DETERMINATION OF TOTAL IRON CONTENT IN IRON ORE BY GLASS DISC FOR X-RAY FLUORESCENCE SPECTROMETRY WITH MATHEMATICAL MASS CORRECTION[1]

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Abstract

The purpose of this study is to improve the precision and accuracy in the determination of total iron content in iron ore by fused glass disc for X-ray fluorescence (XRF), applying mass gain or loss mathematical correction during glass disc preparation. In addition, this study also aims at reducing economic costs of reagent and labor use by applying the new methodology as a routine in-house method for iron ore samples. In the new proposed method, all samples used for tracing the calibration curve and in testing are previously ignited in a muffle furnace at 1,000°C (1,832°F) for one hour. In this way, the samples read on the XRF spectrometer are in ignited base and are corrected by a mathematical factor as a function of mass loss on ignition (LOI). Certified reference materials (CRM) were used for assessing and comparing the method's accuracy, with and without mathematical correction of mass. The method's precision was assessed in samples with total Fe contents of 25% to 65%, in accordance with standard *ISO 3085:2002 - Iron ores - Experimental methods for checking the precision of sampling, sample preparation and measurement*. The results showed that using mathematical mass loss correction reduces the relative bias between the results for the reference materials (CRM) analyzed for total Fe by XRF from 1.12% to 0.10%, improving the method's accuracy. In addition, a precision improvement from 3.05% to 0.32% was noted. Therefore, we conclude that the proposed method improves the results' analytical quality and can be applied as an in-house method for iron ore samples, reducing the response time and testing costs, because the total iron content is, in general, determined by wet analysis.

Key words: X-ray fluorescence; Fused glass disc; Iron ore; Total Fe.

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[1] *Technical contribution to the 3rd International Meeting on Ironmaking, September 22 – 26, 2008, São Luís City – Maranhão State – Brazil*

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1 INTRODUCTION

X-ray fluorescence (XRF) is one of the most used instrumental techniques for chemical analysis of materials, such as ores in general, metals, cement, petroleum, ceramics, organic materials, pigments, plastics, and films. Since its advent, in the middle of the 20th century, XRF equipment has become increasingly robust, advanced and fast, meeting the great demand for chemical analysis in research and production laboratories at major companies, as Vale.

The high initial investment in a XRF equipment yields a good return thanks to the low consumption of man-hour, reagents, standards, consumables, and premises maintenance resources, because, once the equipment is calibrated, the analyses progress at a rate and reproducibility superior to those of other analytical techniques. In this way, XRF equipment is widely used in iron ore laboratories, being applied to many chemical testing processes conducted at laboratories.

However, although instrumental techniques aim at being self-sufficient as to all analytical challenges, there is always a limitation for some element or material, so no single technique is universal. On the other hand, because they are “evolutionary” and not “revolutionary,” no instrumental technique may be discarded in favor of a new method, but supplemented by it, because the range of analytical problems is very wide.

The fused glass disc XRF technique is proper for chemical analysis of most types of iron ores due to the elimination of chemical bond, mineralogical, granulometrical, and matrix effect interference. However, in spite of the benefits offered by this method, it is not possible to use the analytical result achieved with the element iron (total Fe) due to the wide dispersion of the results, which invalidates the technique for this element. At large, in addition to other chemical analysis techniques, iron ore laboratories use the fused glass disc XRF to analyze the chemical composition of iron ore samples. The calibration curve of the X-ray equipment is plotted based on data from reference material samples in dry base and unknown routine samples as well. Nevertheless, in general, this method has excellent precision and accuracy for most of the pertinent elements, except for the total Fe content, which shows a high variability of results, not meeting the uncertainty requirement for total Fe content. Thus, when the sample is analyzed by fused glass disc XRF, it is necessary to determine the total Fe content applying the wet analysis (primary method).

In this study, the influence of mass loss or gain (oxidation) during the iron ore sample fusion on the determination of the total Fe content via fused glass disc XRF is described. It is important to make clear that mass gain is related to the oxidation of chemical elements in iron ore, for example, the oxidation of Fe^{+2} (Fe_2O_3) into Fe^{+3} (Fe_3O_4) during LOI testing. This study also proposes a mathematical correction of mass in the iron content measured as a function of the loss on ignition (LOI) value, with the purpose of improving the analytical technique’s precision and accuracy. Since XRF is a comparative technique, the proposed method is to work with calibration curves and testing samples previously ignited i.e. in the same ignited base (CB) and, then, make the mathematical correction for dry base (DB).

Taking into account the numerous testing processes for wet analysis of total Fe conducted in iron ore laboratories, this study also assessed the potential for cost reduction, environment protection, safety, and response time of the new method.

2 MATERIALS AND METHODS

The testing processes conducted in this study used dry base iron ore samples i.e. samples with units of approximately 0% (oven-dried at 100°C (212°F)) and ignited base iron ore samples (muffle-ignited at 1,000°C (1,832°F)) i.e. samples with LOI of approximately 0%. In this way, a calibration curve was plotted for dry base with 33 iron ore certified reference materials (CRM) with all samples in dry base i.e. without ignition. In general, this methodology is adopted in iron ore laboratories as a routine. For tracing the XRF equipment's calibration curve, applying the new proposed method, 33 iron ore CRM's were selected and ignited at 1,000 ± 50°C (1,832 ± 122°F) for 1 hour in muffle furnace before fused glass disc formation. Both X-ray equipment's calibration curves were plotted based on the flux mixture comprising Li2B4O7/LiBO2 (66%/33%) from Claisse at a flux/sample ratio of 12:1. Thus, the glass discs were formed with 8.4000 ± 0.0002 g of flux plus 0.7000 ± 0.0002 g of ignited sample without surfactant added. The surfactant is used to reduce the surface tension between the platinum crucible and the fused glass disc, facilitating its removal. However, in general, surfactants, such as KI and NaBr, cause interference in the spectral lines of the elements Ti and Al, respectively, resulting in systematic errors in the measurement of the contents of these elements. It is important to emphasize that, before being entered into the equipment's software, the CRM reference values were mathematically corrected as a function of the LOI, because the glass discs were formed with samples in ignited base. Equation 4 for mathematical mass correction is demonstrated in item 3.1 of this report.

Once the calibration curve was plotted, some reference standards and geological research routine samples were read using the ignited base and dry base fused glass disc XRF technique. The total Fe content of the samples was also determined by wet analysis, based on standard *ISO 9507:1990 - Iron ores - Determination of total iron content - Titanium (III) chloride reduction method.* For the LOI testing of each sample, an amount of 2.0000 ± 0.0002 g of iron ore was ignited for 1 hour in muffle furnace at 1,000 ± 50°C (1,832 ± 122°F).

All testing activities were conducted using RIGAKU X-ray fluorescence equipment, model Simultix-12, Claisse machine, model M3-Fluxy, and Analógica muffle furnace, model AM1222-W61.

3 RESULTS AND DISCUSSION

3.1 Mathematical Correction Factor as a Function of Mass Loss (LOI)

Assuming an iron ore sample with total mass m_{total}, atom mass of element X m_x, and volatile mass m_v, we define:

- The content of an element X in a dry base (DB) sample is the atom mass of this element, m_x, divided by the total mass of the sample, m_{total}, times 100, as shown in Equation 1.

$$TeorX_{BS} = \frac{m_X}{m_{total}}100 \qquad 1$$

- The content of an element X in a ignited base (CB) sample is the atom mass of this element, m_x, divided by the total mass of the sample, m_{total}, minus the volatile mass, m_v, times 100, as shown in Equation 2.

$$TeorX_{BC} = \frac{m_X}{m_{total} - m_v} 100 \qquad 2$$

- The loss on ignition (LOI) in a sample is defined as the volatile mass, m_v, divided by the total mass of the sample, m_{total}, times 100, as shown in Equation 3.

$$PPC = \frac{m_v}{m_{total}} * 100 \qquad 3$$

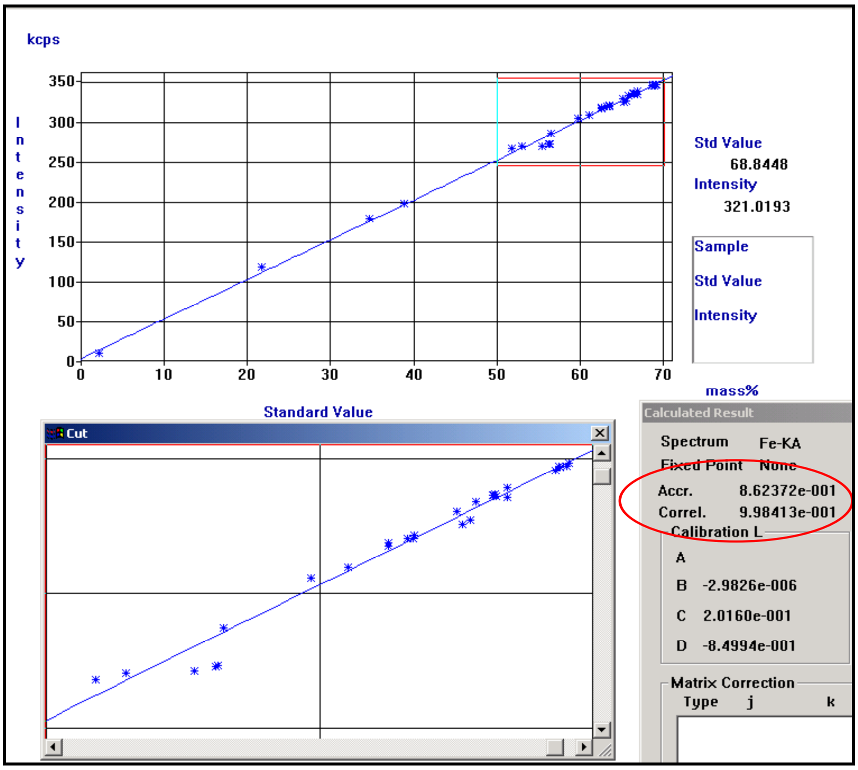
Dividing Equation 1 by Equation 2 and applying Equation 3 to the ratio, we have Equation 4, which is the mathematical correction of mass loss on ignition.

$$TeorX_{BS} = \frac{TeorX_{BC}(100 - PPC)}{100} \qquad 4$$

3.2 XRF Equipment Calibration Curve

Figures 1 and 2 show the calibration curves for dry base and ignited base fused glass disc XRF.

The accuracy and the polynomial regression correlation coefficient of the curve linking the points are optimal when ignited samples are used, as shown in table 1. Thus, it is possible to note that the reference, the calibration curve in this instance, is more reliable when ignited sample standards are used.



Std Value
68.8448
Intensity
321.0193

Sample
Std Value
Intensity

Spectrum Fe-KA
Fixed Point None
Accr. 8.62372e-001
Correl. 9.98413e-001

A
B -2.9826e-006
C 2.0160e-001
D -8.4994e-001

Figure 1. Calibration curve with dry base standards.

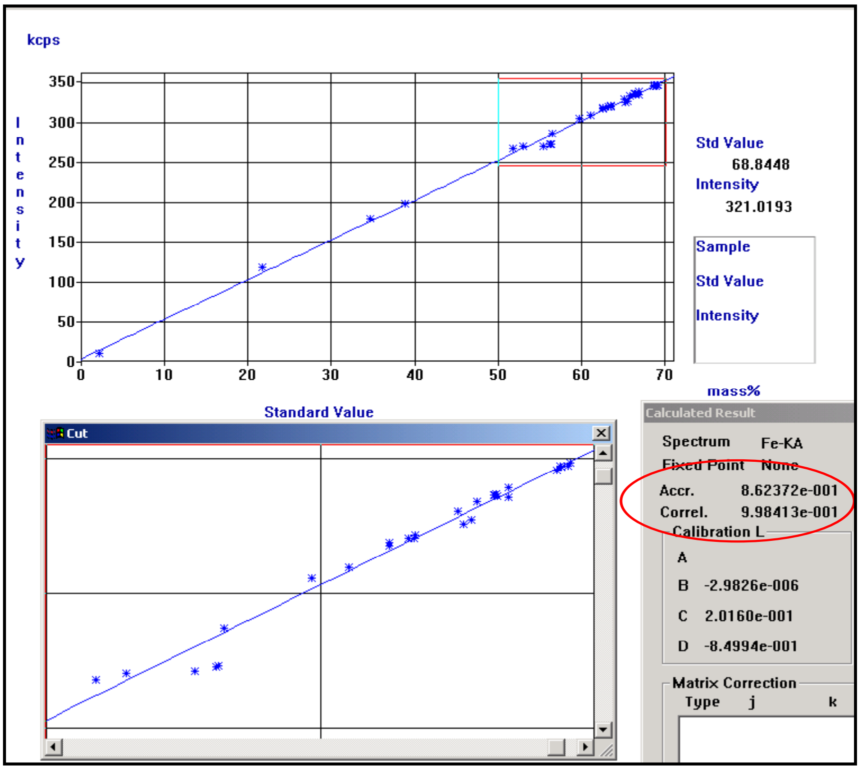


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Figure 2. Calibration curve with ignited base standards.

The graph in Figure 1, for dry base sample, also shows a trend towards a wider dispersion of the curve points due to the increase in iron content concentration in the die after fusion on the fused glass disc machine. This happens because the mass of iron atoms remains the same in the sample after fusion, while the total mass (sample plus flux) is reduced due to the loss of volatile mass at 1,000°C (1,832°F). Thus, the ratio between the mass of iron atoms and the total mass increases, resulting in an error in the determination of total Fe content.

Table 1. Accuracy and correlation coefficient of DB and CB calibration curves.

Statistic Parameters	Calibration Curve-DB	Calibration Curve-CB
Accuracy	1.65945	0.86237
Correlation Coefficient	0.99428	0.99841

3.3 Dry base and ignited base method accuracy test

In order to check the ignited base and dry base methods for accuracy or deviations, CRM reference standards were used and statistic treatments were carried out using 1:1 or X-Y graphs, Student’s paired t-test with Box-Plot graphs, and residue and chemical complementary graphs. Graph plotting and statistic treatments were conducted with Minitab software version 14.

Table 2 lists the results of the Student’s paired t-test, with significance of 5%, used for assessing the statistic differences between the results of dry base and ignited base for the element total Fe. The result for P-Value was over 5%, confirming that both data sets, reference values and ignited base values, are statistically equal or that there is no significant evidence for discarding the neutral hypothesis. In order to apply the Student’s paired t-test, the goodness of fit test (Kolmogorov-Smirnov) and the F test were conducted previously, for difference residues and achieved results, respectively, showing that the data are normally distributed and homoscedastic. Figures 3 and 4 show the histograms for differences and the Box-Plot. The red circle indicates the neutral hypothesis H_o (ignited base = reference value), or in other words, Difference = (0). The blue line indicates the mean value with the reliability interval of 95%. If the neutral hypothesis H_o is within the mean reliability interval, it is not possible to affirm that there is a statistic difference between the sets.

Table 2. Results of the Student's paired t-test.

Paired T-Test and CI: Total Fe – CRM value; Total Fe - CB

Paired T for Total Fe – CRM value – Total Fe – CB

	N	Mean	StDev	SE Mean
Total Fe - Value	35	62.2134	5.4307	0.9180
Total Fe - CB	35	62.1878	5.3651	0.9069
Difference	35	0.025657	0.253651	0.042875

95% CI for mean difference: (-0.061475; 0.112789)

T-Test of mean difference = 0 (vs not = 0): T-Value = 0.60 P-Value = 0.554

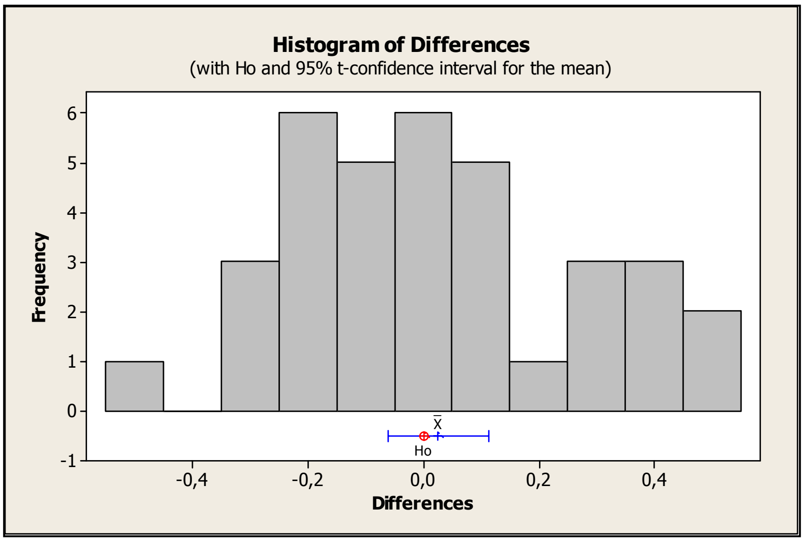

Figure 3. Histogram of differences between the certified reference value and the ignited base methodology.

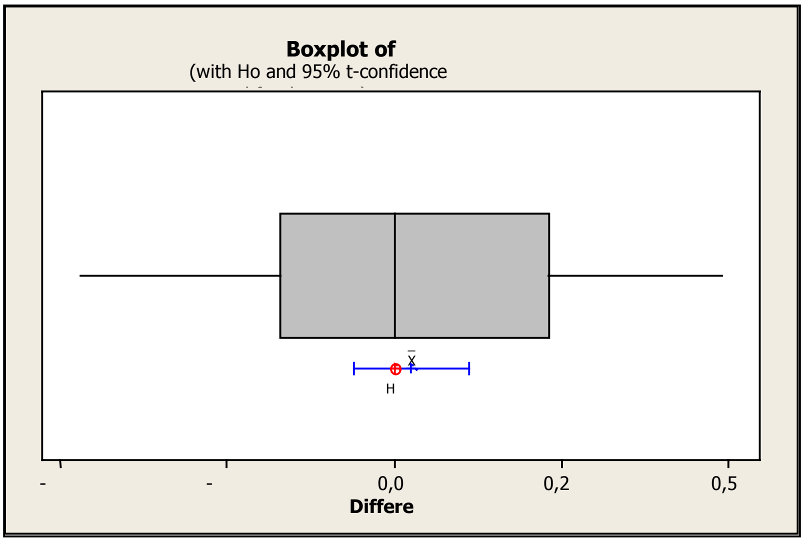

Figure 4. Box-Plot of differences between the certified reference value and the ignited base methodology.

Figure 5 shows the 1:1 graph plotting the results for the certified value and the ignited base method on the abscissa and ordinate axes, respectively, in ascending order of values. An 1:1 line with a 45-degree slope serves as a reference, representing the optimal situation i.e. certified results equal to ignited base. These graphs represent the data behavior, showing potential trends and outliers.

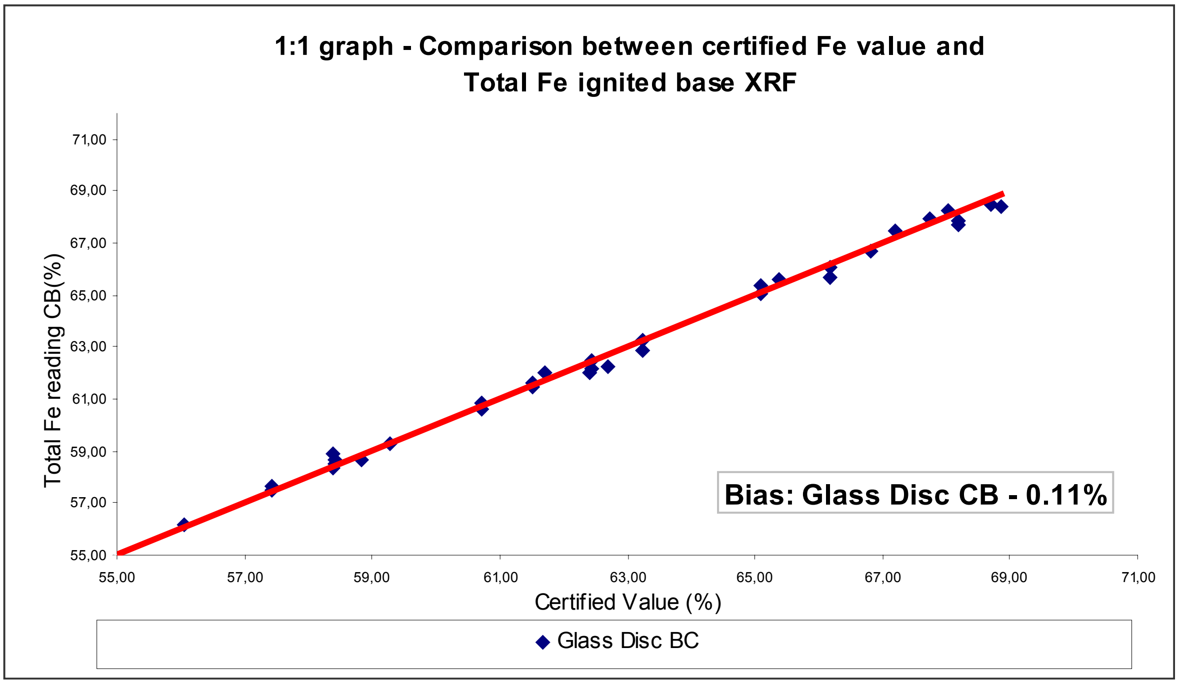

Figure 5. 1:1 graph – Comparison between certified Fe value and total Fe via ignited base XRF.

One may say that deviations (mean deviation from actual or exact value) are inherent to chemical analysis activities. These deviations may result from calibration details, measurement equipment building aspects, the analytical method itself, the analyst conducting the testing procedures, the reagent batch's quality or simply from factors out of the laboratory's control, which actuate in predefined periods. Thus, it is necessary to verify if the deviation is actually significant from a statistical (t-test) or relative (relative bias) point of view and as to trends (results consistently higher or lower). It is a consensus among some statisticians in the mining industry that a relative bias lower than 2% for iron ore samples represents an insignificant deviation. The graph in Figure 5 shows that the standard certified values and the results achieved with the ignited base methodology have an excellent closeness, because the relative bias of 0.11% is very low.
The relative bias is calculated according to Equation 5:

$$Viés = \frac{\left| \sum \left(Certificado_i - FRX\_BC \right) \right| \times 100\%}{\sum \left(Certificado_i \right)} \qquad 5$$

- Certified$_i$ – Reference value for standard i;
- XRF_BC – Result of total Fe achieved using ignited base XRF for standard i;
- i – sample sequential identification

In this way, using the statistical testing, it was observed that the fused glass disc XRF methodology for the element total Fe, using ignited samples, has no significant deviations and can be applied as an analytical technique, depending on the required accuracy. Item 3.5 of this study evaluates the analytical βm precision of this technique.

3.4 Test with Geological Research Samples Using Ignited Base XRF

In order to analyze the behavior of the fused glass disc XRF methodology with previously ignited samples, a test using long-term geological research routine samples was conducted. The total Fe contents of 105 samples with total Fe concentrations from 20% to 68% and LOI from 0.2% to 8% were determined, using dry base and ignited base fused glass disc XRF techniques. The samples were also analyzed based on the reference method in compliance with standard *ISO 9507:1990 - Iron ores - Determination of total iron content - Titanium (III) chloride reduction method*, in order to make it possible to assess the accuracy of the methods in relation to a primary reference. Figures 6 and 7 show the 1:1 and residue graphs, respectively, comparing the total Fe by wet analysis to the total Fe by dry base and ignited base fused glass disc XRF. It is shown that the relative bias of the ignited base method, 0.11%, is much lower than that of the dry base, 1.12%. Therefore, the mathematical mass correction significantly improved the method's accuracy. The graphs in Figures 6 and 7 also show that the results achieved by dry base XRF have an upward systematic error. This is, as explained above, due to the concentration of iron atoms after mass loss in the sample during fusion. It is possible that, for samples characterized by a very low LOI, less than 0.20%, the dry base and ignited base XRF methods have the same behavior, because the mass loss phenomenon during fusion is minimized. The residue graph in Figure 7 shows that the dry base XRF methodology has additive and multiplicative errors. This is due to the fact that the calibration curve is not a good reference for comparison, because mass loss took place during the preparation of the standards, increasing the concentration of total Fe content in the sample. Therefore, the curve's uncertainty has its share in the deviation detected. Analyzing Equation 4, one can affirm that, in the dry base methodology, part of the error (deviation) is directly proportional to the LOI and the sample's total Fe content. It can be noted in the graphs of Figures 6 and 7. As to the ignited base methodology, it was noted that the deviation is insignificant.

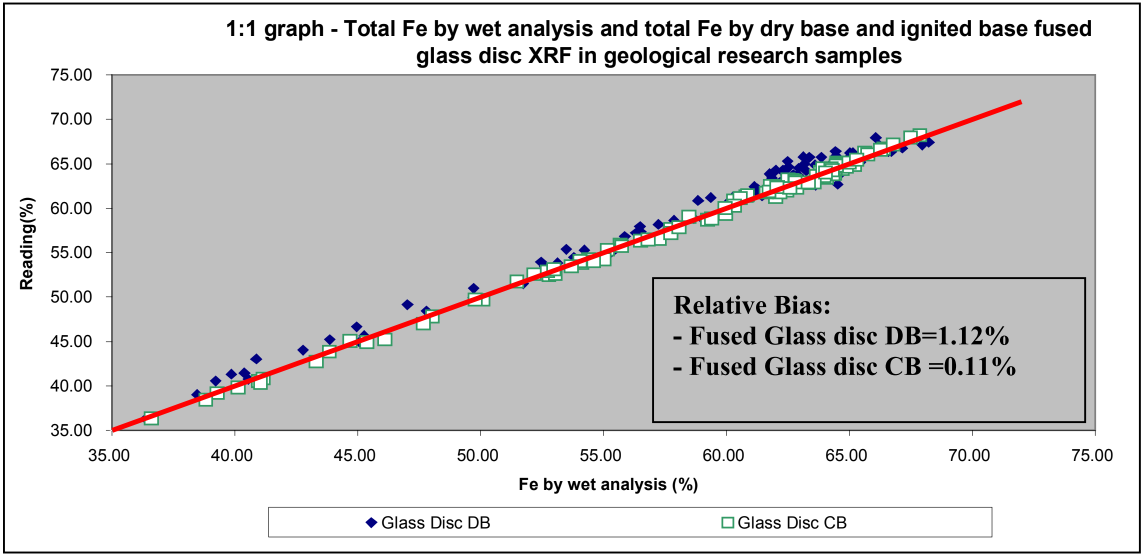

Figure 6. – 1:1 graph – Comparison between total Fe by wet analysis and total Fe by ignited base and dry base XRF (glass disc) in geological research samples.

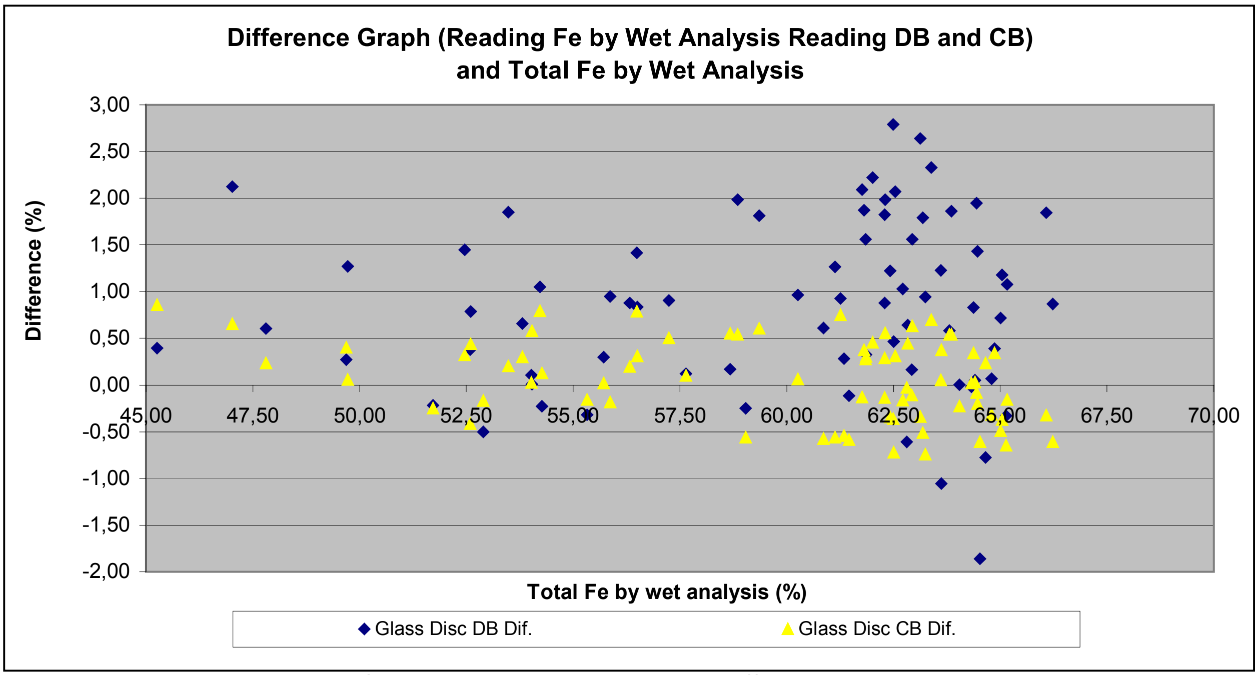

Figure 7. Residue graph – Comparison between reading differences in total Fe by wet analysis and total Fe by ignited base and dry base XRF (Glass Disc).

It is important to emphasize that systematic and random errors due to LOI determination testing are directly propagated to results from XRF with mathematical mass correction technique. In order to ensure that this technique has good accuracy and precision, the results from LOI testing must be reliable.

3.5 Evaluation of Ignited Base XRF Technique's Measurement βm Precision

Testing for determination of the measurement βm precision (error relative to result repeatability) was conducted in compliance with standard *ISO 3085:2002 - Iron ores - Experimental methods for checking the precision of sampling, sample preparation and measurement* for total Fe by wet analysis and total Fe by ignited base and dry base XRF (fusion) techniques, the values of which were 0.18%, 0.32%, and 3.05%, respectively. The XRF with mathematical mass correction improved the βm precision for total Fe by ignited base fused glass disc XRF. Nevertheless, it still is approximately 2 times the precision of total Fe testing by wet analysis (primary reference method). This difference between the methods' precision values is due to the lack of control over testing conditions, which results in problems such as humidity reabsorption after sample ignition, improper sample ignition, and errors in LOI determination, among other faults.

3.6 XRF with Mathematical Mass Correction in Dry Base Samples

This item discusses a third alternative for determining the total Fe by XRF with mathematical mass correction in fused glass discs prepared with dry base samples, assuming that the mass loss or gain phenomenon taking place during the sample LOI testing is reproduced during the fusion at approximately 1,300°C (2,372°F) on the glass disc machine, which is similar to that occurring when samples are exposed in a muffle furnace during 1 hour.

This is possible because the principle of the fused glass disc XRF technique with mass correction involves the plotting of a calibration curve with all standards set to the same LOI condition equal to zero. Since the measurement reference is fixed, it is possible to determine the total iron content, preparing a fused glass disc with dry base sample and correcting the total Fe content read on the X-ray equipment as a function of LOI. It must be emphasized that it is assumed that all volatile material of the sample is lost during fusion at approximately 1,300°C (2,372°F) on the glass disc machine.

All fused glass discs were prepared with a fixed mass of 8.4000 $\pm$ 0.0002 g of flux and 0.7000 $\pm$ 0.0002 g of dry base sample, without ignition, and their data were read in the ignited glass disc curve. The read results were corrected according to Equation 6. However, since the mass loss of the sample on the glass disc fusion machine has a high variability, the method's βm precision is of 0.50%, as shown in Figure 8, which is approximately 2 times the βm precision for samples ignited in a muffle furnace. It occurs due to the temperature variation of the flame from the fusion machine's nozzles and the short sample exposition time, about 10 minutes. Nevertheless, it is an excellent methodology option to be studied and developed, because it reduces the response time of the chemical analysis and makes the technique simpler to be applied as a routine procedure, dispensing with the need for previously ignited the routine sample to prepare the fused glass disc.

3.6.1 Equation of mathematical mass correction in dry base samples

Let us assume a fused glass disc prepared with an iron ore sample with dry base total mass m_{total}, flux mass m_F, and mass loss LOI.

Equation 5 provides the mathematical correction factor for the difference between the result provided by the equipment (variable base - VB) and the actual dry base value. The variable base is the value read from the X-ray of the fused glass disc prepared with dry base sample in the calibration curve with ignited base standards. In order to determine the actual value, it is necessary to transform the variable base value into the dry base value, which is the actual value of total Fe content in an iron ore sample.

$$TeorX_{BS} = TeorX_{BV} \frac{((m_{Total} + m_F)100 - m_F PPC)}{((m_{Total} + m_F)100 - (m_{Total} + m_F)PPC)} \qquad 5$$

Since the glass disc preparation used a dry base sample mass m_{total}=0.7000 g and a flux mass m_F=8.4000 g, Equation 5 can be written as Equation 6.

$$TeorX_{BS} = TeorX_{BV} \frac{(910 - 0.7PPC)}{(910 - 9.1PPC)} \qquad 6$$

Figure 8 shows the graph for the correlation between the reference total Fe value by the wet analysis primary method and the total Fe by fused glass disc XRF with correction, according to Equation 6, in dry base samples read in the ignited base calibration curve.

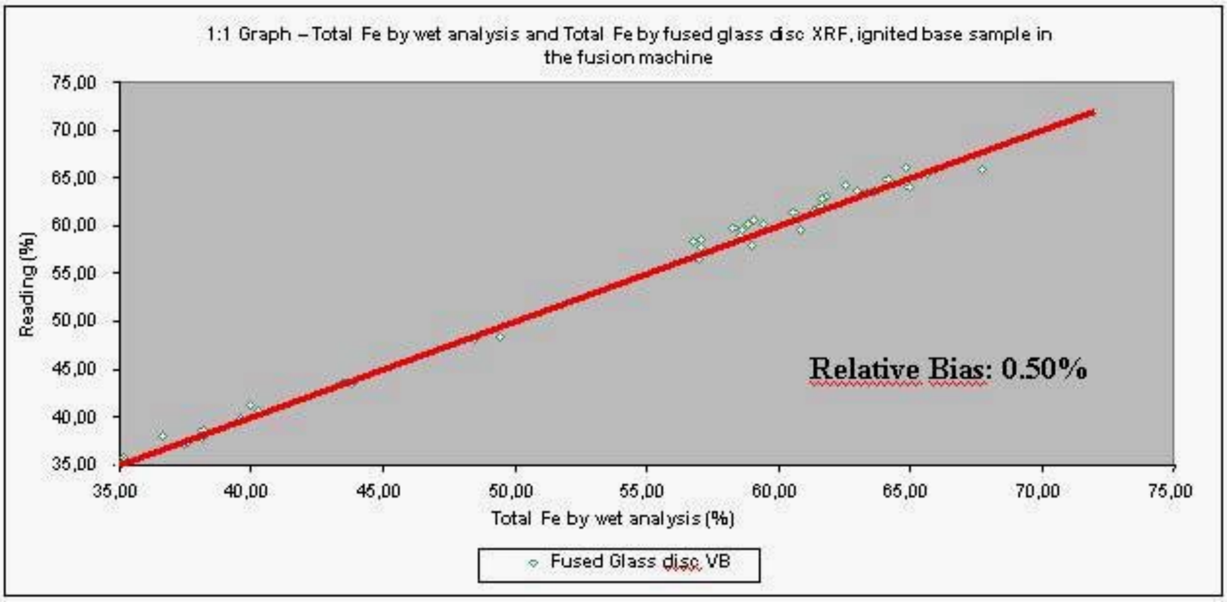

Figure 8. 1:1 graph – Comparison between total Fe by wet analysis and total Fe by ignited base XRF (fusion) on the fusion machine for geological research samples

3.8 Comparison Between Methodologies

Table 3 lists a summary of precision and bias values achieved by each methodology using fused glass disc XRF. The highest precision is achieved by the wet analysis primary method with 0.11% in accordance with standard *ISO 9507:1990 - Iron ores - Determination of total iron content - Titanium (III) chloride reduction method*. Nevertheless, the improvement in precision and accuracy is obvious when ignited base samples are used, showing that it is possible to use this technique for determining the total Fe content in the sample, provided that the required precision and accuracy are not so demanding.

Table 3. Comparison between the βm precision and bias values of the various methodologies

Methodology	βm Precision Total Fe (%)	Bias Total Fe (%)
XRF – Dry Base	3.05	1.12
XRF – Ignited Base	0.32	0.11
XRF – Variable Base	0.48	0.50
Wet Analysis	0.11	-

3.9 Environment Protection and Safety

In general, at iron ore laboratories, some testing procedures for geological research samples are conducted using the wet analysis technique, for example, the total Fe testing by wet analysis. Therefore, thanks to the improvement in the analytical quality of the total Fe determination by fused glass disc XRF, it will be possible to dispense with the need for carrying out numerous testing activities for total Fe by wet analysis. This represents a potential for minimizing by approximately 50% the treated effluent and sludge from the Effluent Treatment Stations at laboratories, without increasing the volume of fused glass disc waste. As to the environment, it is an enormous benefit, because it minimizes the impact of the treated effluent discharged into the water and reduces the volume of sludge deposited in the sterile matter piles at mines. In addition, when wet analysis and XRF are compared from an environmental perspective, the fused glass disc waste treatment is easier than the treatment of acid effluent from testing. Another important benefit to be mentioned is that concerning safety, because potential hazards are much greater in wet analysis testing than in XRF due to the handling of acid solutions, which can result in burns.

3.8 Cost Reduction

As aforementioned, the use of the new method for determining total Fe by XRF with mass correction reduces the number of testing activities for iron ore samples from geological researches. It represents a potential for reducing the high costs of labor, chemical reagents (total Fe by wet analysis), and caustic soda used in effluent treatment stations.

4 CONCLUSION

The method for analyzing total Fe by fused glass disc XRF with mass correction showed no significant statistical deviation (Student’s paired t-test) from the wet analysis primary reference method, the relative deviation of which is 0.11%.

It was confirmed that the mathematical mass correction used in the technique for determining the total Fe by fused glass disc XRF with ignited samples improved the accuracy and precision of the technique when compared to the testing conducted with dry base samples without mass correction, because the βm precision was improved from 3.05% to 0.32%.

Using the new methodology for determining the total Fe in iron ore has the potential for reducing costs of labor, chemical reagents, and caustic soda.

It was also confirmed that the determination of total Fe with mass correction in dry base samples is an excellent option to be developed, because good results were achieved for βm precision and relative bias. The advantages offered by this methodology are its ability to reduce the chemical analysis’ response time and its usefulness as a laboratory routine procedure, dispensing with the need for previously ignited the sample to prepare the fused glass disc.

It is also important to emphasize the benefits for the environment and safety offered by the new methodology, because it is possible to reduce by approximately 50% the treated effluent and the sludge from iron ore laboratories, without increasing the volume of fused glass disc waste, minimizing the impact of the treated effluent discharged into the water and the sludge deposited in the sterile matter piles at mines. In addition, when wet analysis and XRF are compared from an environmental perspective, the fused glass disc waste treatment is easier than the treatment of acid effluent from testing.

Another important benefit to be mentioned is that concerning safety, because potential hazards are much greater in wet analysis testing than in XRF due to the handling of acid solutions, which can result in burns.

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