ORIGINAL PAPER

Ti^{+4} determination in Ziegler Natta Polymerization Catalysts by UV-vis spectrometric method

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ABSTRACT

Determination of Ti^{+4} in Ziegler-Natta catalysts is very relevant for industrial plants that use the Ziegler Natta (ZN) catalysts based on $TiCl_4$ as a source of titanium. The catalyst preparation step requires analytical monitoring during the dilution processes for the morphological effect according to the relationship between Ti^{+3} and Ti^{+4} concentration in the polymerization process, which in turn depend on a variety of intended grades for different market applications. Spectrophotometry in the visible region was evaluated as a potential analytical technique for the quantification of Ti^{+4} in ZN catalysts. The present study proposes to make use of an easily accessible, reliable and low-cost validated instrumental method for Ti^{+4} determinations. Therefore, technical details regarding sample preparation, instrumental analytical parameters and performance characteristics of method were descriptively addressed. The quantitative evaluation of performance parameters (namely:specificity, linearity, detection and quantification limits, precision, accuracy and robustness) demonstrated successful results when compared to the theoretical values of the studied reference sample.The precision of the method by visible spectrophotometry was estimated at 0.4% for the relative error and the accuracy presented within an IC of 95% the LOC ± 1.7 mmolTi $\cdot L^{-1}$ for the average concentration of 339.5 mmolTi$\cdot L^{-1}$ in reference to the Tyzor ® TnBT sample with a theoretical concentration of 337mmol/L study solution from this work. The method proved to be a supporting tool to quantitative Ti^{+4} species determination in the control of industrial processes.

Keywords: Ziegler Natta, Ti, spectrophotometry, titration, analytical validation.

INTRODUCTION

In recent years, the production and development of new types of polyethylene has been increasing as a result of market demands and constant changes in product processability in the manufacturing industry. In this context, the use of Ziegler-Natta (ZN) catalysts stands out, which has been used for more than half a century in industrial processes for the synthesis of polyolefin compounds in Petrochemical Plants worldwide.

The development of catalysts has been possible with the progressive knowledge of coordination chemistry and organometallic compounds, which made it possible to arrive at the exact structure of the complex that will catalyze in a given reaction, resulting in efficient and selective catalysts in terms of transition metal complexes: (generally) Ti, V, Cr or Zr combined with organometallic cocatalyst, resulting for instance: $TiCl_4 + (C_2H_5)_3Al$ as a catalyst/cocatalyst system.

In the industrial context, for the effectiveness and control of polymerization processes on industrial scale, analyzes of the concentrations of Ti^{+3} and Ti^{+4} species are decisive for the preparation of the catalyst [1, 2]. Different techniques have been reported in the literature for Ti quantification or characterization in Ziegler-Natta catalysts. For instance, UV–vis diffuse reflectance spectroscopy (UV–vis-DRS) and X-ray photoelectron spectra (XPS) have been employed for $MgCl_2$-supported Ziegler–Natta catalysts [3]. Extended X-ray absorption fine structure analysis (EXAFS) [4], Inductively coupled plasma atomic emission spectrometry (ICP OES), Rutherford backscattering spectrometry (RBS) [5], X-ray fluorescence (XRF) [6] and electron paramagnetic resonance (EPR) [7,8] are also examples of potential instrumental techniques applicable for ZN characterization. Such techniques demand complex instrumental designs, high cost equipments and complex sample preparation, which in sum, cannot be available in an industrial context for routine analysis. Recent published works mention titrimetric techniques to correlate the co-presence of Ti (III) and Ti (IV) species, whose relative determinations of more advanced techniques are in agreement with that determined by titration in Hoff's first works [9]. FT-IR spectroscopy was also employed to monitor the insertion of CO into Ti^{3+}-alkyl bond, both in the absence and in the presence of olefin monomer [10]. In a similar goal, FT-IR has also been exploited to characterize and to differentiate ZN catalysts aiming to predict catalyst reactivity for control testing at industrial facilities [11].

As long as we know, in the open literature, there is no cleardescription for Ti^{+4} quantification in Ziegler-Natta catalyst systems. In the present study we discuss the potentialities and limitations of a spectrophotometer Ti^{+4}determinations in such catalyst systems. Sample preparation technical details, the role of instrumental analytical parameters and validation of the spectroscopic validated method were here discussed.

EXPERIMENTAL

Materials

All the samples and solutions used analytical grade reagents.Deionized water (MilliQ -® Integral 5 system with resistivity >18M Ω cm $^{-1}$), Sulfuric Acid (Merck 95-97%), Hydrogen Peroxide (Merck), Cerium Sulfate (Merck), Diphenylamine (Vetec 98%), Tyzor® TnBT (tetra - *n* - butyl titanate) - $Ti(Obt)_4$, Nitrogen (5.0 – White Martins), Cylindrical Magnets (70 mm × 5 mm), 100 mL Volumetric Flask, 250 mL Volumetric Flask (250 mL glass bottle) were used in the preparation of samples, standards and auxiliary solutions. Sulfuric acid solutions were prepared at concentrations of 10% and 6N. Hydrogen peroxide of 3% Hydrogen.

Instrumental Analysis

Spectrophotometry analyses were carried out in Agilent UV-VIS spectrophotometer, model Cary 100, with double-beam optical configuration, wavelength 190 to 900 nm (± 0.04 nm) bearing Czerny - Turner monochromator (0.278m). PMT detector and halogen light source. The experimental parameters were determined using a quartz cuvette with an internal volume of approximately 4.0 mL and an optical path of 1 cm. Appliedwavelengthsource was 386nm.

Preparation of the calibration standard curve

To prepare the standard curve, a blank solution and eight standard solutions were prepared from the Ti standard solution - Titrisol® (1000 ppm) in concentrations from 0.20 mmol•L^{-1} to 3.33 mmol•L^{-1} .

Reference and sample preparation

For precision and accuracy tests, a solution of Tyzor® TnBT - $Ti(OC_4H_9)_4$, (99.9%) diluted in *n*-Hexane was prepared at a theoretical concentration of 337 mmol•L^{-1}. The catalyst sample containing Ti was suspended in n-Hexane (250 mL screw-top glass vial containing a metallic magnet). Initially the sample was submitted to constant stirring for 10 minutes and then a 10 mL aliquot was collected using a volumetric pipette, transferring it to a 100 mL volumetric flask previously prepared with the addition of metallic magnet and 70 mL of 6N sulfuric acid solution. The flask containing the sample in acidic medium forms two distinct phases: (i) An organic phase originated from the catalyst suspension in *n*-Hexane and (ii) an inorganic one originated from the acidic solution. The phase system present in the flask remained under vigorously stirring for one hour to carry out the extraction process. Then, the metal magnet was removed from the flask and then, with the aid of a vacuum pump, only the upper fraction (organic) contained in the flask was sucked out for disposal, then swelling it to 100 mL with deionized Milli-Q® water. In another 100 mL volumetric flask, 75 mL of 10% H_2SO_4 solution and 10 mL of3% H_2O_2 solution were added. Then, sample extraction step was carried out by adding 10 mL aliquot from the extracted sample.

The presence of H_2O_2 produces a yellow color solution when Ti(IV)-containing species are present. These colored species are recognized as $[TiO(SO_4)_2]^{-2}$ or similar ion, formulated as $[Ti(H_2O_2)]^{+4}$ or similar complex. The intensity of the coloring is directly proportional to the concentration of Ti present in the sample. This final stage of the test is called the ion complexation stage [2]. Sample readings were performed in a quartz cuvette on an Agilent spectrophotometer configured with the parameters indicated in Table 1.

Method validation

In quantitative method validation studies, the addressed performance parameterswere: Specificity, linearity, limits of detection and quantification, precision, accuracy and robustness [12,13]. The investigated parameters were defined as:

Specificity

evaluated from the comparison between the baseline of the reagents used in preparing the standard solution *versus* the solution containing Ti(IV) at the 386 nm.

Precision and Accuracy

Tyzor® TNBT 337 mmol/L reference sample has been subjected to seven triplicate readings and its concentration extrapolated through the use of the analytical curve for titanium determination (IV). Accuracy was evaluated with the estimated relative standard deviation (RSD) or coefficient of variation (CV) described in equation 1. The accuracy was estimated by calculating relative error (RE) for the analysis of the referenced sample performed in triplicate according to equation 2.

$$\%RSD = S_{x_0} \times 100 / C_{x_0} \quad (1)$$

where: S_{x_0} = average standard deviation of the analyte concentration in the sample; C_{x_0} = average concentration of the analyte in the sample.

$$\%RE = [med] - [theoretical] \times 100/[theoretical] \quad (2)$$

where: *[med]* = measured average concentration of the analyte in the sample; *[theoretical]* = theoretical concentration of the analyte in the sample.

Calibration curve

For the calibration curve, eight standards (Ti standard solution - Titrisol® 1000 ppm) concentrations between 0.20 mmol•L^{-1} to 3.33 mmol•L^{-1}) were prepared and read in quintuplicate. The calibration curve generated a function $y = 0.6959x – 0.0124$ ($R^2 = 0.9998$). When observing the dilutions performed during the sample preparation stage, the equation x must be used for the calculation and final expression of the results.

$$[Ti^{+4}] = [u] \times 100 \qquad (3)$$

where: $[Ti^{+4}]$ = Sample result (mmol•L^{-1}); [u] = absorbance read on the instrument.

Limits of Detection (LOD) and Quantification (LOQ)

The limits of detection (LOD) and of quantification (LOQ) were determined by Equation 4 and 5, respectively.

$$LOD = k' \times s/ a \qquad (4)$$

$$LOQ = k'' \times s / a \qquad (5)$$

where: k = constant for the limit of detection (k' = 3.3) and for quantification (k'' = 10); s = standard error; a = is the slope of the linear regression between [mmol•L^{-1}] *versus* absorbance.

Robustness

The Placket-Burmann design was employed to detect the main effects of the robustness change. An experimental matrix that uses a factorial design and modeled in the Minitab 21 ® statistical software [14] was employed. For this test, twelve experiments combining seven factors at two different levels were carried out. The analyses were performed in triplicate between two analysts. The following parameters were taken into account, namely: Extraction time (30 and 60 minutes); Reading time waiting for sample stabilization (2 and 20 minutes); Wavenumber (386nm and 388nm); Sample vial - sampled content (level and uneven); type of pipette tip (narrow and wide), Blank reading (done and not done); Equipment stabilization (accomplished and not performed). The parameters and levels of the experiments are shown in Table 1.

Table 1. Placket-Burmann experimental matrix for the robustness test.

Parameters	**Experiments**											
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**
Extraction time (min)	60	30	30	30	30	60	60	30	60	30	60	60
Reading time (min)	2	2	2	2	20	20	2	20	20	20	20	2
Wavelength (ʎ)	388	386	388	388	388	388	386	386	386	388	386	388
Sample bottlecontent	uneven	level	level	uneven	uneven	uneven	uneven	uneven	level	Level	level	level
Pipette - nozzletype	narrow	wide	wide	narrow	wide	wide	wide	narrow	narrow	Narrow	wide	narrow
Blankreading	notdone	done	notdone	notdone	notdone	done	done	done	notdone	Done	notdone	done
Equipmentstabilization	done	notdone	done	notdone	notdone	notdone	done	done	notdone	Done	done	notdone

RESULTS AND DISCUSSION

To establish the best analysis condition in the spectrophotometer, a spectral scan in the visible region was carried out in a Quartz cuvette (10 mm × 10 mm). The absorbance maximum was chosen: 386 nm.The results obtained for each validation parameter are discussed in the sequence.

Specificity

The exploratory experiments carried out showed that the reagents used in sample preparation presented a noise of 0.0674 in the absorbance chosen for the determination of Ti (IV). To correct this effect, blank was read in wavelength value was deducted from each sample reading, thus reducing the noise generated by the reagents to zero, leaving only the signal generated by the presence of Ti complex solution. In Figure 1 we have the scan in the region between 350nm and 600nm. Figure 1 shows the blank and sample 50 ppm) readings.

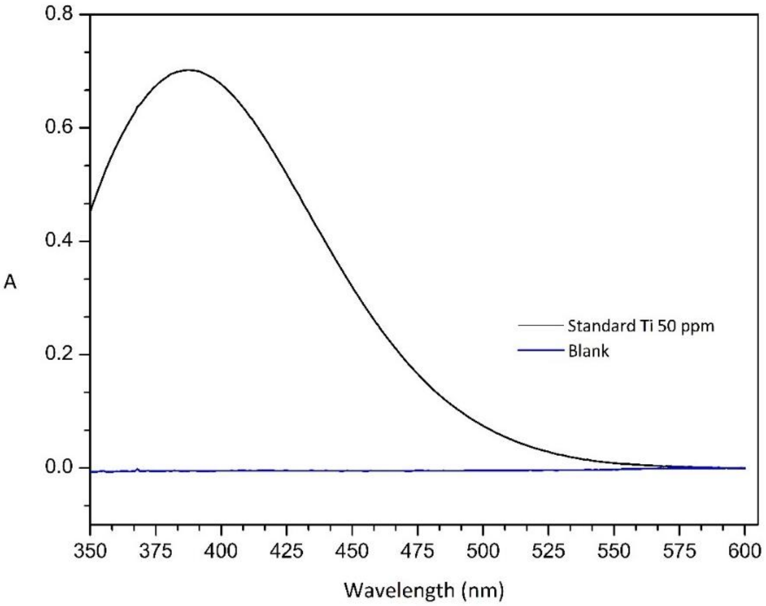

Figure 1. Scan containing the blank sample and 50ppm Ti standard sample.

Precision

The precision of the method was assessed by repeatability intra-run, where the agreement among the results of successive measurements of the method under the same measurement conditions was assessed. Seven triplicate repetitions of a reference sample (Tyzor ® TnBT 337 mmol/L) were used to calculate the estimated standard deviation. The results are presented in Table 2.

Table 2. Intra-run precision assessment.

Precision - Repeatability **A1, A2, A3, A average - signalabsorbance**					
Replica	**A1**	**A2**	**A3**	**Aaverage**	**C (mmol Ti·L^{-1})**
1	1.1699	1.1723	1.1754	1.1701	339.9
2	1.1677	1.1672	1.1620	1.1678	339.2
3	1.1689	1.1697	1.1729	1.1721	340.4
4	1.1642	1.1698	1.1654	1.1632	337.9
5	1.1628	1.1622	1.1625	1.1625	337.7
6	1.1653	1.1632	1.1701	1.1639	338.1
7	1.1739	1.1736	1,16,94	1.1738	340.9
				Average	**339.2± 1.3**
				RSD (%)	**0.4**

For the RSD, a value of approximately 0.4% was estimated, which is within the precision range applied to spectrophotometric techniques in industrial processes.

Accuracy

To represent the degree of agreement between the individual results found in the absorbance readings of the reference sample, the results are presented in Table 3.

Table3. Confidence Interval.

95% Confidence Interval	
Replica	C (mmol Ti•L^{-1})
1	339.9
2	339.2
3	340.4
4	337.9
Average	339.5 ± 1.1
L.C.	1.7

The confidence limit (CL) value (339.5 mmolTi•L^{-1} ± 1.7) is suitable for quantification of Ti^{+4} in process control samples for ZN catalysts, however, due to time constraints and equipment availability, it was not possible to consider a wider range of concentration levels, which would be ideal to obtain a better assessment of the confidence interval.

Linearity

The estimated linearity was determined by the least squares method using a series of standard solutions (N = 8), ranging from 0.20 mmol•L^{-1} to 3.33 mmol•L^{-1} of the Ti standard solution - Titrisol® 1000ppm. The method presented a resulting standard curve with function y = 0.6959x – 0,0124 (R^2 = 0.9998) in a confidence interval of 95% results within the parameters of acceptance for this work. Simple regression assumes that there is no significant deviation and the concentrations among the standards are considered accurate due to the normal distribution of residuals [15-17] as shown in Figure 2 with the analytical curve. The calibration curve was shown in Equation 5.

$$y = 0.6959x - 0.0124 \qquad (5)$$

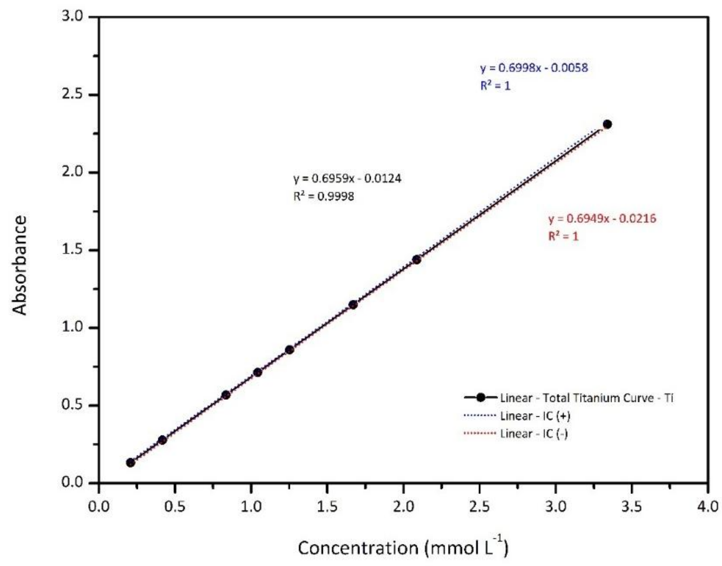

Figure 2. Analytical curve for determining Ti (IV) with confidence interval.

Limits of Detection (LOD) and Quantification (LOQ)

The LOD and LOQ were determined using Equation 3 and 4. The readings of eight samples at concentrations between 0.20 mmol•L^{-1} and 3.33 mmol•L^{-1} of Ti (IV) were analyzed in quintuplicate. The linear equation was determined by correlating the theoretical concentration of Ti in mmol•L^{-1} with the average of the analytical signal measured in five readings. Table 4 presents the results of standard error (s), LOD and LOQ obtained with the standard samples.

Table 4. Standard Error(s), LOD and LOQ Results.

Determination of Standard Error (s), LOD e LOQ							
N	**C (mmol•L^{-1})**	**A_1**	**A_2**	**A_3**	**A_4**	**A_5**	**Average**
1	0.20870	0.14025	0.14490	0.14360	0.14030	0.14610	0.14303
2	0.41740	0.28790	0.28550	0.29000	0.28490	0.25000	0.27966
3	0.83480	0.57932	0.55965	0.58345	0.54345	0.54456	0.56209
4	1.04310	0.70387	0.71097	0.70197	0.72234	0.74357	0.71654
5	1.25220	0.86898	0.85321	0.84378	0.82768	0.86658	0.85205
6	1.66960	1.15860	1.14876	1.14567	1.16870	1.14766	1.15388
7	2.08710	1.40237	1.42136	1.43534	1.44108	1.41634	1.42330
8	3.33920	2.31730	2.33750	2.32520	2.31210	2.31650	2.32172

a	0.6958
b	-0.0124
error (s)	0.0101
LOD	0.0479 mmol•L^{-1}
LOQ	0.1451 mmol•L^{-1}

Robustness

Placket-Burmann experimental matrix bearing twelve experiments were carried out combining seven factors at two different levels in factorial combination to determine the influence of each parameter on the results. The Pareto chart obtained by modeling the test in the Minitab 21® software allows us to evaluate that five of the seven factors (parameters) studied are considering a significance level of 0.1. The bars presented in Figure 3 represent the significant factors that exert the greatest influence on the variation in the result of the Ti (IV) content present in the sample. The ability to explain the variation in titanium concentration in the sample within the parameters studied by the model is $R^2 = 97\%$.

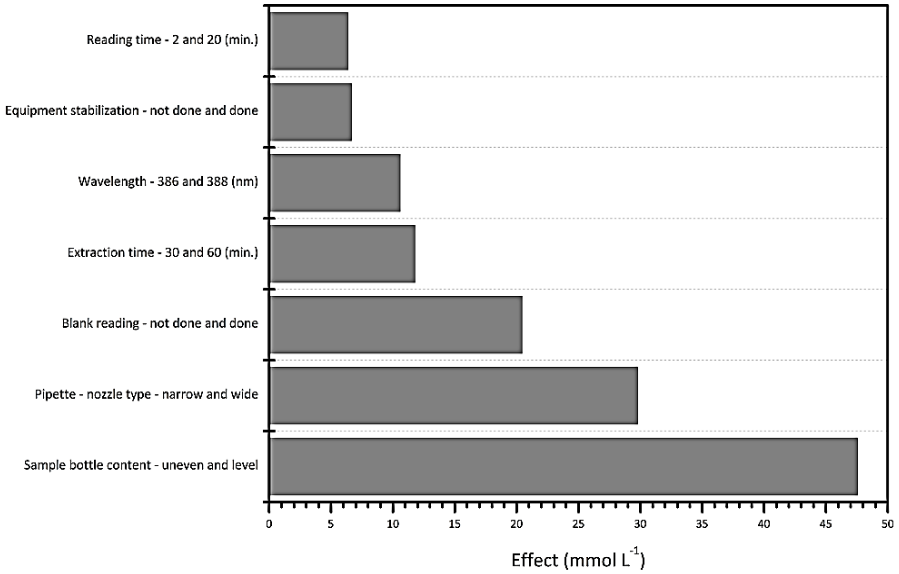

Figure 3. Pareto chart relationship between the parameters and the effect of variations of each parameter on the concentration of Ti (IV) in the sample.

The Placket-Burmann test combined with the statistical software made it possible to individually graphically evaluate the effect of each parameter. Figure 4 describes how these changes affect the result of the Ti (IV) content present in the sample. The three parameters with the greatest source of variability are: Level of catalyst present in the sampling bottle; the type of nozzle of the sample collection pipette(narrow and wide) and the reading of the blank before the sample (discounting it or not). These factors were responsible for the variability in results at 48, 30 and 20 mmolTi•L^{-1}, respectively. Two effects calculated for the method confirming the visual observations and practice carried out in the technique: Sampling bottles containing catalyst precipitate below the standard level having lower analyte content. The sample bottles, when stirred, maintain a suspension of the catalyst in hexane solution and consequently a smaller amount of catalyst when the aliquot is removed for the extraction process. The other main observed factorswere the type of pipette nozzle, narrow-nozzle pipettes by restriction and gravitational effect, which favors the preferential passage of the liquid (hexane) to the solid (catalyst) that is present in the suspension of the solution. This effect produces lower levels of Ti (IV) at the end of the test. Such behavior is not observed in wide-mouth pipettes, since these tools remove the aliquot of the suspension without causing interference to the Ti (IV) content present in the sample. The extraction time was set at 30 minutes based on the observation that this interval was sufficient to promote the efficient transfer of the analyte from the organic solvent to the acidic solution, achieving a satisfactory extraction equilibrium compared to the reference sample.

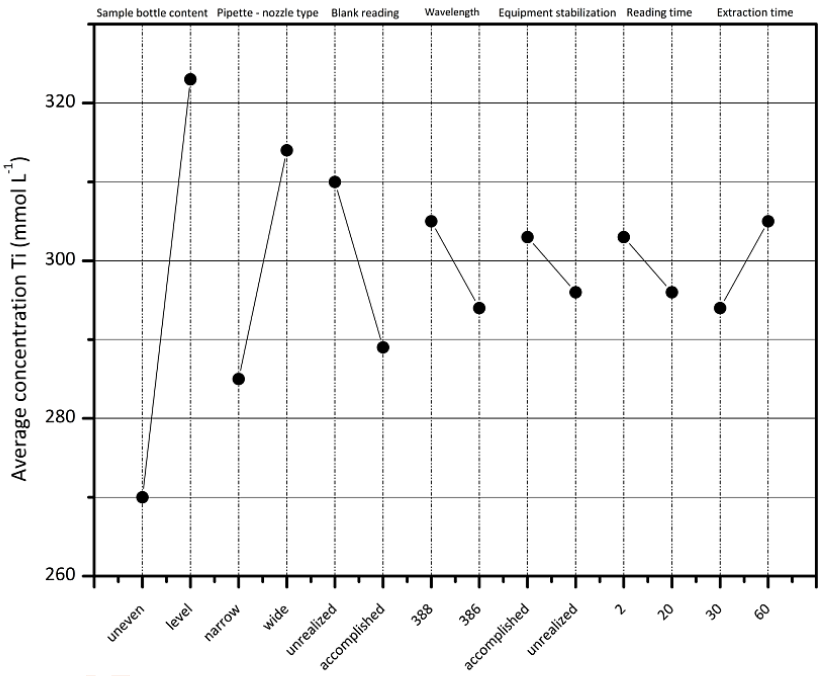

Figure 4. Individual parameter effects in the robustness test.

Figure 4 presents the analysis of the residual model generated by the software. The graphical analysis presents randomly distributed residuals with constant variance on both sides of zero with no recognizable patterns at the points for the twelve experiments carried out. Figures 5 presents the residuals in the order in which the data were collected and the assumption that the residuals are independent of each other.

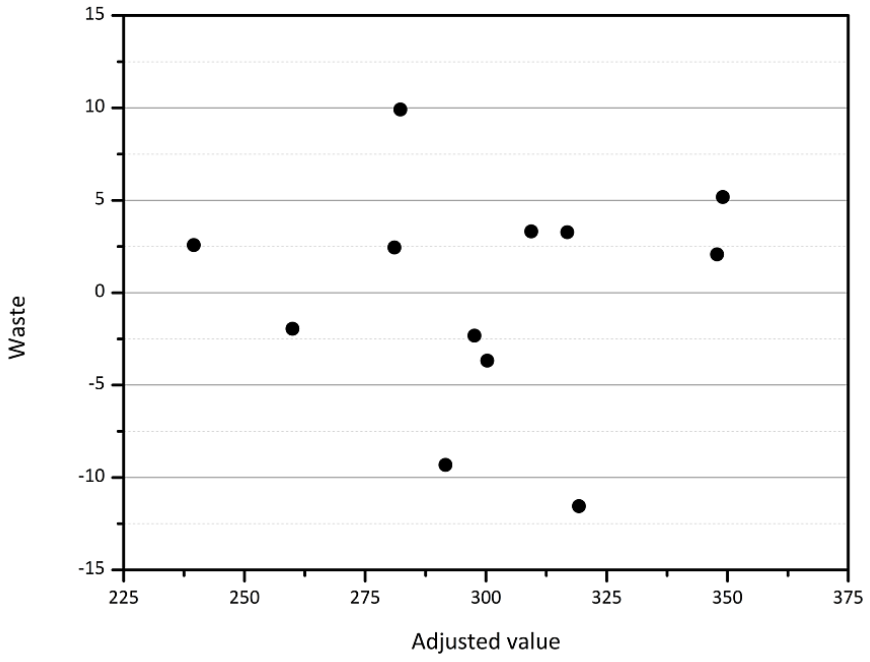

Figure 5. Residual values.

The graphical representation shows that the simple linear regression model evaluated the main effect of each factor, after adjustment, so that the software calculated the residuals according to Equation 6.

$$R = (V_o - V_a) \quad (6)$$

where: R = Residual; V_o = Observed value; V_a = value adjusted by the model.

Graphically, the X axis represents the values adjusted by the regression model, i.e., the predicted responses based on the effects of the factors; on the Y axis, residuals, which are the difference between observed and adjusted values. The graphical interpretation presented in Figure 5 indicates that the results are randomly scattered around the “zero” line, without the formation of systematic patterns such as curves, funnels or data clusters.

The randomness of the data in the graph suggests that the regression model adjusted to the Placket-Burman experiment is adequate, assuming homodedasticity (constant error variance) is met and the absence of unmodeled interaction effects or significant curvature of the system.

Method performance

The method was subjected to tests with samples of catalysts containing Ti (IV) from an industrial process for the production of PE over a period of one year. It is worth mentioning that this study did not address the possibility of using a Ti^{+3} solution because it is understood that the method is restricted to the determination of Ti species in their oxidation state (IV), and species in the Ti^{+3} state would be completely oxidized by the non-inertization of the medium and by the final addition of H_2O_2 in the colored complex formation stage.

During this period, 37 samples were collected and analyzed in duplicate using the validated method in this study. Figure 6 shows the process control chart for the determination of Ti^{+4}, where graphically, in the central line, we have the target concentration of Ti (IV), with the adjacent lines representing the maximum and minimum specification limits for the production process. In this context, 96.4% of the samples analyzed in 12 months remained in compliance with the specification ranges and only 5.4% presented a non-compliant content above the maximum limit specified. For reasons of industrial confidentiality, the process targets were not presented.

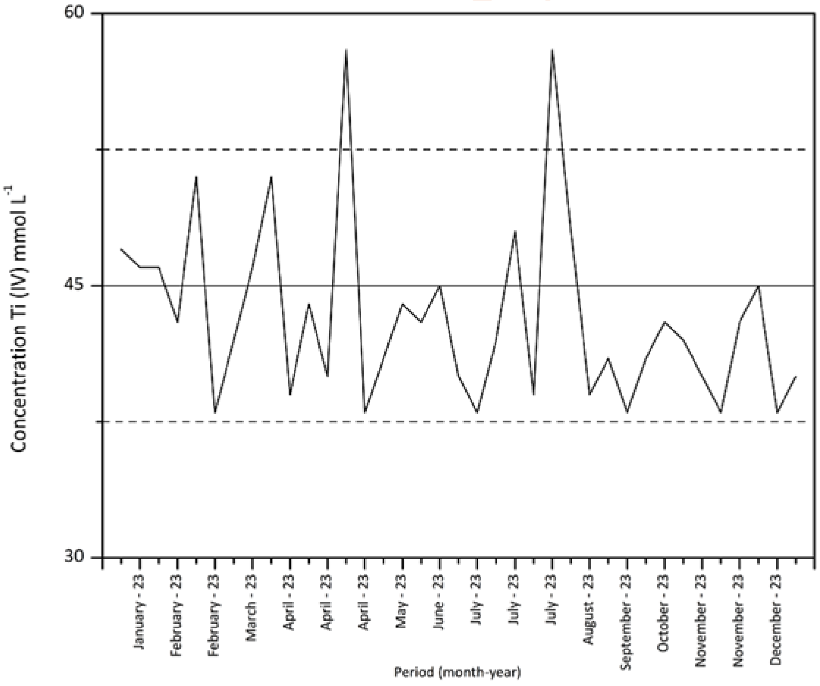

Figure 6. Performance of the method for process control.

It is worth remarking that the sign of out control is due to the rule off six points or more in a row steadily increasing or decreasing. This behavior may be due to the industrial catalyst preparation process.

From the analytical point of view, one cannot neglect the potentialities of other techniques which may provide alternative measurement in terms of sample preparation or analytical sensibility. In this scope, atomic absorption spectrometry (AAS) or inductively coupled plasma (ICP OES), allowing the quantification of Ti^{+4}, the target species of this study. Both techniques present alternative design allowing solid sample measurements. One cannot neglect the potentiality of voltammetry which can provide complementary information regarding Ti species. In the case of XRF, direct pressing was shown to be unsuitable for sample preparation due to catalyst decomposition. For Ti measurements, the catalyst sample preparation due to catalyst decomposition. For Ti measurements, catalyst samples are calcinated at 1000 ^{0}C and pressed at 275 MPa. Its determination by the fundamental parameters based on Ti Kα line measurement has shown to be equivalent to those results obtained by univariate calibration [6].

CONCLUSION

The results demonstrate that the use of the visible spectrometry technique is a simple and applicable method for the routine quantitative determination of Ti^{+4} species present in Ziegler-Natta catalysts. The study presents satisfactory results for the performance parameters addressed in the method validation, demonstrating specificity in relation to the reagents used in the evaluation of the signal-to-noise ratio of the absorbance of complexed titanium in relation to the reagents used in the analysis. The linearity of the standard curve within a 95% CI presented an R^2 value greater than 0.99 and a non-significant deviation according to the normal distribution of the residual analysis. The LOD was 0.0479 mmol/L and the LOQ was 0.14 mmol/L, values that allow the detection and quantification of Ti^{+4} within the usual ranges of process targets. The robustness evaluated by the Placket-Burmann test demonstrated in the Pareto diagram presents three parameters with result variability greater than 5%. The parameters: Sampled content level; The type of pipette used and the blank reading between samples are responsible for a variability of 48, 30 and 20 $mmolTi{\cdot}L^{-1}$, respectively, for the effect parameters that have the greatest impact on the variability of the results.

In the context of polyethylene production by the suspension process, where Ziegler-Natta catalysts are dispersed in n-hexane, acid digestion with sulfuric acid solutions is an efficient strategy for the extraction of titanium present in the n-hexane suspension. The use of sulfuric acid promoted the rupture of the catalytic matrix, solubilizing the metallic components, especially titanium, which is released from the supported structure, such as $MgCl_2$. The aggressiveness of the sulfuric acid promoted the effective disintegration of the solid-organic system, allowing the transfer of titanium to the acid phase. This approach has proven to be efficient for the visible region spectrometry technique, and its application in future studies using techniques such as atomic absorption spectrometry (AAS) or inductively coupled plasma (ICP-OES) can be evaluated.

The study proves the viability of using visible region spectrophotometry as a method for determining Ti^{+4}, a simple, reliable and low-cost instrumental technique for determining titanium in Ziegler Natta catalysts, which can be applied in industry and academia.

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Figure Captions

Figure 1. Scan containing the blank sample and 50ppm Ti standard sample.
Figure 2. Analytical curve for determining Ti (IV) with confidence interval.
Figure 3. Pareto chart relationship between the parameters and the effect of variations of each parameter on the concentration of Ti (IV) in the sample.
Figure 4. Individual parameter effects in the robustness test.
Figure 5. Residual values.
Figura 6. Performance of the method for process control.

Table Captions

Table 1. Placket-Burmann experimental matrix for the robustness test.
Table 2. Intra-run precision assessment.
Table 3. Confidence Interval.
Table 4. Standard Error(s), LOD and LOQ Results.