

# IRON ORES CHARACTERIZATION – A STATISTICAL TOOL FOR ANALYTICAL METHODS COMPARISON AND VALIDATION

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## Abstract

An X-ray fluorescence (XRF) study comparing the performance of standardless analysis in relation to the traditional standard-based analysis technique is presented. The comparison using precision line regression analyses, and simultaneous confidence intervals provides reliable information about the precision and trueness that each method can achieve. This study enables to compare the results obtained with two different analytical approaches for iron ore samples, in terms of precision and accuracy of results, time in preparing samples and availability of standards. In this study, as a new technique for assessing the accuracy of an analytical method using linear regression, the results of both analyses are regressed against certified reference materials (CRM's). The statistical test is based on the joint confidence interval for the slope and the intercept of the regression line calculated taking into account the uncertainties in both axes or, in both analytical methods. The slope, intercept, and variances associated with the regression coefficients are calculated with bivariate least-squares regression (BLS) instead of the traditional ordinary least squares regression (OLS). After each calibration procedure, some chosen standard-samples are analysed for statistical validation of the methods. These samples have sufficient replicates to perform the calculations and later statistical comparison between the accuracy (precision and trueness) of each analytical method and evaluation of its precision line.

Keywords: mineral technology; iron ores characterisation; method validation and comparison.

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## **Introduction**

For an Ore Characterisation Laboratory, the validation of an analytical method provides a standardised, non-subjective means to ensure that the data quality objectives are met. It also assures management, staff and clients that an appropriate level of quality of the results is achieved. Above all, a validation procedure proves the applicability of a given method.

Firstly, the validation provides a standardised way to determine the statistical figures for an analytical method and thus can be used to compare methods. It becomes a vital overall component of the delivery of a quality product to a client. Consistent product quality increases client confidence in and satisfaction with a laboratory. Secondly, it convinces the laboratory staff that an appropriate level of expertise is achieved for any given method and that the method is working in an appropriate manner. Finally, it provides a consistent way to compare analytical methods in terms of their accuracy, limit of detection/quantification, sample preparation, standards availability and time-effectiveness, as well.

After the calibration procedure, the chosen standard-samples are analysed for the statistical validation of the analytical method. These samples must be sufficiently replicated, according to a previous plan of the experiment, to make the calculations and later statistical assessment of the accuracy of the analytical methods and the evaluation of their precision lines possible (Richardson and Morrison, 1995). This statistical assessment and comparison of the accuracy with other known analytical methods are performed using modern statistical models. The full statistical study performed in this study uses the models proposed in ISO 5725 parts 2 and 4 (1990), and the methods proposed by Riu and Rius (1996) and Deming, In Cornbleet and Gochman (1979). Nalimov (1963) proposed the comparison between precision lines also used.

Method validation in analytical chemistry is the last step in method development. Once a candidate method has been obtained one has to show that it meets the requirements of the user, namely to measure a specific substance with a given precision, accuracy, detection limit, etc. Method validation is carried out to ensure the quality and applicability of a method. It is therefore an essential part of any quality assurance program in a laboratory.

## **Background and Theory**

### *Standardless analysis*

Semiquantitative analysis, or standardless analysis, is based on mathematical methods also used to proceed matrix corrections. The present study method is based on the fundamental parameter method that uses physical parameters along with instrument parameters to calculate the instrumental sensitivity. It is a mathematical method of calibration, in which all the matrix-effects are accounted for, using physical theory only (Vrebos, 1987).

In a first step, the sensitivity of the spectrometer is determined, using some few standards. Any combination of standards is allowed: one can use the pure elements or oxides but also multi-element standards can be used. By measuring these standards of known concentration the instrumental sensitivity is assessed for each

element. After this calibration procedure these standards can be put aside since the instrument sensitivity relies only on the equipment and physical parameters and not on the samples. This independence of standards led to the use of the term "standardless analysis" and made it possible to carry on a calibration that somehow differs from the traditional quantitative, or "standard-based analysis" (Ratti and Rizzo, 1996).

This calibration allows the assessment of a rough initial concentration of any kind of material, no matter if it is not of the same mineralogy of the standard samples used in the calibration step. Afterwards, the software based on the fundamental parameters method improves these data, providing a semiquantitative result.

#### *Method validation*

Method validation is the process used to ensure that a particular analytical methodology using a specific combination of procedures will yield a particular analytical result that has been proven to be correct (Taylor, 1989). As such, a method validation is a form of certification ensuring that a specified method will produce precise and true analytical results for certain sample types during routine analytical conditions. Precision is a measure of how closely one measurement agrees with a replicate generated by repeated application of the same method under specified conditions. Trueness, meanwhile, is an absolute measurement of how closely a determined value approaches the known or certified value.

It can be undertaken in four ways. Acceptable results can be obtained by the analysis of synthetic formulations, analysis of spiked samples, and comparison of obtained results with those achieved by official or standard methods or by the analysis of certified reference materials (CRMs). The usefulness of any of these approaches depends on the sample types expected and the availability of methods or standards. Thus, any method validation must certify that the method in study can indeed generate data of sufficiently high quality (Richardson and Morrison, 1979).

#### **Accuracy Assessment of Analytical Methods**

Assessing accuracy is a fundamental step in the method validation process. The analyte concentration value obtained with a new method is often compared with the result of a reference method by replicating measurements and applying a statistical test to compare its variances. However, if the validity of a new method is checked with a range of analyte concentrations, the linear regression also gives additional statistical information. These are the presence of proportional errors, the need of including a blank correction for the constant error, and the calculation of a confidence interval for the regression coefficients (Montgomery and Peck, 1991).

A statistical test that compares the intercept and slope values obtained by linear calibration with the theoretical values of zero and unity, bearing in mind the correlation between the two regression coefficients, was firstly applied by Mandel and Linning, (1957) to analytical results. This procedure, extensively used up to now, is based on the linear regression hypotheses being fulfilled by ordinary least-squares or, whenever a correlation between the errors is present in the dependent variable, by weighed least-squares Draper and Smith, (1981) or Deming's method, as detailed in Hartman *et al*, (1997). The values obtained from the reference samples, over the

range of concentration chosen, which are analysed by the two methods, should give a straight line of approximately unity slope and zero intercept if the results are not statistically different at a given level of significance.

But when applied to method comparison, this procedure has the drawback that it regards the reference method as being free not only of systematic errors but of random ones, as well. Nevertheless, this reference method often includes random errors of the same order of magnitude as the new method to be validated. As a result, the literature is full of methods that are considered to be correct but which may contain systematic errors. Considering this, Riu and Rius, (1996) proposed a joint confidence test for the intercept and the slope to assess the accuracy of new analytical methods. These regression coefficients are calculated by applying calibration regression methods that consider errors in both axes and that, therefore, take into account the uncertainty in the results that both methods may have.

Furthermore, in view of the strong correlation between slope and intercept, any proposed value for the intercept restricts the choice of acceptable values for the slope and vice-versa. This fact is ignored in the usual method of examining slope and intercept separately. So, when assessing the accuracy of an analytical method using linear regression, it is advisable to plot a confidence region for the straight-line regression coefficients rather than individual confidence intervals. This region corresponds to an ellipse defined by the regression coefficients and which has its centre at the point (intercept, slope).

The joint confidence test consists of checking the presence of the theoretical point (0,1) within the limits of the joint confidence region spanned by the ellipse described above. The parameters of the regression line, which are the centre point or the ellipse are calculated using a regression method that takes into account that, in the validation of analytical methods, there are errors in both axes, represented by the method to be validated and the reference method available. Such errors should be taken into account by using Bivariate Least Squares (BLS), instead of Ordinary Least Squares (OLS) to achieve the regression line.

## **Experimental**

### *Methodology*

For each element analysed by X-ray fluorescence (XRF), two graphs are generated together with the precision line data. By means of these graphs the following steps perform the validation of each method:

Firstly some comments are drawn concerning the precision straight line that was built for each element measured though each method. The equation of this line together with its correlation factor is presented for each major element and some comments are carried on.

Secondly, the even figures show the linear regression of the results of the analyses, of chosen CRM's obtained by quantitative and semiquantitative XRF analyses against the certified values. The straight line is compared with the identity straight line, represented in dotted line. The squares or, sometimes rectangles, which are seen around each point, represent the precision of analysis. If the method tested had no error associated with its measurements, its straight line would lie exactly over the

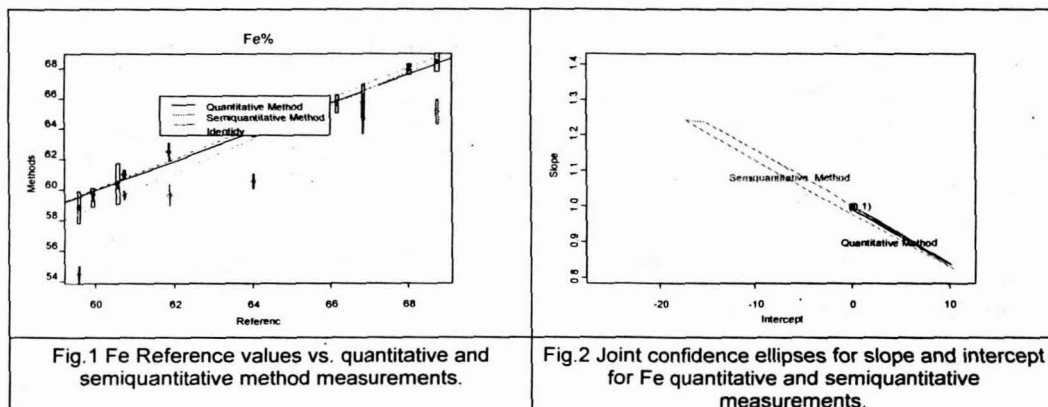
identity one. But this is an ideal situation and what is actually done is an analysis of the position of the straight line of the proposed method in relation to the identity straight line.

Finally, the odd figures show joint confidence regions for the slope and the intercept of the straight lines described above. The boundary of the ellipse is determined by the precision of the analytical method and by the degree of confidence, or the "confidence coefficient" with which one wishes to state that the theoretical point lay in the interior of the ellipse. In the present study it was chosen a degree of confidence of 95 %.

Although a fully study was carried out, it will be shown here only the validation discussion for Fe, SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>, contents of iron ores analysed by X-ray fluorescence spectrometry.

## Method validation discussion

### Iron



The precision straight lines obtained for iron analysis between 58 to 70% with 0,00183 correlation coefficient for quantitative method and with 0,0032 correlation for semiquantitative method are shown below:

$$\text{Conc (\%)} = 0,00139 + 0,0028 s_a$$

$$R^2 = 0,00183$$

$$\text{Conc (\%)} = 0,3196 + 0,008 * s_a$$

$$R^2 = 0,0032$$

Where Conc. is the concentration of Fe in %,  $s_a$  is the absolute standard deviation and  $R^2$  is the correlation factor.

In this special situation, where  $R^2$  tends to the 0,00 value or almost a straight line parallel to the abscissa axis, it is advisable to take the mean of the standard deviations to represent precision. So, the precision for iron quantitative and semiquantitative analysis into the concentration range performed is 0,1897 and 0,8160, respectively. The precision is higher in the quantitative rather than in semiquantitative method.

It can also be seen, through the squares and rectangles in Figure 1, that the precision of the reference method is better than the quantitative measurements which is better than semiquantitative measurements along the concentration range performed.

Considering a horizontal line of **slope=1** and another one of **intercept=0**, Figure 2 shows that there is such a region inside the ellipse for Fe analysis. It means that the method is statistically accurate for Fe for both quantitative and semiquantitative methods, although there are constant and proportional errors related to both sequences of measurements. The values of these errors are shown as individual confidence intervals for each one, either in the abscissa or the ordinate, which represents the intercept and the slope, respectively.

The 95% confidence interval for the constant error of the quantitative method of analysis is (-0,0094; 0,0128) and it's the expected value (centre of the interval) for is 0,0017% absolute. Considering no constant errors present (intercept=1 straight line), meanwhile, its proportional error lies between 0,03 and 0,37 % relative. The same intervals for semiquantitative method are (-1,5897 – 0,2381%) absolute for the constant errors and 0,29 and 0,25% relative for the proportional ones. It is also shown in Figure 2 that both methods are statistically accurate since their confidence ellipses both contain the theoretical point (0,1).

Finally, the iron analysis in iron ores is considered statistically accurate, although there is a stronger contribution of both constant and proportional errors for the accuracy of semiquantitative method. Consequently, its confidence ellipse stands graphically larger than the quantitative's one.

### Silicon

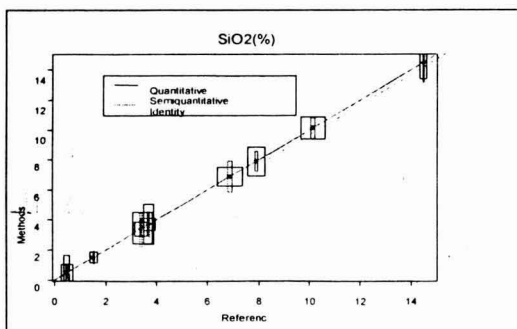


Fig.3 SiO<sub>2</sub> Reference values vs. quantitative and semiquantitative method measurements.

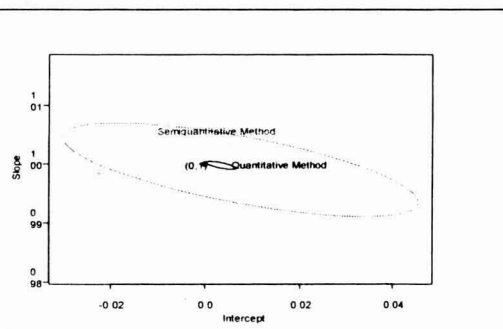


Fig.4 Joint confidence ellipses for slope and intercept for SiO<sub>2</sub> quantitative and semiquantitative

Two straight lines that represent the precision of silicon analysis between 0,4 to 15% were built for both the quantitative and semiquantitative measurements and are shown below.

Quantitative method:

$$\text{Conc (\%)} = 0,0452 + 0,0012 s_a$$

$$R^2 = 0,0573$$

Semiquantitative method:

$$\text{Conc (\%)} = 0,1972 + 0,0161 s_a$$

$$R^2 = 0,4198$$

Where Conc. is the concentration in % and  $s_a$  is the absolute standard deviation of the results.

Because its slope is almost null, the intercept is taken as the average value for the precision. It means that the precision for the silicon analysis is 0,1346 over the concentration range studied.

Taking into account only Figure 3, it can roughly figured out that both methods have a good accuracy for Si analysis, since their straight lines rely very closely on the identity one. Actually, their correlation coefficients between the reference and the measurements are 0,9999 for both. Therefore, Figure 4 provides more detailed information:

- On one hand, both methods can be considered statistically accurate since their joint confidence intervals contain the point (0,1). On the other hand, however, the tight dimension of the confidence interval for the quantitative method confirms its better precision (0,051). It is also advisable to pay closer attention to the dimensions of the constant and proportional errors through their 95% confidence intervals.
- The straight line of **slope = 1** (condition of no proportional error) intercepts the ellipses determining a confidence interval for the constant error of 0,0006 – 0,0047 % absolute for the quantitative method and of -0,0226 – 0,0316 % absolute for the semiquantitative one.
- Finally, the straight line of **intercept = 0** (condition of no constant error) touches the ellipses in only one point determining an expected value for the proportional error of 0,0003 % absolute, which means 0,03 % relative, for the quantitative method. The semiquantitative one meanwhile shows higher proportional errors that lie on the interval 0,9945 – 1,0058 % absolute, meaning 0,65% – 5,79%.

This all means that both methods are statistically accurate for silicon analysis in iron ores, although the semiquantitative one carries higher proportional and constant errors as it was expected. However, depending on the client's proposes this might not be a problem, taking into account how much easier the calibration and sample preparation are in the latter method of analysis.

## Aluminium

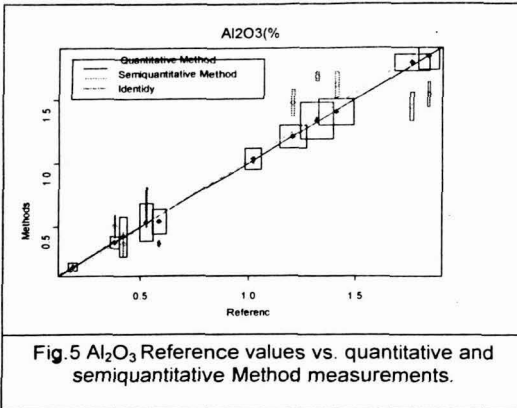


Fig.5 Al<sub>2</sub>O<sub>3</sub> Reference values vs. quantitative and semiquantitative Method measurements.

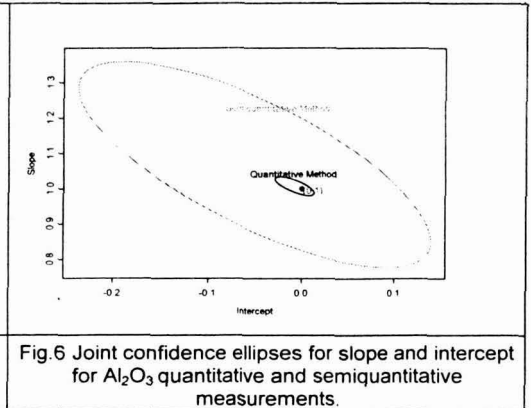


Fig.6 Joint confidence ellipses for slope and intercept for Al<sub>2</sub>O<sub>3</sub> quantitative and semiquantitative measurements.

The straight line of 0,00573 correlation coefficient represents the precision of Al quantitative analysis between 0,03 to 0,105%:

$$\text{Conc. (\%)} = 0,0452 + 0,0012 \cdot s_a$$

$$R^2 = 0,00573$$

Again due to its almost null slope, the intercept is taken as the average value for the precision. It means that the precision for aluminium quantitative analysis is 0,045 over the concentration range studied (0 – 1,7%). In this situation, the average of standard deviations can also be taken as the precision over the performed concentration range. So, the precision is 0,051 what is almost the same value of the intercept itself. This statement can also be checked out through the fairly constant dimensions of the squares around the points in Figure 5.

Since there is a strong correlation between the measured results and the certified results for the quantitative method, 0,9996 (Figure 5), and the theoretical true point (0,1) lies inside the confidence ellipse (Figure 6), the aluminium quantitative analysis is considered statistically accurate. Although this correlation is lower for the semiquantitative analysis, 0,9241 (Figure 5), the theoretical true point also lies inside its confidence ellipse (Figure 6). This all means that both methods are accurate for aluminium analysis, yet the semiquantitative one carries a worse precision compared to the quantitative one. The right choice between them will again be fully dependent on the client objectives.

The differences between the methods' precision can also be seen from Figure 6, where the 95% confidence interval for the constant error (taken the straight line of slope = 1 as a reference) is -0,0156 – 0,0102 % absolute for the quantitative method and -0,1356 – 0,1063 % absolute for the semiquantitative one. Taking another straight line of intercept = 0 as reference, Figure 5, it also shows that the proportional error lies in its confidence interval of 0,9842 – 1,0171 %, or 2,68 – 1,71 % relative for the quantitative and 0,8266 – 1,1996 % or 17,34 – 19,95% relative for the semiquantitative method.



It means that although both methods are statistically accurate for aluminium, there are proportional errors of 2,65% maximum relative related to the quantitative measurements and of 19,95% maximum relative associated to the semiquantitative ones. The constant and proportional errors together should be understood as the two main aspects of accuracy of an analytical method.

## Conclusions

Based on the statistical calibration and validation methodology presented for each method, a proposal for a broader analytical procedure for characterisation of mineral technology and similar samples can be made, using the potential benefits of each one. For an Ore Characterisation Laboratory, a method validation would provide a standardised, non-subjective means to ensure that the data quality objectives of the facility are met. It can also convince management, staff and clients that an appropriate level of expertise is achieved.

While the basic theory of joint confidence regions has been known for a number of years, its practical usefulness seems to have been largely overlooked. The present validation exercise is attempted to fill this gap and to present a practical use of the theoretical ideas and principles of this approach. It is hoped that this exposition will also throw some light on the analytical importance of statistical tools mainly concerning quality assurance of results.

From this validation exercise it is seen that both quantitative and semiquantitative methods serve different purposes, and are better suited for different applications since they are based on different principles of operation and calibration. A similar distinction holds for the standards: for quantitative methods they must be similar to the unknowns, and ought to be selected before the measurements. With semiquantitative methods, meanwhile, the database of all standards is searched for the best-suited ones. They can be quite different from the unknown and, furthermore, they are selected and settled only once.

Finally, it must be emphasised that semiquantitative and quantitative analyses can be complementary techniques in a chemical characterisation laboratory, designed to attend different demands as well as different analytical problems. In general, because of the easiness concerning calibration and samples preparation, semiquantitative analysis must be seen as automated qualitative analysis, followed by a highly qualified estimation of sample composition. Moreover, it can be applied to any kind of unknown sample that might appear in the laboratory. Quantitative analysis meanwhile is better suited for highly accurate analysis of routine well known samples.

Furthermore, there can be a more flexible use of the quantitative and semiquantitative analytical methods, separately or together, as tools for chemical characterisation of mineral samples, regarding the real needs of clients and the particularities of the samples. In other words, the clients can reach their specific objectives with the analysis reliability required and within the best cost-benefit laboratory relationship.

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