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RESEARCH ARTICLE

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DEVELOPMENT AND VALIDATION OF AN ANALYTICAL METHODOLOGY FOR QUANTIFICATION OF Al IN ALUMINA-BASED MATERIALS BY ^{27}Al SOLID-STATE NMR

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ABSTRACT

In this work, a simple protocol for counting the Al spins present in diamagnetic materials used as carriers and catalysts based on ^{27}Al solid-state nuclear magnetic resonance using routine 4 mm rotors was developed and validated. The acquisition parameters were optimized, and validation tests were performed using a standard sample of γ -alumina with a known aluminium concentration. The validation results indicated that solid-state NMR can be used for the quantification of quadrupolar aluminium (mmol Al.g^{-1} material) in diamagnetic materials by employing non-special tools with satisfactory results, similar to the NMR quantitative analysis of dipolar nuclei in solids.

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INTRODUCTION

Nuclear magnetic resonance (NMR) spectroscopy is one of the most important tools of structural characterization and has also been used for quantitative purposes. The advantage of NMR over other analytical techniques is that it is a primary standardization method, similar to gravimetry, titration techniques and coulometry, among others. For this reason, the construction of an analytical curve and the use of reference standards identical to the analytes are in principle unnecessary (Malz et al., 2005). The use of NMR for quantification allows the substances under investigation to be identified and quantified directly from the spectrum obtained since the NMR signal area is directly proportional to the number of nuclei that contribute to the observed signal (Liu et al., 1996; Mingyue et al., 2021; Wawer et al., 2008). Although NMR is a primary quantification technique, its use for the evaluation of samples in solid form (MAS NMR) is mainly focused on nuclei with spin = $\frac{1}{2}$.

For ^{13}C quantification, usually a combination of cross-polarization (CP MAS, in which the signal detection is modulated by the H population near the site) and direct polarization (DP MAS) spectra is used to obtain quantitative data (Bakhmutov et al., 2006; Smerniket et al., 2000; Wang et al., 2018; Wawer, 2008). ^{27}Al is a nucleus with spin $I = 5/2$ (therefore quadrupolar), with a natural abundance of 100% and a quadrupole moment of $0.1466 \times 10^{-28} \text{ m}^2$. In the presence of an external magnetic field B_0 , ^{27}Al nuclei possess six Zeeman states defined by the $m = 5/2, 3/2, 1/2, -1/2, -3/2$ and $-5/2$ orientational quantum numbers (Benndorf et al., 2017) and five transitions ($n \rightarrow n+1; n = -I$ to $I-1$). Although for quantitative NMR analysis of spin $I=1/2$ nuclei, the use of $\pi/2$ single pulse excitation is indicated, in quadrupolar nuclei the quadrupolar interactions are orientation dependent, and the extent to which they are excited affects the intensities observed (Haouas et al., 2016). In this situation, the line intensity could be measured for quantification purposes following the protocol based on a reduced pulse angle such that $(I+1/2)w_1T_p/6$ to obtain a less than 5% error, as noted by Smith and van Eck (1999), by using single pulse excitation, and the resulting signal (FID – 'free

induction decay⁷) is recorded as the spins return to equilibrium. The spin system relaxes back to equilibrium state by first-order processes characterized by two relaxation times, T1 and T2 (Wawer, 2008). T1 is the longitudinal relaxation time, that measures how rapidly the spins return to the equilibrium and is experimentally determined for each signal. Additionally, the recycle delay (D1) must be adjusted to a value of at least $5 \times T1$. In addition, the position of the centre of gravity is dependent on the electric field produced by the environment, so the quantitative detection of ^{27}Al in solid samples is hampered by the possibility of a loss of signal area due to, among other factors, the presence of sites with distorted symmetry (Gee et al., 2001). Fortunately, for diamagnetic samples, the effect can be neglected, as is the case for the samples investigated in this work.

Aluminium oxide, Al_2O_3 , generally known as alumina, is a very important industrial material with several applications. These applications range from electronics, optics and mechanical engineering to biomedicine (Ananthanarayanan et al., 2010; Saini et al., 2017). Many polymorphs of alumina are known as transition aluminas and are traditionally obtained from the calcination of their precursors, usually hydroxides or oxy-hydroxides (Chagas et al., 2014; Liu et al., 2015). In petrochemical industries, $\gamma\text{-Al}_2\text{O}_3$ is used as a catalyst or catalyst support (Rocha et al., 2007; Li et al., 2009; Liu et al., 2010; Arias et al., 2013).

The characterization of heterogeneous catalysts is fundamental to explain and predict some of their main properties. Quantitative NMR data of quadrupolar nuclei such as ^{27}Al are relevant information that can help in understanding the catalytic phenomenon (Fyfe et al., 2001; Lima et al., 2014; Man et al., 1988). A significant portion of the starting materials for the preparation of catalysts have Al in their composition, such as alumina (Firdous et al., 2019; Paglia et al., 2003), metal-supported aluminas (Al-Fatesh et al., 2018; Claude et al., 2020; Weissman et al., 1996), bauxite and Al-containing mixed oxides. Bauxite is a natural mineral and is the main source of aluminium. It is a heterogeneous mixture of trihydroxides (gibbsite) and oxyhydroxides (diaspore and boehmite), predominantly gibbsite, aluminium silicates, iron and/or titanium dioxide (Constantino et al., 2002; Crosson et al., 2006). Many problems related to NMR quantification through spin counting can be avoided by considering the sample as part of the circuit involved in signal generation and detection.

The amplitude variation due to the dielectric constant and conductivity is temperature dependent and can be inferred based on the evolution of the quality factor of the probe. By controlling the probe head temperature, this factor can be considered constant (Haouas et al., 2018). For the rotor sample holder, Ziarelli et al. (2007), Sanchez et al. (2008), and recently Brinkmann et al. (2019) developed procedures to perform quantitative measurements of ^{13}C and ^{19}F by solid-state NMR such that the entire sample contributed to signal formation. They measured the contribution to the signal from different areas of a 4 mm rotor, and it was evidenced that a higher sensitivity is present in the central part that homogeneously responds to the excitation. The lower signal contributions from the top and bottom of the rotor were attributed to the effects of the inhomogeneity of the radiofrequency field, and the exclusion of those volumes contributes to reliable quantitative analysis. Thus, the authors used a specially designed rotor that excluded the top and bottom rotor areas. Regardless of the satisfactory results, this protocol is not practicable in routine solid-state NMR labs due to the unconventional rotors and inserts.

Considering the potential of the solid-state NMR technique as an analytical tool, the importance of following validated protocols during quantitative work and the use of alumina worldwide, the objective of this work was to present the development and validation of a methodology for Al quantification by this method, following the protocols recommended by distinct resolutions (ABNT, 2016; ANVISA, 2003; EURACHEM/CITAC, 2012; EUROLAB, 1/2014; INMETRO, 2001). Although there are some examples of spin counting of quadrupolar nuclei by solid-state NMR (Haouas et al.,

2016; Fitzgerald et al., 1994; Jiao et al., 2005), to the best of our knowledge, this is the first time a validated protocol for Al quantification has been reported using a routine 4 mm device. Success was achieved in the quantification of Al present in samples of alumina-based supports and catalysts in which diamagnetic nuclei are dominant.

Experimental

Preparation of samples: A sample of Pural Alumina (from Sasol Inc., USA) with known alumina content was used as a reference for the validation tests. The developed protocol was applied for the quantification of Al in the following materials: an alumina synthesized in the laboratory, a sample of certified bauxite (no. NCS DC 61105 provided by China National Analysis Center, China) and supports containing Nb_2O_5 in Al_2O_3 with 11% Nb_2O_5 and 20% Nb_2O_5 , provided by the Heterogeneous Catalysis Laboratory of the Institute of Chemistry (IQ) of the Universidade Federal do Rio de Janeiro (UFRJ, Brazil). Table 1 shows the details of the materials used, while the chemical composition is indicated in Table S1 (Supplementary Material). Sodium chloride Sigma Aldrich (PA) was used as the diluent in the preparation of solid solutions with an Al percentage in the range of 5 to 100%.

All samples were pulverized and weighed on a Shimadzu brand AY220 semi-analytical balance (220 g capacity and 0.01 mg/0.1 mg accuracy).

Table 1. Diamagnetic materials studied in this work

Material	Formula	Origin
γ -alumina Pural	Al_2O_3	Sasol Inc. USA
γ -aluminaS	Al_2O_3	Synthesis product
Bauxite	$\text{AlO}_2(\text{OH})$	China National Anal.Center
11 $\text{Nb}_2\text{O}_5/\text{Al}_2\text{O}_3$	$\text{Nb}_2\text{O}_5/\text{Al}_2\text{O}_3$	Lima et al. (2014)
20 $\text{Nb}_2\text{O}_5/\text{Al}_2\text{O}_3$	$\text{Nb}_2\text{O}_5/\text{Al}_2\text{O}_3$	Lima et al. (2014)
MoAl	$\text{Mo}/\text{Al}_2\text{O}_3$	Rocha et al. (2007)
MoAlNb	$\text{Mo}/\text{Nb}_2\text{O}_5/\text{Al}_2\text{O}_3$	Rocha et al. (2007)

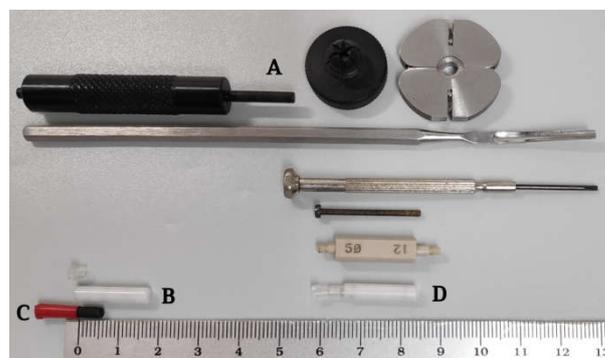


Figure 1. Materials used for sample packaging: (A) hand tools; (B) routine 4 mm r-rotor; (C) plastic cylinder for free volume control; and (D) special 50 μL HRMAS 4 mm c-rotor

Acquisition of ^{27}Al solid-state NMR spectra (^{27}Al MAS NMR): The ^{27}Al MAS NMR spectra were acquired on a Bruker instrument, model Avance III 400WB (9.4T) switched at a frequency of 104.23 MHz (ν_{Larmor} of ^{27}Al), equipped with a Bruker CPMAS triple channel 4mm probe. The samples were analysed at the same temperature, thus excluding error due to variation in the Q factor of the probe head (Haouas et al., 2018). Since all the samples were spun at a rotation speed of 12 kHz and the bearing air was maintained at 293-294 K, the samples were analysed at 306 K (Grimmer et al., 1997), taking into account the effect of frictional heating during the rotation at this spinning rate. This spinning speed was sufficient to avoid the need of correction for sidebands in integral region data. The chemical shifts were referenced to the $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ signal and expressed in the ppm units defined in Equation 1:

$$ppm = \frac{\nu_{obs}(Hz) - \nu_{ref}(Hz)}{\nu_{Larmor\ 27Al}(MHz)} \cdot 10^6 \quad (\text{Eq. 1})$$

Where ν_{obs} is the frequency observed for the signal, ν_{ref} is the frequency of the reference sample (0.0 Hz) and ν_{Larmor} is the Larmor frequency of ^{27}Al , which depends on the magnetic field B_0 . We used a single pulse sequence (Bloch decay) with an excitation pulse of $1.03\ \mu\text{s}$ ($\pi/12$) and a 1s recycle time (D1). This value was more than five times the longest longitudinal relaxation times (T1) for the Al sites, which were measured by inversion-recovery pulse sequence (Figure S1, Supplementary Material) as 0.0157 s (Al^{IV}) and 0.0195 s (Al^{VI}). The probe was re-tuned after each sample change. To ensure good spectral quality, the processing was performed with manual phase correction and automatic correction of the baseline, and integrations were performed manually. In solution-state NMR, it is advisable to use an integration range wider than at least $25 \times \frac{1}{2}$ (Suiter et al., 2019). Unfortunately, our signals have widths on the order of 2 kHz, so this condition could not be fulfilled. The integration was performed in the range of 90 ppm to -80 ppm to cover only the signal areas. The contributions of spinning sidebands (ssb) from the central transitions and from satellite excitations were addressed through a series of integrations, measured by considering or not the first-order ssb. The results (Table S2, Supplementary Material) showed that approximately 99% of the Al response area was covered when only the first-order signals of each type of Al were integrated, in accordance with Malz and Jancke (2005). Between 512 and 2048 scans (NS) were used in a 100 kHz spectral window to maintain a signal/noise ratio (S/N) greater than 200 in all spectra. The signal/noise (S/N) ratio was measured electronically by using the TopSpin 3.2 Software, following Equation 2:

$$\frac{\text{signal}}{\text{noise}} = \frac{NS}{\sqrt{NS}}, \quad \text{where NS is the number of scans} \quad (\text{Eq. 2})$$

Validation: In the selectivity/specificity assays, the blank of the reference substance and the diluent (NaCl, Sigma Aldrich P.A., 99%) were analysed. The working range and linearity were determined according to the specifications (ABNT, 2016; ANVISA, 2003; EURACHEM/CITAC, 2012; EUROLAB, 1/2014; INMETRO, 2001). In the linearity test, seven different amounts of the reference sample were weighed together with a given amount of the diluent to cover a range between 5% and 100% by weight. The mixtures were ground in a mortar for 30 minutes. A curve was constructed using Al_2O_3 and NaCl (diluent) at seven concentrations (5%, 15%, 25%, 35%, 50%, 75%, and 100%). The linearity of the method was determined from the working range curve and calculated from the linear regression equation (Equation 3):

$$y = ax + b \quad (\text{Eq. 3})$$

where:

y = Absolute area (from Topspin 3.2 software)

x = Concentration

a = Slope of the calibration curve (sensitivity)

b = Intersection with the y-axis

Repeatability assays were performed with seven samples of different concentrations on two consecutive days by different operators. The precision can be expressed as the relative standard deviation (RDS) or coefficient of variation (CV%), and all parameters were calculated using spreadsheet methods (Teófilo et al., 2006). The maximum acceptable value, not exceeding 5%, is defined according to the methodology used, the concentration of the analyte in the sample, the type of matrix and the purpose of the method (INMETRO, 2011). The analyses for these tests were performed in triplicate, with three different masses, in the same way as described for the linearity and working range tests.

RESULTS AND DISCUSSION

Initially, the MAS NMR ^{27}Al spectrum of the reference sample was obtained (Figure 2, left). Two signals were observed at 63.9 ppm and

7.5 ppm, corresponding to the Al^{IV} and Al^{VI} sites, respectively, which are characteristic of this material (Fitzgerald et al., 1994). Parallel to the acquisition of the blank, measurements were performed to estimate the number of scans and the recycle time to establish the ideal parameters for acquisition of NMR spectra with S/N >200 and determine the absolute area factor (Equation 4), which was calculated for each type of rotor evaluated (theroutine r-rotor and c-rotor, containing ceramics and Kel-F inserts).

$$\text{Absolute area factor} = \frac{\text{absolute area (from Topspin software)}}{NS \times \text{sample mass} \times 19.62} \quad (\text{Eq. 4})$$

From the absolute area measured electronically and provided by the TopSpin 3.2 software, it was established for the NMR spectra that the quantification would be based on the average spin count (area) per mmol Al, the number of scans (defined by S/N >200) and the absolute area factor generated for each rotor per gram of material (Equation 4), where '19.62' is the amount (in mmol) of aluminium in a 1g sample with 100% Al_2O_3 content. In this way, the reported results were normalized to mmol Al per gram of sample. The absolute area factor was measured on different days by using a reference sample, as shown in Table S3 (Supplementary Material).

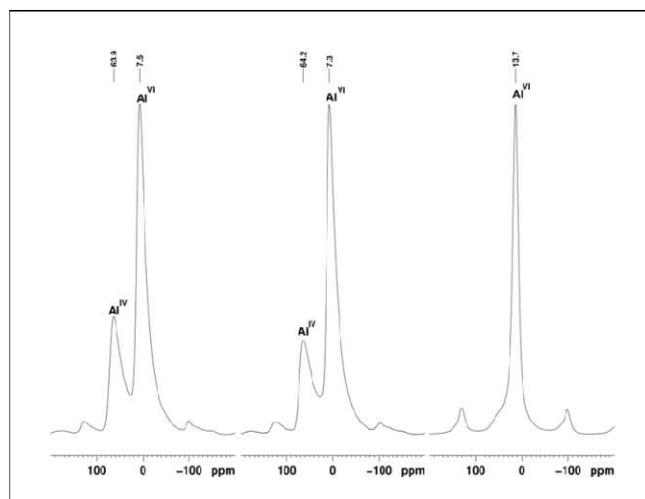


Figure 2. ^{27}Al MAS NMR spectra of the reference γ -alumina sample (left), γ -aluminaS (centre) and bauxite (right)

Analytical Method Validation: The method was validated according to distinct resolutions (ABNT, 2016; ANVISA, 2003; EURACHEM/CITAC, 2012; EUROLAB, 1/2014; INMETRO, 2001), whose purpose is to establish quantitative tests for raw materials. One of these resolutions, ANVISA advocates that the purpose of a validation is to demonstrate that the method is appropriate for the intended purpose, i.e., qualitative, semiquantitative or quantitative determination. The purpose of the specificity/selectivity assay is to ensure that the signals to be integrated for quantification correspond only to the analyte. For this purpose, the spectra of the reference substance and of the blank were separately obtained. It was evident from the extent of the signal areas in alumina that the signals present at 7.5 ppm corresponds to octahedral sites and at 63.9 ppm corresponds to tetrahedral aluminium sites, and that the analyte of interest do not exhibit interference from the diluent. The linearity curve was constructed with seven different concentrations of the analyte (Table S4, Supplementary Material), thus satisfying the recommendation of Resolution ANVISA RE No. 899 and EUROLAB. The interval was established by the smallest (≈ 1 mmol Al) and highest (19.6 mmol Al) points of this curve, which resulted in a correlation coefficient (R^2) equal to 0.9939 (Figure 3).

As the value obtained was higher than the minimum acceptance criterion described in RE No. 899 ($r \geq 0.99$), the linearity test was considered valid. The nonzero y-intercept value, although intriguing, was already reported in the literature, as in the work of Bharti and Roy (2012), who found a linear coefficient during solution ^1H NMR quantitative determination. In our case, we believe that the observed

linear coefficient could be due to the presence of trace amounts of Al in the coil region of the probe.

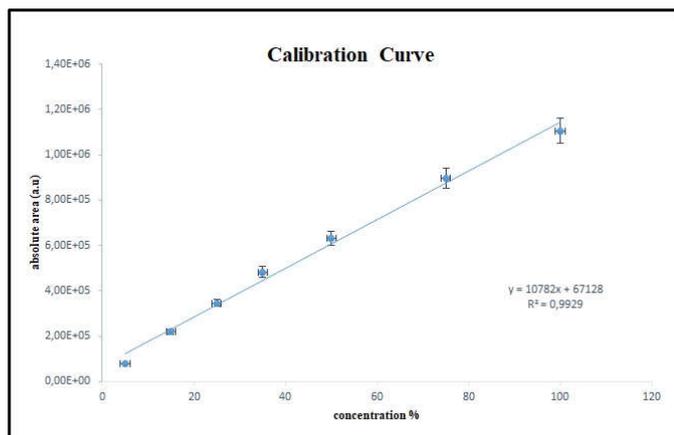


Figure 2. ^{27}Al MAS NMR spectra of the reference γ -alumina sample (left), γ -aluminaS (centre) and bauxite (right)

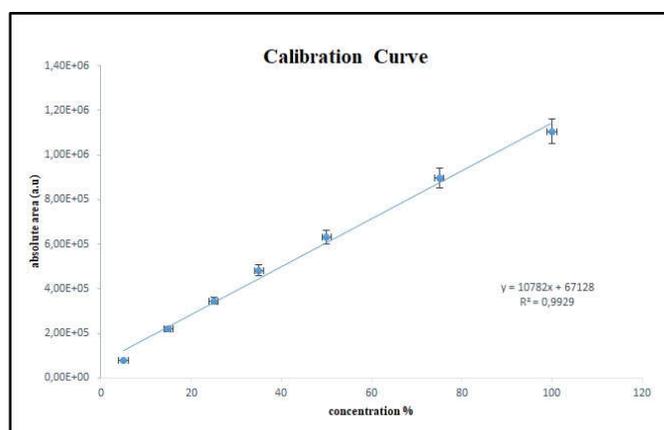


Figure 3. Linearity analytical curve for the quantification of Al by ^{27}Al MAS NMR

It is noteworthy that although the standards require the linearity test, in the case of the use of NMR, the need for this assay may be questioned due to the particularities of this analytical tool. In spectroscopic techniques such as UV and IR, the signal areas depend on specific properties of the molecules, such as the molar absorbance (for UV and IR) and the dipole moment (for IR), in addition to the respective concentrations (Roggo et al., 2007). This phenomenon does not occur for the area of the NMR signals of the same sample, which depends only on the number of nuclei that absorb energy in the radiofrequency region, that is, the concentration.

Accuracy: The accuracy test was carried out by applying the proposed analytical method to the analysis of a substance of known purity: the alumina reference sample. The mean experimental concentration values were calculated, and the accuracy was determined from Equation 5. The mean result found in the accuracy test was 97.8% - 98%. Although some international references do not establish accuracy parameters, our results are in accordance with the range of values accepted for the test (98% - 102%) according to the ABNT (2016).

$$\text{Accuracy (\%)} = \frac{\text{experimental mean concentration}}{\text{theoretical concentration}} \cdot 100 \quad (\text{Eq.5})$$

Precision: The repeatability, reproducibility and intermediate accuracy tests evaluate the accuracy of an analytical method, which can be expressed as the relative standard deviation (RSD%) or coefficient of variation (CV%). The precision in the working range is presented in the form of the repeatability and intermediate accuracy, and the relative standard deviation of the obtained results is evaluated

INMETRO (2011). The intermediate accuracy test was performed by a second analyst after two days, according to what is recommended in the regulations. In this work, the reproducibility test was not performed since it is not required for the granting of registration. The results obtained in both assays are presented in Table S5 (Supplementary Material) and were considered adequate, as they resulted in an RSD of less than 5.0%, according to the international resolution ANVISA (2003). In the repeatability assay, a value of 0.6% was obtained, and in the intermediate accuracy assays, a value of 2.1% was obtained (analyst A = 0.6% and analyst B = 2.1%). The knowledge of these values allows the uncertainty of the method to be estimated when necessary, thus guaranteeing better security in decision making.

Limits of Detection and Quantification: The limit of detection is the lowest concentration of analyte in a sample that is adequate for detection but not necessarily quantified. The limit of quantification is the lowest concentration of analyte in a sample that can be quantitatively determined with suitable precision and accuracy. The limits of detection and quantification (LOD and LOQ, respectively) are not applicable to major component methods but can be calculated based on the standard deviation of the response σ and the slope S of a calibration curve obtained in a linearity study (INMETRO, 2011). The results for the limits of detection and quantification at the 95, 99 and 99.9% confidence levels are, respectively 1.9, 2.7 and 3.6 mmol $\text{Al}\cdot\text{g}^{-1}$ for the LOD and 1.9, 3.3 and 3.9 mmol $\text{Al}\cdot\text{g}^{-1}$ for the LOQ.

Robustness: The robustness test is important to verify the susceptibility of the method to variations in the analytical conditions. These variations should be controlled, and precautions should be taken in the procedure ANVISA (2003). The robustness of the method was estimated by independently varying three parameters: (i) the number of scans; (ii) the relaxation delay; and (iii) the pulse width. The results showed that this method was quite robust because they presented little variation with the parameters (Table S6, Supplementary Material). Table 2 shows the mean results obtained in the validation tests of the analytical method proposed in this work.

Table 2. Mean results of the validation parameters for qNMR

Test	Result	Accepted value ^a
Linearity	0.9975	$r \geq 0.99$
Accuracy	$\approx 98\%$	98-102%
Repeatability	RSD 0.6%	RSD $\leq 5.0\%$
Intermediate Accuracy	RSD 2.1%	-
Robustness	RSD 2.6%	-

^aref [(EUROLAB, 1/2014; ANVISA, 2003; INMETRO, 2001; EURACHEM/CITAC, 2012; ABNT, 2016)]

Quantification: As an application of the developed protocol for quantification of Al in diamagnetic samples by ^{27}Al MAS NMR, some diamagnetic samples were analysed: a sample of certified bauxite, a γ -aluminaS sample synthesized in the laboratory, and a series of alumina and diamagnetic niobium and molybdenum metal supported alumina samples with distinct compositions to characterize and quantify the Al sites present. The ^{27}Al MAS NMR spectra of the γ -aluminaS and bauxite samples are shown in Figure 2 (centre and right, respectively). The synthesized γ -alumina displays a profile similar to that of the reference alumina, with maxima at 64.2 ppm (Al^{IV}) and 7.3 ppm (Al^{VI}). The spectrum obtained for bauxite shows an Al^{VI} signal with a maximum at 13.7 ppm and a broad low intensity signal at approximately 60 ppm (Al^{IV}). The Al levels obtained are listed in Table S7 (Supplementary Material). For the quantifications, the signals located in the range of 90 ppm to -80 ppm, corresponding to the central transition (+1/2 \rightarrow -1/2) excitation, were integrated. The mean values of the results for the synthesized γ -alumina and bauxite samples obtained by counting the aluminium spins by NMR of solids using the routine rotor were in good agreement with those obtained by XRF, considering an error percentage of up to 5% as acceptable for a semiquantitative analysis.

Table 3. Results of the MAS NMR quantification of ^{27}Al in the diamagnetic samples studied

Sample	Al Content by XRF		Al Content by NMR			S/N	
	Al_2O_3 (%)	mmol Al g^{-1}	r-rotor mmol Al g^{-1}	c-rotor (%) ^c	c-rotor mmol Al g^{-1}		
γ -aluminaS	99.4 ^a	19.5	18.8±0.02	96.3	19.3±0.02	99.1	361.8
11Nb ₂ O ₅ /Al ₂ O ₃	88.9 ^b	17.4	16.7±0.02	95.6	17.6±0.02	101.0	246.8
20Nb ₂ O ₅ /Al ₂ O ₃	80.0 ^b	15.7	15.0±0.02	95.5	15.4±0.01	98.4	235.6
MoAl	80.6 ^b	15.8	15.0±0.03	95.1	15.4±0.01	97.1	246.1
MoNbAl	65.9 ^b	12.9	12.3±0.02	94.9	12.6±0.01	97.2	275.7

^a obtained by XRF (CETEM, RJ, Brazil).

^b nominal.

^c relationship between the Al content detected by NMR and the theoretical or XRF analysis result.

It can be verified that the presence of iron at a concentration of 1.2% did not alter the results, in agreement with the report of Bakhmutov (2012), whose results showed that materials in which the concentration of paramagnetic centres are $\leq 0.5\%$ - 1% by weight can be considered as diamagnetic systems. Samples of Nb₂O₅/Al₂O₃ carriers containing 11% and 20% Nb₂O₅ and Mo supported on Al₂O₃ and on the Nb₂O₅/Al₂O₃ support showed ^{27}Al MAS NMR spectra with the same profile (Figure 4), with the two signals typical of alumina, with distinction of the tetrahedral and octahedral aluminium coordination in the structure, and without any overlap of the signals, which makes the quantification possible. The spectra of the supports were integrated in the region of 90 ppm to -80 ppm after processing, and calculations were performed based on the mass of each sample on the routine rotor and the special rotor, the number of scans and the integrated area. The values of the aluminium content in mmol Al per gram were compared with the results obtained by chemical analysis and are presented in Table 3.

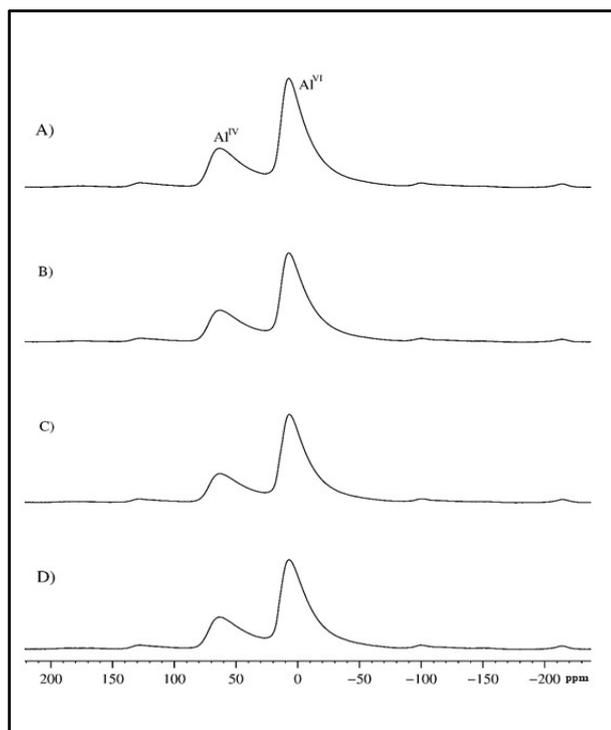


Figure 4. ^{27}Al MAS NMR spectra of supports and catalysts containing Nb and/or Mo: A) 11Nb₂O₅/Al₂O₃, B) 20Nb₂O₅/Al₂O₃, C) MoAl and D) MoNbAl.

The niobium-containing aluminas presented aluminium spin count values relative to the Al content obtained by XRF of 95.6% for 11Nb₂O₅/Al₂O₃ and 95.5% for 20Nb₂O₅/Al₂O₃ with the routine rotor and of 101.0% for 11Nb₂O₅/Al₂O₃ and 98.4% for 20Nb₂O₅/Al₂O₃ for the special rotor. It can be noted that the presence of niobium in the support did not hamper the quantification of aluminium. For the supported molybdenum catalysts, again in relation to the XRF results, 95.1% was obtained for MoAl and 94.9% for MoNbAl with the r-rotor, and 97.1% was obtained for MoAl and 97.2% for MoNbAl with

the c-rotor. Thus, it can be seen that the impregnation of molybdenum in the alumina-containing supports does not disturb the quantification by counting of the Al spins. These results were similar to those reported by Ziarelli et al. (2007), in the quantification of drug samples using ^{13}C CP MAS NMR and Brinkmann et al. (2019), in ^{19}F quantitative solid-state NMR, demonstrating that the quadrupolar nuclei in solid-state NMR can be used in the quantitative evaluation of detectable aluminium, similar to the quantitative analysis of dipolar nuclei in solids. It was observed that the quantification of aluminium in this series of diamagnetic samples using ^{27}Al MAS NMR was satisfactory for both types of rotors; considering a percentage error of up to 5% as being acceptable, both presented values $<5\%$. The slightly worse results obtained for routine rotors could be due to the presence of a small volume of detected sample located in a lower region of the routine 4 mm rotors. In contrast, in the specially designed rotor used by Ziarelli et al. this region contains no sample due to the introduction of inserts, Kel-F inserts and Kel-F spacers, as seen in Ziarelli et al. (2007) report. This result is very important considering that in solid-state NMR laboratories, ordinary 4 mm ZrO₂ solid rotors are available for routine analysis. Our results showed that routine rotors can be used not only for qualitative experiments but also for quantitative determinations of the different types of quadrupolar Al sites present in diamagnetic samples. Application of this procedure to alumina-based materials containing paramagnetic sites is in progress and will be shown in a forthcoming publication.

CONCLUSION

It was possible to develop and validate an Al quantification protocol involving spin counting based on ^{27}Al MAS NMR spectra. The viability of using commercial and routine 4 mm rotors was demonstrated. The values obtained in the quantification of Al by ^{27}Al MAS NMR using 4 mm ZrO₂ rotors were considered excellent compared to those obtained with special ZrO₂ rotors containing ceramics and Kel-F inserts, with satisfactory results being obtained with errors of up to 5%. The sample has to be preferably located in the coil region so that the ^{27}Al solid NMR analysis response corresponds to the amount of Al present. This is achieved through compact packaging and "dead volume" control between the Kel-F cap and the sample. The obtained results showed that it is possible to apply the NMR method to quadrupolar nuclei in diamagnetic materials for the quantitative evaluation of detectable aluminium, similar to the method used for dipolar nuclei.

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Table S4. Results of the Repeatability and Intermediate Accuracy tests

Sample (%p/p)	replicate	Repeatability			Intermediate Accuracy		
		Area byNS	NMR AlContent exp. (%) AnalystA	NMR AlContent exp. (%) AnalystB	Area byNS	NMR Al Content exp. (%) AnalystA	NMR AlContent exp. (%) AnalystB
25	rep1	358884.2	4.7	98.1	345000.8	4.6	93.1
25	rep2	359819.4	4.8	98.1	342805.7	4.5	92.5
25	rep3	363686.4	4.8	98.0	344299.2	4.6	92.9
50	rep1	634370.7	9.5	97.1	638358.2	9.5	97.3
50	rep2	635627.0	9.5	97.0	619882.1	9.3	94.6
50	rep3	636428.9	9.5	97.1	642682.4	9.6	98.1
100	rep1	1109871.6	19.1	98.5	1066645.6	18.3	93.5
100	rep2	1106209.5	19.0	98.2	1073948.1	18.5	94.1
100	rep3	1104215.2	19.0	97.2	1078222.4	18.5	94.5
			Average	97.8		Average	94.5
			SD	0.6		SD	2.0
			RSD(%)	0.6		RSD (%)	2.1

Table S5. Results of robustness tests

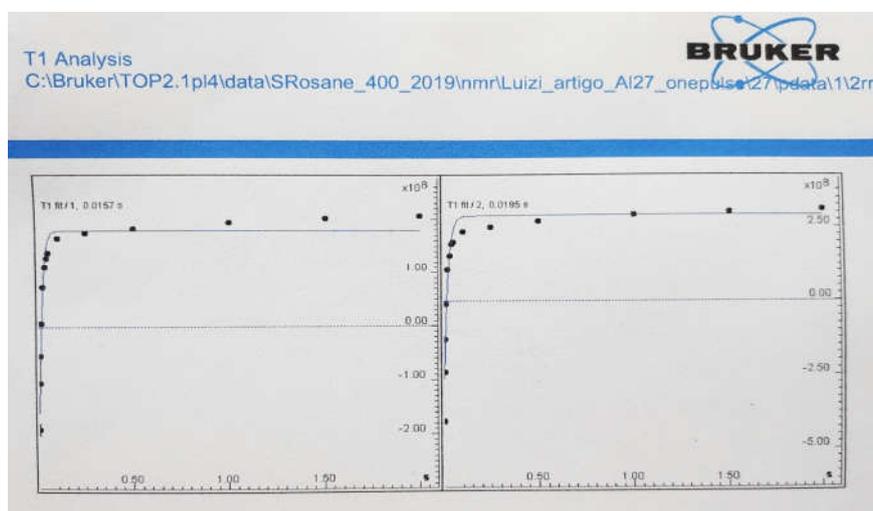
Parameter	Change	Recoverd (mmol Al g ⁻¹) ^a	mass (%)
Relaxation Delay	0.5	19.05	97.09
	1.0	19.44	99.09
	1.5	19.70	100.42
	2.0	19.68	100.33
	3.0	19.58	99.77
	4.0	19.90	101.41
		Average	19.55
	SD	0.23	
	RSD(%)	1.49	
NumberofScans	4	19.59	99.83
	16	19.78	100.83
	64	19.14	97.55
	128	19.17	100.46
	256	19.69	100.37
	512	19.70	100.41
		Average	19.60
	SD	0.23	
	RSD(%)	1.19	

^a Average of three determinations.

Table S6 - Results of ²⁷Al NMR-MAS quantification of samples of synthesized γ -aluminaS and certified Bauxite.^a

Sample	ContentAl ^b		Signal Area by NS	Content Al by NMR		Average		SD ^c	RSD ^d
	% Al ₂ O ₃	mmol Al g ⁻¹		mmol Al g ⁻¹	% ^e	mmol Al g ⁻¹	% ^e		
			1240229.1	18.7	95.9				
γ -aluminaS	99.4	19.5	1246440.6	18.8	96.4	18.8	96.2	0.2	0.3
			1245385.4	18.8	96.3				
			2170538.1	16.2	97.4				
Bauxite	85.0	16.7	2157984.8	16.1	96.9	16.2	96.8	0.6	0.7
			2160254.0	16.2	96.9				

^ar-rotor ^bXRF. ^cSD- Standard Deviation. ^dRSD - Relative Standard Deviation. ^e relationship between the Al content detected by NMR by XRF analysis.

Figure S1–Measurement of T₁ of ²⁷Al sites present in a reference sample of alumina by inversion-recovery pulse sequence.
