

A Straightforward Method for Determination of Al and Na in Aluminosilicates Using ICP OES

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The improvements on aluminosilicates dissolution through microwave-assisted acid decomposition procedures for Na and Al quantification by inductively coupled plasma optical emission spectrometry (ICP OES) are reported here. Complete dissolution of the samples is achieved employing 4 mL of HNO₃ and 3-4 mL of HF thus reducing the total amount of these reactants in comparison with procedures found in the literature. Additionally, the type of crucibles used in the calcination for sample preparation step is also evaluated. Na and Al concentrations are in agreement with the expected values on the samples. Estimated silicon amount is achieved by difference of sodium and aluminum, and then Si/Al molar ratios were calculated for samples calcined in both porcelain (Si/Al is in the range 22-42) and platinum (Si/Al is in the range 27-40) crucibles, showing no difference between these procedures.

Keywords: sample preparation, ICP OES, microwave digestion, acid dissolution

Introduction

Inductively coupled plasma optical emission spectrometry (ICP OES) is a powerful multi-elemental technique applied to chemical analysis¹ which requires a sample preparation step involving only a simple dilution or total dissolution if the sample is a solid.^{1,2} Concerning solid samples, methodologies involving suspensions prepared from finely powdered samples (slurries) have become acceptable^{1,3,4} as well as the application of extraction methods⁵ depending the nature of sample. ICP OES presents some advantages such as low degree of matrix-interference, high analytical frequency, linearity of calibration curves over several orders of magnitude and excellent reproducibility.¹ Additionally, detection and quantification limits allow the determination of a diversity of metals and nonmetals in a myriad of sample types such as cements, ceramics, silicates, geological materials, metallosilicates, refractory compounds, aluminophosphates, silicoaluminophosphates, clays, phyllosilicates, and coals.^{4,6-14}

The chemical analysis of the inorganic solids mentioned above by ICP OES using conventional acid dissolution methods, in open flasks on hot plate,¹⁵ usually involves costly and time-consuming procedures for sample preparation,³ requiring a long analysis time and large amounts of reagents. Additionally, such conventional procedures do not assure complete dissolution of some solid inorganic samples, especially geological samples^{15,16} (including silicates^{8,13,17} and aluminosilicates)^{14,16} even when a large amount of concentrated acids is used.^{3,8} Moreover, these procedures allow analytes loses and samples contamination,⁴ with the accuracy, reproducibility, and precision being affected.⁸ Another negative point of using a large amount of acid mixture in open systems is a potential source of systematic error because of the use of ultra-pure reagents. HNO₃ presents 1 and 0.01 µg L⁻¹ of Al and Na, respectively, while these values are 0.5 and 0.6 µg L⁻¹ of Al and Na, respectively, for HF.¹⁸ These impurities affect the detectability method, making it impossible to determine elements in low concentrations.

In this way, microwave radiation has been also used for extraction procedures (microwave-assisted extraction, MAE)^{19,20} besides synthesis of different

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materials,²¹⁻²³ as carbon nanotubes²⁴ and organo-functionalized magnesium phyllosilicate.²⁵ It is also widely and successfully applied to sample decomposition, when combined with the use of sealed-vessels^{15,16,26} and concentrated, strong, oxidizing and/or non-oxidizing acids (e.g., HNO₃, HCl, HF, H₂SO₄, HClO₄, etc.).^{14,16,27-30} Microwave-assisted digestion is a promising method to achieve this critical step of solids analysis^{10,31} because it attains fast dissolution rate while avoiding analyte losses (mainly the volatile analytes),³² minimizes possible contamination of the digest,²⁹ increases reproducibility³² and assures safety procedure. Closed systems for sample decomposition require a lower acid volume, increases the reliability of the method, and, consequently, the figures of merit (accuracy, precision, sensitivity). Furthermore, digestion procedures performed in closed vessels are efficient because such systems can reach higher temperatures since the boiling points of the acids are raised by the pressure generated within the vessel.³³ Both, increased temperature and pressure, lead to a higher reactivity of the reactants^{30,33} and a significantly decreased time of analysis.³³

Different inorganic solids can require different acid mixtures;³⁰ both silicate and aluminosilicate matrixes are dissolved only in the presence of HF.^{15,30} The strong Si–O bonds are broken by complexing F⁻ ions, forming SiF₄ which volatilizes upon heating.³⁰ Although HF has been effective by itself, its combination with other strong mineral acids (HClO₄, HNO₃, HCl, aqua regia or H₂SO₄) increases the capability of this non-oxidizing acid in sample decomposition.³⁰

Yafa and Farmer⁵ performed microwave-assisted dissolution of peat samples using acid mixtures of a range of compositions depending on the composition of the analyzed solids (Table 1). The peat sample with aluminosilicates in its composition required concentrated HNO₃ (9 mL) and concentrated HF (0.5 mL). Totland *et al.*³⁴ reported that a

combination of 29, 16 and 12 mol L⁻¹ of HF, HNO₃ and HClO₄, respectively, and three microwave digestion runs was sufficient to obtain total dissolution of geological samples (Table 1). On the other hand, Navarro *et al.*¹⁶ used a combination of 15, 15 and 15 mL of HF, HNO₃ and water to assure total dissolution of geological samples, following a decomposition procedure, which involved at least four microwave run steps, which took almost 5 h (Table 1).

Digestion of ceramic samples in open vessels took 7.5, 7.5, 7 and 10 mL of H₂O, HNO₃ (65%), HClO₄ and HF (48%), respectively.⁸ When the same samples were submitted to microwave digestion (Table 1) the effective acidic mixture was: 3 mL of HNO₃ (65%) and 10 mL of HF (48%).⁸

Despite numerous reports concerning solid sample decomposition, an intensive development, dissemination of information besides improvements of methods is still very much necessary. In this way, the present study aims to develop/optimize the amount and relative acid composition (HNO₃ + HF) in the mixture applied for dissolution of aluminosilicate samples of Na-RUB-18 structure (also known as octosilicate) and quantify aluminum and sodium via ICP OES.

For these determinations, a microwave-assisted decomposition method was applied as an alternative to the traditional sample preparation procedures, which comprise dissolution steps in open flasks using hot plates. The limitations observed in these procedures, such as the incomplete sample decomposition, high probability of contamination, among others prompted the present study. The estimation of silicon concentration was made by taking into account aluminum and sodium concentration in calcined samples, and then, Si/Al molar ratios were calculated. Si/Al_{ICP} of these zeolitic materials is an important property related to the acidity of these solids. Additionally, the calcination pre-treatment was performed

Table 1. Microwave decomposition to geological samples

Material	Mass / g	Amount of acid / mL				time for total digestion / h	Reference
		HF	HCl	HNO ₃	HClO ₄		
Peat	0.25	–	–	10	–	0.83	5
Peat	0.25	–	3	9	–	0.83	5
Peat	0.25	0.5	–	10	–	0.83	5
Andesite ^a	0.50	4	–	8	2	1.05	34
Serpentinite	0.50	8	–	4	2	1.05	34
Basalts, amphibolites ^b	0.10	15	–	15	–	4.83	16
Ceramic ^c	0.10	10	–	3	–	0.42	8

^aThe geological materials limestone, dolomite, Hawaiian basalt, granite marine mud, cody shale, nepheline and seyenite were dissolved following the same procedure above; ^bbesides the acid mixture, this procedure used 15 mL of water; samples from Niquelândia Complex; ^canalyzed samples have at least the followed mineralogical composition: quartz, dolomite, calcite, hematite, plagioclase feldspar, analcime, plagioclase, amphibole, clinoenstatite, spinel, mullite.

in both porcelain and platinum crucibles in order to evaluate the influence of the crucible material in the obtained results. The hypothesis was that porcelain could decompose in the calcination temperature. This effect was proven absent and it was advantageous because platinum is quite expensive when compared to porcelain, using the last for the calcination in the sample preparation step allowed the simultaneous examination of repetition experiments.

Experimental

Reagents, materials and solutions

All reagents were of analytical grade, including HNO_3 (65%, Sigma-Aldrich), HF (40%, Sigma-Aldrich), NaCl (>99%, Sigma-Aldrich), and H_3BO_3 (Vetec). Deionized water ($18.2 \text{ M}\Omega \text{ cm}$), obtained in a Milli-Q Millipore system was used to prepare all solutions. An aluminum standard solution of 1000 mg L^{-1} (Fluka Sigma-Aldrich) was used to prepare a series of calibration standard solutions. A standard solution of 2000 mg L^{-1} Na was prepared, using dry NaCl (Sigma-Aldrich). Then, 100 mg L^{-1} stock solutions of Al and Na were prepared by diluting the above standard solutions. The six standard solutions of the analytical curves with concentrations ranging between 0.5 and 10 mg L^{-1} were obtained through dilution of 100 mg L^{-1} stock solutions of Al and Na. The volumes of all solutions were completed with 1% (v/v) HNO_3 aqueous solution, which was used as a blank.

Aluminosilicates with the RUB-18 crystalline structure were previously synthesized with nominal Si/Al molar ratios of 15, 30 and 60 and named as [15Al]-RUB, [30Al]-RUB, and [60Al]-RUB, respectively.

Instrumentation

The pre-treatment step of the samples described below (Sample preparation sub-section) was performed in a muffle furnace model EDGCON 5P. The solid decomposition was performed using a Provecto Analítica DGT 100 Plus oven equipped with a twelve-positions tray for Teflon® PTFE digestion vessels and a magnetron of $2450 \pm 13 \text{ MHz}$ with a nominal power of 1200 W . Measurements were performed in a Thermo Scientific iCAP 6000 ICP OES. The instrumental conditions used for quantitative determination of the elements are given in Table 2.

Sample preparation

The preparation of samples for the ICP OES analysis comprised a pre-treatment step and microwave digestion part described below.

Table 2. Operating conditions of the ICP OES for quantitative Al and Na determinations

Power RF / kW	1.3
Viewing	
Al	axial
Na	axial
Plasma gas flow rate / (L min^{-1})	0.5
Emission line / nm	
Al	396.152
Na	589.592

Pre-treatment

First, each previously synthesized sample was distributed in both platinum and porcelain crucibles and heated from room temperature to $900 \text{ }^\circ\text{C}$ in a muffle furnace model EDGCON 5P, under argon atmosphere, at $2 \text{ }^\circ\text{C min}^{-1}$ heating rate. Then, the samples were maintained at this temperature for 10 h under oxygen atmosphere and cooled down to room temperature. The oxygen was used in order to burn out any organic material present in the samples before the digestion step. After that, the samples were ground using an agate mortar and pestle to obtain fine powders (less than $500 \mu\text{m}$), increasing the contact area of the samples with the solvents to guarantee complete dissolution in the digestion step.

The calcination procedure was performed in order to destroy the crystalline structure of the solids and to obtain the oxides (Na_2O , SiO_2 and Al_2O_3). In the next step, the samples were submitted to acidic decomposition (a mixture of 65% (v/v) HNO_3 and 40% (v/v) HF) assisted by microwave radiation as described below.

Optimization of the acid decomposition method assisted by microwave radiation of synthesized aluminosilicates

RUB-18 aluminosilicate samples, previously calcined in both platinum and porcelain capsules as described above, were submitted to the same acidic microwave decomposition program shown in Table 3.

Table 3. Microwave program for aluminosilicates decomposition

Step	Power / W	Plateau time / min
1	400	5
2	790	8
3	320	4
4	0	3

The amount of each calcined sample used in the procedures was calculated to afford solutions with

concentrations of 20–50 mg L⁻¹ of Al³⁺, as shown in Table 4. Then, diluted solutions of the totally dissolved samples were analyzed by ICP OES. The concentrations of both aluminum and sodium were calculated taking into account the amount of sample shown in Table 4 and two considerations: that the unit cell composition was Na₈[Si_yAl_x(OH)₈]·32H₂O, y = 30 – 31.5; x = 0.5 – 2.0 and that all the aluminum added to the synthesis of the Na-RUB-18 was incorporated into the framework; the concentration of sodium was maintained as shown in the unit cell composition. After ICP OES analysis, the real concentrations of the both aluminum and sodium were compared with the expected values, to indicate the success of the synthesis procedure.

The nomenclature of the samples [15Al]-RUB, [30Al]-RUB and [60Al]-RUB was increased by “pt” and “por”, respectively, for better identification of each type of crucible, platinum or porcelain, used (Table 4).

Table 4. Sample mass^a in each procedure

Sample	Mass / g
[15Al]-RUB/por	0.1001 ± 0.0001
[15Al]-RUB/pt	0.1004 ± 0.0025
[30Al]-RUB/por	0.1693 ± 0.0120
[30Al]-RUB/pt	0.1738 ± 0.0014
[60Al]-RUB/por	0.1384 ± 0.0005
[60Al]-RUB/pt	0.1382 ± 0.0002

^aCalcined material; pt: platinum; por: porcelain.

Procedure 1

Optimization 1: interaction of microwave energy and acid volume

This optimization step involved the interaction of microwave energy and acid volume being applied to the samples [30Al]-RUB/por and [30Al]-RUB/pt.

A desired mass (Table 4) of the calcined sample [30Al]-RUB/por for obtaining 50 mL of a solution with ca. 50 mg L⁻¹ of Al³⁺, was weighed into Teflon® PTFE digestion vessels. Then 2 mL of 65% (v/v) HNO₃ and 1 mL of 40% (v/v) HF were added initially to the vessels, which corresponds to triplicate analyses of the sample [30Al]-RUB/por, and the PTFE bombs were tightly sealed (Table 5). The vessels corresponding to triplicate analyses of [30Al]-RUB/por and nine Teflon® PTFE digestion vessels with only the same amount of acid mixture (2 mL of 65% (v/v) HNO₃ and 1 mL of 40% (v/v) HF) were transferred to the microwave system, amounting to twelve bombs (Table 5, line 1), filling the whole microwave tray. The nine vessels containing only the acid mixture were

needed to ensure the same interaction of the microwave energy with all of them, as well as to dilute its intensity reducing the exposure time.

Table 5. Digestion procedure for [30]-RUB-18/pt and [30]-RUB-18/por samples

Run	Amount of acid / mL		Teflon® PTFE / unit	Aspect of the digested
	40% (v/v) HF	65% (v/v) HNO ₃		
I	1	2	12	undissolved sample
II	0	0	12	undissolved sample
III	1	2	6	undissolved sample
IV	0	0	6	undissolved sample
V	1	0	6	transparent/total dissolution
Total	3	4		

Then, the system was submitted to the first digestion run following the microwave program described in Table 3 using the masses shown in Table 4. Then the system was cooled down; visual inspection indicated that undissolved sample was still present in the flasks. Thus, a second run was performed, without any further addition of acids, to try to promote the total dissolution of samples. The procedure was not successful, undissolved solid was still found at the vessel (Table 5, run II).

In order to increase the exposure time of each vessel to the microwave radiation, from the third run onwards, only six Teflon® PTFE vessels were maintained in the oven, alternating voids and vessels in the tray, thereby increasing the amount of microwave energy received by each one of them and, consequently, reducing the consumption of sample and reagents. Then 1 mL of 40% (v/v) HF + 2 mL 65% (v/v) of HNO₃ were added to each vessel initially submitted to a run equal to the first run program: three vessels corresponding to the triplicate of the sample and three other with only the acid mixture (Table 5, run III). Again, undissolved solid was observed in the bombs. The fourth run was the same as run II with six Teflon® PTFE vessels in the tray (Table 5, run IV) to attempt complete dissolution of the sample. No success in the run IV since visual inspection showed undissolved sample.

After these failed runs, 1 mL of 40% (v/v) HF was added to each vessel and the system was submitted to the run V, Table 5. Finally, total dissolution of the sample was observed.

After total acid decomposition of the samples [30Al]-RUB/por and [30Al]-RUB/pt (Table 5, run V) and slight cooling, 900 mg of H₃BO₃ were added to each Teflon® PTFE vessels, including the blank. A period of

ca. 40 min elapsed and the contents (including the blank) were transferred to volumetric flasks using filter paper, and the volume was completed to 50 mL with 1% (v/v) HNO₃. Each solution was diluted to prepare a new one with ca. 5 mg L⁻¹ of Na⁺. This procedure was carried out to allow for the measurement of the analyte within the linear range (1-10 mg L⁻¹) in the ICP OES equipment.

Teflon® PTFE digestion vessels were placed in the microwave system in alternate positions in the tray in all runs performed by this procedure.

All the steps described in such procedure above were also performed with the sample [30Al]-RUB/pt.

Procedure 2

Optimization 2: acid volume

This procedure was performed with the sample with Si/Al_{nominal} molar nominal ratio of 60. Approximately 140 mg (Table 4) of sample were weighted into Teflon® PTFE vessels and 4 mL 65% (v/v) HNO₃ + 3 mL of 40% (v/v) HF were added. The vessels were sealed tightly and submitted to microwave decomposition according to the program described in Table 3. In order to promote total sample dissolution, 1 mL of 40% (v/v) HF was added, and the system submitted to a second run at the same conditions as above. At the end of the run, a solution was obtained. [15Al]-RUB samples were prepared with 4 mL 65% (v/v) HNO₃ + 4 mL of 40% (v/v) HF in a single microwave-assisted decomposition step.

Results and Discussion

The decomposition procedures performed in this study aimed to reduce the acid amount involved in the dissolution of these samples, to diminish volatilization and/or precipitation of analytes, to avoid both a long time of analysis^{3,29} and the damage of the vessels. All these efforts were made by focusing on an efficient decomposition, leading to good recoveries²⁹ of the analytes.

Table 6. Concentrations of Al and Na in the calcined samples submitted to microwave-assisted digestion and determined using ICP OES

RUB-18	Al _{calc} ^a / (mg L ⁻¹)	Al _{ICP} / (mg L ⁻¹)	Na _{calc} ^a / (mg L ⁻¹)	Na _{ICP} / (mg L ⁻¹)
[15Al]/por ^a	1.52 ± 0.001	1.05 ± 0.09	5.02 ± 0.002	4.87 ± 0.31
[15Al]/pt ^a	1.52 ± 0.001	0.88 ± 0.04	5.03 ± 0.002	5.44 ± 0.46
[30Al]/por ^a	0.70 ± 0.05	0.51 ± 0.06	4.61 ± 0.33	4.73 ± 0.11
[30Al]/pt ^a	0.80 ± 0.006	0.55 ± 0.01	4.73 ± 0.04	4.59 ± 0.10
[60Al]/por ^a	0.44 ± 0.002	0.58 ± 0.02	5.25 ± 0.02	6.20 ± 0.15
[60Al]/pt ^a	0.44 ± 0.001	0.64 ± 0.08	5.24 ± 0.01	7.12 ± 1.80

^aNot compared to a certified material.

H₃BO₃ was added after total dissolution of the solids to form a fluoride complex in the medium, resulting in the volatile BF₃, avoiding the formation of precipitates. This step also avoids the damage of the quartz torch by fluoride compounds as well as any other component of the ICP OES when the sample solution is introduced into the system and pre-optic interface. Additionally, the measurement using diluted samples is preferable for three reasons: (*i*) to make sure that the equipment detector will not be saturated; (*ii*) to avoid damages to the ICP OES apparatus due to concentrated acidic mixture; (*iii*) to make sure that the elements will be determined within the linear range of the analytical curve.

Progressive microwave-assisted acid decomposition steps were performed in the Procedure 1 until total dissolution of the samples was achieved (Table 5). In this way, five runs were performed with the initial amount of solid, adding acid, as shown in Table 5. The total digestion of the samples [30Al]-RUB/por and [30Al]-RUB/pt required 4 mL of 40% (v/v) HF and 3 mL of 65% (v/v) HNO₃. Once aluminosilicates dissolution of the type [30]-RUB was optimized, the digestion of [15Al]-RUB/por and [15Al]-RUB/pt was performed in a single microwave-assisted run with 4 mL of 40% (v/v) HF and 4 mL of 65% (v/v) HNO₃.

The aluminum and sodium calibration curves presented linear correlation coefficient of 0.9999 and 0.9998, respectively (Figures S1 and S2, Supplementary Information section). The results obtained for the samples are shown in Table 6 and good agreement was attained with expected concentrations when the samples were treated in both, platinum and porcelain crucibles, showing good recovery degrees of the elements examined after dissolution procedures.

The higher SiO₂ concentration in [60Al]-RUB required a larger amount of HF for its total dissolution. Even in that case, the amount of the acidic mixture and time are smaller than the ones used in procedures reported for similar materials.^{8,29}

The present study showed an improvement on aluminosilicates dissolution, as well as considerable reduction on total analyses time, which is a limiting step for sample preparation focusing on ICP OES analysis. In contrast, when using conventional decomposition method in open flasks over hot plate, long times are currently devoted for sample dissolution. Ceramics, soil, silicates, and aluminosilicates demand large amounts of acids and lengthy heat treatments in comparison to the method described here sometimes without success.

The acid dissolution of aluminosilicates [Al]-RUB-18 was performed in our laboratory in open flasks using hot plate as heating source. Generally, after adding a large amount of a mixture of concentrated HClO_4 , HNO_3 and HF, at least three times more acid than what was described here, during several days, undissolved sample was still observed in the flasks.

Tsolakidou *et al.*⁸ also have spent a large amount of acid in dissolving ceramics (0.15 g) in open vessels: 5, 5, 10 and 2 mL of HNO_3 65%, H_2O , HF and HClO_4 , respectively, in a first digestion step. The addition of HF 48% and HClO_4 , 10 and 2 mL, respectively, was performed in each subsequent digestion step until total dissolution of the solid. Then 5 mL of HClO_4 and, at the final step, HNO_3 (2.5 mL) and deionized water (2.5 mL) were added. This approach consumed 36.5 mL of acids to achieve dissolution of the material. Dissolution by the method proposed here employed ca. 4 times less volume of acid. Even through the authors used microwave digestion, a higher amount of acid mixture was used compared with our study: 3 mL of HNO_3 65% and 10 mL of HF 48% to dissolve 0.1 g of ceramic.

Having optimized the microwave-assisted acid decomposition procedure for Na-[Al]-RUB-18 layered aluminosilicates, such straightforward method was applied to dissolve pillared-layered aluminosilicates and to quantify Al and Na. The dissolution of these solids was performed with the microwave program shown in Table S1 (Supplementary Information section), using only 300 mg of H_3BO_3 after the single dissolution step. Si/Al_{ICP} ratios were determined as described above with [Al]-RUB samples (Table S2, Supplementary Information section). This approach can be applied to the dissolution of synthetic talc, a well known 2:1 phyllosilicate, a clay. Since the 2:1 phyllosilicates lose their brucite layer in acid media, the silica layers remain free and are dissolved by the working up of the process. In fact, the procedure is simpler and faster for phyllosilicates; the octosilicate is very difficult to dissolve and analyze, and that was precisely the reason why we decided to report it as the main subject of this procedure.

Furthermore, the acid dissolution process studied here was used to dissolve mordenite and omega zeolites (Table S3,

Supplementary Information section), aluminophosphates and silicoaluminophosphates (results not shown).

Additionally, it is noteworthy that the proposed method complies with the concepts of Green Chemistry because it reduces the use of reactants and generation of hazardous substances for the quantification of Al and Na in aluminosilicates.³⁵

In this study, silicon was determined indirectly, and the Si/Al molar ratio was calculated by difference (Table 7),³⁶ taking into account the amount of calcined sample in both type of crucibles, from aluminum and sodium values quantified by ICP OES (Table 6). The differences between the values obtained and calculated were not related to problems involving the recovery of the elements but to the synthesis method of the solids studied. The amount of heteroatom incorporated into zeolites and/or molecular sieves depends of the method of incorporation, framework type and nature of the heteroatom (Al^{3+} , B^{3+} , V^{5+} , Ti^{4+} , Fe^{3+} , etc.) to be incorporated, as observed in the literature.³⁷⁻³⁹

Table 7. Si/Al molar ratio calculated from results obtained by ICP OES

Sample	Si/Al _{nominal}	Si/Al _{ICP}	
		Porcelain	Platinum
[15Al]-RUB	15	22 ± 2	27 ± 2
[30Al]-RUB	30	42 ± 8	40 ± 1
[60Al]-RUB	60	40 ± 1	36 ± 6

In order to evaluate if there is a difference between platinum and porcelain crucibles, the *t*-test was applied. There is no significant difference at 99% confidence level for sample [15Al]-RUB and 95% for [30Al]-RUB and [60Al]-RUB for results obtained using platinum and porcelain crucibles. In this way, aluminosilicates can be calcined at 900 °C in porcelain crucibles because the material does not interfere in the quantification of Na and Al.

Conclusions

The microwave-assisted decomposition procedures optimized in this study for aluminosilicates was shown to be effective, since a complete dissolution of the solids in a short period of time was observed while the consumption of acids was kept to a minimum. The procedures were applied to layered Na-[Al]-RUB-18 and to their pillared derivative, to two zeolite structures and are also adequate for clays, phosphates and aluminophosphates. By using porcelain or platinum crucibles for the calcination step, there was no difference on Si/Al molar ratios when the silicon concentration was obtained by difference of the

amount of calcined sample. Finally, the strategies of sample preparation for Na and Al quantification by ICP OES allow high analytical frequency.

Supplementary Information

Supplementary information is available free of charge at <http://jbcs.sbn.org.br> as PDF file

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