

## Preparation of in-house reference material of Fe, Ca, Ni, and Si in carbon samples from an aluminum industrial facility and the results of a proficiency test

*Preparação de material de referência interno de Fe, Ca, Ni e Si em amostras de carbono de uma instalação industrial de alumínio e os resultados de um teste de proficiência*

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### Abstract

This study presents the preparation of reference material for Fe, Ca, Ni, and Si to ensure the quality of the analysis of these elements in routine samples of carbonaceous materials in the aluminum industry. The sample was fractionated and bottled for homogeneity and stability studies before being shipped to interlaboratory certification. We then sent a bottle to each of the seven participating laboratories to determine the reference values. The results of concentration for Fe, Ca, Ni, and Si after outlier exclusion were  $589.1 \pm 25.3$ ,  $142.9 \pm 12.0$ ,  $178.1 \pm 9.3$ , and  $134.2 \pm 6.6$  ppm, respectively. Lastly, we applied a technique called z-score to evaluate the performance of the participating laboratories. After the results of this study, we can conclude that the carbon material can be used as reference material for in-house control of Fe, Ca, Ni, and Si analyses.

**Keywords:** reference material; interlaboratory certification; carbon material.

### Resumo

Este estudo apresenta a preparação do material de referência para Fe, Ca, Ni e Si para garantir a qualidade da análise desses elementos em amostras de rotina de materiais carbonáceos na indústria de alumínio. A amostra foi fracionada e engarrafada para estudos de homogeneidade e estabilidade antes de ser enviado para a certificação interlaboratorial. Em seguida, foi enviada uma garrafa para cada um dos sete laboratórios participantes para determinar os valores de referência. Os resultados da concentração para Fe, Ca, Ni e Si após a exclusão externa foram  $589,1 \pm 25,3$ ,  $142,9 \pm 12,0$ ,  $178,1 \pm 9,3$  e  $134,2 \pm 6,6$  ppm, respectivamente. Por fim, foi aplicada uma técnica chamada Z-Score para avaliar o desempenho dos laboratórios participantes. Após os resultados deste estudo, podemos concluir que o material de carbono pode ser usado como material de referência para o controle interno das análises de Fe, Ca, Ni e Si.

**Palavras-chave:** material de referência; certificação interlaboratorial; material de carbono.

## 1. INTRODUCTION

Industrial laboratories must constantly evaluate and optimize their analytical methods to ensure the quality of their measurements. The use of certified reference materials (CRMs) is one way to ensure the effectiveness of these analyses (THOMPSON et al., 2002). Furthermore, certified reference materials can be used to validate analytical methods, improve the accuracy and comparability of measurement data, and establish the metrological traceability of the analytical results (DURAN et al., 2009). When laboratories have a specific material to analyze, the use of CRMs is difficult, because in some cases there may be significantly different matrices between analyzed samples and certified standards (SANTOS et al., 2011). Thus, a few laboratories choose to produce their own in-house reference materials (RMs) from their routine samples (BOHM et al., 2011).

Carbon materials are used in the aluminum industry as a raw material for producing anodes; they are composed of pitch and coke (ABAL, 2020). These materials supply the carbon necessary to reduce alumina in aluminum by the following reaction  $2\text{Al}_2\text{O}_3 + 3\text{C} \rightarrow 4\text{Al} + 3\text{CO}_2$  in the Hall-Héroult process (MAJID et al., 2011). The anodes' chemical composition can directly influence the quality of the Al produced. Besides contamination in the aluminum produced, the presence of dross in the anode damages the electrolytic cells and anode-baking furnaces, consequently increasing production costs and environmental impacts. Thus, it is important to control the impurities in aluminum industrial facilities' carbon materials used in anode production. Impurities that must be controlled in these materials are Na, V, P, Fe, Ca, Ni, and Si content (THORNE et al., 2013).

One laboratory in the aluminum industry needed to control the content of Ca, Fe, Si, and Ni in carbon samples by fluorescent X-ray; to do so, they needed CRMs to evaluate the accuracy of their analytical method. They produced their own in-house reference material from a routine sample to solve problems with differences in matrices between analyzed samples and certified standards. These materials' production occurred through the samples' homogeneity and stability studies (ZELENY et al., 2006).

The production of solid reference material is an activity that consists of four steps: preparation of the material in the desired particle size, distribution of this material in bottles, verification of its homogeneity and stability through analytical tests over time, and certification of the sought property values. (KOUNBACH et al., 2021). Determining the necessary parameters may be done by an interlaboratory program (WASITO et al., 2022).

Given the above, this study sought to produce a reference material for Fe, Ca, Ni, and Si from anode samples from the aluminum industry through an interlaboratory certification program.

## 2. EXPERIMENTAL AND METHODS

The carbon materials used in preparing this reference material were a mixture between coke and pitch from the aluminum industry in Brazil. Firstly, the sample was prepared and evaluated for homogeneity and stability. Afterward, the samples were sent to seven laboratories, where Fe, Ca, Ni, and Si content was determined. The certified value of these elements in the sample was defined by consensus concentration after excluding outliers.

## 2.1 Sample preparation

About 13 kg of the sample was broken in a jaw crusher (model PE60-100 Shuliy), and the sample was then sprayed in an AMEF mill (model AMP1-A). The entire sample was passed through 0.250-mm sieves (Dafratec model). The material with particle sizes below 0.250 mm was sent for quartering, and material with particle sizes above 0.250 mm was discarded. Hence, at the end of the grinding and sieving process, approximately 12.7 kg of the sample remained. The sample was then kept in an oven at 60 °C for 48 h to remove moisture. A rotating device (model PT100, Retsch) with eight positions performed the quartering. Finally, all of the material was placed in polyethylene bottles — 95 g were filled into each of the 128 bottles.

## 2.2 Homogeneity test

The homogeneity test was performed before delivering the material to interlaboratory certification. The main aim was to verify any problems with the sample preparation, and the test's purpose was to verify significant differences between samples. Ten bottles were randomly selected, and the content of Fe, Ca, Ni, and Si were analyzed in triplicate by X-ray fluorescence (XRF) using the method described in standard D4326-11 of the American Society for Testing and Materials (ASTM) for pressed powder (ASTM, 2011).

In this study, 2 g of each sample were weighed and mixed with 2 g of stearic acid from Merck, which works as a binder in preparing tablets for XRF analysis. The mixture was ground in a tungsten carbide mill pot (model AMP1-A, AMEF), and each sample was then pressed in a hydraulic press (model HTP 40, Herzog) for tablet preparation. Concentrations of the elements of interest were measured on an X-ray spectrometer (WDX-

RF PW2420, Philips, PANalytical). After the analyses, analysis of variance (ANOVA) was applied, which is the appropriate statistical test for multiple comparisons such as homogeneity between bottles (MAJID et al., 2011).

## 2.3 Stability test

The stability test was performed monthly for four consecutive months. During this study, seven bottles stored at room temperature were analyzed for Ca, Si, Fe, and Ni by XRF. After the analysis, graphs were constructed in which the concentrations in ppm were converted to  $\text{Log}_{10}$  and plotted on the y-axis; they were then correlated with the variable study time elapsed plotted on the x-axis. Linear regression was applied for statistical analysis. Thus, lower and upper 95% confidence limits were obtained from the slope (THOMPSON et al., 2006).

## 2.4 Interlaboratory certification program

The Fe, Ca, Ni, and Si contents in the material were defined by an interlaboratory program. Seven laboratories, four in Brazil, one in Spain, one in Switzerland, and one in the USA participated in the certification program. Each laboratory received one sample bottle and performed the analysis six times according to their routine using their standard methodologies. After analysis, the results were compiled and treated with statistical techniques suitable for determining the consensus concentration among laboratories. Each laboratory received a numeric code to ensure the confidentiality of their results.

## 2.5 Statistical methods

The certified value for a reference material cannot be defined simply by averaging

the results of all laboratories participating in the interlaboratory certification program. Several statistical tools are applied to data from an interlaboratory procedure to ensure the results' accuracy. Among them, Cochran and Grubbs' tests were applied to exclude outliers, and the variance analysis technique was used to verify the existence of significant differences between the samples analyzed in the interlaboratory program. Lastly, we used the z-score to evaluate the technical performance of the participating laboratories (CARDOSO et al., 2010).

## 2.6 One-way ANOVA

One-way ANOVA is a robust and reliable method used in multiple comparisons as in tests performed in interlaboratory analyses (ZUCCHINI et al., 2003). Seven laboratories analyzed a sample in the interlaboratory tests. Therefore, the variance within the group or variance of repeatability and the variance between groups or reproducibility are considered (FARRANT, 1997).

The variance components are defined by Equations (1) and (2) as follows:

$$(1) s^2_{within} = MS_{within}$$

$$(2) s^2 = MS_{between} - MS_{within} \div n$$

Where:

*SM within*: mean squares within levels or groups;

*SM between*: mean squares between levels or groups;

*n*: number of replicates.

The proper use of ANOVA is based on two critical assumptions. The first is that the averages obtained by each laboratory follow the normal trend, and the second is that there is homoscedasticity between the

results (i.e., the variances for each laboratory are the same). Therefore, it is vital to apply the Cochran test preliminarily to the analysis of variance (single factor test) (CHUI et al., 2009).

## 2.7 Cochran and Grubbs' tests

The Cochran test excludes laboratories with significantly greater variance than the other participating laboratories (CHUI et al., 2009). It should be noted that the Cochran test is unilateral, as it only evaluates the maximum value (FARRANT, 1997). This test evaluates the highest value when the highest variance is related to the total sum of variances. The null hypothesis is verified by the Cochran coefficient (C) (LOPES, 2003).

The Cochran coefficient is calculated by dividing the maximum variance between the values measured for each laboratory by the sum of the variances of all laboratories.

$$(3) C = \frac{\max Si^2}{\sum Si^2}$$

The calculated value of C is compared with the critical values ( $C_c$ ) tabulated for tests of 1 and 5% of significance. The decision-making criteria are as follows:

$C < C_c(5\%)$ : the null hypothesis is accepted;

$C_c(1\%) > C > C_c(5\%)$ : suspicious situation;

$C > C_c(1\%)$ : the null hypothesis is rejected.

After applying the Cochran test, the Grubbs test was applied; it is applied to both ends of a set to exclude outliers. Thus, after excluding laboratories that showed high values of means, the Grubbs test was applied to check whether higher or lower values measured in the interlaboratory program are considered discrepant. For the lowest value:

$$(4) G_l = \frac{\bar{x} - x_l}{s}$$

For the highest value:

$$(5) G_n = \frac{x_n - \bar{x}}{s}$$

The evaluation criteria of Grubbs were then applied. At this moment, the Grubbs criteria are: the values of Grubbs coefficient (G) greater than Gc(1%) are considered discrepant, the values of G between Gc(1%) and Gc(5%) are considered suspicious, and the values of G minor than Gc(5%) accept the null hypothesis.

If the null hypothesis is accepted, the second step of the Grubbs test is carried out: the sum of the squares of the differences in relation to its mean ( $SQ_i$ ) is calculated considering all the results, and the sum of the squares of the differences in relation to the new mean excluding the two lowest values ( $SQ_{1,2}$ ).

$$(6) G' = \frac{SQ_{1,2}}{SQ_i}$$

Then, the sum of the squares of the differences in relation to the mean is calculated, excluding the two largest values and divided by the sum of the squares of the differences in relation to the mean, considering all the values of the set.

$$(7) G'' = \frac{SQ_{p-1,p}}{SQ_i}$$

Then, the values of G' and G'' are compared with the values of Gc tabulated with a confidence level between 1 and 5%. The decision-making criteria are: if G' (or G'') < Gc (5%) value considered anomalous, if Gc (1%) > G' (or G'') > Gc (5%) value is suspicious, and if G' (or G'') > Gc (1%) the null hypothesis is accepted (CHUI et al., 2009).

### 3. RESULTS AND DISCUSSIONS

#### 3.1 Homogeneity test

Contents of Ca, Fe, Si, and Ni were measured in three subsamples of ten different bottles randomly selected. Between-bottle variation was evaluated using triplicate results of each interest element. The results of Ca, Fe, Ni, and Si were tested for homogeneity study using ANOVA. The mean squares within bottles ( $MS_{\text{within}}$ ), mean squares between bottles ( $MS_{\text{between}}$ ), F calculation ( $F_{\text{cal}}$ ), F critical ( $F_{\text{crit}}$ ), p value, and the relative standard uncertainty due to inhomogeneity ( $u_{\text{bb}}$ ) for each element are listed in Table 1.

Table 1: ANOVA table for between-bottle homogeneity study of Ca, Fe, Ni, and Si in carbon reference material.

ELEMENTS	MS <sub>WITHIN</sub>	MS <sub>BETWEEN</sub>	F <sub>CAL</sub>	F <sub>CRIT</sub>	P VALUE	U <sub>BB</sub>
Ca	4.37	2.06	0.47	2.39	0.88	0.88%
Fe	42.80	13.37	0.31	2.39	0.96	3.13%
Si	55.03	76.26	1.39	2.39	0.26	2.66%
Ni	1.77	0.63	0.35	2.39	0.94	0.62%

Source: From the author

As shown in Table 1,  $F_{cal}$  does not exceed  $F_{crit}$ , and the  $p$  value is greater than 0.05, indicating the material is homogeneous for Fe, Ca, Ni, and Si at a 95% confidence level. The relative standard uncertainties due to inhomogeneity ranged from 0.62 to 3.13%.

### 3.2 Stability test

This study was proposed to evaluate the stability of the carbon material during storage time. Thus, seven bottles were analyzed and stored in the same conditions for four months. Table 2 and Figure 1 show the four-month experimental data for Ca, Fe, Si, and Ni.

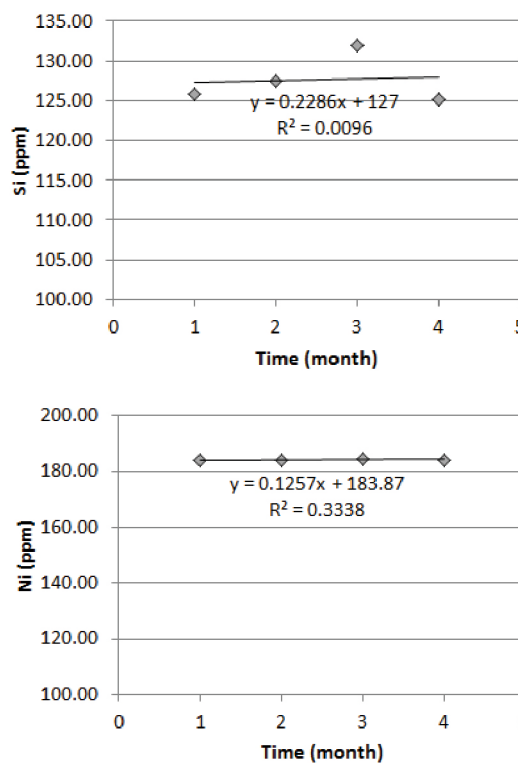
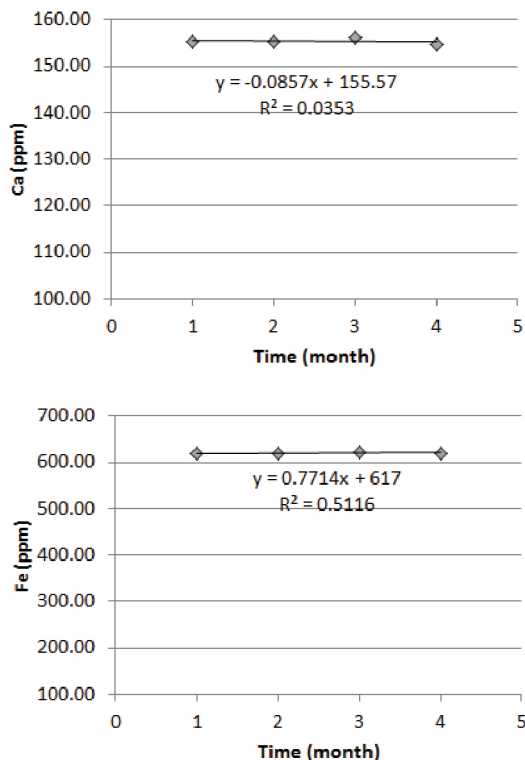
Table 2: Experimental data and standard deviation for contents of Si, Ca, Fe, and Ni during four months

TIME (MONTHS)	SI (PPM)			CA (PPM)			FE (PPM)			NI (PPM)		
1	125.9	±	3.3	155.3	±	3.2	618.0	±	2.5	183.8	±	0.7
2	127.4	±	10.3	155.3	±	1.6	617.6	±	2.5	184.2	±	0.4
3	131.9	±	12.0	156.1	±	2.2	620.6	±	1.7	184.5	±	0.5
4	125.1	±	1.6	154.7	±	2.4	619.6	±	2.8	184.2	±	0.4

Source: From the author

The low  $R^2$  values can be seen in Figure 1, indicating that the material is stable during study time because it shows no relation between the the contents of Ca, Fe, Si, and Ni and time.

Figure 1: Long-term stability results on candidate reference material for four months. Ca, Fe, Si, and Si concentration in ppm of the candidate reference material.



Source: From the author

Stability can be confirmed by slope and intercept values in Figure 1. Because the slopes of the regression line for elements are not statistically significant, the intercepts of the regression line are also not statistically different from the initial values.

### 3.3 Interlaboratory certification program

Each laboratory received a sample bottle and analyzed the content of Fe, Ca, Ni, and Si according to their standard routine six times. Table 3 lists interlaboratory results in ppm.

Table 3: Interlaboratory results in ppm and standard deviation for each laboratory

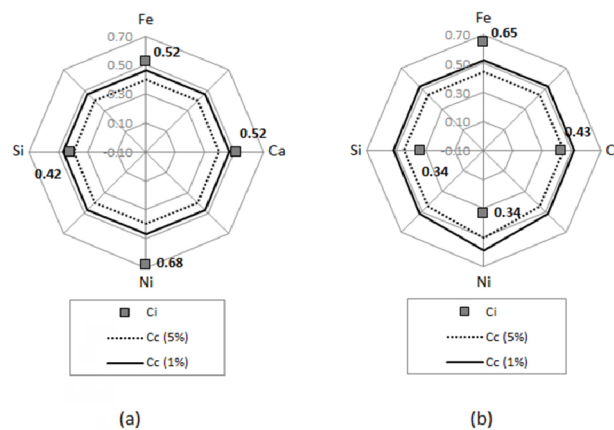
LABORATORIES	SI (PPM)			CA (PPM)			FE (PPM)			NI (PPM)		
1	173.8	±	9.6	149.5	±	5.5	582.0	±	13.1	175.8	±	3.5
2	133.5	±	4.5	158.5	±	3.6	614.0	±	2.0	183.2	±	0.8
3	137.0	±	6.3	145.0	±	0.9	580.7	±	17.1	181.3	±	1.0
4	140.0	±	6.5	143.3	±	3.0	591.5	±	6.3	175.0	±	0.9
5	127.7	±	3.4	138.7	±	8.7	618.9	±	1.4	162.2	±	1.2
6	127.8	±	3.1	120.8	±	1.2	541.8	±	4.5	188.7	±	0.5
7	139.0	±	1.8	140.2	±	4.0	594.7	±	5.1	182.8	±	1.5

Source: From the author

These findings are not enough to show the real concentration in the sample. Some errors are associated with the methods, routines, and equipment, among other factors. Thus, to determine the Ca, Fe, Si, and Ni contents, it would be necessary to apply a statistical test to delete discrepant values.

The Cochran test was the first test applied, which is a sided test because it is used to verify the major variance in relation to the sum of variances. From Figure 2, one can observe that after the exclusion, the major variance values for Fe (Cochran index: 0.65) were even higher than before the exclusion (0.52) because the variance values were significantly different between laboratories.

Figure 2: Cochran indices before exclusion of discrepant variances (a) and after exclusion of discrepant variances (b)

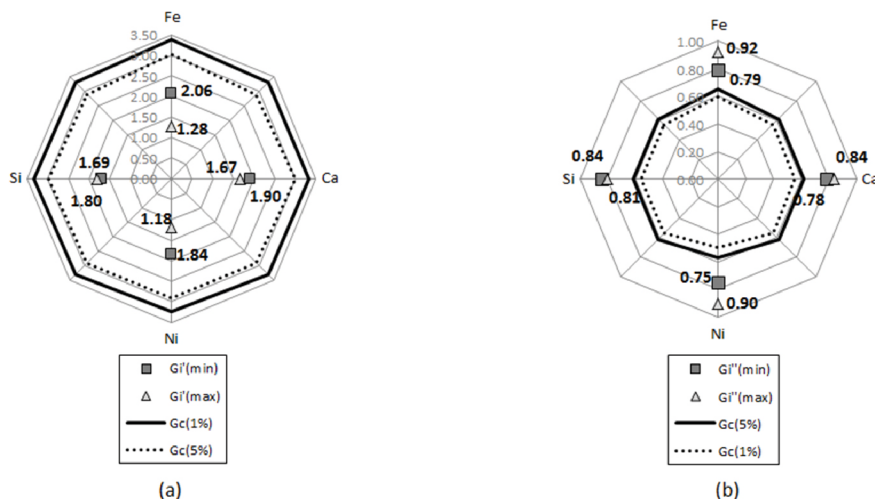


Source: From the author

Thus, we opted for the non-exclusion of laboratory 3 for Fe analysis. Nevertheless, when discrepant variances for the other elements were excluded, the homoscedasticity of the data improved. Because Cochran indices calculated (Ci), 0.43 for Ca and 0.34 for Ni and Si, were less than Cochran indices tabulated (Cc) at 5% confidence, 0.44 for Ca and Si and 0.51 for Ni. Therefore, we opted to exclude laboratory 5 for Ca analysis, laboratories 1 and 7 for Ni analysis, and laboratory 1 for Si analysis.

After applying the Cochran test, the Grubbs test was applied. It is applied to both ends of a set to exclude outliers. Thus, after excluding laboratories that showed high values of means, the Grubbs test was applied to check whether higher or lower values measured in the interlaboratory program are considered discrepant. Figure 3a shows criteria Grubbs applied before and after excluding discrepant variances.

Figure 3: The first step of Grubbs test applied to the highest and lowest values of the data set (a) and the second step applied to the sum of differences squared after excluding major and minor values of each set (b)



Source: From the author

According to Figure 3a, none of the values of the ends of the data sets were considered outliers due to the Grubbs indices ( $G_i'_{(min)}$  or  $G_i'_{(max)}$ ) of all elements being less than tabulated  $G_c$  (5%). Hence, we proceeded to the second stage of the Grubbs test.

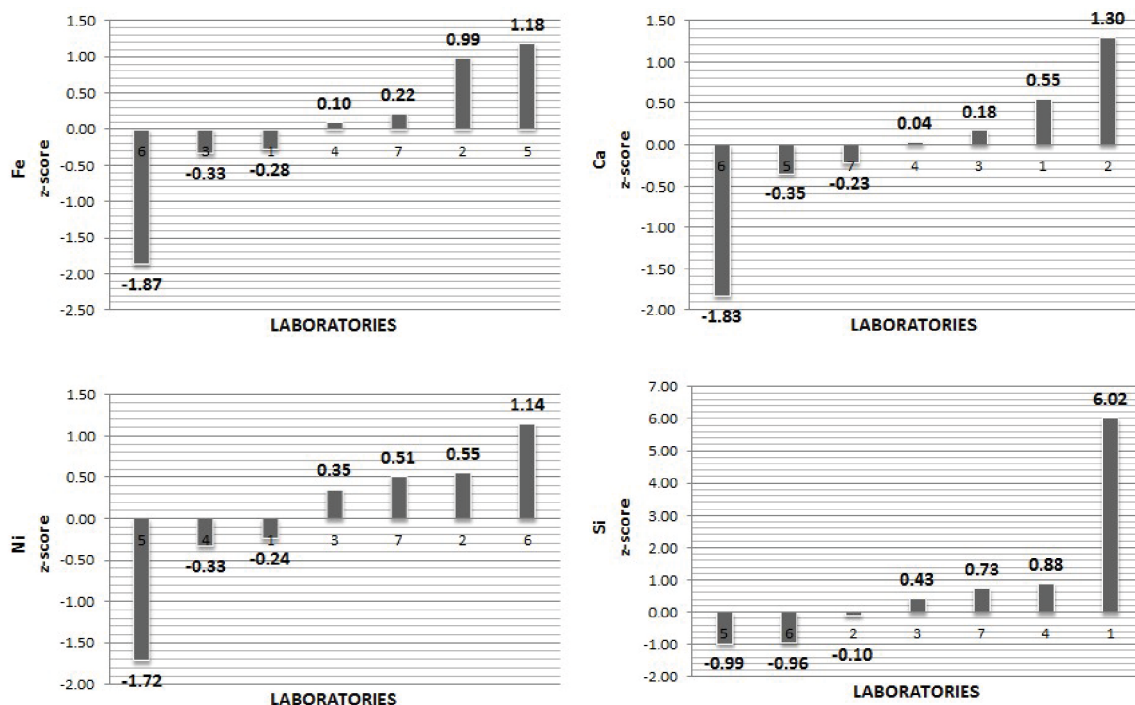
Then, excluding the two largest values, we repeated the procedure. Figure 3b shows the results of the second stage of the Grubbs test. As shown in the figure, no discrepant values at the ends of the sets for the highest and lowest values of each element were observed. By excluding the two lower values,  $G_i''(min)$  values were 0.79, 0.78, 0.75, and 0.84, and  $G_i''(max)$  values were 0.92, 0.84, 0.90, and 0.81, for Fe, Ca, Ni, and Si, respectively. These values are greater than the tabulated values, 0.66 for Fe, 0.62 for Ca and Si, and 0.57 for Ni. Thus, the  $G_i''$  values met the criteria for acceptance of the mean.

Finally, it was possible to determine the certified concentration of the interest elements in the sample. The concentration was determined by the average of the remaining values after the Cochran and Grubbs test. The results of concentration in ppm for Fe, Ca, Ni, and Si, after outlier exclusion, are  $589.1 \pm 25.3$ ,  $142.9 \pm 12.0$ ,  $178.1 \pm 9.3$ , and  $134.2 \pm 6.6$ , respectively.

After certification of the material, the participating laboratories were evaluated for performance by z-score test. The z-score test is used to measure the performance of laboratories in an interlaboratory program. This test was applied after determining the consensus concentration for interest elements. Moreover, the certified value was used as a reference to evaluate the laboratories.



Figure 4: Graphical representation of the z-scores



Source: From the author

Figure 4 shows the laboratories' performance in measuring the elements of interest. There was one case of significant deviation when the z-score  $> 2$ . In general, all laboratories performed well in measuring the elements of interest.

## 4. CONCLUSIONS

After preparing the sample, evaluation of homogeneity and stability, and sending samples for interlaboratory certification, we can conclude that the carbon material can be used as reference material for internal control of Fe, Ca, Ni, and Si analyses in a laboratory of an aluminum industrial facility.

The reference material produced "in-house" is an interesting alternative for laboratories and industries seeking to maintain the reliability of their measurements and can be used in calibration and tighter controls without the high costs of certified reference

materials. Another advantage is that the material produced has similar characteristics to samples analyzed routinely in the laboratory, avoiding differences between sample matrices and analytical standards.

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