

# Determination of Mg, Ti and Cl in Ziegler-Natta catalysts by WDXRF

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## Abstract

A method for determination of Mg, Ti and Cl in Ziegler-Natta (ZN) catalysts by wavelength dispersive X-ray fluorescence (WDXRF) spectrometry was developed. For comparative reasons, Ti was determined by spectrophotometry, Mg by complexometry and Cl by argentometric titration. Direct pressing was shown to be unsuitable for sample preparation due to catalyst decomposition. For Ti and Mg measurements, catalyst samples were calcinated at 1000 °C and pressed at 275 MPa. Their determination by the fundamental parameters based on the Ti K $\alpha$  line measurement was shown to be equivalent to those results obtained by univariate calibration or by the classical methods. Cl was determined by aqueous extraction, followed by deposition on a support. Chloride loss was observed. Fixation of Cl as AgCl on polytetrafluoroethylene (FHL) millipore membrane afforded the best results. Nevertheless, measurements by WDXRF were shown to be inferior to those obtained by argentometric titration.

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## 1. Introduction

Ziegler-Natta (ZN) catalyst is a generic term to describe a variety of catalysts based on transition metal moieties, which are active in  $\alpha$ -olefins polymerization and copolymerization. Polymers produced by Ziegler-Natta catalysts include products, such as engineering plastics, synthetic rubber and elastomers [1]. Most of ZN catalysts are constituted essentially of two components: the catalyst itself and its cocatalyst. The catalyst is derived from transition metal complexes (in particular Ti or V), such as TiCl<sub>4</sub>, TiCl<sub>3</sub>, Ti(OR)<sub>4</sub>, VCl<sub>4</sub>, VOCl<sub>3</sub>, VCl<sub>3</sub> and ZrCl<sub>4</sub>. The cocatalyst is an organometallic compound, generally alkylaluminum, which role is to react as scavenger of the milieu impurities (oxygen, water), to alkylate the transition metal catalysts, generating and stabilizing the active catalyst site. Examples of typical cocatalysts are: Al(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>, Al(*i*-C<sub>4</sub>H<sub>9</sub>)<sub>3</sub>, Al(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>Cl and Al<sub>2</sub>(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>Cl<sub>3</sub>. None of these two components is lonely capable to promote polymerization [2].

In addition to these two components, other ones can also be present, namely: supports, carriers and modifiers. Supports, although inactive, interact chemically with the active components of the catalyst system, influencing on the catalyst activity. Among the most used supports, MgCl<sub>2</sub>, SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> can be cited. Carriers, such as spherical silica are employed for technological reasons and can improve the transportation along the tubes in industrial plant. Modifiers (also named as *donors*) are compounds which aims at modifying the catalyst site by steric and/or electronic effect leading to more specific catalysts, as in the case of the addition of silicon alcoxides to obtain highly isotactic propylene [1].

Metal content determination in catalysts is an important parameter in order to evaluate catalyst performance in terms of activity, defined as the capacity of the catalyst to convert feedstock in products, normally expressed as the quantity of obtained product by mass of catalyst (or mole of metal). Metal catalyst content can be determined by many techniques [3]. Procedures of elemental analysis of ZN catalysts are not described in details in the specialized literature. Most of the articles just mention that the elements were determined by “routine techniques”. Among those which describe

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sample preparation, basically three preparative routes can be evidenced: pyrolysis, fusion and dissolution in mineral acids. ZN catalysts based on Ti supported on Mg derivatives were submitted to pyrolysis, followed by dissolution in HCl [4]. Similar catalysts were melt with  $\text{LiBO}_3$  at  $900^\circ\text{C}$ , followed by dissolution in  $\text{H}_2\text{SO}_4$  or melt with  $\text{Na}_2\text{SO}_4$  at  $650^\circ\text{C}$  and dissolved in concentrated  $\text{H}_2\text{SO}_4$  [5]. Direct catalyst dissolution in  $\text{H}_2\text{SO}_4$  [6,7] or HCl [8] were also reported.

Concerning metal content determination, most of the articles deal with Ti, Mg and Cl determination. Ti is usually determined by spectrophotometric method, after reaction with  $\text{H}_2\text{O}_2$  and  $\text{H}_2\text{SO}_4$  and measurement at 410 nm [5,9,10–15]. In some studies, Ti was determined by atomic absorption spectroscopy (AAS) [6,8,16,17]. Mg is usually determined by AAS [6,8,15,17,18]. Other reports mention Mg determination by EDTA titrimetry [13], nuclear activation analysis (NAA) [5] or X-ray photoelectron spectroscopy (XPS) [19]. In ZN catalysts, Cl has been determined by volumetric analysis [8–10,15]. NAA was also employed for Cl determination [18].

Most of the examples of elemental analysis previously reported demands that metal content must be first extracted and dissolved (digestion step). This procedure can be tedious, time-demanding and might engender some systematic errors due to incomplete metal extraction and incomplete solubility. Such inconveniences can be overcome by determination of analyte concentrations through direct methods, in which heterogeneous catalysts are analyzed in their solid state, without digestion step. Moreover, in some techniques, the use of external standards can be avoided by expressing the final results in terms of atomic ratio. Many techniques can provide elemental analysis of catalysts, differing in measurement principle, and thus in probed depths along the catalyst grain. Among them, X-ray fluorescence spectrometry (XRF) is a technique which allows qualitative and quantitative determination of elemental composition of a variety of samples. Minimal sample preparation, wide dynamic range and non-destructive methodology make XRF the method of choice for many industrial analyses [20].

The application of XRF to catalyst characterization has been widely reported in the literature. For instance, XRF was employed to quantify analytes in chromium-containing silicate catalysts for cyclohexane oxydation [21], in Pd-based automotive catalysts [22] and in Co- and Fe-based catalysts for ammonia synthesis [23], just to mention a few. As long as we know, only two studies report the use of XRF for ZN catalysts characterization. Zohuri et al. [24] mentioned XRF for determination of Ti in ZN catalysts, but no information neither concerning sample preparation, nor analytical parameters were provided. Chirinos et al. comparably determined Ti by spectrophotometry, AAS and XRF. The authors concluded that there is no advantage of the two latter in comparison to spectrophotometry, although no concrete data were presented [25].

In a previous study, we determined Zr, Nb and Al in supported metallocene catalysts which are also active for olefin

polymerization by wavelength dispersive X-ray fluorescence (WDXRF) spectroscopy [26]. In the present work, we studied Ti, Mg and Cl determination in Ziegler-Natta catalysts by WDXRF spectroscopy. The samples were pressed as pellets (for Ti and Mg) or preconcentrated on membrane (for Cl). For comparative reasons, Ti was determined by spectrophotometry, Mg by complexometry and Cl by titration with  $\text{AgNO}_3$ .

## 2. Experimental section

### 2.1. Samples and reagents

Ziegler-Natta catalysts were prepared at Ipiranga Petroquímica S.A. (Triunfo, Brazil). The three employed ZN catalysts differed in chemical composition and in preparative conditions. High purity oxides: MgO (Merck),  $\text{TiO}_2$  (Merck) and  $\text{H}_3\text{BO}_3$  (Merck) were used to prepare the standards. Standard Ti and Mg  $1.000\text{ mg l}^{-1}$  (Titrisol, Merck) were also employed. HCl (37%),  $\text{H}_2\text{SO}_4$  (98%),  $\text{H}_2\text{O}_2$  (30%), NaCl,  $\text{Na}_2\text{CrO}_4$ , NaOH,  $\text{AgNO}_3$ , EDTA,  $\text{Li}_2\text{B}_4\text{O}_7$  and  $\text{Na}_2\text{B}_4\text{O}_7$  were purchased from Merck. Milli Q water conductivity was  $18.2\text{ m}\Omega\text{ cm}^{-1}$ . Nitrogen (99.999%) was provided by Air Liquide. The supports: polytetrafluoroethylene (FHLC), polyvinylidene fluoride, mixed cellulose ester and nylon membrane filter were purchased from Millipore. Polyester (Mylar<sup>®</sup>) and polyimide (Kapton<sup>®</sup>) films were purchased from DuPont, while quantitative filter paper from Framex.

### 2.2. Sample preparation

#### 2.2.1. Pressing and calcination

For quantitative analysis, the catalyst sample (ca. 1.0 g) was weighted under inert atmosphere ( $\text{N}_2$ ) and transferred to porcelain or Vycor crucible. The calcination loss at  $1000^\circ\text{C}$  was determined. The calcinated sample was mixed to  $\text{H}_3\text{BO}_3$  in 1:4 ratio (sample: flux) based on preliminary tests. The mixture was homogenized for 10 min in Sepx mill, affording particle size of  $74\text{ }\mu\text{m}$  (200 mesh). Then ca. 2.0 g of the mixture was pressed under 15 ton for 60 s in a sampler ( $\text{Ø} = 25\text{ mm}$ ). Standards were prepared by mixing weighed pure Mg and Ti oxides previously calcinated at  $1000^\circ\text{C}$  and pressed as the samples.

#### 2.2.2. Direct deposition

Ca. 0.2 g of catalyst sample was dispersed into water,  $\text{H}_2\text{SO}_4$  or  $\text{HNO}_3$ , under stirring for 1 h and made up to 100 ml. Twenty-five microliter of the dispersion was deposited onto the support, following by drying for 2 h. The same procedure was employed for precipitation of Cl with  $\text{AgNO}_3$  (0.04979 M). NaCl solution was employed for the calibration curve. The standards were prepared in the same manner as a AgCl slurry: 10, 20, 30, 40 and  $50\text{ }\mu\text{l}$  of NaCl solution ( $2000\text{ mg l}^{-1}$  Cl) were treated with  $\text{AgNO}_3$

Table 1  
X-ray operation conditions and spectrometer parameters

Element	Mg	Ti	Cl
Line	KL <sub>III</sub>	KL <sub>III</sub>	KL <sub>III</sub>
Angle (°)	20.995	86.110	92.275
Crystal	RX35 <sup>a</sup>	LiF200	Ge
Counting time (s)	40	10	40
Detector	PC	SC	PC
Voltage (kV)	50	50	50
Current (mA)	50	50	50

<sup>a</sup> Plumb estearate; PC: flow proportional detector; SC: scintillation detector (NaI (Tl)).

(0.04979 M). Limits of detection was 151.4 mg l<sup>-1</sup> and the evaluated concentration range was 0.0–1200 mg l<sup>-1</sup>.

### 2.2.3. Classical methods

Ca. 0.25 g of dried catalyst sample was dissolved in 60 ml of H<sub>2</sub>SO<sub>4</sub> (6 M) and stirred for 1 h. The volume was made up to 250 ml and the resulting solution was employed for Ti, Mg and Cl determination.

Ti determination was performed by diluting 5 ml of acid solution in a 50 ml volumetric flask, containing 3.8 ml of H<sub>2</sub>SO<sub>4</sub> (10% v/v) solution and 5 ml of H<sub>2</sub>O<sub>2</sub> (3% v/v) reagent. The resulting yellow complex, [Ti(H<sub>2</sub>O<sub>2</sub>)]<sup>4+</sup>, was measured at 400 nm.

Mg was determined by titration with EDTA in the presence of eriochrome black T. Twenty-five milliliter of aliquot of the acid solution was transferred to a Becker and pH was raised to 4.0–4.5 in order to precipitate Ti in hydroxide form. The solution was filtered and made up to 50 ml. A 25 ml aliquot was titrated with EDTA (0.01989 M).

For Cl the same procedure for Ti removal was carried on. A 10 ml aliquot was titrated with AgNO<sub>3</sub> 0.04979 M, using Na<sub>2</sub>CrO<sub>4</sub> (0.1%) as indicator.

### 2.2.4. Instrumentation

The XRF analyses were carried out a Rigaku (RIX 3100) wavelength dispersive X-ray fluorescence spectrometer equipped with a Rh X-ray tube, 4 kW generator and eight position crystal changer. The spectrometer was interfaced to an PC with a RIX for Windows software. Operating conditions and spectrometer parameters are described in Table 1. The calibration curves were performed using five synthetic standards prepared by mixing MgO and TiO<sub>2</sub> under different ratio. The correlation coefficient was 0.9999 and 0.9952, for Ti and Mg, respectively.

The XRD analyses were performed in a Rigaku (DMAX 2200) diffractometer equipped with a Cu tube and secondary monochromator, theta–theta Ultima goniometer and scintillation (NaI (Tl)) detector.

Thermal analyses were performed in an Universal V2.6D (Ta Instruments) analyzer. Samples were heated from 0 to 1000 °C at 20 °C min<sup>-1</sup> rate under N<sub>2</sub> atmosphere.

UV-Vis spectrophotometric measurements were carried out in Zeiss (PMQ 3) spectrophotometer equipped with W

source and a photomultiplier detector. Measurements were performed in quartz cuvet (1 cm) at 400 nm.

## 3. Results and discussion

The Ziegler-Natta catalysts were pressed and submitted to a qualitative analysis. The resolution of spectral lines of Ti, Cl and Mg is acceptable for quantitative measurements. However, the direct pressing method was shown to be unsuitable for these samples, due to their decomposition in the presence of air and to their hygroscopic character. Therefore, the samples were pressed under N<sub>2</sub> atmosphere and placed in the vacuum pre-chamber. According to this procedure, no sample alteration was observed during sample transfer. Nevertheless, after the measurement, samples were visibly altered showing color change and rough surface, probably due to sample transfer to the measurement chamber in the presence of air and to heating caused by the radiation beam (50 kV and 50 mA), enhanced by the low pressure condition (4 Pa). Thus, direct pressing was rejected as a method for Ziegler-Natta catalysts sample preparation.

The use of binder is an alternative approach for XRF sample preparation based on pressing pellets procedures. Ti in ZN catalysts was already determined by mixing the catalyst with polymer powder, which was used as binder. Results were shown to be comparable to those obtained by spectrophotometry [25]. In the present study, the use of H<sub>3</sub>BO<sub>3</sub> and Hoescht C Wax indeed avoided catalyst decomposition, but the pellets presented surface roughness after measurement. The use of these binders did not afford samples with good reproducibility, when compared to those results obtained with the classical methods.

Considering Ziegler-Natta catalyst instability, the samples were then calcinated, followed by pressing, aiming at transforming the catalyst in a more stable structure. Thermal stability of the ZN catalysts was first evaluated by thermogravimetric analysis. A typical thermogram is shown in Fig. 1.

According to Fig. 1, ZN1 thermal decomposition starts slightly above 50 °C. A continuous mass loss is observed up to 700–800 °C. Similar thermal behavior was observed for ZN2 and ZN3. Taking into account TGA results, calcination temperature was established to be at 1000 °C in order to guarantee total sample decomposition. The XRD patterns obtained on the catalyst samples after calcination is presented in Fig. 2.

The resulting XRD patterns differs for each ZN sample, although all the three sample employed the same starting material. The observed XRD patterns indicates the presence of pure oxides (MgO, TiO<sub>2</sub>, Ti<sub>4</sub>O<sub>7</sub>) or mixed oxides (MgTiO<sub>3</sub>, MgTi<sub>2</sub>O<sub>5</sub>). The XRD patterns of ZN1 (Fig. 2a) evidences a more complex crystallographic structure if compared to those of ZN2 and ZN3. Besides no chlorine-containing phase was observed, indicating that this element was completely eliminated after thermal treatment.

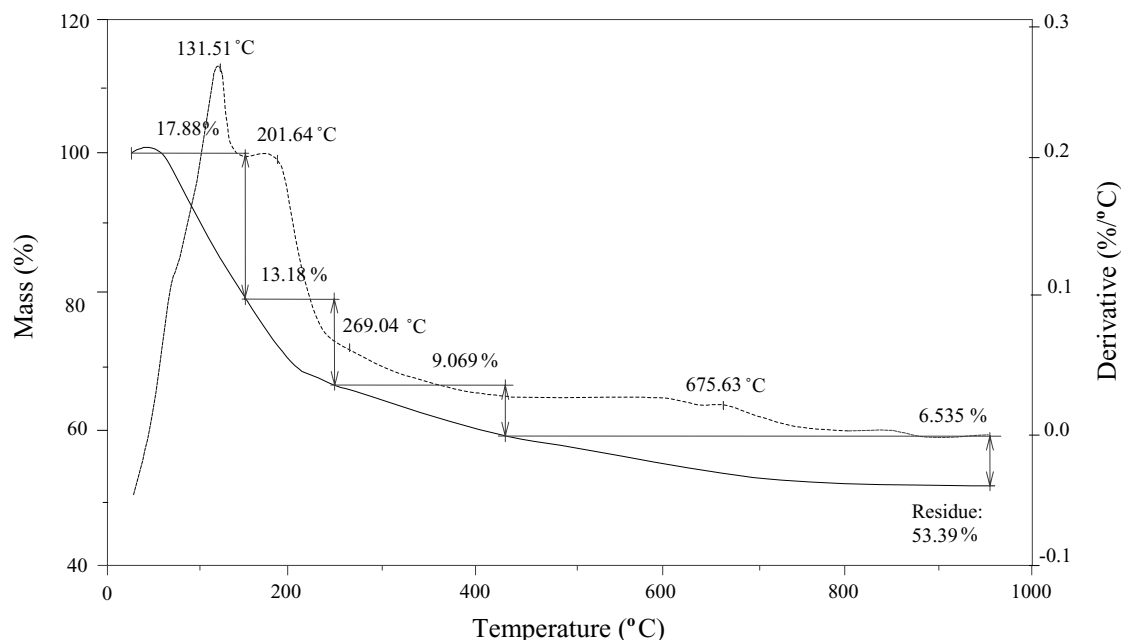


Fig. 1. Thermogram of ZN1 catalyst in the 0–1000 °C range. Heating rate: 20 °C min<sup>-1</sup> under N<sub>2</sub> atmosphere. TGA (—); DTGA (---).

Based on XRD results, calibration curve was constructed by using synthetic patterns prepared by the mixture of pure TiO<sub>2</sub> and MgO, since there was no certificate material available for this kind of catalyst. Calcinated samples were pressed with H<sub>3</sub>BO<sub>3</sub> (binder) at 200 MPa for 60 s. After same essays, the best calcinated sample/binder ratio was found to be 1:4, which afforded a non-brittle and homogeneous sample. In the case of pressed samples, the effect of particle size and of pressure might influence the spectral line intensity: smaller the particle size, higher the intensity of the analytical line. Therefore, it is expected that the increase in pressure might enhance the line intensity [27–29]. The effect of the particle size and the influence of the pressure was reported, for instance, in the case of compacting muscovite. The authors reported better results for pressures above 12 ton cm<sup>-2</sup> and particle size lower than 200 mesh (75 μm) [30].

Fig. 3 shows the effect of the pressure on the Mg Kα and Ti Kα line intensity. Pressure was varied from 78 to 300 MPa. Comparing Fig. 3a and b, the effect was shown to be more pronounced in the case of Mg. Considering the

three catalysts, ZN1 exhibited the highest variation in counts both for Ti and Mg. Regarding the Mg Kα line, both ZN1 and ZN3 suffered a more important pressure effect than ZN2 and standard ZN2. Besides, ZN2 counts remained practically constant for both analytes. It is worth noting that taking into account the crystallographic structure observed in the diffractogram patterns observed after calcination (see Fig. 2) in comparison to those obtained for the pure oxides, the crystallographic complexity of ZN1 might influence in the intensity of the analytical lines of Mg Kα and Ti Kα.

According to Fig. 3, a minimum pressure of 200 MPa might be applied during the confection of the pellets in order to guarantee higher counts intensity. Therefore, 275 MPa was chosen as working pressure for pressing the catalyst sample.

Table 2 shows Mg and Ti content in the studied catalysts, expressed in terms of Mg/Ti ratio for the 3 ZN samples determined by univariate calibration, by the fundamental parameters based on the Mg Kα and on the Ti Kα line measurement and by the classical methods.

According to Table 2, Mg/Ti ratio measurement is equivalent whether it is determined by the calibration curve, by

Table 2  
Mg/Ti ratio determined by different methods

Sample	Univariate calibration <sup>a</sup>	Fundamental parameters (Mg Kα) <sup>b</sup>	Fundamental parameters (Ti Kα) <sup>c</sup>	Classical methods <sup>d</sup>
ZN1	0.44	0.04	0.44	0.43
ZN2	1.90	0.10	1.9	1.8
ZN3	4.9	0.31	4.9	4.7

<sup>a</sup> Mean of three replicates, each one measured twice.

<sup>b</sup> Mg Kα line measured.

<sup>c</sup> Ti Kα line measured.

<sup>d</sup> Mg determined by EDTA complexometry and Ti by spectrophotometry.

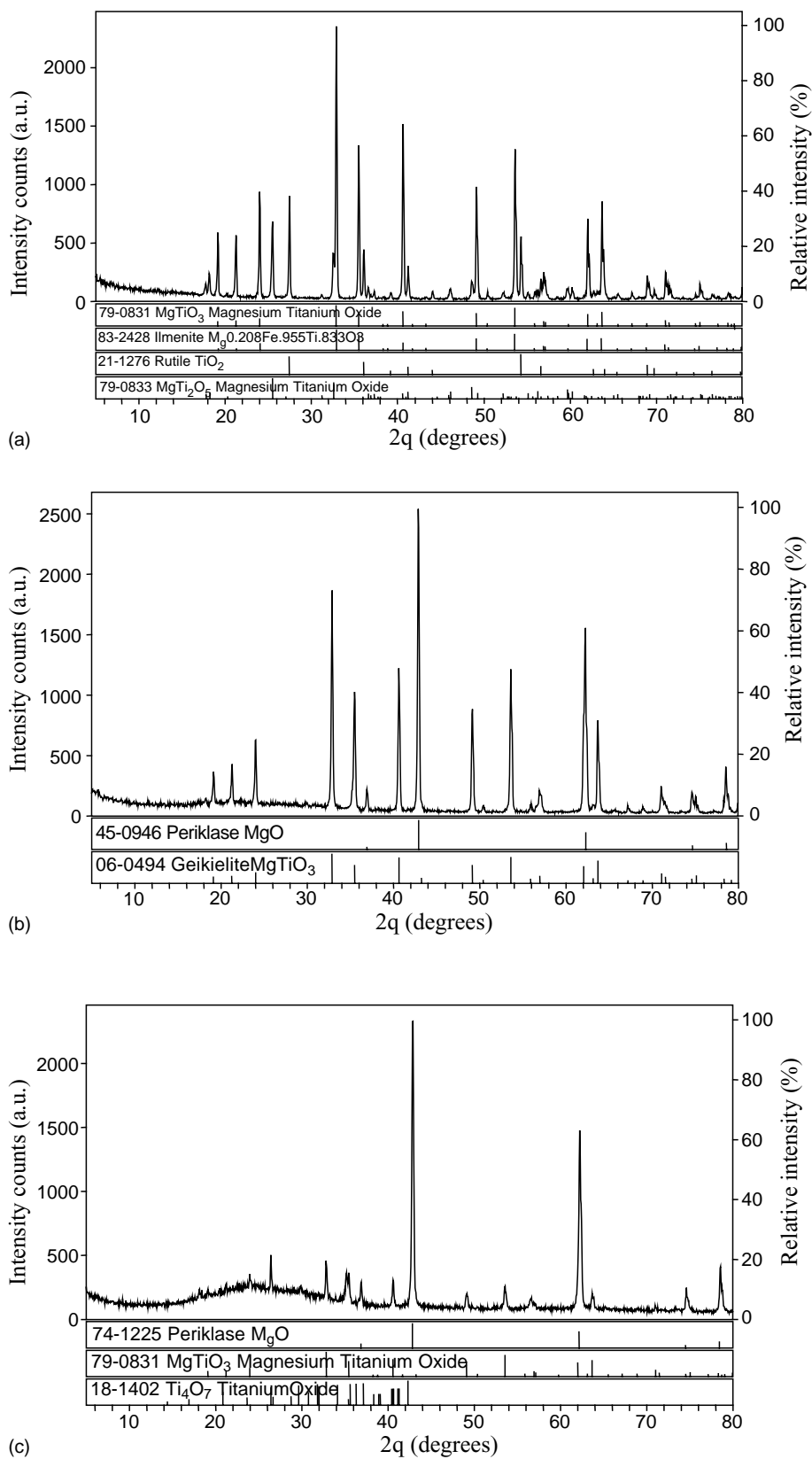


Fig. 2. Powder diffraction patterns from ZN catalysts after calcination at  $1000^\circ\text{C}$ : (a) ZN1; (b) ZN2 and (c) ZN3.

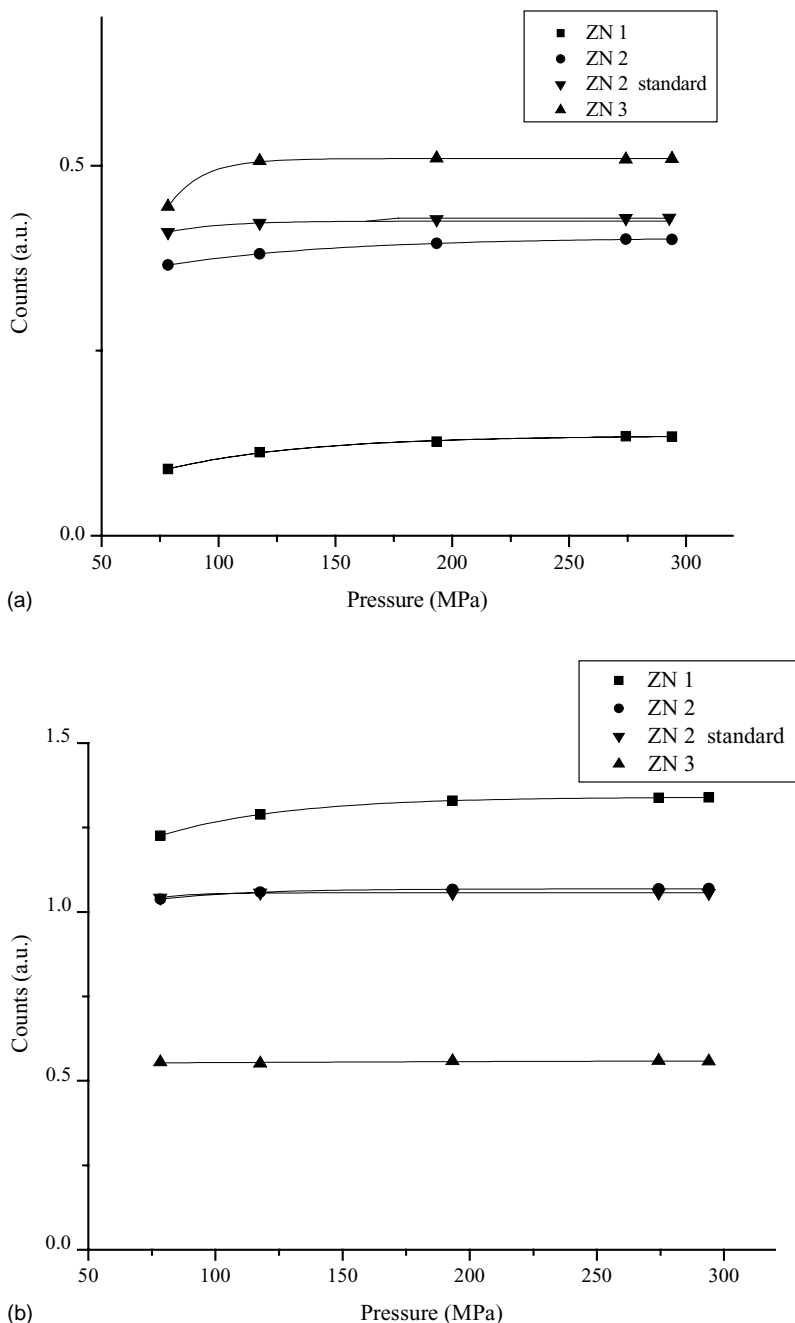


Fig. 3. Effect of the pressure on the spectral line intensity: (a) Mg K $\alpha$ ; (b) Ti K $\alpha$ .

the fundamental parameters based on measuring the Ti K $\alpha$  line or through the classical methods. On the other hand, Mg/Ti determination based on the fundamental parameters taking into account the Mg K $\alpha$  line measurement was shown to be unsuitable. This behavior could be owing to the low atomic number of Mg ( $Z = 12$ ) in which the quantum yield in fluorescence is lower than that associated to Auger electron emission one [29]. Therefore, WDXRF measurements were performed taking into account Ti K $\alpha$  emission line.

It is worth mentioning that ZN1, ZN2 and ZN3 differ on the preparative method and on the chemical

composition. In the calcinated samples, MgO content varied from 25 to 80%, while TiO<sub>2</sub> from 20 to 75%. Data obtained from both WDXRF and classical methods was seemed to be equivalent. A better evaluation for que-equivalence of both methods was performed through  $F$ - and  $t$ -test [31]. Table 3 reports the accuracy obtained for Mg and Ti determined by the classical and WDXRF methods.

According to Table 3, the calculated value did not exceed the critical value for  $F$  distribution. Thus, the results accuracy obtained by WDXRF is equivalent to that observed using



Table 3  
Evaluation of the accuracy of the results obtained for Mg and Ti determined by the classical methods and WDXRF;  $\alpha = 0.05$  [31]

Sample	Method	Variance ( $s^2$ )	Calculated value	Critical value ( $F$ ) <sup>a</sup>
ZN1	Classical	0.0006		
	WDXRF	0.0001	6.00	6.39
ZN2	Classical	0.0004		
	WDXRF	0.0016	0.25	6.39
ZN3	Classical	0.0004		
	WDXRF	0.0003	1.33	6.39

<sup>a</sup> Degrees of freedom = 4.

the classical methods for Mg and Ti measurements in the calcinated ZN samples.

Table 4 reports the mean results for both analytes determined by both techniques. For the  $t$  distribution, the calculated values did not exceed the critical value. Therefore, both classical and WDXRF methods provide mean equivalent values for the three evaluated samples.

### 3.1. Determination of Cl

For Cl determination, the catalyst samples were dissolved in water or in acidified water solution, followed by deposition on an inert support, and finally by solvent evaporation. Initial tests using quantitative filter paper as support have shown that dissolution in sulfuric or nitric acid milieu were unsuitable for Cl determination. The precipitation of Cl as AgCl using a AgNO<sub>3</sub> solution, although bearing a visible precipitated, did not afford quantitative recuperation. It seems that Cl was lost as HCl in the vacuum chamber owing to vacuum itself or to heating during X-ray incidence. Therefore, dissolution in acid solution was rejected.

The Cl determination after deposition of a filter support was measured ten times, each one three times. The oscillation of the mean in the 10 measurements suggested the possibility of problems of Cl extraction with water. Two alternative approaches were tested: extraction with hot water assisted or not by ultra-sound bath. For both procedures, it was observed oscillations in the mean measurements, similar to those previously detected. Therefore, it was necessary to investigate the efficiency of extraction with water. Cl concentration was determined by argentometric titration comparing the extraction with water and acidic water solu-

Table 4  
Evaluation results mean obtained for Mg and Ti determined by the classical methods and WDXRF employing  $t$ -test;  $\alpha = 0.05$  [31]

Sample	Differences mean ( $d$ )	Standard deviation (S.D.)	Calculated value	Critical value ( $t$ ) <sup>a</sup>
ZN1	0.0008	0.0164	1.089	2.78
ZN2	0.0020	0.0409	0.109	2.78
ZN3	-0.002	0.0179	-0.250	2.78

<sup>a</sup> Degrees of freedom = 4.

Table 5  
Cl determination after water and acidic water extraction by argentometric titration

Sample	Extraction with water	Extraction with acidic water
ZN1	46.6 ± 0.165	46.6 ± 0.062
ZN2	52.3 ± 0.086	52.4 ± 0.038
ZN3	62.7 ± 0.138	62.8 ± 0.038

tion, using the Mohr method [32]. The results are shown in Table 5.

Comparison between both extraction procedures were respectively evaluated by  $F$ - and  $t$ -tests. The calculated values did not exceed the critical value. Then, the results obtained by both extraction protocols were equivalent in terms of precision for a confidence level of 95%. Similar behavior was observed employing the  $t$ -test. Both the extraction using water or acidic water reproduce the Cl contents, which are equivalent in terms of mean and accuracy.

The oscillations observed during WDXRF measurement using the deposition method could be owing to contamination of the support itself. Therefore, different supports were evaluated in order to verify the presence of Cl and the possibility of its use as a blank for further corrections. Fig. 4 shows the results employing 10 different units using FHLC Millipore (Teflon<sup>®</sup> film) and quantitative Framex<sup>®</sup> filter paper. The irradiated area was 25 mm. Each support was analyzed as received (blank) and after the addition of a fixed volume (50  $\mu$ l) of aqueous solution (2000 mg l<sup>-1</sup>) containing the analyte.

According to Fig. 4 the background radiation in the case of Framex filter paper is much higher than that of FHLC Millipore membrane. Besides, for each tested support, the counts number oscillated for each unit containing the analyte. Therefore, the use of blank did not solve the problem, since each support unit corresponded to different net Cl counts (discounted the background radiation). Similar behavior was observed for Millipore polyvinylidene fluoride, mixed cellulose ester and nylon Millipore membranes and polyimide (Kapton<sup>®</sup>). On the other hand, FHLC millipore membrane did not show much oscillation. Then Mylar<sup>®</sup> and FHLC millipore membrane were considered being exempt of chloride for the present experimental conditions and suitable for Cl determination in ZN catalysts. It is worth mentioning that Cl concentration varied from 5 to 80 mg l<sup>-1</sup>.

Aqueous solution of the ZN samples were directly deposited on FHLC millipore membrane, dried and analyzed by WDXRF. Nevertheless, successive measurements evidenced analyte loss, even when the sample was protected by Mylar<sup>®</sup>, as shown in Table 6.

In the literature the use of Kapton<sup>®</sup> tape is reported for measurements in vacuum [33]. Nevertheless, its use was not possible in the present study due to the presence of Cl contamination in this support.

An attempt to fix the Cl was performed through the addition of NaNO<sub>3</sub> solution on the support. Similar results

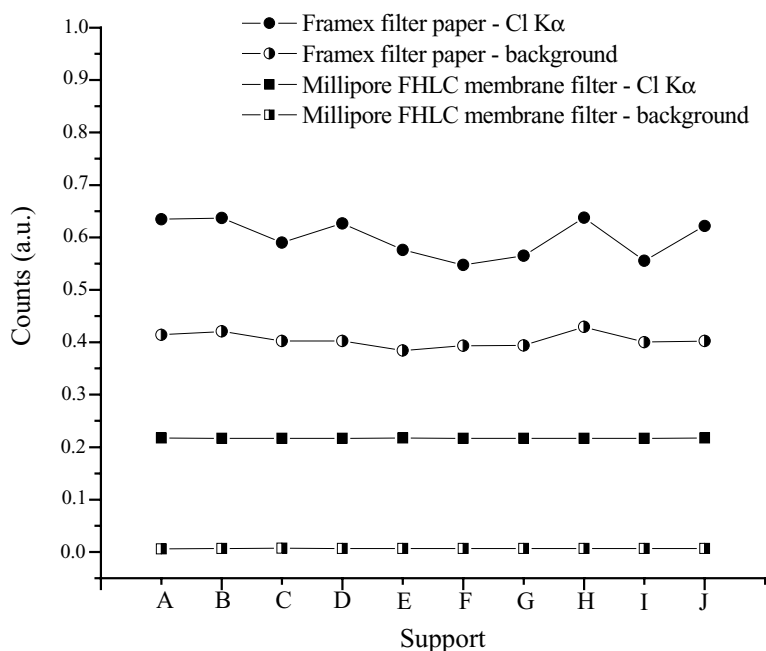


Fig. 4. Cl K $\alpha$  line measurement of the blanket (background) and of Cl solution deposited on the supports. Ten different units (A–J) of each support were evaluated.

as those reported in Table 6 were observed, indicating analyte loss. Besides, analyte loss from acidic solutions was shown to be higher than that in aqueous ones. Analyte loss in both cases was associated to Cl volatilization during the measurement conditions: vacuum and primary X-ray beam irradiation.

Taking into account these results, the fixation of the analyte in the form of AgCl was opted [34]. Then a catalyst slurry was deposited on FHLC Millipore membrane was dried and analyzed. Successive measurements did not indicate analyte loss and the calibration curve presented a correlation coefficient of  $R = 0.9997$ . Table 7 present Cl in the three samples, determined by WDXRF. For comparative reasons, Cl was also determined by argentometric titration.

Table 6  
Evaluation of the accuracy of the results obtained for Cl determined by argentometric titration using the  $F$ -test;  $\alpha = 0.05$  [31]

Support	Intensity counts (a.m.u.)		
	I	II	II
FHLC millipore membrane	4.0106	3.2763	3.0674
FHLC millipore membrane between 2 Mylar <sup>®</sup> films	1.9501	1.5754	1.3519

Table 7  
Cl (% , w/w) determined by WDXRF and by argentometric titration

Sample	WDXRF	Argentometric titration
ZN1	43.7 $\pm$ 0.114	46.6 $\pm$ 0.062
ZN2	50.9 $\pm$ 0.290	52.4 $\pm$ 0.038
ZN3	59.8 $\pm$ 0.298	62.8 $\pm$ 0.038

These results were also evaluated in terms of mean (Table 8) and accuracy (Table 9).

The calculated values for ZN2 and ZN3 exceeded the critical value and only for ZN1 both methods indicate equivalence in the accuracy of the results. According to Table 9,

Table 8  
Evaluation of the accuracy of the results obtained for Cl determined by the WDXRF and argentometric titration employing the  $F$ -test for  $\alpha = 0.05$  [31]

Sample	Method	Variance ( $s^2$ )	Calculated value	Critical value ( $F$ ) <sup>a</sup>
ZN1	Argentometric Titration	0.0006	3.5	19.0
	WDXRF	0.0021		
ZN2	Argentometric Titration	0.0004	34	19.0
	WDXRF	0.0139		
ZN3	Argentometric Titration	0.0002	70	19.0
	WDXRF	0.0144		

<sup>a</sup> Degrees of freedom = 2.

Table 9  
Evaluation results mean obtained for Cl determined by argentometric titration and WDXRF employing  $t$ -test for  $\alpha = 0.05$  [31]

Sample	Differences mean ( $d$ )	Standard deviation (S.D.)	Calculated value	Critical value ( $t$ ) <sup>a</sup>
ZN1	2.867	0.0321	154	4.30
ZN2	1.523	0.1201	22	4.30
ZN3	2.920	0.1054	48	4.30

<sup>a</sup> Degrees of freedom = 2.



the calculated values for the three catalysts exceeded the critical values, i.e. WDXRF results were considered to be distinguished from those obtained from argentometric titration.

The use of FHLC support limits the aliquot volume to be deposited on, since it can not absorb volume higher than 40  $\mu$ l, without spreading the sample in an area which is broader than that of analysis ( $\phi = 25$  mm). Although Cl fixation as AgCl was shown to be more efficient in accordance to Table 9, the results obtained by WDXRF and by argentometric titration were considered to be different in terms of mean and accuracy for a confidence level of 95%. The dilution magnitude could be a likely cause for the observed divergences.

#### 4. Conclusions

Direct pressing ZN catalysts was shown to be unsuitable for WDXRF measurement due to sample decomposition during irradiation time. Better results were obtained when ZN catalysts were calcinated, and the resulting oxides were pressed with H<sub>3</sub>BO<sub>3</sub>. Quantitative determination based on the fundamental parameters showed that better results were observed when the Ti analytical line measurement was considered. The determination of Mg and Ti in such catalysts, expressed in terms of Mg/Ti ratio was shown to be practicable.

For Cl determination in ZN catalysts, sample deposition on support was shown to be the best method. Nevertheless, among the evaluated test, only FHLC Millipore and Mylar<sup>®</sup> were shown to be exempt of Cl. Subsequent measurements showed that there is Cl loss along the measurement time. Better results were observed then Cl was fixed as AgCl. Nevertheless, the obtained results were lower than that using argentometric titration, probably due to errors due to sample dilution and limited absorption capacity of the support.

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