

DETERMINATION OF THE SURFACE FUNCTIONALITY OF NANOCARBON ALLOTROPES BY BOEHM TITRATION

M. HERNANDEZ-ORTIZ*, H. A. DURÁN-MUÑOZ†, J. D. LOZANO-LÓPEZ‡,
S. M. DURÓN‡, M. GALVÁN-VALENCIA‡, Y. ESTEVEZ-MARTÍNEZ§,
I. ORTIZ-MEDINA*, L. A. RAMÍREZ-HERNÁNDEZ¶, O. CRUZ-DOMÍNGUEZ†
and V. M. CASTAÑO||,**

*Unidad Académica de Economía,
Universidad Autónoma de Zacatecas (UAZ),
Av. Preparatoria S/N Col. Hidráulica,
C.P. 98068 Zacatecas, Zac. Mexico

†Carrera de Ingeniería Industrial,
Universidad Politécnica de Zacatecas (UPZ),
Plan de Pardillo Sn, Parque Industrial,
99059 Fresnillo, Zac. Mexico

‡Unidad Académica de Ciencias,
Químicas Campus Siglo XXI,
UAZ, Km 6 Carretera Zacatecas-Guadalajara Ejido la Escondida,
98160 Zacatecas, Zac. Mexico

§Departamento de Ingeniería Electrónica,
Instituto Tecnológico Superior de Acatlán de Osorio,
Carretera Acatlán-San Juan Ixcaquixtla km 5.5,
Acatlán de Osorio, Puebla, Mexico

¶Unidad Académica de Matemáticas,
UAZ, Czda. Solidaridad y Paseo La Bufa S/N,
98060 Zacatecas, Zac. Mexico

||Departamento de Ingeniería Molecular de Materiales del Centro de Física,
Aplicada y Tecnología Avanzada Campus Juriquilla,
Universidad Nacional Autónoma de México,
Boulevard Juriquilla No. 3001, Querétaro, Qro., Mexico

**vmcastano@unam.mx

Received 28 January 2019

Accepted 30 October 2019

Published 31 December 2019

Critical point (CP) in a titration curve to quantify carboxylic, lactonic, and phenolic groups on multi-walled carbon nanotube (CNT) and Vulcan carbon (VC). Titration technique used was Boehm type and tipping point measurement from titration curve was done by second derivative method. The calculation functional groups on nanocarbons (NCs) presents lowest uncertainty

**Corresponding author.

previously published. An order of $\pm 10^{-4}$ meq/g is the precision of the values obtained, one order of magnitude below reported. Both NCs display a high quantity of carboxylic groups created after being treated with regard to the other functional groups generated, mainly for functionalized Vulcan carbon VC-F.

Keywords: Surface functionality; nanocarbons; Boehm titration.

1. Introduction

Carbonaceous materials with the presence of functional groups on their surface generate new properties, mainly adsorption process; and in some cases, their increasing applications are interesting and unique in the interdisciplinary sciences.¹⁻³

Precise determination of carboxylic, lactonic, and phenolic groups on treated nanocarbons (NCs) is essential for a controlled application.⁴ An effective and frequently used method for quantification of oxygen-containing surface groups is the titration Boehm.⁵⁻⁷ However, the accuracy of quantifying functional groups is still variable and depends on experimental alternatives that are made to the above titration technique.

The aim of this paper is to present the possibility to bring down the measurement error of the critical point (CP), that determines the quantitative values of the surface groups on NCs, by applying the second derivative and varying a parameter of the Boehm titration.

2. Materials and Methods

2.1. Materials and solutions

Vulcan carbon (VC), XC-72 carbon black (Sigma-Aldrich Co., USA) and carbon nanotubes (CNTs) were obtained from Sun Nanotech Co. Ltd. These NCs were activated as reported in our previous job.⁸ The treated specimen were referred to as CNT-F and CV-F.

The solutions used for titration process were NaOH (Sigma-Aldrich, $\geq 97\%$), Na_2CO_3 (Sigma-Aldrich, $\geq 99\%$), NaHCO_3 (HYCEL México, $\geq 99.7\%$), and HCl (Meyer, 36.5–38%).

2.2. Titration

Solutions made by 30 mg of treated and untreated NCs into 30 ml of each reaction bases (NaHCO_3 ,

Na_2CO_3 , and NaOH) in deionized water with 0.05 M concentration, were stirred for 24 h and filtered to remove the carbon. The samples were dried at 100°C for 24 h at environmental pressure. Titration of aliquots of the reaction bases (10 ml) was directly with 0.05 M HCl, previously it bubbled for 2 h with N_2 . Later, the aliquots were covered with Parafilm to avoid CO_2 into the sample. Further, the degasification continued during the potentiometric titrations. Solutions without carbon were used as targets. Each experiment was carried out three times.

Above mentioned is Boehm titration technique taking into account the standardized titration realized by Goertzen *et al.*^{9,10} and a recent study.¹¹ However, in this titration there was a modification in an experimental process, the filtration step is used without acidified to remove dissolved CO_2 .

Potentiometric measurements were done using a potentiometer HANNA instruments with a pH 210 microprocessor pHMeter. CP was calculated from the titration curve, pH-volume (pH-V) plot, applying first and second derivative techniques.

2.3. CP determination

Experimental data were computerized, next, first and second derivatives were measured using the slope equation (see Eq. (1)).

$$\frac{d\text{pH}}{dV} \cong \frac{\Delta\text{pH}}{\Delta V} = \frac{\text{pH}_{i+1} - \text{pH}_i}{V_{i+1} - V_i}, \quad (1)$$

where $i = 1, 2, \dots$, is the value measurement in a pH-V.

CP was determined by average of two points, before and after which the second derivative is zero, based on the proportionality of triangles,¹² view Fig. 1. By subtraction of the value of the abscissa in the point M, the value of MN, given by Eq. (2), gets the value of CP.

$$\text{MN} = \frac{(\text{BC} \cdot \text{AM})}{\text{AB}}. \quad (2)$$

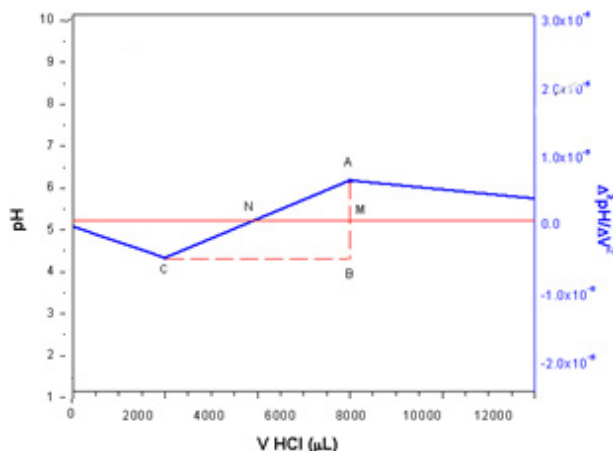


Fig. 1. Rendering of proportionality of triangle view around where second derivative vanishes ($\text{pH}/\Delta V^2 = 0$).

Concentrations of the surface groups on functionalized and unfunctionalized NCs, as was done in a previous study¹¹ using Eq. (3)

$$n_{\text{FG},\text{B}} = \frac{\text{eq}_{\text{B,pre}} - \text{eq}_{\text{B,post}}}{m_{\text{NCs},\text{B}}}, \quad (3)$$

where $n_{\text{FG},\text{B}}$ is measured in meq/g and this is equivalent to the difference between the base equivalence before ($\text{eq}_{\text{B,pre}}$) and after ($\text{eq}_{\text{B,post}}$) of the reaction base B (NaOH, Na_2CO_3 , and NaHCO_3), given by the product of the HCl concentration with its volume for each of the base equivalence, and $m_{\text{NCs},\text{B}}$ is the effective mass of the specimen subsequent to reaction base. Thus, Eqs. (4)–(6) allowed to obtain the number of carboxylic (n_c), lactonic (n_l), and phenolic (n_p) groups, respectively.

$$n_c = n_{\text{FG},\text{NaHCO}_3}, \quad (4)$$

$$n_l = n_{\text{FG},\text{Na}_2\text{CO}_3} - n_{\text{FG},\text{NaHCO}_3}, \quad (5)$$

$$n_p = n_{\text{FG},\text{NaOH}} - n_{\text{FG},\text{Na}_2\text{CO}_3}. \quad (6)$$

And the typical error in the $n_{\text{FG},\text{B}}$ was determined using the following equations, based on Kim *et al.* report¹³:

$$S_{n_c} = \left[\frac{S_{\text{eqNaHCO}_3,\text{pre}}^2 + S_{\text{eqNaHCO}_3,\text{post}}^2}{m_{\text{NCs},\text{NaHCO}_3}} \right]^{1/2}, \quad (7)$$

$$S_{n_l} = \left[\frac{S_{\text{eqNa}_2\text{CO}_3,\text{pre}}^2 + S_{\text{eqNa}_2\text{CO}_3,\text{post}}^2}{m_{\text{NCs},\text{Na}_2\text{CO}_3}} + \frac{S_{\text{eqNaHCO}_3,\text{pre}}^2 + S_{\text{eqNaHCO}_3,\text{post}}^2}{m_{\text{NCs},\text{NaHCO}_3}} \right]^{1/2}, \quad (8)$$

$$S_{n_p} = \left[\frac{S_{\text{eqNaOH},\text{pre}}^2 + S_{\text{eqNaOH},\text{post}}^2}{m_{\text{NCs},\text{NaOH}}} + \frac{S_{\text{eqNa}_2\text{CO}_3,\text{pre}}^2 + S_{\text{eqNa}_2\text{CO}_3,\text{post}}^2}{m_{\text{NCs},\text{Na}_2\text{CO}_3}} \right]^{1/2}, \quad (9)$$

where S_n is the standard deviation of the respective concentration. These error ranges depend on the measured equivalence of each reaction base. Therefore, the error determined by proportionality of the triangle used in second derivative to estimate this equivalence is part of the results of this work.

3. Results and Discussion

3.1. CP uncertainty

Uncertainty calculations were completed using the typical error equation propagated throughout the partial derivatives, Eq. (10). This equation was applied in each of the calculus realized, from both slopes corresponding to the first and second derivatives; the determination of CP where the second derivative vanishes (Eq. (2)); and for the $n_{\text{FG},\text{B}}$ equation (Eq. (1)).

$$\sigma_f^2 = \left(\frac{\partial f}{\partial a} \right)^2 \cdot \sigma_a^2 + \left(\frac{\partial f}{\partial b} \right)^2 \cdot \sigma_b^2 + \dots, \quad (10)$$

where function f is considered as each of the equations mentioned (4)–(6) and the a, b, \dots values are the variables of f . Also, σ_x is the standard deviation of term x , corresponding to each of the functional groups.

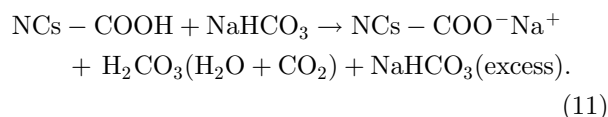
Each experiment was carried out three times, necessary amount to account statistical standard deviations.¹⁴ Although the noise in the signal caused in second derivative is a disadvantage of the method,¹⁵ in this paper, to estimate an error for each of the equations, major precision is assigned to the CP calculation, as shown in Table 1 corresponding to the surface functional groups calculated on samples used. Moreover, the change in the experimental method modifies the accuracy of the results, even if Boehm titration methodology has been standardized.^{9,10} Thus, besides one experimental variation, the location of CP through second derivative, part of the error typically is reduced with respect to that reported until now.

3.2. Titration curves to determinate functional groups

Figure 2 shows the titration curves (pH vs volume) for 0.05 M: (a, b) NaHCO_3 , (c, d) Na_2CO_3 , and (e, f) NaOH as blank aliquots of the reaction with treated and untreated VC and CNT described above (a, c, e) and (b, d, f), respectively; and their second-order derivatives (below). All curves decrease with added titrant. Described below, plots correspond to each reaction base, and finally will a comparison is made of all results.

Starting with NaHCO_3 , blank aliquot of the reaction with functionalized and unfunctionalized NCs are described in Figs. 2(a) and 2(b). Sulfuric/nitric acid treatment is induced on vacancy sites of NCs

that finally get carboxylic groups.¹⁶ These surface groups react with NaHCO_3 leading to the substitution of H^+ corresponding to the carboxyl by Na^+ (carboxylate groups) on NCs surface and the formation of carbonate ion that immediately present a decomposition into water and carbon dioxide,¹⁷ as shown in Eq. (11). This is preferred to degassing that liberate CO_2 from the solution.



When the reaction is completed, the NaHCO_3 excess (titrated with 0.05 M HCl) directly corresponds

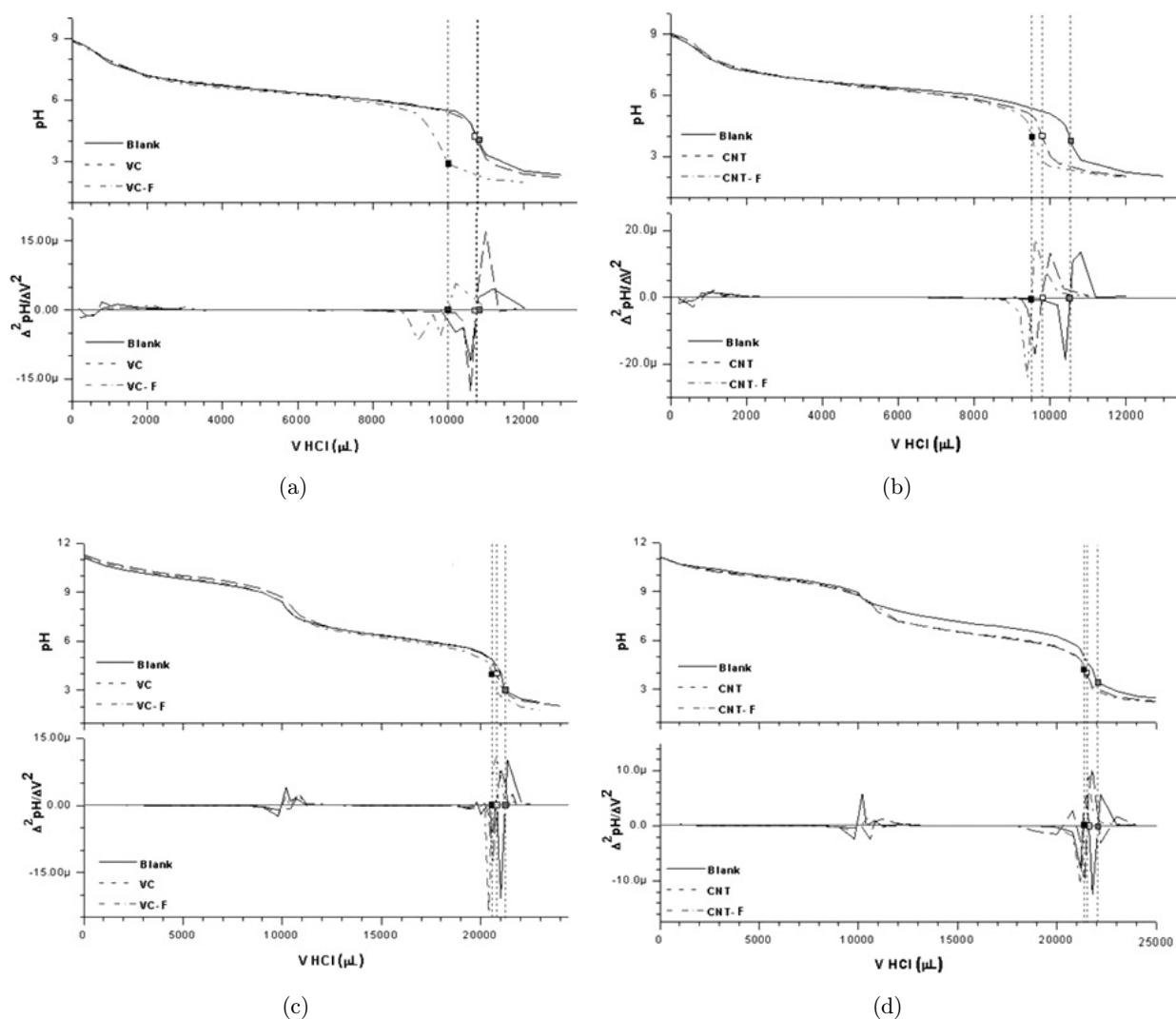


Fig. 2. Titration curves (above) all with their second-order derivatives (below), of: (a, c, e) VC and CV-F, (b, d, f) CNT and CNT-F, and (a-f) blank (continuous line); for reaction bases 0.05 M: (a, b) NaHCO_3 , (c, d) Na_2CO_3 , and (e, f) NaOH .

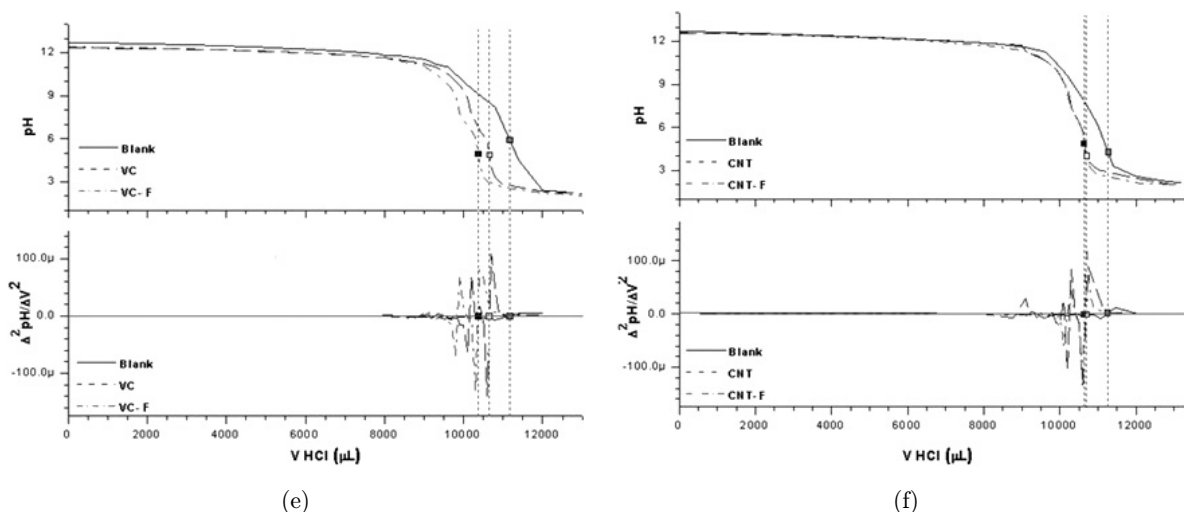
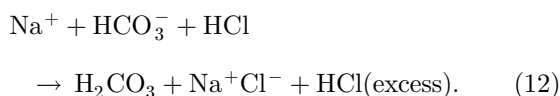
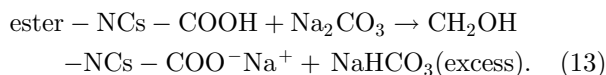


Fig. 2. (Continued)

to the quantity of carboxylic groups at NCs surface, according to Eq. (12).

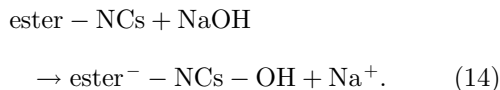


On the other hand, the titration of Na_2CO_3 occurs in two steps. The transformation of carbonate in carboxylate and hydroxyl sites (see Eq. (13)) by saponification, and the neutralization of bicarbonate by the titrating solution, as previously discussed.¹⁷ Therefore, the amount of lactonic group is obtained through subtracting. It is worth mentioning that Na_2CO_3 base is stronger than NaHCO_3 .

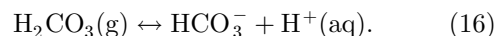
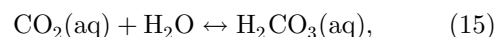


Note that total HCl titrant volume for this reaction base is almost double than other reaction bases used.⁹ However, the same conditions were employed for completing the neutralization between Na_2CO_3 and HCl.

Last case, where reaction base is NaOH, the mechanism in further carboxylic and lactonic groups that occurs is the concentrations of absorbed hydroxide ions. As Eq. (14) indicates, this reaction presents an increase of hydroxyl groups.^{14,18}



The presence of two CPs (about pH 4 and pH 8) for titration curves corresponding to reaction bases Na_2CO_3 and NaHCO_3 , with carbonate ions excess presents a CO_2 saturation that is not released until the HCl dominates.¹³ The degasification did not completely remove the CO_2 . This implies that gaseous CO_2 enters solution and it becomes aqueous CO_2 whose interaction with water generates carbonic acid,^{9,10} as shown in reactions to Eqs. (15) and (16). In this instance, the reason of the two CPs present in the titration curves is associated with the reaction base not being acidified, because otherwise it would allow to remove the CO_2 effect.¹³ This is a situation that does not happen with the base reaction NaOH, simply because of its chemical composition and reaction affinity with HCl. Therefore, $n_{\text{FG,B}}$ was determined by Eq. (3) considering the second CP from all titration curves located where the second derivative intersects in zero value seen in Fig. 2.



Second, all titration curves show displacement variations of each NCs regarding their NCs-F (Fig. 2 superior plots) considering the comparison with their respective reaction base or blank. This implies that the functionalization treatments with a sulfuric/nitric acid mixture yield carboxylic groups on NCs. This is confirmed in Table 1, which shows a change between concentration of functional and unfunctional

Table 1. Quantity of surface functional groups on NCs and NCs-F.

Sample (NC)	Quantity of functional groups (meq/g)		
	COOH	CO	OH
CNT	0.8690 ± 0.0004	0.2996 ± 0.0004	0.3561 ± 0.0002
CNT-F	1.1905 ± 0.0002	0.3360 ± 0.0005	0.1165 ± 0.0006
VC	0.0119 ± 0.0003	1.6366 ± 0.0007	0.4198 ± 0.0009
VC-F	0.9167 ± 0.0007	0.7327 ± 0.0007	0.7170 ± 0.0007

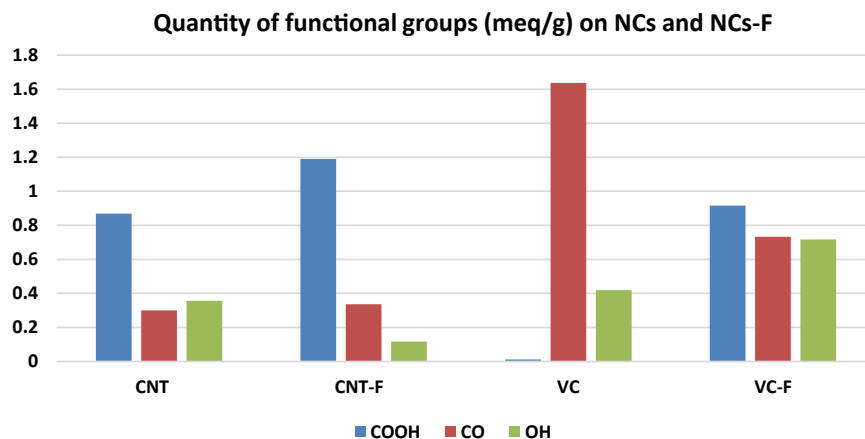


Fig. 3. Comparison by bars of functional groups concentration (meq/g) on treated and untreated NCs.

groups. The amount of carboxyl groups increase with the oxidation of NCs while the quantity of other functional groups does not exhibit the same behavior. Moreover, Fig. 3 presents the change generated in surface functional groups on NCs after their oxidation. Concentration ratio of carboxyl group on VC and functionalized Vulcan carbon (VC-F) is impressively bigger than NTC and NTC-F (1:77 compared to 1:1.4, respectively). This implies that nitric and sulfuric acid mixture treatment increases to a greater extent the quantity of — COOH on VC surface. Raman spectra for CNT and VC presented in our prior work⁸ confirm the oxidative activity of the functional groups over these NCs. VC showed a significantly microcrystalline planar size ($L_a = 21\text{--}22$ nm) compared with all other CNTs ($L_a = 4\text{--}6$ nm). Another deep justification of the results in this job could be focused on analysis of oxygenated sites distribution on the NCs surface as was done by Schmidlin *et al.*¹⁷

Based on the results presented, treated NCs provide a change in oxygen-containing surface groups, mainly an increase in carboxyl groups.

The complementary method of uncertainty calculations (Sec. 3.1) was a good reference to consider within the results, since it was applied the typical error equation propagated to all functions that depend on the standard deviation obtained from the three experimental measurements and that tended to get the CPs. It is noteworthy that the significant experimental and theoretical variation of the Boehm titration methodology used in this paper provides a relatively high precision in determination of the functionalized NCs surface groups never before presented. Namely, two novel experimental factors are considered in this study. First, the filtration step is used without acidified to remove dissolved CO_2 . The second experimental factor was CP determination from the second derivative of the pH-V plot.

4. Conclusions

Two novel experimental factors are used for the quantitative study of functional groups (carboxylic, lactone, and phenols) on some CV, CV-F, CNT, and CNT-F, it can be utilized for the comparisons

between results, without to affect the precision thereof. The determination of CP was using the second derivative of the pH-V plot and the quantification of the oxygenated groups was employing typical equations propagation of error to estimate the uncertainty in the values of surface functional groups. This step presents an error smaller than other reported results. The results presented indicate that, VC-F revealed a prevailing ratio of carboxyl groups regarding treated CNT. This industrial carbon is a NC that competes and excels in its capacity of oxidation and its degree of structural order with respect to the popular NCs. Therefore, the variation in the experimental factors generates benefits in applications that require a control of functionalized NCs.

Acknowledgments

M. Hernandez-Ortiz is a recipient of post-doctoral fellowship from CONACyT and of “For Woman in Science L’Oreal-UNESCO-CONACyT-AMC 2015” fellowship.

References

1. A. M. Kalijadis, M. M. Vukčević, Z. M. Jovanović, Z. V. Laušević and M. D. Laušević, *J. Serbian Chem. Soc.* **76** (2011) 757.
2. Y. Zeng, L. Prasetyo, V. T. Nguyen, T. Horikawa, D. D. Do and D. Nicholson, *Carbon* **81** (2015) 447.
3. X. Peng, J. M. Vicent-Luna, S. K. Jain, Q. Jin and J. K. Singh, *ACS Appl. Nano Mater.* (2019) [citado 4 de noviembre de 2019]; Available in <https://doi.org/10.1021/acsnm.9b01633>.
4. M. M. Doroodmand and Z. Shafie, *Sens. Actuators Phys.* **207** (2014) 32.
5. H. P. Boehm, *Carbon* **40** (2002) 145.
6. J. Schönherr, J. R. Buchheim, P. Scholz and P. Adelhelm, *J. Carbon Res.* **4** (2018) 21.
7. H. Ren, E. Cunha, Q. Sun, Z. Li, I. A. Kinloch, R. J. Young *et al.*, *Nanoscale Adv.* **1** (2019) 1432.
8. M. Hernandez-Ortiz, Y. Estevez-Martínez, S. M. Durón, I. L. Escalante-García, M. Vega-González and V. M. Castaño, *Fuller Nanotub Carbon Nanostruct.* **24** (2016) 345.
9. S. L. Goertzen, K. D. Thériault, A. M. Oickle, A. C. Tarasuk and H. A. Andreas, *Carbon* **48** (2010) 1252.
10. A. M. Oickle, S. L. Goertzen, K. R. Hopper, Y. O. Abdalla and H. A. Andreas, *Carbon* **48** (2010) 3313.
11. Y. S. Kim and C. R. Park, *Carbon* **96** (2016) 729.
12. A. Checchetti and J. Lanzo, *World J. Chem. Educ.* **3** (2015) 64.
13. Y. S. Kim, S. J. Yang, H. J. Lim, T. Kim and C. R. Park, *Carbon* **50** (2012) 3315.
14. S. Hanelt, G. Orts-Gil, J. F. Friedrich and A. Meyer-Plath, *Carbon* **49** (2011) 2978.
15. D. L. Zellmer, *The Derivative Methods* (1997). Available in: <http://zimmer.csufresno.edu/~davidz/Chem102/Derivative/Derivative.html>
16. Z. Zhang, L. Pfefferle and G. L. Haller, *Chin. J. Catal.* **35** (2014) 856.
17. L. Schmidlin, V. Pichot, M. Comet, S. Josset, P. Rabu and D. Spitzer, *Diam. Relat. Mater.* **22** (2012) 113.
18. J. P. Chen and S. Wu, *Langmuir* **20** (2004) 2233.