	4.7	1.9	2.0	5.2	1.8	1.7	-5.5	1	1.0	0		
B and D 5	2.8	0.9	0.9	0	0.9	0.8	-11.1	1	1.1	10		
B and D 7	4.7	0.9	0.9	0	1.8	1.8	0	2	2.0	0		
C and D 1	4.7	1.9	1.9	0	1.8	1.8	0	1	0.9	-10		
C and D 7	4.7	0.93	0.95	21	1.8	1.8	0	2	2.0	0		

$\epsilon_r$  = Relative error



ditions with both air-C<sub>2</sub>H<sub>2</sub> and N<sub>2</sub>O-C<sub>2</sub>H<sub>2</sub> flames (see Table 3). This indicates that the mechanism involved in the aforementioned studies is related to the atomization of calcium from the aqueous part of the slurries.

### References

1. LANGMYHR F.J., WIBETOE G.: Direct analysis of solids by Atomic Absorption Spectrometry. *Prog Analyt Spectrosc* 8: 193-256, 1985.
2. FULLER Z.W., HUTTON R.C., PRESTON B.: Comparison of flame, electrothermal and inductively coupled plasma atomization techniques for the direct analysis of slurries. *Analyst* 106: 913-920, 1981.
3. BENZO Z.A., VELOSO M., CECCARELLI C., DE LA GUARDIA M., SALVADOR A.: Application of the slurry technique to biological materials: A survey of literature. *Fresen J Anal Chem* 339: 235-239, 1991.
4. EBDON L., FOULKES M.E., HILL S.: Fundamental and comparative studies of aerosol sample introduction for solutions and slurries in atomic spectrometry. *Microchem J* 40: 30-64, 1989.
5. EBDON L., COLLIER A.R.: Particle size effects on kaolin slurry analysis by inductively coupled plasma-atomic emission spectrometry. *Spectrochim Acta* 43B: 335-369, 1988.
6. EBDON L., WILKINSON J.R.: Direct atomic spectrometric analysis by slurry atomization. Part 3. Whole coal analysis by inductively coupled plasma atomic emission spectrometry. *J Anal At Spectrom* 2: 325-328, 1987.
7. MARTINEZ-AVILA R., CARBONELL V., SALVADOR A., DE LA GUARDIA M.: Studies on the behaviour of slurries of calcium compounds in different atomization systems. Unpublished results.
8. MAURI A.R., DE LA GUARDIA M., MONGAY C.: Speciation of lead alkyl compounds by FAAS with vapour phase sample introduction. *J Anal At Spectrom* 4: 539-542, 1989.
9. BORJA R., DE LA GUARDIA M., SALVADOR A., BURGUERA M.: Speciation of tetraalkyl lead compounds by FI-atomic absorption spectrometry. *Fresen J Anal Chem* 338: 9-15, 1990.
10. MAURI A.R., DE LA GUARDIA M.: Multi-component determination of La, Ce, Pr and Nd by flame atomic emission spectrometry. *J Anal At Spectrom* 3: 1111-1114, 1988.