

## Clay and Refractory Materials Slurries in Inductively Coupled Plasma Optical Emission Spectrometry: Effects of Mechanochemical Synthesis on Emission Intensities of Analytes

Mirian C. Santos<sup>a</sup>, Ana Rita A. Nogueira<sup>b</sup> and Joaquim A. Nóbrega<sup>\*,a</sup>

<sup>a</sup>Departamento de Química, Universidade Federal de São Carlos, CP 676, 13560-970 São Carlos - SP, Brazil

<sup>b</sup>Embrapa Pecuária Sudeste, São Carlos - SP, Brazil

Neste trabalho foi investigada a aplicação da síntese mecanoquímica para promover reações na amostra e sintetizar novos compostos visando aumentar as intensidades de emissão de elementos presentes em suspensões de argilas e materiais refratários quando introduzidas em espectrômetro de emissão óptica com plasma acoplado indutivamente com configuração axial. A hipótese formulada é que é possível gerar compostos mais voláteis durante a moagem e esses novos compostos causam aumento da intensidade dos sinais de emissão para os analitos em suspensões introduzidas no plasma. A ação de dois modificadores,  $\text{LiBO}_2$  e  $\text{Na}_2\text{CO}_3$ , adicionados durante a etapa de moagem foi investigada. As argilas e materiais refratários foram moídos juntamente com os modificadores químicos durante 2 h usando um moinho de bolas de alto impacto com recipiente e bolas de carbeto de tungstênio. As suspensões foram preparadas dispersando as argilas e os materiais refratários modificados em solução 10% v/v  $\text{HNO}_3$  e, posteriormente, sonicadas em banho de ultra-som para melhorar a homogeneização. Os compostos produzidos durante a etapa de moagem foram caracterizados por difração de raios X e análise termogravimétrica. Ambas as técnicas indicaram a formação de novos compostos nas argilas e materiais refratários por síntese mecanoquímica. Os efeitos da modificação química foram avaliados pelas mudanças nas intensidades de emissão dos analitos Al, Ca, Fe, K, Mg, P, Si e Ti. Ambos modificadores causaram aumento na sensibilidade para todos os analitos de até 665% ( $\text{Na}_2\text{CO}_3$ ) e 583% ( $\text{LiBO}_2$ ) quando comparados às intensidades dos sinais de emissão obtidos para os analitos nas suspensões preparadas com as amostras sem modificação química.

The developed work investigated the application of mechanochemical synthesis for promoting reactions in the samples and for synthesizing new compounds for increment of emission intensities of analytes in clays and refractory materials slurries in inductively coupled plasma optical emission spectrometry with axial viewing. The hypothesis is that it is possible to generate more volatile compounds during the grinding step and these new compounds will increase the intensities of emission signals for slurries introduced in the plasma. The action of two chemical modifiers,  $\text{LiBO}_2$  and  $\text{Na}_2\text{CO}_3$ , added during the grinding step was evaluated. The clays and refractory materials mixed with the chemical modifier were ground for 2 h using a high impact ball mill with a tungsten carbide grinding container and balls. Slurries were prepared by dispersing the modified clays and refractory materials in 10% v/v  $\text{HNO}_3$  solution and by shaking them in an ultrasonic bath to ensure good dispersion. The compounds produced during the grinding step were characterised by X-ray diffraction and thermogravimetric analysis. Both techniques indicated the formation of new compounds in clays and refractory materials by mechanochemical synthesis. Chemical modification effects were evaluated by changes of the emission intensities of Al, Ca, Fe, K, Mg, P, Si, and Ti. Both modifiers caused increments of sensitivities for all analytes in up to 665% ( $\text{Na}_2\text{CO}_3$ ) and 583% ( $\text{LiBO}_2$ ) compared to the emission signals for analytes present in slurries prepared using samples ground without adding modifiers.

**Keywords:** mechanochemical synthesis, slurry, ICP OES, clays, refractory materials

### Introduction

Analysis of inorganic materials using spectroanalytical techniques usually involves conversion of solid samples

\* e-mail: djan@terra.com.br

in representative solutions. Depending on the characteristics of these materials, the digestion procedure can be tedious and can require the use of concentrated acids at high temperatures.<sup>1</sup>

When the sample to be analyzed is insoluble even in hot concentrated acids, a fusion method may be adopted.

A mixture of the sample with a suitable flux in a fine-state division is heated at high temperatures in a furnace. Lithium metaborate or lithium tetraborate, sodium metaborate or sodium tetraborate, and sodium carbonate can be used as efficient fluxes. The time required in these procedures usually is around 4-8 h.<sup>2,3</sup>

Another procedure for analysis of inorganic materials is the direct analysis of slurries by inductively coupled plasma optical emission spectrometry (ICP OES). The slurry technique is based on the idea that a powdered sample of suitable small particle size held in an aqueous suspension of a certain percentage can be directly aspirated into the plasma and analyzed.<sup>4,5</sup>

Taking into account that many types of samples such as silicate minerals, refractory compounds, and ceramics are not easily completely dissolved without contamination and losses of analytes, a number of methods have been developed to introduce slurries into plasmas.<sup>4,6</sup>

Some of the experimental factors that can influence the signal intensities for analytes in slurry nebulization are: the particle size distribution and atomization efficiency.<sup>4-6</sup> In a review Ebdon *et al.* discussed the importance of particle size distribution measurements for the powder to be brought into suspension, the influence of the slurry concentration, and the calibration in slurry nebulization in ICP.<sup>7</sup>

Sanchez *et al.* described a practical method for the direct determination of Al, Ca, Fe, K, Mg, Mn, Na, Si, and Ti in slag samples by the introduction of suspensions into the ICP OES. The effect of particle size distribution on the atomization efficiency of these elements was evaluated. The results obtained showed that when particle sizes decreased, the intensities of emission signals increased around 20-fold for all elements.<sup>8</sup>

As it can be seen above is necessary to place under control a series of parameters, and in general the particle size is the most important. A wide range of grinding techniques and materials have been used to reduce the particle size in slurry preparation before ICP analysis.<sup>5,7</sup>

Atomization efficiency in the plasma is biased towards small particles and mean grain size of  $< 5-10 \mu\text{m}$  is essential to ensure that the slurry has similar transport properties to an aqueous solution.<sup>9</sup>

The grinding time required depends on the type of mill, the intensity of grinding, the ball-to-powder ratio, and the temperature of grinding. The grinding time has to be decided for each combination of the above parameters and for a particular sample material. However, it should be pointed out that the level of contamination increases if the powder is milled for a time interval longer than required.<sup>10</sup>

Suryanarayana discussed in a comprehensive review that some types of reactions can occur during the grinding step.<sup>10</sup> In this process mechanical energy is converted to chemical energy and chemical reactions are promoted during the grinding. This has been referred to in the literature as mechanochemical synthesis or mechanosynthesis.

One example of these processes can be observed when calcium hydroxide,  $\text{Ca}(\text{OH})_2$ , phosphorous oxide,  $\text{P}_2\text{O}_5$ , and calcium fluoride,  $\text{CaF}_2$ , powders (9:3:1 m:m:m) are milled in a planetary ball mill. According to X-ray diffraction measurements, carbonated fluorohydroxyapatite,  $\text{Ca}_{10}(\text{PO}_4)_{1-y}(\text{CO}_3)_y(\text{PO}_4)_5(\text{OH})_{2-2x_1}(\text{F})_{2x_1}$  was formed after 5 h of milling and carbonated fluoroapatite  $\text{Ca}_2(\text{PO}_4)_{1-y}(\text{CO}_3)_y(\text{PO}_4)_5(\text{F})_2$  was formed after 9 h of milling. The X-ray patterns of the sample aliquots removed during different times of grinding had shown a continuous conversion of the original compounds in the new ones.<sup>11</sup>

A characteristic feature of all solid-state reactions is that they involve the formation of new products compounds at the interfaces of the reactants.<sup>10</sup> Mechanochemical reaction can provide the means to substantially increase reaction rates. This is because the repeated welding and fracturing of powder particles increases the area of contact between the reactant powder particles due to a reduction of particle sizes and allows fresh surfaces to come into contact repeatedly. This allows the reaction to proceed without the necessity of diffusion through the product layer. As a consequence, reactions that normally require high temperatures will occur at lower temperatures during mechanochemical reaction without any externally applied heat. In addition, the high defect densities induced by mechanochemical reactions accelerate the diffusion processes. Alternatively, the particle refinement and consequent reduction in diffusion distances (due to microstructural refinement) can at least reduce the reaction temperatures significantly, even if they do not occur at room temperature.

The mechanochemical synthesis process could be exploited to promote chemical modifications in inorganic materials during the grinding step normally employed for preparation of slurries. The common view considers the grinding as an effective process to decrease particle sizes. We propose here that the grinding step could also be seen as a stage to promote chemical reactions and generate new chemical compounds that could improve the efficiency of atomization of slurries in ICP OES.

The procedure here proposed was based on the grinding of clays and refractory materials with added chemical modifiers to promote the formation of new compounds by mechanochemical synthesis. The formation of new

compounds was investigated using X-ray diffraction (XRD) and thermogravimetric analysis (TGA) and the effects of the chemical modifications on the intensities of emission signals for elements in slurries introduced in ICP OES with axial viewing were evaluated.

## Experimental

### Instrumentation

The effects of mechanical synthesis on the emission intensities of analytes were evaluated using a VISTA AX simultaneous ICP OES spectrometer with axial view configuration (Varian, Mulgrave, Australia). The sample introduction system consists of a V-groove nebulizer and a Sturman-Masters type spray chamber made of polytetrafluoroethylene (PTFE). The operating parameters and the selected analytical lines are listed in Table 1.

**Table 1.** Instrumentation and operating conditions for ICP OES with axial viewing

Operating parameters	
RF generator (MHz)	40
Power (kW)	1.3
Plasma flow rate (L min <sup>-1</sup> )	15
Auxiliary flow rate (L min <sup>-1</sup> )	1.5
Nebulizer flow rate (L min <sup>-1</sup> )	0.7
Replicates	3
Injector tube diameter (mm)	2.4
Spray Chamber	Sturman-Masters
Nebulizer	V-groove
Emission lines (nm)	Al I 394.399 Ca II 422.673 Fe I 239.561 K I 766.480 Mg II 280.268 P I 213.618 Si I 288.158 Ti II 334.938

The mechanochemical synthesis reactions were performed in a high impact ball mill (SPEX 8000 CertPrep, Metuchen, NJ, USA). All grinding procedures were carried out using a tungsten carbide recipient and 2 balls (e.d. 10 mm).

X-Ray diffraction spectra of clays and refractory materials were obtained using a Siemens (München, Germany) Model D500 equipped with an X-ray tube with copper target operated at 40 kV and 40 mA, a Ni filter, and the goniometer was set at 0.6° (2θ).

An ultrasonic bath USC (UNIQUE model 1400, SP, Brazil) was used for particle desegregation of slurries, and a vortex mixing (Maxi Mix II, Thermolyne, USA) was used to ensure homogeneity of slurry samples before introduction into the ICP OES.

The thermal decomposition studies were performed over a temperature range of 20 – 1000 °C using a Simultaneous DSC-TGA (model SDT 2960, TA Instruments, USA) thermogravimetric analysis system under an air environment at a flow-rate of 0.1 L min<sup>-1</sup> and a scan rate of 10 °C min<sup>-1</sup>.

### Samples and reagents

All reagents employed were of analytical grade. Nitric acid (Merck, Darmstadt, Germany) was used for slurry preparation. The slurries were prepared with Milli-Q water (Millipore, Bedford, MA, USA). Mechanochemical synthesis reactions were carried out using two chemical modifiers: LiBO<sub>2</sub> (Merck, Rio de Janeiro, RJ, Brazil) and Na<sub>2</sub>CO<sub>3</sub> (Merck).

Clays (IPT-28, IPT-32, and IPT-42) and refractory certified reference materials (IPT-57 and IPT-63) prepared by the Instituto de Pesquisas Tecnológicas, São Paulo, SP, Brazil, were used in this work. The use of these materials will facilitate the evaluation of emission intensities for different analytes and did not imply that they will be employed for assessment of accuracy.

### Procedures

**Grinding step.** Mechanochemical synthesis was utilised to synthesize new compounds in clays and refractory materials. In this study the effects caused by two chemical modifiers, LiBO<sub>2</sub> and Na<sub>2</sub>CO<sub>3</sub>, both anidrous, were evaluated. These modifiers were chosen taking into account their conventional use as fluxes. A mass of 0.5 g of clays or refractory materials was mixed with 2.5 g of each modifier and ground for 0.5-3.0 h using a ball mill with a tungsten carbide grinding container. Two tungsten carbide balls were added to the container.

The effect of the grinding time was investigated by using these conditions and varying the grinding time in 0.5, 1.0, 1.5, 2.0, and 3.0 h.

For a preliminary evaluation of particle size effects, ground samples were screened through a 37 µm (400 mesh) Nylon sieve. Slurries were prepared using the sample fraction with particle sizes lower than 37 µm and using the ground sample without any sieving. Each sample was dried at 105 °C for 1 h after the grinding step.

**Preparation of slurries.** The ground and chemically modified clays and refractory materials were characterized by X-ray diffraction and thermal analysis.

These powders were also used for preparation of slurries by dispersing 0.12 g of sample in 100 ml of 10% v v<sup>-1</sup> HNO<sub>3</sub> solution. Slurries were sonicated for 5 min before introducing them into the plasma. This procedure was

based on a procedure developed by Silva *et al.* for analysis of clays.<sup>12</sup>

Chemical modification effects were evaluated by changes in the emission intensities of Al, Ca, Fe, K, Mg, P, Si, and Ti measured in an ICP OES with axial viewing.

#### *Effect of masses of $\text{LiBO}_2$ and $\text{Na}_2\text{CO}_3$ on emission intensities of analytes*

It is well known that lithium and sodium, frequently called easily ionisable elements, cause appreciable effects on emission intensities of other analytes in ICP OES.<sup>7</sup> Thus it is important to estimate these effects for a better evaluation of the emission intensities measured when introducing modified slurries. In this study the effects caused on emission intensities of analytes by gradual addition of increasing masses of  $\text{LiBO}_2$  and  $\text{Na}_2\text{CO}_3$  in slurries prepared using 20 mg of IPT-42 in 10% v v<sup>-1</sup>  $\text{HNO}_3$  were evaluated. The masses of  $\text{LiBO}_2$  or  $\text{Na}_2\text{CO}_3$  added were 20, 40, 60, 80, and 100 mg. This latter mass was also added to slurries prepared from a modified IPT-42 material for comparison purposes.

## Results and Discussion

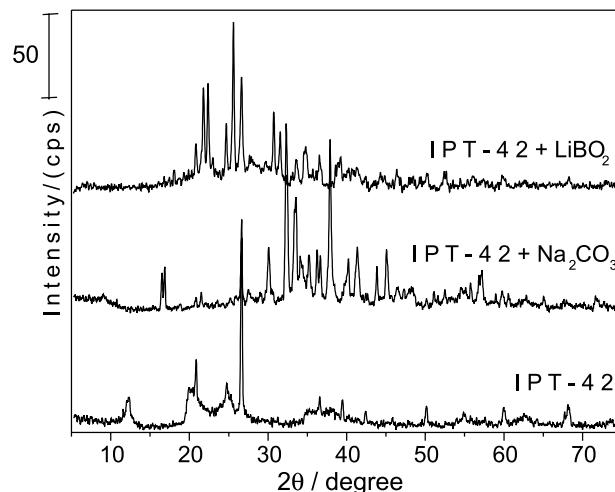
#### *Effects of mechanical alloying on chemical composition*

The mechanochemical synthesis of new compounds in clays and refractory materials ground with either  $\text{Na}_2\text{CO}_3$  or  $\text{LiBO}_2$  were characterised using XRD and TGA. All characterisation experiments were performed using samples ground for 2 h since this grinding time was established as the best one to increase emission intensities of analytes in ICP OES as it will be discussed later on.

The diffractograms showed in Figure 1 demonstrated that the grinding step in the presence of both chemical modifiers was effective for generating new compounds. The diffractogram for IPT-42 clay ground without modifier shows that quartz and kaolinite were present in the sample. On the other hand, when  $\text{LiBO}_2$  was added during the grinding step, cristobalite, ankelite, rutile, and lithium boron hydroxide were produced. The use of  $\text{Na}_2\text{CO}_3$  during the grinding step led to the formation of thermonatrite, muscovite, rutile, and sodium hydrogen oxalate hydrate.

Compounds detected in other samples before and after modification are summarized in Table 2. As it can be seen, all materials produced new compounds when ground with a chemical modifier, indicating the occurrence of chemical reactions in solid phase. Additionally, it can also be seen that some original compounds remained even after grinding with the modifier because they are either present in high

concentrations in the original sample or are chemically more stable.

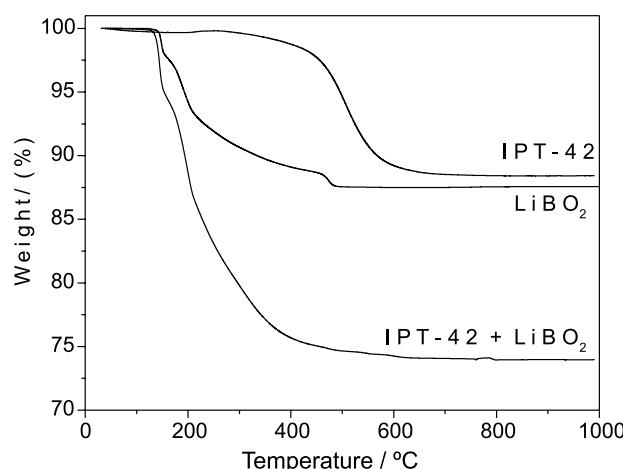


**Figure 1.** X-ray diffraction analysis of IPT-42 unmodified and modified with  $\text{LiBO}_2$  or  $\text{Na}_2\text{CO}_3$ .

Thermogravimetric analysis can be used to a preliminary evaluation of the thermal behavior of the new compounds generated in clays and refractory materials.

The TGA curves, under oxidant atmosphere, for one clay and one refractory material without modification and modified with  $\text{LiBO}_2$  are depicted in Figures 2 and 3. The TGA curves obtained for samples ground with or without adding this modifier showed appreciable differences of thermal stability. For comparison purposes the TGA curve for  $\text{LiBO}_2$  is also shown.

The ground and non-modified clay sample presented a loss of mass caused by thermal degradation around 500 and 600 °C (Figure 2). On the other hand, the loss of mass occurred between 200 and 350 °C for the clay sample ground after adding  $\text{LiBO}_2$ . The residual mass at 1000 °C



**Figure 2.** Thermogravimetric curves for  $\text{LiBO}_2$  and for IPT-42 ground without modifier and with  $\text{LiBO}_2$ .

**Table 2.** Compounds detected by X-ray diffraction analysis in samples ground with and without modifier

Sample Material	Ground without modifier	Ground with $\text{LiBO}_2$	Ground with $\text{Na}_2\text{CO}_3$
Clay IPT-28	Kaolinite	Quartz Lithium boron hydroxide Diomignite	Trona Thermonatrite
Clay IPT-32	Kaolinite	Kaolinite Diomignite Sassolite	Trona Thermonatrite Quartz
Clay IPT-42	Quartz Kaolinite	Cristobalite Ankelite Rutile Lithium boron hydroxide Quartz	Thermonatrite Muscovite Rutile Sodium hydrogen oxalate hydrate Quartz
Refractory material IPT-57	Mulite Quartz Corundum	Quartz Lithium boron hydroxide Mulite Rutile Corundum	Thermonatrite Mulite Quartz Trona Corundum Natrite
Refractory material IPT - 63	Cristobalite Tridymite Rutile	Quartz Cristobalite Tridymite Lithium aluminum silicate $\beta$ -Spumode	Thermonatrite Cristobalite Tridymite

(74%) for the modified clay is smaller than that obtained for the non-modified clay (88%).

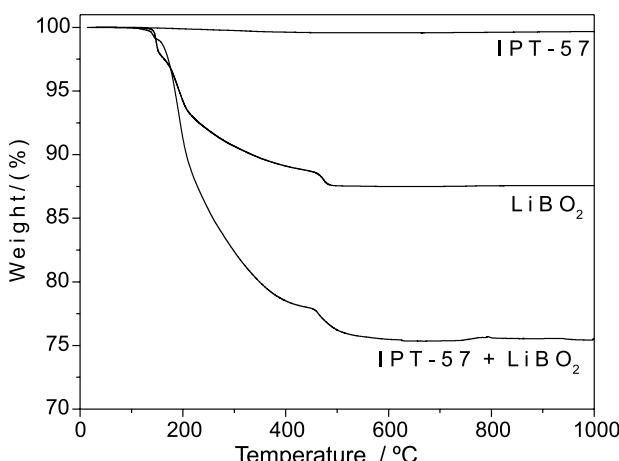
The TGA curve for the IPT-57 refractory material is shown in Figure 3. No stage of loss of mass due to thermal degradation was observed for the sample ground without adding a modifier. After grinding with  $\text{LiBO}_2$ , this sample presented two stages of losses of mass. The first step occurred between 200 and 400 °C, and the second stage of thermal degradation can be observed between 400 and 500 °C. Above 600 °C the percentage of solid residue (75%) for the modified material is appreciably smaller than that observed for the sample ground without adding a modifier

(99%). These results also indicate that mechanochemical synthesis reactions can promote the formation of more volatile compounds.

#### Effects of mechanochemical synthesis on emission intensities of analytes in ICP OES

The effect of the grinding time on the emission intensities of Al, Ca, Fe, K, Mg, P, Si, and Ti was investigated. Tables 3 and 4 show the percentage of variation in emission signal intensities for IPT-42 clay slurries modified with  $\text{LiBO}_2$  and  $\text{Na}_2\text{CO}_3$ , respectively. The emission intensities increased up to 718% depending on the analyte when the grinding time was 3 h. Results obtained for slurries prepared after 2 or 3 h of grinding for almost of elements were similar, consequently all further experiments were carried out adopting 2 h of grinding.

As expected, chemical modification affected the emission intensities for Al, Ca, Fe, K, Mg, P, Si, and Ti. Increments on emission intensities for slurries of IPT-42, a clay material, and of IPT-57, a refractory material, can be seen in Tables 5 and 6, respectively. Both chemical modifiers caused appreciable increment in emission intensities for most elements in both standard reference materials. Comparing the emission intensities for analytes in slurries prepared using samples ground with and without modifier, it was observed that for all analytes the emission intensities increased in the 140 to 665% range when



**Figure 3.** Thermogravimetric curves for  $\text{LiBO}_2$  and for IPT-57 ground without modifier and with  $\text{LiBO}_2$ .

$\text{Na}_2\text{CO}_3$  or in the 115 to 583% range when  $\text{LiBO}_2$  were added during the grinding step. This was particularly significant in the case of Al, Ti, and Si. Measurements of slurries prepared using IPT-42 sample modified during

grinding led to enhancements of emission intensities of 155% ( $\text{LiBO}_2$ ) and 211% ( $\text{Na}_2\text{CO}_3$ ) for Al, 583% ( $\text{LiBO}_2$ ) and 665% ( $\text{Na}_2\text{CO}_3$ ) for Ti, and 98% ( $\text{LiBO}_2$ ) and 140% ( $\text{Na}_2\text{CO}_3$ ) for Si.

**Table 3.** Effect of the grinding time on percentage of increment of emission intensities of analytes for IPT-42 clay slurries modified with  $\text{LiBO}_2$

Analyte	time / h									
	0.5		1.0		1.5		2.0		3.0	
Mean	RSD	Mean	RSD	Mean	RSD	Mean	RSD	Mean	RSD	
Al	131	1.3	146	0.9	156	1.3	160	1.8	163	1.9
Ca	124	2.9	139	3.9	150	3.1	160	4.8	165	6.1
Fe	135	4.7	153	3.5	157	4.2	170	4.1	178	5.9
K	328	5.1	374	4.2	386	4.3	405	3.9	435	5.3
Mg	123	1.3	134	2.1	142	2.4	150	1.9	162	2.1
P	49.5	1.6	68.5	2.7	85.8	1.9	100	3.1	109	4.0
Si	495	2.3	472	3.3	528	2.9	590	4.1	634	3.7
Ti	131	5.9	146	4.3	156	4.5	160	5.7	163	6.7

All values were based on 3 measurements and calculated by comparison with emission intensities obtained for a IPT-42 clay slurry ground without adding any modifier. RSD: relative standard deviation.

**Table 4.** Effect of the grinding time on percentage of increment of emission intensities of analytes for IPT-42 clay slurries modified with  $\text{Na}_2\text{CO}_3$

Analyte	time / h									
	0.5		1.0		1.5		2.0		3.0	
Mean	RSD	Mean	RSD	Mean	RSD	Mean	RSD	Mean	RSD	
Al	187	2.3	187	1.4	207	2.9	210	2.1	210	1.8
Ca	214	3.4	234	3.2	291	3.5	300	4.8	314	6.1
Fe	195	4.4	182	4.7	221	5.2	240	6.1	249	6.5
K	258	5.3	259	4.9	290	4.2	300	5.1	315	5.8
Mg	188	1.7	181	2.2	215	2.4	230	1.9	238	2.1
P	112	3.1	118	2.9	130	3.3	140	4.1	146	4.6
Si	569	3.2	448	3.9	575	4.9	660	4.5	718	4.7
Ti	187	5.3	187	4.9	207	5.5	210	6.7	210	7.1

All values were based on 3 measurements and calculated by comparison with emission intensities obtained for a IPT-42 clay slurry ground without adding any modifier. RSD: relative standard deviation.

**Table 5.** Effect of chemical modification during grinding on emission intensities of analytes for slurries of IPT-42. All data are based on 3 measurements

		Al	Ca	Fe	K	Mg	P	Si	Ti
IPT-42 + $\text{LiBO}_2$	%	155	156	168	405	147	115	98	583
	RSD	0.8	2.9	5.6	7.0	2.2	0.1	3.0	17.0
IPT-42 + $\text{Na}_2\text{CO}_3$	%	211	297	235	603	227	172	140	665
	RSD	0.9	9.5	3.9	1.3	0.6	3.4	2.3	6.8

**Table 6.** Effect of chemical modification during grinding on emission intensities of analytes for slurries of IPT-57. All data are based on 3 measurements

		Al	Ca	Fe	K	Mg	P	Si	Ti
IPT-57 + $\text{LiBO}_2$	%	161	125	144	134	200	328	122	135
	RSD	4.2	6.0	4.0	8.0	5.9	47.8	2.0	1.3
IPT-57 + $\text{Na}_2\text{CO}_3$	%	177	161	169	167	216	214	144	148
	RSD	7.6	2.7	10.2	0.13	8.7	48.2	5.0	8.7

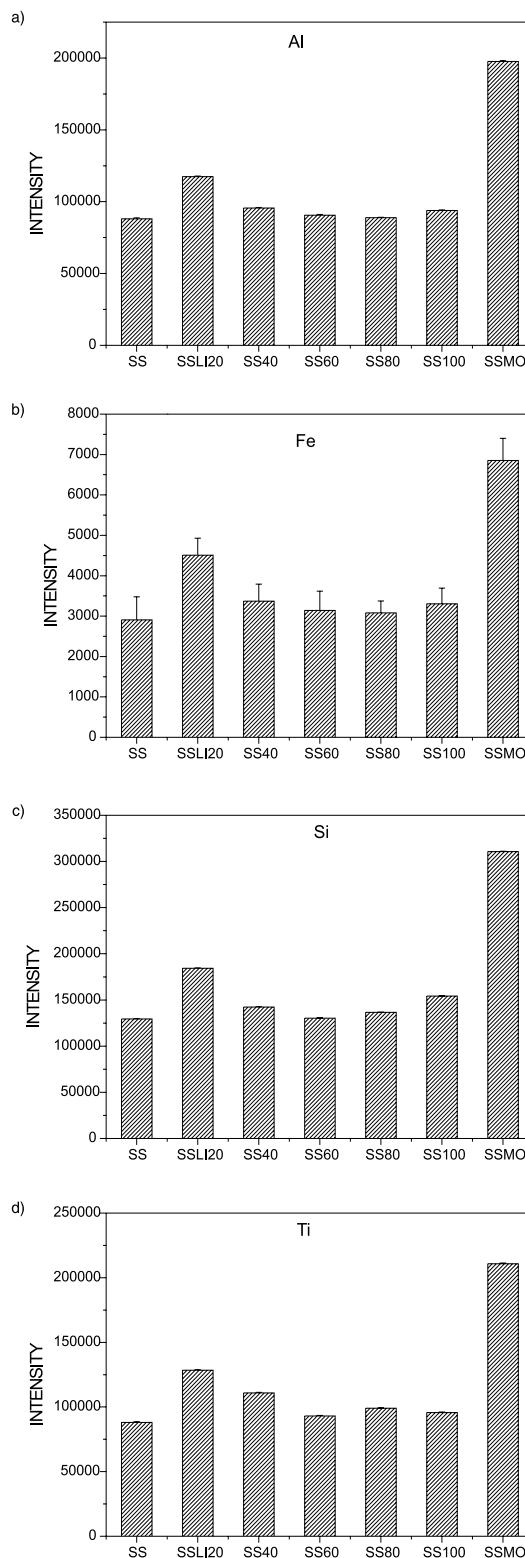
It could be supposed that these increments on analyte emission intensities were caused by the presence of lithium and sodium in the slurries, since these cations are present in the modifiers.

An experiment was performed to evaluate this hypothesis by adding  $\text{LiBO}_2$  or  $\text{Na}_2\text{CO}_3$  to slurries prepared using unmodified samples. The emission intensities obtained for Al, Fe, Si, and Ti after addition of  $\text{LiBO}_2$  and  $\text{Na}_2\text{CO}_3$  are shown in Figures 4 and 5, respectively.

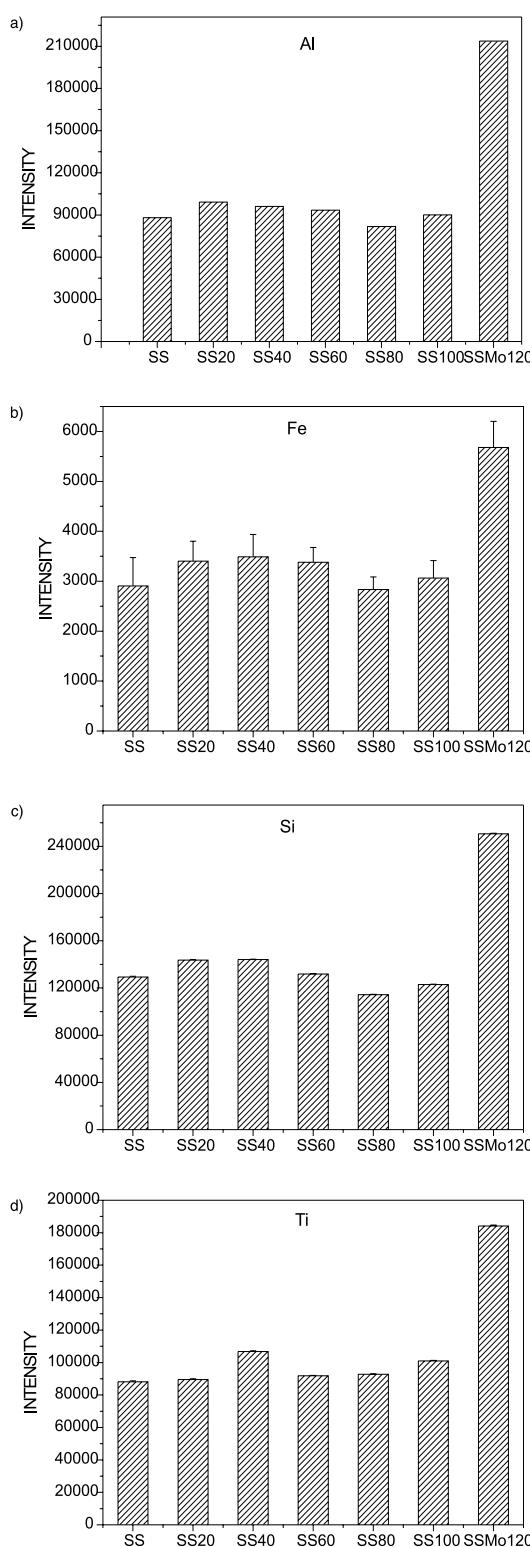
As it can be seen the gradual increase of masses of  $\text{LiBO}_2$  or  $\text{Na}_2\text{CO}_3$  in an unmodified clay sample, IPT-42, did not cause appreciable changes in the emission intensities of analytes. However, when each one of the modifiers was added before the grinding step, the emission intensities for all analytes were appreciably increased as already shown. Comparing the emission intensities for slurries prepared using chemically modified materials in an 1:5 clay:chemical modifier ratio and unmodified materials mixed with the same modifiers and ratios, the increase of emission intensities varied from 70 to 100% for all analytes. This is another indication of the occurrence of mechanochemical synthesis and implied that the observed gains in emission intensities are not caused by spectral interferences in ICP OES measurements.

Finally, it is well known that the particle size distribution of a slurry is the limiting factor controlling analytical performance. Considering atomization-excitation processes in plasma, Raeymaekers *et al.* showed for refractory oxide slurries that the efficiency of atomization improves when working with slurries containing smaller particles.<sup>13</sup> Ebdon and Collier studied particle size effects in kaolin slurries with a wide-range of particle sizes using ICP OES and they found that kaolin particles up to  $8 \mu\text{m}$  can be completely atomised in the ICP.<sup>14</sup>

In the present study two different sizes fractions of a ground clay (IPT-42) were tested, one fraction without any separation of particle size after grinding and the other fraction with particle sizes smaller than  $37 \mu\text{m}$ . Both fractions were chemically modified during the grinding step with  $\text{LiBO}_2$  and  $\text{Na}_2\text{CO}_3$ . Emission intensities for Al, Si, and Ti are shown in Figure 6. As it can be seen, after the chemical modification the difference in the intensity values between the two fractions is not significant. This is a preliminary indication that when using mechanochemical synthesis, the main factor controlling the efficiency of atomization is the thermal behavior of the particle that reached the plasma. However, these data are not conclusive because the distribution of particle sizes is not known, but it can also be mentioned that when a ground sample was sieved through the  $37 \mu\text{m}$  Nylon sieve,

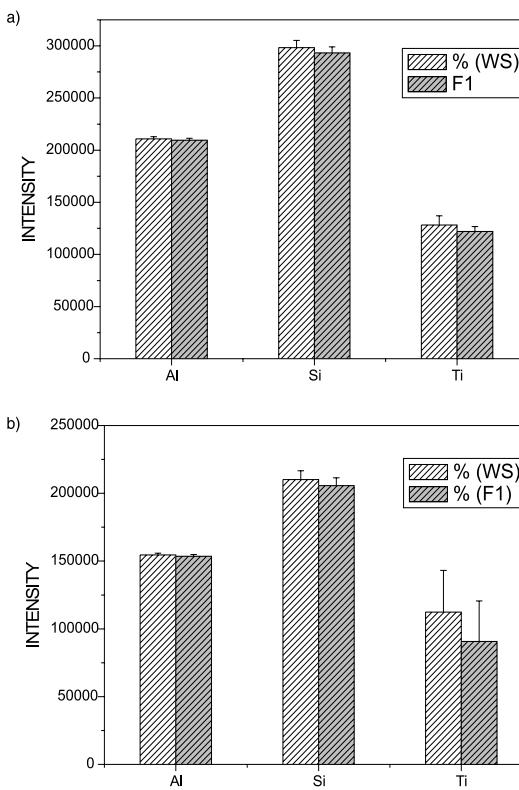


**Figure 4.** Emission intensities and relative standard deviations for (a) Al, (b) Fe, (c) Si, and (d) Ti from IPT-42 slurries,  $20 \text{ mg L}^{-1}$  in  $10\% \text{ v v}^{-1} \text{ HNO}_3$  solution with gradual addition of  $\text{LiBO}_2$ . SS - without  $\text{LiBO}_2$  (sample:modifier ratio, 1:0 m:m), SS20 - with  $20 \text{ mg LiBO}_2$  (1:1 m:m), SS40 - with  $40 \text{ mg LiBO}_2$  (1:2 m:m), SS60 - with  $60 \text{ mg LiBO}_2$  (1:3 m:m), SS80 - with  $80 \text{ mg LiBO}_2$  (1:4 m:m), SS100 - with  $100 \text{ mg LiBO}_2$  (1:5 m:m), and SSMO -  $120 \text{ mg IPT-42}$  modified with  $\text{LiBO}_2$  in  $10\% \text{ v v}^{-1} \text{ HNO}_3$  solution (1:5 m:m).



**Figure 5.** Emission intensities and relative standard deviations for (a) Al, (b) Fe, (c) Si, and (d) Ti from IPT-42 slurries, 20 mg L<sup>-1</sup> in 10% v v<sup>-1</sup> HNO<sub>3</sub> solution with gradual addition of Na<sub>2</sub>CO<sub>3</sub>. SS - without Na<sub>2</sub>CO<sub>3</sub> (sample:modifier ratio, 1:0 m:m), SS20 - with 20 mg Na<sub>2</sub>CO<sub>3</sub> (1:1 m:m), SS40 - with 40 mg Na<sub>2</sub>CO<sub>3</sub> (1:2 m:m), SS60 - with 60 mg Na<sub>2</sub>CO<sub>3</sub> (1:3 m:m), SS80 - with 80 mg Na<sub>2</sub>CO<sub>3</sub> (1:4 m:m), SS100 - with 100 mg Na<sub>2</sub>CO<sub>3</sub> (1:5 m:m), and SSMo - 120 mg IPT-42 modified with Na<sub>2</sub>CO<sub>3</sub> in 10% v v<sup>-1</sup> HNO<sub>3</sub> solution (1:5 m:m).

a percentage of 45 – 60% of the original powder did not pass through the sieve pores.



**Figure 6.** Emission intensities and relative standard deviations for Al, Si, and Ti (n = 3). Slurries prepared from IPT-42 using (a) Na<sub>2</sub>CO<sub>3</sub> or (b) LiBO<sub>2</sub>. WS – without separation of particle sizes and F1 – particles sizes lower than 37  $\mu$ m.

## Conclusions

It was demonstrated that mechanochemical synthesis processes were operative for generating new compounds when clays and refractory materials were ground in a high impact ball mill by adding either LiBO<sub>2</sub> or Na<sub>2</sub>CO<sub>3</sub> as chemical modifiers.

The formation of new compounds was confirmed by X-ray diffraction and the higher volatilities of these when compared to samples ground without adding chemical modifiers were demonstrated by TGA measurements.

Slurries were prepared using these samples modified by grinding in the presence of chemical modifiers and the emission intensities of their constituents were measured by ICP OES with axial viewing. It was observed a significant increase of signals for all elements in all samples ground with either LiBO<sub>2</sub> or Na<sub>2</sub>CO<sub>3</sub>.

Further developments will focus on the feasibility of this procedure for improving the calibration strategy when dealing with the direct introduction of slurries in ICP OES.

## Acknowledgements

The authors wish to express their appreciation to Fundação de Amparo à Pesquisa do Estado de São Paulo (São Paulo, SP, Brazil) for financial support of this research (FAPESP, Processes 02/04473-6 and 03/04502-9). We would like to thank M. Sc. Leandro Martins and Prof. Dr. Dilson Cardoso (Department of Chemical Engineering, Universidade Federal de São Carlos, São Carlos, SP, Brazil) for thermogravimetric analysis. J.A.N. and A.R.A.N. express their gratitude to Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq, Brasília, DF, Brazil) for the researchships provided.

## References

1. Ingle, J.D.; Crouch, S.R.; *Spectrochemical Analysis*, Prentice Hall: New Jersey, 1988.
2. Abollino, O.; Braglia, M.; Contardi, C.; Dai, G.; Mentasti, E.; Mosso, S.; Sarzanini, C.; *Anal. Chim. Acta* **1999**, 383, 243.
3. Lau, O.; Lam, L.; Luk, S.; *Talanta* **2000**, 51, 1009.
4. Borszéki, J.; Halmos, P.; Gegus, E.; *Can. J. Anal. Sci. Spectrosc.* **1997**, 42, 165.
5. Jarvis, K.E.; *Chem. Geol.* **1992**, 95, 73.
6. Nickel, H.; Broekaert, J.A.C.; *Fresenius J. Anal. Chem.* **1999**, 363, 145.
7. Ebdon, L.; Foulkes, M.; Sutton, K.; *J. Anal. At. Spectrom.* **1997**, 12, 213.
8. Sanchez, M.L.F.; Fairman, B.; Sanz-Medel, A.; *J. Anal. At. Spectrom.* **1991**, 6, 397.
9. Totland, M.; Jarvis, I.; Jarvis, K.E.; *Chem. Geol.* **1993**, 104, 175.
10. Suryanarayana, C.; *Prog. Materials Sci.* **2001**, 46, 1.
11. Nikcevic, I.; Jokanovic, V.; Mitric, M.; Nedic, Z.; Makovec, D.; Uskokovic, D.; *J. Solid State Chem.* **2004**, 177, 2565.
12. Silva, C. S.; Blanco, T.; Nóbrega, J.A.; *Quím. Nova* **2002**, 25, 1194.
13. Raeymaekers, B.; Graule, T.; Broekaert, J.A.C.; Adams, F.; Tschöpel, P.; *Spectrochim. Acta* **1988**, 43B, 923.
14. Ebdon, L.; Collier, A.R.; *Spectrochim. Acta* **1988**, 43B, 355.

Received: December 2, 2004

Published on the web: April 6, 2005

**FAPESP helped in meeting the publication costs of this article.**