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 Ka 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 (FTLC) 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 α-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 TiCl₄, TiCl₃, Ti(OR)₄, VCl₄, VOCl₃, VCl₃ and ZrCl₄. The cocatalyst is an organometallic compound, generally alkylaluminium, 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(C₂H₅)₃, Al(η-C₃H₅)₃, Al(C₂H₅)₂Cl and Al₂(C₂H₅)₃Cl. 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, MgCl₂, SiO₂ and Al₂O₃ 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 alcoxydes to obtain highly isotactic propylene [1].

Metal content determination in catalyts 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
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 LiBO₂ at 900 °C, followed by dissolution in H₂SO₄ or melt with Na₂SO₄ at 650 °C and dissolved in concentrated H₂SO₄ [5]. Direct catalyst dissolution in H₂SO₄ [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 H₂O₂ and H₂SO₄ and measurement at 410 nm [5,9,10–15]. Magnesium is usually 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 determining 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 oxidation [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 AgNO₃.

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), TiO₂ (Merck) and H₄BO₄ (Merck) were used to prepare the standards. Standard Ti and Mg 1.000 mg 1⁻¹ (Titrisol, Merck) were also employed. HCl (37%), H₂SO₄ (98%), H₂O₂ (30%), NaCl, Na₂CO₃, NaOH, AgNO₃, EDTA, Li₂B₄O₇ and Na₂B₄O₇ were purchased from Merck. Milli-Q water conductivity was 18.2 mΩ cm⁻¹. Nitrogen (99.999%) was provided by Air Liquide. The supports: polytetrafluoroethylene (Framex), polystyrene and cellulose ester and nylon membrane filter were purchased from Millipore. Polyester (Mylar) and polyimide (Kapton) 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 weighed under inert atmosphere (N₂) and transferred to porcelain or Vycor crucible. The calcination loss at 1000 °C was determined. The calcinated sample was mixed with H₃BO₃ 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 µm (200 mesh). Then ca. 2.0 g of the mixture was pressed under 15 ton for 60 s in a sampler (Ø = 25 mm). Standards were prepared by mixing weighed pure Mg and Ti oxides previously calcinated at 1000 °C and pressed as the samples.

2.2.2. Direct deposition

Ca. 0.2 g of catalyst sample was dispersed into water, H₂SO₄ or HNO₃, 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 AgNO₃ (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 µl of NaCl solution (2000 mg 1⁻¹ Cl) were treated with AgNO₃.
Table 1. X-ray operation conditions and spectrometer parameters.

<table>
<thead>
<tr>
<th>Element</th>
<th>Mg</th>
<th>Ti</th>
<th>Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Line</td>
<td>Kα1, Kβ1</td>
<td>Kα2, Kβ2</td>
<td>Kα1</td>
</tr>
<tr>
<td>Angle (°)</td>
<td>20.995</td>
<td>86.110</td>
<td>92.275</td>
</tr>
<tr>
<td>Crystal</td>
<td>R315*</td>
<td>LiF200</td>
<td>Ge</td>
</tr>
<tr>
<td>Counting time (s)</td>
<td>40</td>
<td>10</td>
<td>40</td>
</tr>
<tr>
<td>Detector</td>
<td>PC</td>
<td>SC</td>
<td>PC</td>
</tr>
<tr>
<td>Voltage (kV)</td>
<td>50</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>Current (mA)</td>
<td>50</td>
<td>50</td>
<td>50</td>
</tr>
</tbody>
</table>

* Plumb estearate; PC: flow proportional detector; SC: scintillation detector.

(0.04979 M). Limits of detection was 151.4 mg l⁻¹ and the evaluated concentration range was 0.1–1200 mg l⁻¹.  

2.2.3. Classical methods  
Ca. 0.25 g of dried catalyst sample was dissolved in 60 ml of H₂SO₄ (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 H₂SO₄ (10% v/v) solution and 5 ml of H₂O₂ (3% v/v) reagent. The resulting yellow complex, [Ti(H₂O₂)₄]⁺⁺, 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 AgNO₃ 0.04979 M, using Na₂CrO₄ (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 TiO₂ 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⁻¹ rate under N₂ 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 N₂ 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 H₃BO₃ 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, TiO₂, Ti₃O₇) or mixed oxides (Mg₂TiO₄, Mg₂TiO₇). 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.
Based on XRD results, calibration curve was constructed by using synthetic patterns prepared by the mixture of pure TiO\textsubscript{2} and MgO, since there was no certificate material available for this kind of catalyst. Calcinated samples were pressed with H\textsubscript{3}BO\textsubscript{3} (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\textsuperscript{-2} and particle size lower than 200 mesh (75 um) [30].

Fig. 3 shows the effect of the pressure on the Mg K\textsubscript{α} and Ti K\textsubscript{α} 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 K\textsubscript{α} 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 K\textsubscript{α} and Ti K\textsubscript{α}.

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 univariated calibration, by the fundamental parameters based on the Mg K\textsubscript{α} and on the Ti K\textsubscript{α} 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

\[ \text{Table 2} \]

<table>
<thead>
<tr>
<th>Sample</th>
<th>Univariate calibration\textsuperscript{a}</th>
<th>Fundamental parameters (Mg K\textsubscript{α})\textsuperscript{b}</th>
<th>Fundamental parameters (Ti K\textsubscript{α})\textsuperscript{c}</th>
<th>Classical methods\textsuperscript{d}</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZN1</td>
<td>0.44</td>
<td>0.04</td>
<td>0.44</td>
<td>0.43</td>
</tr>
<tr>
<td>ZN2</td>
<td>1.90</td>
<td>0.10</td>
<td>1.90</td>
<td>1.8</td>
</tr>
<tr>
<td>ZN3</td>
<td>4.9</td>
<td>0.31</td>
<td>4.9</td>
<td>4.7</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Mean of three replicates, each one measured twice.

\textsuperscript{b} Mg K\textsubscript{α} line measured.

\textsuperscript{c} Ti K\textsubscript{α} line measured.

\textsuperscript{d} Mg determined by EDTA complexometry and Ti by spectrophotometry.
Fig. 2. Powder diffraction patterns from ZN catalysts after calcination at 1000°C: (a) ZN1, (b) ZN2 and (c) ZN3.
the fundamental parameters based on measuring the Ti Kα line or through the classical methods. On the other hand, Mg/Ti determination based on the fundamental parameters taking into account the Mg Kα 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 Kα 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\(_2\) 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; α = 0.05 [31]

<table>
<thead>
<tr>
<th>Sample</th>
<th>Method</th>
<th>Variance (F²)</th>
<th>Calculated value</th>
<th>Critical value (F)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZN3</td>
<td>Classical</td>
<td>0.0006</td>
<td>6.00</td>
<td>6.39</td>
</tr>
<tr>
<td></td>
<td>WDXRF</td>
<td>0.0001</td>
<td>0.25</td>
<td>6.39</td>
</tr>
<tr>
<td>ZN4</td>
<td>Classical</td>
<td>0.0004</td>
<td>1.33</td>
<td>6.39</td>
</tr>
<tr>
<td></td>
<td>WDXRF</td>
<td>0.0003</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a Degrees of freedom = 4.

Table 4
Evaluation results mean obtained for Mg and Ti determined by the classical methods and WDXRF employing α = 0.05 [31]

<table>
<thead>
<tr>
<th>Sample</th>
<th>Differences mean (d)</th>
<th>Standard deviation (S.D.)</th>
<th>Calculated value</th>
<th>Critical value (F)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZN1</td>
<td>0.0008</td>
<td>0.0164</td>
<td>1.089</td>
<td>2.78</td>
</tr>
<tr>
<td>ZN2</td>
<td>0.0020</td>
<td>0.0499</td>
<td>0.109</td>
<td>2.78</td>
</tr>
<tr>
<td>ZN3</td>
<td>-0.002</td>
<td>0.0179</td>
<td>-0.250</td>
<td>2.78</td>
</tr>
</tbody>
</table>

a Degrees of freedom = 4.

The classical methods for Mg and Ti measurements in the calculated 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 AgNO₃ solution, although bearing a visible precipitate, 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 argendometric titration comparing the extraction with water and acidic water solution, 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. Therefore, 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® film) and quantitative Framex® filter paper. The irradiated area was 25 mm. Each support was analyzed as received (blank) and after the addition of a fixed volume (50 µl) of aqueous solution (2000 mg l⁻¹) 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®). On the other hand, FHLC millipore membrane did not show much oscillation. Then Mylar® 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⁻¹.

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®, as shown in Table 6.

In the literature the use of Kapton® 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 NaNO₃ solution on the support. Similar results

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

<table>
<thead>
<tr>
<th>Sample</th>
<th>Extraction with water</th>
<th>Extraction with acidic water</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZN1</td>
<td>46.6 ± 0.165</td>
<td>46.6 ± 0.082</td>
</tr>
<tr>
<td>ZN2</td>
<td>52.3 ± 0.086</td>
<td>52.4 ± 0.038</td>
</tr>
<tr>
<td>ZN3</td>
<td>62.7 ± 0.138</td>
<td>62.8 ± 0.038</td>
</tr>
</tbody>
</table>
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 $R^2 = 0.9997$. Table 7 present Cl in the three samples, determined by WDXRF. For comparative reasons, Cl was also determined by argentometric titration.

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

<table>
<thead>
<tr>
<th>Support</th>
<th>Intensity counts (a.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FHLC millipore membrane</td>
<td>1.9501 1.5754 1.3519</td>
</tr>
<tr>
<td>FHLC millipore membrane between 2 Mylar® films</td>
<td>4.0106 3.2763 3.0674</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Sample</th>
<th>WDXRF</th>
<th>Argentometric titration</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZN1</td>
<td>43.7 ± 0.114</td>
<td>46.6 ± 0.062</td>
</tr>
<tr>
<td>ZN2</td>
<td>50.9 ± 0.290</td>
<td>52.4 ± 0.038</td>
</tr>
<tr>
<td>ZN3</td>
<td>59.8 ± 0.298</td>
<td>62.8 ± 0.038</td>
</tr>
</tbody>
</table>

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].

<table>
<thead>
<tr>
<th>Sample</th>
<th>Method</th>
<th>Variance ($s^2$)</th>
<th>Calculated value</th>
<th>Critical value ($F$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZN1</td>
<td>Argentometric Titration</td>
<td>0.0006</td>
<td>3.5</td>
<td>19.0</td>
</tr>
<tr>
<td>ZN2</td>
<td>Argentometric Titration</td>
<td>0.0004</td>
<td>34</td>
<td>19.0</td>
</tr>
<tr>
<td>ZN3</td>
<td>Argentometric Titration</td>
<td>0.0002</td>
<td>70</td>
<td>19.0</td>
</tr>
</tbody>
</table>

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

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

* 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 FHL(X) support limits the aliquot volume to be deposited on, since it can not absorb volumes higher than 40 μl, without spreading the sample in an area which is broader than that of analysis (φ = 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 H3BO3. Quantitative determination based on ZN catalysts were calcinated, and the resulting oxides were expressed in terms of Mg/Ti ratio was shown to be practical.

Acknowledgements

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References