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Article

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

***Mirian C. Santos*[a]*, Ana Rita A. Nogueira*[b] *and Joaquim A. Nóbrega**[*,a]**

[a]*Departamento de Química, Universidade Federal de São Carlos, CP 676, 13560-970 São Carlos - SP, Brazil*

[b]*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, $LiBO_2$ e Na_2CO_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^{-1} 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% (Na_2CO_3) e 583% ($LiBO_2$) 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, $LiBO_2$ and Na_2CO_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^{-1} 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% (Na_2CO_3) and 583% ($LiBO_2$) 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 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.[1]

When the sample to be analyzed is insoluble even in

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.[2,3]

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 aspired into the plasma and analyzed.[4,5]

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.[4-6]

Some of the experimental factors that can influence the signal intensities for analytes in slurry nebulization are: the particle size distribution and atomization efficiency.[4-6] 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.[7]

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 shown that when particle sizes decreased, the intensities of emission signals increased around 20-fold for all elements.[8]

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.[5,7]

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

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.[10]

Suryanarayana discussed in a comprehensive rev
that some types of reactions can occur during the grin
step.[10] In this process mechanical energy is converte
chemical energy and chemical reactions are prom
during the grinding. This has been referred to in
literature as mechanochemical synthesis
mechanosynthesis.

One example of these processes can be observed w
calcium hydroxide, $Ca(OH)_2$, phosphorous oxide, P_2O_5
calcium fluoride, CaF_2, powders (9:3:1 m:m:m) are m
in a planetary ball mill. According to X-ray diffrac
measurements, carbonated fluorhydroxyapa
$Ca_{10}(PO_4)_{1-y}(CO_3)_y(PO_4)_5(OH)_{2-2x1}(F)_{2x1}$ was formed afte
of milling and carbonated fluoroapatite Ca_2(P
$(CO_3)_y(PO_4)_5(F)_2$ was formed after 9 h of milling. The X
patterns of the sample aliquots removed during diffe
times of grinding had shown a continuous conversio
the original compounds in the new ones.[11]

A characteristic feature of all solid-state reactio
that they involve the formation of new products compo
at the interfaces of the reactants.[10] Mechanochem
reaction can provide the means to substantially incr
reaction rates. This is because the repeated welding
fracturing of powder particles increases the area of co
between the reactant powder particles due to a reduc
of particle sizes and allows fresh surfaces to come
contact repeatedly. This allows the reaction to pro
without the necessity of diffusion through the product l
As a consequence, reactions that normally require
temperatures will occur at lower temperatures du
mechanochemical reaction without any externally ap
heat. In addition, the high defect densities induce
mechanochemical reactions accelerate the diffu
processes. Alternatively, the particle refinement
consequent reduction in diffusion distances (du
microstructural refinement) can at least reduce the rea
temperatures significantly, even if they do not occ
room temperature.

The mechanochemical synthesis process coul
exploited to promote chemical modifications in inorg
materials during the grinding step normally employe
preparation of slurries. The common view consider
grinding as an effective process to decrease particle s
We propose here that the grinding step could also be
as a stage to promote chemical reactions and generate
chemical compounds that could improve the efficien
atomization of slurries in ICP OES.

The procedure here proposed was based on the grin
of clays and refractory materials with added chem
modifiers to promote the formation of new compoun
mechanochemical synthesis. The formation of

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 polytetrafluorethylene (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^{-1})	15	
Auxiliary flow rate (L min^{-1})	1.5	
Nebulizer flow rate (L min^{-1})	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^{-1} and a scan rate of 10 °C min^{-1}.

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: $LiBO_2$ (Merck, Rio de Janeiro, RJ, Brazil) and Na_2CO_3 (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, $LiBO_2$ and Na_2CO_3 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^{-1} HNO_3 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.[12]

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 $LiBO_2$ and Na_2CO_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.[7] 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 $LiBO_2$ and Na_2CO_3 in slurries prepared using 20 mg of IPT-42 in 10% v v^{-1} HNO_3 were evaluated. The masses of $LiBO_2$ or Na_2CO_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 Na_2CO_3 or $LiBO_2$ 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 difractograms showed in Figure 1 demonstrated that the grinding step in the presence of both chemical modifiers was effective for generating new compounds. The difractogram for IPT-42 clay ground without modifier shows that quartz and kaolinite were present in the sample. On the other hand, when $LiBO_2$ was added during the grinding step, cristobalite, ankelite, rutile, and lithium boron hydroxide were produced. The use of Na_2CO_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 chemic
more stable.

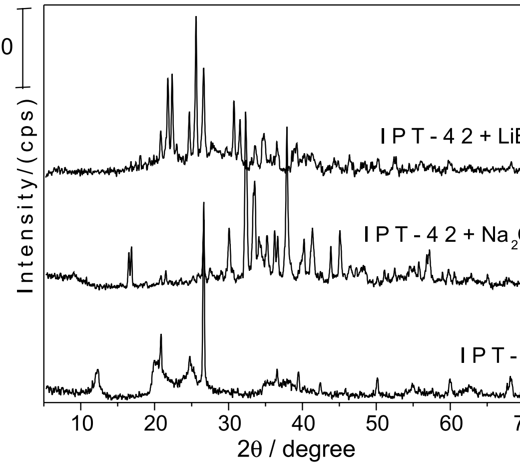

Figure 1. X-ray diffraction analysis of IPT-42 unmodifie
modified with $LiBO_2$ or Na_2CO_3.

Thermogravimetric analysis can be used
preliminary evaluation of the thermal behavior of the
compounds generated in clays and refractory materia

The TGA curves, under oxidant atmosphere, for
clay and one refractory material without modification
modified with $LiBO_2$ are depicted in Figures 2 and 3.
TGA curves obtained for samples ground with or wit
adding this modifier showed appreciable difference
thermal stability. For comparison purposes the TGA c
for $LiBO_2$ is also shown.

The ground and non-modified clay sample present
loss of mass caused by thermal degradation around
and 600 °C (Figure 2). On the other hand, the loss of
occurred between 200 and 350 °C for the clay sa
ground after adding $LiBO_2$. The residual mass at 100

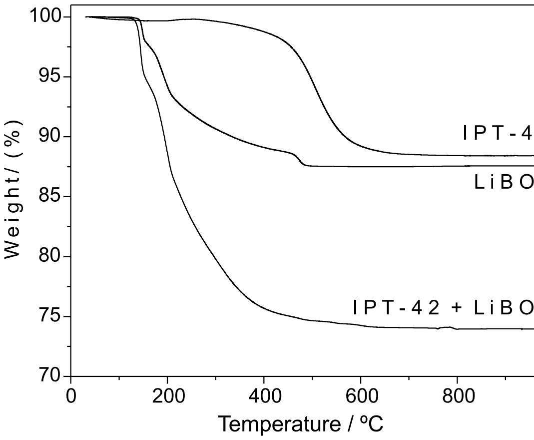

Figure 2. Thermogravimetric curves for $LiBO_2$ and for IP

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

Sample Material	Ground without modifier	Ground with $LiBO_2$	Ground with Na_2CO_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 β-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 $LiBO_2$, 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

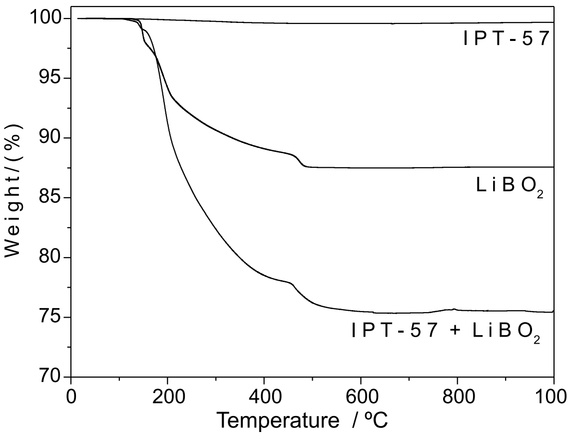

Figure 3. Thermogravimetric curves for $LiBO_2$ and for IPT-57

(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 $LiBO_2$ and Na_2CO_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

Na_2CO_3 or in the 115 to 583% range when $LiBO_2$ 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 intensitie 155% ($LiBO_2$) and 211% (Na_2CO_3) for Al, 583% (Li and 665% (Na_2CO_3) for Ti, and 98% ($LiBO_2$) and 1 (Na_2CO_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 L

	time / h									
	0.5		1.0		1.5		2.0		3.0	
Analyte	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 gr 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 Na

	time / h									
	0.5		1.0		1.5		2.0		3.0	
Analyte	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 gr 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 measurements

		Al	Ca	Fe	K	Mg	P	Si	Ti
IPT-42 + $LiBO_2$	%	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 + Na_2CO_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 measurements

		Al	Ca	Fe	K	Mg	P	Si	Ti
IPT-57 + $LiBO_2$	%	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 + Na_2CO_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 $LiBO_2$ or Na_2CO_3 to slurries prepared using unmodified samples. The emission intensities obtained for Al, Fe, Si, and Ti after addition of $LiBO_2$ and Na_2CO_3 are shown in Figures 4 and 5, respectively.

As it can be seen the gradual increase of masses of $LiBO_2$ or Na_2CO_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.[13] 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 μm can be completely atomised in the ICP.[14]

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 μm. Both fractions were chemically modified during the grinding step with $LiBO_2$ and Na_2CO_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 μm Nylon sieve,

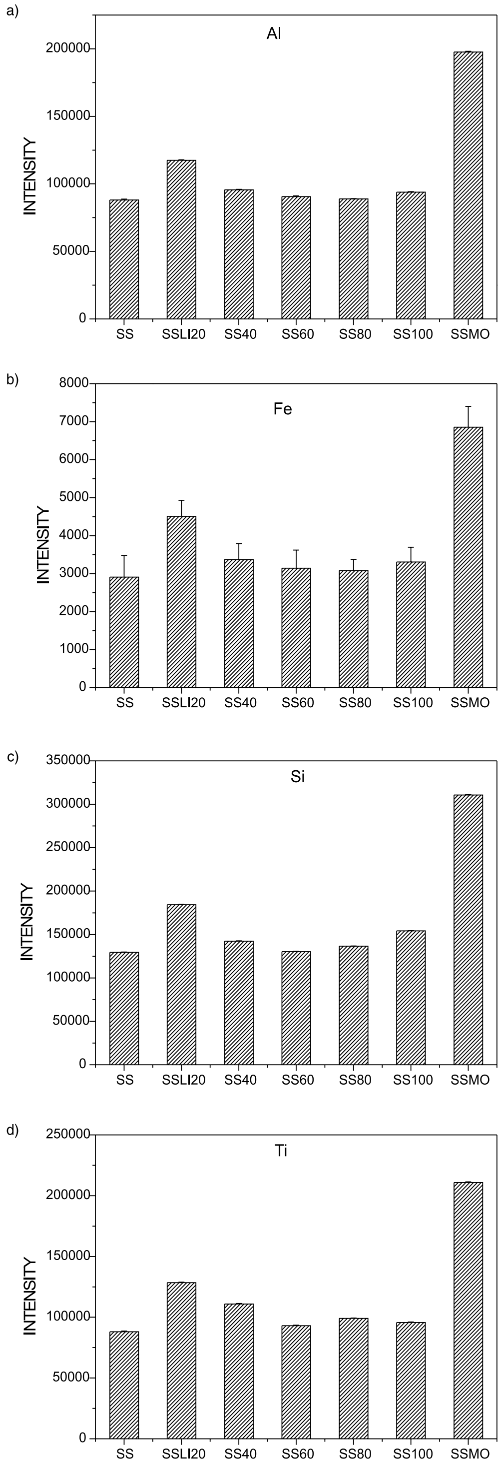

Figure 4. Emission intensities and relative standard deviations for (a) Al, (b) Fe, (c) Si, and (d) Ti from IPT-42 slurries, 20 mg L^{-1} in 10% v v^{-1} HNO_3 solution with gradual addition of $LiBO_2$. SS - without $LiBO_2$ (sample:modifier ratio, 1:0 m:m), SS20 - with 20 mg $LiBO_2$ (1:1 m:m), SS40 - with 40 mg $LiBO_2$ (1:2 m:m), SS60 - with 60 mg $LiBO_2$ (1:3 m:m), SS80 - with 80 mg $LiBO_2$ (1:4 m:m), SS100 - with 100 mg $LiBO_2$ (1:5 m:m), and SSMo - 120 mg IPT-42 modi-

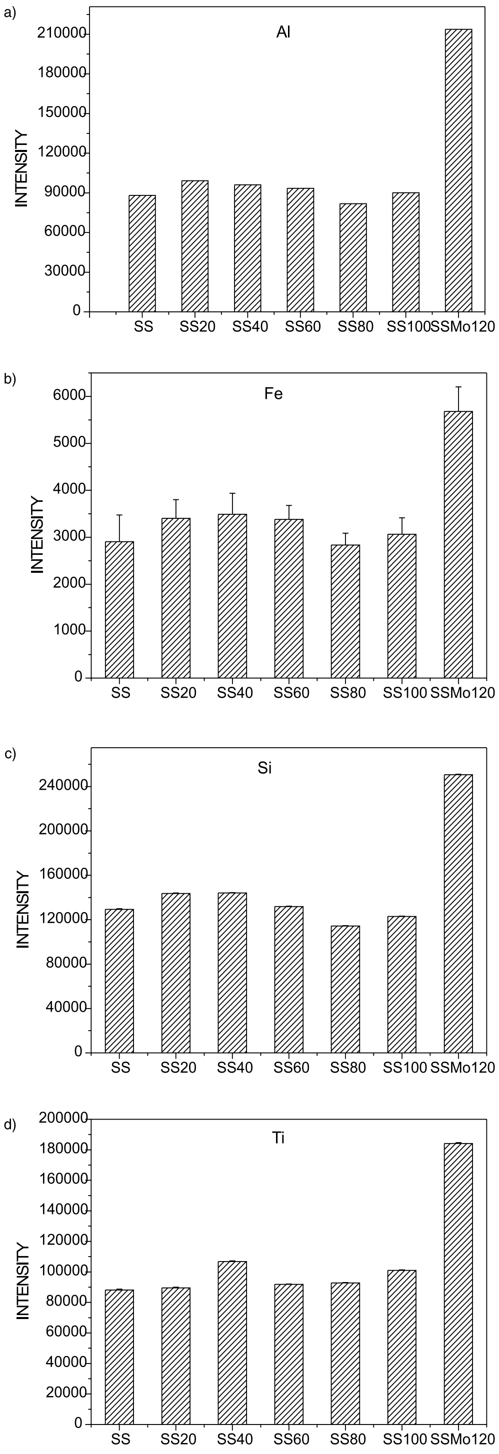

Figure 5. Emission intensities and relative standard deviations for (a) Al, (b) Fe, (c) Si, and (d) Ti from IPT-42 slurries, 20 mg L^{-1} in 10% v v^{-1} HNO_3 solution with gradual addition of Na_2CO_3. SS - without Na_2CO_3 (sample:modifier ratio, 1:0 m:m), SS20 - with 20 mg Na_2CO_3 (1:1 m:m), SS40 - with 40 mg Na_2CO_3 (1:2 m:m), SS60 - with 60 mg Na_2CO_3 (1:3 m:m), SS80 - with 80 mg Na_2CO_3 (1:4 m:m), SS100 - with 100 mg Na_2CO_3 (1:5 m:m), and SSMo - 120 mg

a percentage of 45 – 60% of the original powder did pass through the sieve pores.

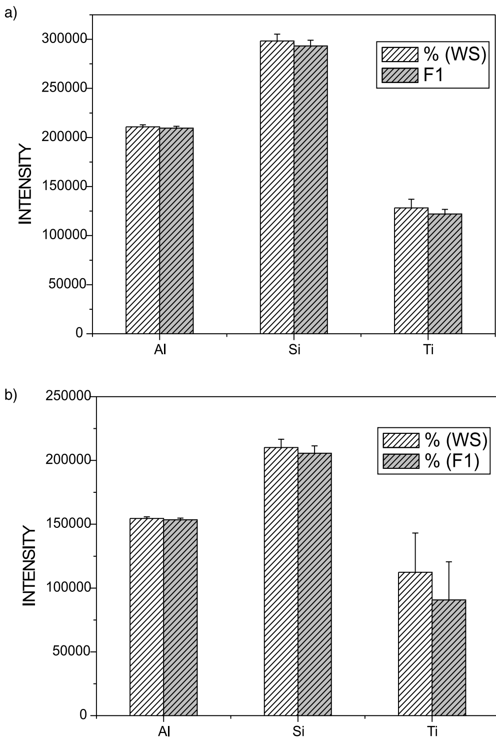

Figure 6. Emission intensities and relative standard deviation Al, Si, and Ti (n = 3). Slurries prepared from IPT-42 usin Na_2CO_3 or (b) $LiBO_2$. WS – without separation of particle size F1 – particles sizes lower than 37 μm.

Conclusions

It was demonstrated that mechanochemical synth processes were operative for generating new compou when clays and refractory materials were ground in a impact ball mill by adding either $LiBO_2$ or Na_2CO chemical modifiers.

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

Slurries were prepared using these samples modi by grinding in the presence of chemical modifiers and emission intensities of their constituents were meas by ICP OES with axial viewing. It was observed a signifi increase of signals for all elements in all samples gro with either $LiBO_2$ or Na_2CO_3.

Further developments will focus on the feasibilit this procedure for improving the calibration strategy w dealing with the direct introduction of slurries in ICP O

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