

DETECTION LIMIT AND ESTIMATE OF UNCERTAINTY OF ANALYTICAL XRF RESULTS*

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Some tools for estimating the uncertainty of XRF results are described. As introduction to the subject, the detection limit is treated even if this parameter and the uncertainty of a result describe different characteristics of an analytical method. The expression "detection limit" is probably one of the most widely misunderstood in XRF analysis. Not only is there a general lack of agreement about the order of magnitude of detection-limit data, but also the international convention for calculating such data is not always respected and the way of naming them is questionable. If a consensus exists on the meaning of this expression (the smallest amount of an analyte that can be detected in a specimen), the interpretation of data varies greatly. This paper attempts to suppress all this confusion. The basic philosophy behind the interpretation of the concept is reviewed and a new realistic and representative way to name it is proposed. The distinction between the limit of detection and the limit of determination is clearly established. General considerations for evaluating the uncertainty associated with the sample preparation are also discussed. Finally, a few comments on the way of reporting analytical results are presented.

1. Introduction

The basic requirement of quantitative X-ray fluorescence (XRF) analysis is first to prepare suitable specimens from the samples to be analyzed. Then, to measure the intensity I_p of the peak of the element to be determined (or analyte) since this intensity is related to the concentration by means of the calibration procedure [1]. However, this analyte peak intensity must be first corrected for dead time, which is normally done automatically by contemporary instruments. If necessary, particularly for trace element determination, it must also be corrected for background beneath the peak, any spectral overlap(s) and blank. Finally, if necessary, the net intensity must be multiplied by the term M_{is} to correct for matrix effects [2]. However, a description of this last step, and also calibration procedures, will be ignored in the present paper on the uncertainty associated with analytical XRF results, that having already been treated in other papers [1, 2]. We will consider, instead, how to estimate the uncertainty introduced in the analytical results during all these steps. .

In quantitative XRF analysis, the global (or overall) uncertainty of an analytical result depends

Certain instrument manufacturers are identified in this paper to specify adequately the source of experimental data. Such identification does not imply recommendation or endorsement by the author, nor does it imply that the instruments used are necessarily the best available for the purpose.

on the combination of errors introduced mainly by the sample preparation, the measurement of both peak and background intensities, the slope "m" of the calibration line and the corrections for matrix effects. All these errors can be grouped in two main categories. The first one is the random error, represented by the precision, which can arise, for example, from random fluctuations associated to the process of measurement of X-ray peak intensities.

These are called counting statistical errors [3] (CSE). The other category is the systematic error, represented by the accuracy, whereby a certain bias is present in the results, as could happen if a badly determined calibration curve is used. Precision can be considered as a measure of the repeatability [4,8] (replicate determinations made under conditions as nearly identical as possible) of a result, while accuracy is a measure of the closeness of the results with its true value. As an analogy, if we have a ruler with an incorrectly engraved scale, we could repeat with precision the measurement of the length of an object, but the results will be inaccurate. The combination of these two types of errors, precision and accuracy, enables us to estimate the global uncertainty of each concentration to be determined. In practice, precision can be improved by controlling the random errors introduced during sample preparation and by the analytical instrument within the range of stability of the generator and of the X-ray tube, to such an extent that the main source of random errors remaining is due to

counting statistical errors. Accuracy can also be improved to a large extent by controlling systematic errors introduced by sample preparation, the instrument itself and the calibration procedure. These errors can be reduced within certain limits by optimizing the use of the analytical instrument and by improving the reliability of the calibration procedure. As a result, only residual systematic errors due to the specimens themselves are then important, which are matrix effects (absorption and enhancement) and physical state effects (heterogeneity, surface, thickness, particle size, mineralogy). This paper deals mainly with the uncertainty introduced in a series of results by the random and systematic errors of all the mentioned sources. Some tools will be described hereafter for estimating this global uncertainty.

However, the first subject to be treated is the detection limit in spite of both parameters, uncertainty of a result and detection limit, describe different characteristics of an analytical method. This first preliminary step is necessary for evaluating the total performance of an analytical system. It is also important to talk about this parameter because the expression "detection limit" is probably one of the most widely misunderstood in XRF analysis. Not only is there a general lack of agreement about the order of magnitude of detection-limit data, but also the international convention for calculating such data is not always respected and the way of naming them is questionable. The detection limit is usually defined as the smallest amount of an analyte that can be detected in a specimen. However, it is often misinterpreted as the smallest concentration of an analyte that can be determined with reliability in a given sample. Furthermore, the detection limit calculations are based on background measurements, which are below any peak intensity used for a possible determination. This paper attempts to clarify all this confusion. The basic philosophy behind the calculations of the different limit types is reviewed and a new realistic and representative way to name them is proposed. It must be emphasized that the terminology used here is presented to prevent ambiguity, but does not have any international ratification. Potts [5] has already tried to do this, but without much success.

Three types of limits are considered: the instrumental limit of detection, the limit of determination of a method and the theoretical or experimental analytical precision. General considerations

for evaluating the uncertainty associated with the sample preparation will also be discussed. Finally, few comments on the way for reporting analytical results are presented. The analysts must absolutely employ an explicit way of reporting results and assessing the capabilities and limits of the analytical method.

The present paper is not a proposal for a new terminology or new mathematical definitions for calculating detection limits applicable to all analytical techniques, but rather to show how the complex jargon of statisticians, often disconnected from the physical reality, should be adapted to the field of XRF analysis. We are more interested to supply to the XRF analyst the necessary tools for evaluating the quality of her/his results rather than getting international recognition. For a more general and thorough discussion on the subject, you may refer to the paper by the International Union of Pure and Applied Chemistry (IUPAC) [6]. This paper also contains other interesting references, which are not repeated here.

2. Sensitivity of an Instrument

An important tool needed for the determination of the three limit types is the sensitivity of an instrument for a given analyte in a given specimen. It is defined as being the net intensity obtained per unit of concentration. For calculating it, the peak intensities of the analyte have to be measured on certified reference materials (erroneously known in popular language as standards) of composition similar to that of the unknown samples to be analyzed. To calculate the sensitivity, the measured intensities must not be corrected for matrix effects and one must assume a linear relation between intensity and concentration. The sensitivity for each analyte *i* is calculated from the slope *m_i* of the calibration line as follows. The general form of the equation for a straight line is

$$Y = mX + b \quad (1)$$

If the calibration line is a plot of the peak intensity *I_p* of an analyte *i* as a function of the concentration *C_i*, the equation (1) becomes

$$I_p = m_i C_i + I_b$$

where the true background intensity *I_b* is given by the intercept of the calibration line on the Yaxis. The slope *m_i* is then given by

$$m_i = \frac{I_p - I_b}{C_i} \quad (2)$$

where C_i is the concentration of the analyte i in % or ppm. It is the slope of the calibration line that enables to convert measured net intensities into concentrations.

3. Instrumental Limit of Detection

An important statistical consideration in XRF analysis is the capability of an instrument to merely detect whether an element is present or not in a specimen. In fact, one wants only to be able to claim with some defined statistical certainty that a given element is present if its concentration is greater than a certain limit. This limit is the limit of detection. This last limit is much smaller than, even under the best analytical conditions, the limit of determination that is the smallest concentration that can be determined (or quantified) with reliability in a sample (more on this subject in Section 5).

When an XRF analyst develops a new analytical program, she or he must calculate the smallest concentration of the analytes that can be detected in a specimen to check if the instrument is sensitive enough to detect all the concentration range of the elements to be determined. The most current detection limit used in XRF analysis is the lower limit of detection, which is assumed to be the concentration equivalent to three standard counting errors [3] (σ_b) of a set of measurements of the background intensity [7]. It will be shown that this limit IS an over-optimistic estimate of true limits of detection met in practice mainly favored by instrument manufacturers and that should be abandoned [5].

The expression "Lower Limit of Detection" (LLD) is often used in X-ray literature to represent the smallest amount of an element in a given specimen that can be detected by an instrument in a specific statistical context for a given matrix. It is unfortunate that many analysts use this limit in practice for the three following reasons.

Firstly, there is no such thing in real life like the LOWER limit of detection or HIGHER limit of detection or any other unrealistic term to qualify the expression "Limit of Detection". For example, when a car, a plane, a helicopter, a train, etc., reaches its maximum speed limit, it cannot travel any faster. A limit is a limit. The association of the word "lower" with the expression "limit of detection" is redundant, a non sequitur! It is like saying lithe lowest low limit". Their combination is irrelevant and meaningless. In practical situations,

the LLD expression makes no sense.

Secondly, the LLD is defined as being the lowest net peak intensity of an analyte, expressed in concentration unit, that can be detected by an instrument in a given analytical context with a 95% confidence level. This minimum intensity is assumed to be equivalent, for a 95% confidence level, to two standard counting errors (σ_b) of a set of measurements of the background intensity (I_b) under the analyte peak [7], i.e., in terms of intensity, assuming no error in the time of the background measurement (T_b):

$$2\sigma_b \Rightarrow 2 \cdot \sqrt{\frac{I_b}{T_b}}$$

and in terms of concentration:

$$2\sigma_b \Rightarrow \frac{2}{m_i} \cdot \sqrt{\frac{I_b}{T_b}}$$

where m_i is the slope of the calibration line or the sensitivity of the spectrometer in cps/% for an analyte i . When two measurements are required, as with XRF analysis where it is frequent to have to measure peak and background intensities, the error is increased by a factor $\sqrt{2}$, so the lower limit of detection is equal to

$$LLD = \frac{2 \times \sqrt{2}}{m_i} \cdot \sqrt{\frac{I_b}{T_b}} \approx \frac{3}{m_i} \cdot \sqrt{\frac{I_b}{T_b}} \quad (3)$$

or replacing m_i by the equation (2), it comes:

$$LLD = \frac{3 \times C_i}{I_p - I_b} \cdot \sqrt{\frac{I_b}{T_b}} \quad (4)$$

Thus, the current LLD used by manufacturers is equal to **three** times the standard counting error of the background intensity. The "fictitious numbers" calculated by the expression (3) or (4) are not representative of the limits of detection met in practice. It is important to emphasize that the LLD is not representative of **true** experimental results but only of a **minimum theoretical estimation**. Quantitative analysis is not possible at the LLD level for the following reasons. Because the number of real measurements is always limited to a finite number, the uncertainty in the mean background intensity, measured on a blank specimen, is assumed negligible and the experimental standard deviation S_b is estimated by the theoretical standard counting error σ_b . Now, σ_b is calculated from measurements that are assumed to respect to the letter statistical rules.

In practical situations it is unrealistic to assume that such measurements will exactly follow a Gaussian (or normal) distribution [3]. Also, a detection limit calculated with a 95% confidence level ($2\sigma_b$) is not usually considered to afford sufficient security of confidence for analytical measurements. Finally, the background counting time (T_b) is often replaced by the total time (n to measure the peak and background (where $T=T_p+T_b$ and $T_p=T_b=T/2$) and the value used in this case by most instrument manufacturers is 100 s. The only reason for doing that is obviously to reduce still more the LLD value, which decreases when the counting time increases. All these "artifices" have only as objective to make fictitious numbers look better, not to better represent the reality.

Thirdly, the meaning of the lower limit of detection is most of the time completely misunderstood. A limit of detection is **not** a limit of determination. The expressions "limit of detection", which is based on background measurements and "limit of determination", which is based on the measurement of any peak intensity above the background are often misused and frequently interchanged, which is a big mistake. In other words, the smallest concentration of an analyte in a given sample that can be determined by an instrument cannot be estimated from the measurement of only the background intensity. It takes at least the measurement of a characteristic line to be able to determine the value of this concentration.

We suggest replacing the artificial expression LLD by another more realistic one with a different name, a different definition and calculated by a different mathematical expression in order to make it more representative of the reality. We suggest using the expression Instrumental Limit of Detection (ILD), which is defined as being the minimum **net** peak intensity of an analyte, expressed in concentration unit, that can be detected by an instrument in a given analytical context with a 99.95% confidence level. The ILD depends on the instrument, the specimen matrix composition and the analyte. But the reading by different instruments of the same element peak in the same specimen, and in the same experimental conditions, will give different ILD values. It does not depend on the mathematical method used to calculate concentration values. For a given analyte in a given specimen, the ILD depends only on the instrument. That is why we suggest calling it the **instrumental** de-

tection limit.

The limit of detection is related to the capability of the instrument to distinguish a peak intensity (I_p) from the fluctuations of the background intensity (I_b) due to counting statistics, or the background noise. The question then arises: «What is the lowest peak intensity of an analyte that can be measured to be recognized as **distinct** from the background noise?» If a large number of measurements of a background intensity I_b is made, all measurements are subject to counting statistical errors and fluctuate around a mean value \bar{I}_b . Thus, many repeated measurements of a background intensity will result in a distribution of data that approximates to a Gaussian (or normal) distribution characterized by a mean value \bar{I}_b and a standard counting error [3, 5] σ_b . Thus, the standard counting error σ_b represents the fluctuations of I_b due to counting statistics, or the background noise.

Furthermore, the XRF analyst must select the confidence level to associate with any assertion that the analyte is present in the specimen. For example, a 95% confidence level means that, for a large number of observations, 95% of the observations indicate the presence of the analyte, whereas 5% of these observations reflect only random fluctuations in background intensity. However, ninety-five percent is an insufficient confidence level to be sure that any measured intensity is distinct from the background noise. That is why the value recommended by IUPAC [6] is 99.95%.

In practical analytical situations, a characteristic line intensity I_p decreases with decreasing concentration of the analyte and finally disappears in the background noise in the case of a blank sample (see the position 0 of Fig. 1). To be significantly different from the background, the peak intensity I_p must not only be larger than \bar{I}_b , but also be statistically distinguishable from the background noise. Based on Gaussian distribution statistics [3], the probability that the analyte to be present is 99.95% if the peak intensity I_p is larger than $(\bar{I}_b + 3.29\sigma_b)$ [6]. In this case, the probability that a background measurement may exceed $(\bar{I}_b + 3.29\sigma_b)$ is only 0.05%.

Any peak intensity will be detected with a confidence level of 99.95% when higher than $(\bar{I}_b + 3.29\sigma_b)$ and will not be detected, for the same

level of confidence, when smaller than ($\bar{I}_b + 3.29\sigma_b$). The decision "detected" or "not detected" is thus established by comparison to a threshold, or a limit of detection, which is the combination of the mean background intensity and the background noise. The ILD represents then a threshold above which a peak intensity can be distinguished from the background noise at a specified level of confidence. Under this threshold the peak intensity is assumed to be indistinguishable from the background noise.

In XRF analysis, any concentration is calculated from the net peak intensity (I_{net} , which is equal to the difference between the measured peak intensity (I_p) and the background intensity (I_b). However, there is a standard counting error (σ_p) attached to any measurement of the peak intensity. Likewise, any measurement of the background intensity is also accompanied by a standard counting error (σ_b). Therefore, the XRF analyst is confronted with the problem of distinguishing the true net peak intensities from the random fluctuations in peak and background intensities. To calculate the limit of detection in terms of net intensities, first, let us remind ourselves that the variance [3] of the sum of (or the difference between) two values taken from statistically independent distributions is equal to the sum of the variances of the two distributions. Thus, for net intensities,

$$s_{net}^2 = s_p^2 + s_b^2$$

where σ_{net} is the standard counting error of the net intensity for the peak of interest.

We can ask, «What must be the minimum value of the net peak intensity to be sure (or 99.95% sure) that we are not merely measuring the statistical fluctuations of the background intensity?» The answer is that the net intensity must exceed 3.29 times the standard counting error of the net intensity, otherwise, there is at least 0.05% of chance that the measured net intensity arises merely from statistical fluctuations in peak and background intensities. This requires that

$$I_{net} = 3.29\sigma_{net}$$

The combination of the two last equations gives:

$$I_{net} \geq 3.29\sqrt{s_b^2 + s_p^2}$$

or, assuming that the measured intensities are close to their respective means and that, for very small net peak intensities, $I_b \gg I_{net}$, or $I_p \sim I_b$, or $\sigma_p \sim \sigma_b$,

$$I_{net} \geq 3.29\sqrt{2s_b^2} = 3.29\sqrt{2}s_b \cong 4.65s_b$$

The ILD is the concentration corresponding to I_{net} , i.e.,

$$ILD = \frac{4.65}{m_i} \sqrt{\frac{I_b}{T_b}} \quad (5)$$

This approach yields minimum detection limits in terms of concentration that can be observed under the best analytical conditions. Conveniently, we have a 99.95% confidence level to distinguish a net intensity from the background noise if this net intensity is larger than a "fluctuation" of $4.65\sigma_b$ above the mean background intensity. It is still a **minimum theoretical estimation** but the chances are better (as compared to the LLD) to detect it in practice.

The instrumental limit of detection is only useful to the analyst for estimating the lowest net intensity, expressed in concentration unit, that can be **detected** by an instrument. This value is not equal to and is in fact much lower than the smallest concentration of the analyte that can be actually **determined** by the instrument. It is important to emphasize that fact. In practice, this limit is used only for checking if the instrument is sensitive enough to detect all the concentration range of the elements to be determined in a particular sample type. This limit can also be used for comparing the performance of different instruments used in the same analytical context. It must **never** be given to the customer submitting samples for analysis who may confuse it with the smallest concentration of the analyte that can actually be determined.

The real physical meaning of the instrumental limit of detection is shown by Fig. 1. Suppose that a series of samples containing a trace element at different concentration values is prepared where the concentration decreases, from sample to sample, from a given value to zero. The intensities of a line are measured and decrease with the decreasing concentrations of this element from the position 18 to the position 0, which represents a sample that does not contain any concentration of the element. At this last position, no peak is measured, but only the background, because the element is absent from the sample. We have reached the point at which a peak intensity is indistinguishable from the background noise. At this position, we are far below the "limit" (or the threshold) of detection, which is located at $4.65\sigma_b$ above the mean back-

ground intensity with a confidence level of 99.95%.

The statistical meaning of the instrumental limit of detection is as follows. Let us suppose that the peak and background intensities of an analytical line are measured and the calculated value of the ILD gives for example 3 ppm. If these measurements are repeated in exactly the same analytical context, one can assume with a 99.95% confidence level that the new ILD value will be in an interval of $\pm 4.65\sigma_b$, in equivalent concentration unit, of the first calculated value. The author confesses that he cannot do the calculation here of σ_b but he knows enough to say that the $4.65\sigma_b$ value will be more than 3 ppm. Let us say to be conservative that it is equal to 3 ppm. The new ILD value will be therefore between 0 and 6 ppm. The ILD value means nothing else statistically. Any other interpretation of this limit would be wrong and disconnected from reality. For example, saying that the limit of determination is equal to 6 times the standard deviation of the background measurements is completely arbitrary and unfounded.

Note that the instrumental limit of detection defined by the equation (5) is associated to a 99.95% confidence level (or $4.65\sigma_b$) and that the total measurement time T is equal to $2T_b$. This follows from the following equation [8]:

$$\frac{T_p}{T_b} = \sqrt{\frac{I_p}{I_b}} \quad (6)$$

which allows to calculate the optimal split of

counting time on peak (T_p) and background (T_b). Since at the detection limit, $I_p \sim I_b$, thus $T_p \sim T_b \sim T/2$. Thus T_b in equation (5) is one half of the available total counting time. Equation (5) can then be written as follows:

$$ILD = \frac{4.65}{m_i} \cdot \sqrt{\frac{I_b}{T/2}} = \frac{4.65 \times \sqrt{2} \times C_i}{I_p - I_b} \cdot \sqrt{\frac{I_b}{T}} \quad (7)$$

$$\approx \frac{6.58 \times C_i}{I_p - I_b} \cdot \sqrt{\frac{I_b}{T}}$$

By selecting the **optimal** counting time split on peak and background, the relative counting error [8] on the net intensity is calculated by

$$(e\%)_{net} = \frac{100}{\sqrt{T}} \cdot \frac{1}{\sqrt{I_p} - \sqrt{I_b}} \quad (8)$$

A consequence of the equation (8) is that, as the peak intensity (I_p) approaches the background intensity (I_b), the net relative counting error becomes **infinite**. Now, this is precisely what happens at or near the detection limit: I_p is getting close to I_b . Consequently, reliable measurements close to the detection limit level become "an impossible dream..." as so well said by the famous song of Jacques Brel.

Note also from equation (7) that, for a fixed counting time, the ILD will be smallest when the expression

$$\frac{I_p - I_b}{\sqrt{I_b}} \quad (9)$$

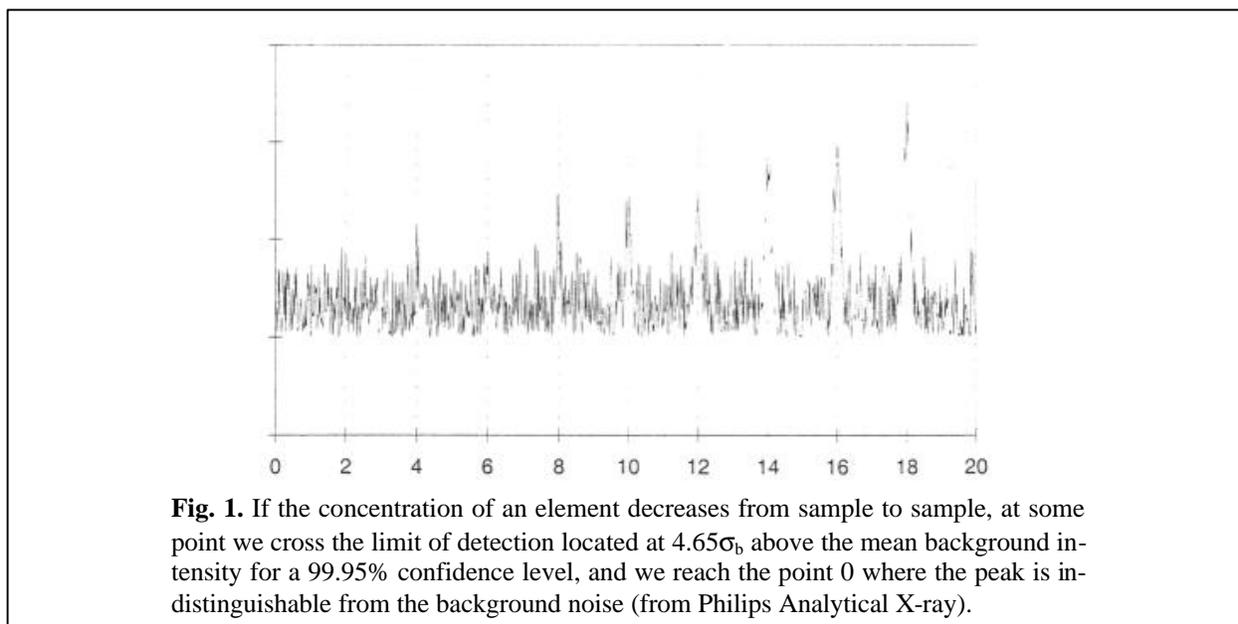


Fig. 1. If the concentration of an element decreases from sample to sample, at some point we cross the limit of detection located at $4.65\sigma_b$ above the mean background intensity for a 99.95% confidence level, and we reach the point 0 where the peak is indistinguishable from the background noise (from Philips Analytical X-ray).

is as large as possible, For this reason, Spielberg and Bradenstein [9] proposed the equation (9) as the definition of Figure of Merit (FOM), which is mainly used to optimize excitation conditions for trace element determination.

As a numerical example, if a given element at a concentration of 0.2%, gives a peak intensity of 330 cps and a background of 30 cps, for a total counting time of 120s, the ILD is:

$$ILD = \frac{4.65 \times 0.2\%}{330 - 30} \cdot \sqrt{\frac{30}{60}} = 0.0022\% = 22 \text{ ppm}$$

An ILD of 22 ppm does not follow, however, that one could in practice determine 22 ppm of the element. This value is just a theoretical estimation of the lowest net intensity, translated in concentration unit, that the instrument can detect with a statistical certainty. Furthermore, as it has already been pointed out, at or near the detection limit the error becomes infinite. For these reasons, the theoretical limit of detection is a somewhat arbitrary or artificial concept and "meaningless" from an analytical viewpoint. A limit more useful in practice is the one defined by the *limit of determination* of a method (LDM). This last concept will be explained in Section 5.

It is unfortunate that among beginner users the following popular belief is largely held:

$$\text{uncertainty} = \text{analytical result} \pm \text{ILD}$$

i.e., that the uncertainty of a reported analytical result (% or ppm) is within the ILD limits in 99.95% of the cases. This belief is misleading and in no case it can be true.

From equation (5), it can be deduced that the limit of detection decreases as the background intensity decreases, as the slope of the calibration line increases and through longer counting times.

Table 1. Instrumental detection limits for low atomic number elements. The ILD is calculated for the 99.95% confidence limit with 100 s as total counting time. Data taken from Ref. [10].

Element	Matrix	m_i (cps/%)	I_b (cps)	ILD (ppm)
Na	Al ₂ O ₃	108	42	395
Mg	Limestone	646	60	79
Mg	Al	1360	470	105
Si	Steel	2300	105	29
Si	Limestone	2950	90	21
P	Oil	24000	450	6
P	Nylon	10000	13	2.4
S	Oil	63000	170	1.4

The ILD also varies with the specimen matrix composition. In general, for a given analytical context, and for a given concentration of a given analyte, the ILD will be smaller when the matrix composition becomes lighter. One observes this phenomenon simply because the degree of absorption decreases with light matrices and, therefore, the measured intensity is higher from samples with light matrices. As an example, Table 1 lists a few ILD data for some low atomic number (Z) elements. It can be seen that the ILD varies not only with Z of the analyte but also with the specimen matrix composition. Taking Mg as an example, as the background intensity for Mg in Al metal is 7.8 times greater than that in limestone, the ILD is only marginally higher by a factor of 1.3. Also for P in oil and nylon, an increase in background intensity by a factor of 35 results in an increase in ILD by a factor of only 2.5.

The ILD also varies with the atomic number (Z) of the analyte and the slope of the calibration line. ILD values may change with different X-ray tube anodes, mainly because the sensitivity factor will be affected by how efficiently the characteristic lines of the tube excite the element(s) of interest, but the final conclusion will stay the same: the ILD varies with the Z of the analyte. For illustrating it, let us take a given X-ray tube anode and divide the periodic table in three wavelength regions. The short wavelength region (0.3-0.8 Å), i.e., for Zr (40) to Ba (56), is characterized by a moderate slope value, high background and excitation conditions far from optimum, which lead to moderate ILD values. The medium wavelength region (0.8-3 Å), i.e., for Ca (20) to Zr (40) for K lines and for Ba (56) to U (92) for L lines, is characterized by a high slope value, low background and optimum excitation conditions, which lead to the best ILD values. The long wavelength region (3-12 Å), i.e., for Na (11) to Ca (20), is characterized by a small slope value, low background and the poorer excitation conditions, which lead to the poorest ILD values [10].

Thus the ILD varies with the matrix composition of the specimen and with the atomic number of the element to be determined. It means that the ILD determined from a specimen is valid **only** for this specimen and any other determination of the same element in other specimens, with different matrix compositions, will lead to different values of ILD. The analyst must be aware that the ILD is

equivalent to a pure hypothetical and theoretical concentration value, which will probably never be determined in practice; or if measurements can be made down to the detection limit, uncertainties would normally be regarded as unacceptable.

4. Theoretical and Experimental Analytical Precision

Two other useful limits to estimate the precision of the analytical process are the theoretical and experimental analytical precision. The theoretical analytical precision is used especially for trace element determination to check whether the differences in concentration from sample to sample are significant. The experimental analytical precision is calculated when the analyst wants to evaluate the quality of the sample preparation (see more information at the end of Section 5). Note that both analytical terms are part of commonly used terminology and have not received international (ISO) approval. They have the merit, however, to apply in an elegant and practical way some definitions recognized by ISO, such as the Poisson distribution, standard deviation and repeatability (precision) [4].

The theoretical analytical precision (TAP) of an element in a given specimen, determined by a given analytical method, is the concentration equivalent to two standard counting errors on the **net** intensity of the analytical line. The TAP is a theoretical estimation of the precision of peak and background measurements, expressed in concentration unit of the analyte, that does not take into account the random errors introduced by the instrument and the sample preparation.

To determine it, measure for each specimen, peak and background intensities of the element of interest by applying the complete procedure of measurement.

The theoretical analytical precision (TAP) expressed in terms of concentration unit for an element in a given specimen, to be determined by a given analytical method, is calculated by

$$TAP = \frac{2}{m_i} \times \sqrt{\frac{I_p}{T_p} + \frac{I_b}{T_b}} \quad (10)$$

where the sensitivity m_i is calculated by the equation (2). This TAP value is valid only for the analyte i in the specimen used for determining it. It is used to evaluate if the differences in concentration from sample to sample are significant. In this case,

it must be calculated for each analyte and for each sample to be analyzed in a given analytical context.

To calculate the experimental analytical precision (EAP), repeat the measurement of the net intensity of the analyte between 10 and 15 times on the **same** specimen, in the same analytical context, and calculate the standard deviation of the distribution of measurements in terms of concentration unit for a 95.4% confidence level from the following expression:

$$EAP = \frac{2}{m_i} \sqrt{\frac{\sum_{m=1}^n (I_m - \bar{I})^2}{n-1}} \quad (11)$$

where I_m is the m^{th} measurement of the net intensity of the element i and \bar{I} is the mean value of the n measured values of the net intensity. This experimental value (EAP) enables us to estimate the random errors due to the instrument and counting statistics. It does not take into account the variability introduced by the sample preparation. As the instrumental precision should be negligible for modern instruments, the experimental value (EAP) should not differ of the theoretical value (TAP) by more than 50%. If it is the case, then there is another error source than counting statistics (for example, the instability of the instrument). It must be investigated, found and corrected.

5. Limit of Determination of a Method

Regarding the determination limit concept, there is a very significant difference between the terms **detection** and **determination**. The limit of detection is a theoretical estimation of the lowest net intensity that can be measured (or detected) by an instrument from a given specimen at the peak position of a given analyte, with a specified level of confidence. This last limit is much smaller than, even under the best analytical conditions, the limit of determination that is the smallest concentration of an analyte that can be determined (or quantified) with reliability in practice in a given analytical context.

Statisticians usually define the limit of determination as six times the theoretical standard counting error above the mean background intensity ($I_b + 6\sigma_b$) [5, 6]. It cannot be quantified, however, only from the measurement of the background intensity I_b . To do so can be extremely misleading. The correct quantitative definition must

take into account the level of confidence and the distribution of data as influenced by factors such as the repeatability of the sample preparation, the instrument, the type of matrix to be analyzed, the calibration procedure, the analytical method and the analyte concentration range. The author understands precisely why the above definition has been proposed [5, 6], but have to respectfully disagree with it and its use should even be discouraged. The traditional definition of the determination limit ($I_b+6\sigma_b$) is not representative of the smallest concentration of an element that can be determined in practice in a given analytical context. Indeed, it makes no sense to claim that the determination limit for an element is only 2 ppm when the result cannot be reproduced better than ± 20 ppm.

As opposed to the limit of detection (ILD) and the statisticians' definition of the limit of determination ($I_b+6\sigma_b$), which give the "illusion" that the performance of an instrument is better than it is in reality, the limit of determination of a method (LDM) is defined as the smallest concentration of an analyte in a given sample that can be reliably quantified in practice by a given analytical method with a 95.4% confidence level. In practice, a confidence level of 95.4% is enough. Our definition for calculating the limit of determination enables us to estimate in practice how well an analytical method can **repeat** a given result. It takes into account the errors introduced by the sample preparation, instrument and counting statistics. It is the smallest uncertainty introduced by an analytical method taken as a whole. It is this uncertainty that must be given aside of any analytical result with the famous "plus-or-minus" (\pm), as for example $0.022\% \pm 0.002\%$. We quantitatively define the limit of determination of a method as the concentration of an element equivalent to two standard deviations of a set of determinations of the same representative concentration. It is calculated from a series of n replicate specimens ($n = 10$) prepared from the same representative sample in the same experimental conditions. For a given element, we have

$$LDM = 2 \cdot \sqrt{\frac{\sum_{m=1}^n (C_m - \bar{C})^2}{n-1}} \quad (12)$$

where the mean concentration value is given by

$$\bar{C} = \frac{\sum_{m=1}^n C_m}{n} \quad (13)$$

The LDM value calculated using the equation (12) will, for a particular element, vary according to the concentration present in the specimen on which measurements are made. It is why the selected sample must be representative of the series of samples to be analyzed. A good practice is to select a sample containing the mid-value of the calibration range of the analyte.

Equation (12) calculates the standard deviation of the distribution of a series of calculated concentrations. A 95.4% confidence level is associated to this standard deviation. This means that there is a probability of 95.4% that, if the determination of the analyte is repeated using the same analytical method, the new concentration value will be within the limits of the LDM value, i.e., between the result \pm the LDM value. On the other hand, this does not guarantee in no circumstance the accuracy of this concentration value. We will come back on this subject in Section 7.

For the XRF analyst, the LDM represents the minimum concentration that can be determined and reported with a specific level of confidence. This is the only limit that should be reported to customers with every determination. The determination limit is particularly useful for the determination of trace elements. If it is unknown, there is a serious risk of reporting meaningless analytical results when they are below the determination limit. For geochemical determinations, where many varieties of matrices are analyzed, it is even appropriated to calculate subdetermination limit data, otherwise the statistical assessment of only one set of data to all matrices will be biased.

There is no theoretical concept that enables us to pretend that the limit of determination of a method can be defined by the equation (12). We were looking for a limit that was taking into account the sample preparation and, based on our experience, was representative of the analytical reality of a given XRF laboratory. The choice of equation (12) is based on the fact that it is reasonable to think that the LDM is reached when the coefficient of variation [8] is 100%. Note that this definition of the LDM is purely a suggestion. Another coefficient of variation of 200% could easily be chosen. Our definition has at least the merit to

be a practical scientific approach, at the limit between a theoretical and empirical approach, rather than to purely and simply claim that it is 6 times the standard counting error of the background measurements [5, 6] above the mean background intensity ($\bar{I}_b + 6\sigma_b$).

One frequently finds in literature [5, 6] the expression "Limit of Quantitation" as proposed by the American Chemical Society Committee on Environmental Improvements (1980) and set at a level $10\sigma_b$ above \bar{I}_b . It is supposed to represent the smallest concentration of an analyte that can be quantitatively determined. In many practical analytical situations, this theoretical definition gives a false result. That is why its use is not recommended. Furthermore, the expression

"Limit of Quantitation" is ambiguous by itself. There are many parameters that can be quantified in XRF analysis and when this expression is used it is not obvious that we are talking about the quantification of the amount of an analyte in samples. On the other hand, the expression "Determination

Limit" has no other possible meaning than the analytical determination of an analyte in samples. Finally the limit of quantitation is superfluous. The two other limits as defined by us, detection and determination limits, are sufficient to determine the capabilities of an analytical system.

As the ILD, the LDM varies with the specimen matrix composition, the atomic number (Z) of the analyte and the analytical context. However contrary to the ILD, the LDM varies also with the level of the concentration of the considered analyte in the selected testing sample. It is then very important, for calculating the limit of determination of a method, to select a real **representative** sample of the series of samples to be analyzed. Table 2 compares the ILD and the LDM of different elements in different certified reference materials.

Furthermore, a comparison of results obtained with equations (11) and (12) enables one to evaluate the quality of the sample preparation. Indeed, from the addition law of the variance [3], the total standard deviation is equal to

$$s_{total} = \sqrt{s_{prep}^2 + s_{inst}^2 + s_{stat}^2} \quad (14)$$

Modern instruments are stable enough for one to assume that the standard deviation s_{inst} due to the instrumental errors (generator, tube, crystal, detector, goniometer, specimen chamber, etc.) is negligible compared to s_{prep} and s_{stat} . Then $s_{inst} \sim 0$ and

$$s_{prep} = \sqrt{s_{total}^2 - s_{stat}^2} \quad (15)$$

where the total standard deviation s_{Total} is calculated by the determination limit (Eqn 12) and the standard deviation s_{stat} due to the counting statistical errors is calculated by the experimental analytical precision (Eqn 11). The standard deviation s_{prep} represents the level of variability introduced by the sample preparation and should never exceed 0.5% in relative value. Its relative value should be ideally around 0.1% or 0.2%. This subject will be explained in more detail in the next section.

6. The Uncertainty Introduced by Sample Preparation

With modern instruments, it is possible to "iJ,] control the different sources of errors that originate from the instrument and the method of concentration calculation. Indeed, random errors due to instrumental and operational errors can be minimized. The counting statistical errors usually can be made very small by selecting appropriate counting times. Regarding systematic errors, they

Table 2. Comparison of the Instrumental Limit of Detection (ILD) and the Limit of Determination of a Method (LDM). X-ray tube: Rh Tube (s.w.). Specimens: fused disc, 1 g sample+5 g $Li_2B_4O_7$ +0.3g LiF. The ILD and LDM have been calculated for a 95.4% confidence level and for a background counting time of 100s.

Element	Z	Reference material	Concentration (ppm)	ILD (ppm)	LDM (ppm)
S	16	BCR-1	400	3.9	267
Cl	17	NS-1	500	0.4	
Sc	21	BX-N	60	8.0	
Cr	24	BR	380	9.8	20
Co	27	NIM-D	210	6.6	
Ni	28	NIM-D	2050	5.1	43
Cu	29	GSD-3	175	2.7	24
Zn	30	SY-2	250	2.9	19
Ga	31	BX-N	70	2.7	
Rb	37	SY-2	220	1.3	7
Sr	38	SY-2	275	1.3	19
Y	39	SY-2	130	1.0	4
Zr	40	SY-2	280	1.0	9
Nb	41	STM-1	270	1.2	5
Mo	42	GSD-3	93	1.7	
Ba	56	GSP-1	1300	27.6	34
La	57	BX-N	390	18.3	
Ce	58	GSP-1	360	14.8	
Nd	60	GSP-1	190	10.7	
Pb	82	GSD-7	350	3.1	18
Th	90	SY-2	380	2.3	
U	92	SY-2	290	2.8	

can be greatly minimized when the instrument is operated by an experienced analyst, the composition of reference materials is accurately known and the matrix effects are corrected effectively.

Finally, the last and most important source of errors that must be eliminated, or at least reduced as much as possible, is due to sample preparation. The uncertainty introduced by this error source may limit considerably the accuracy and precision of the analytical results if we are not attentive to it. In this section, techniques for improving and controlling the quality of the sample preparation itself will not be discussed, but only general considerations for evaluating the uncertainty introduced by random and systematic errors due to the preparation of samples to be analyzed will be considered.

As a first precaution, since X-ray fluorescence spectrometry, like most instrumental methods of analysis, is essentially a comparative technique, it is absolutely vital that both calibration reference materials and samples to be analyzed are prepared in an identical and reproducible manner and presented to a spectrometer that must be operated under the same experimental conditions.

The second important precaution is to check that the repeatability of the prepared specimens is sufficiently good. This means that the uncertainty due to the sample preparation must be smaller than the acceptable global analytical uncertainty. It is therefore essential that even the simplest method of sample preparation be tested for its repeatability. Only after verification that the preparation method is sufficiently reproducible should one start preparing the (expensive) calibration reference materials.

The following general procedure can be used to test the repeatability of the sample preparation method:

1. Select a large amount of a homogeneous "production sample" to test. The selected sample does not have to be a calibration reference material.
2. Prepare 10 specimens from this single sample, using the same preparation method for all 10 specimens.
3. Prepare an analytical program to measure the intensities of all elements of interest. Carry out the following two series of measurements, preferably on the same day, using the same analytical program:
 - 3.1 Measure each of the 10 specimens once.
 - 3.2 Measure one of the specimens 10 times.

Table 3. Comparison of the results of 1 measurement on 10 different fused disc specimens and of 10 measurements on the same fused disc. Data taken from Ref. [11]

	10 fused discs 1 measurement/disc	1 fused disc 10 measurements
Mean intensity (cps)	213,110	212,996
Total standard deviation (cps)	585	185
Total counting time/mea. (s)	---	12

4. Calculate the relative standard deviation [8] as explained hereafter for both series of measurements.
5. If the relative standard deviation obtained in experiment 3.1 is sufficiently low, the method of sample preparation is suitable. Pay special attention to the results for the major constituents.
6. If for a particular element the obtained relative standard deviation is too high, the results of experiment 3.1 can be compared with those of 3.2 in order to determine whether the spread is due to the sample preparation or to the instrument and counting statistics.

If required, other sample preparation methods can be tested using a similar testing procedure. For example, for testing a new binder in the preparation of pressed powder pellets, the surfacing of metal specimens, a new flux for the preparation of fused discs, etc. To do so, select another representative homogeneous sample. Repeat the preparation and measurement of 10 new specimens, and additionally, measure one of the prepared specimens 10 times. Compare both series of results as described hereafter. Whatever sample preparation method you choose, always verify its repeatability before to begin preparing the calibration reference materials.

As a numerical example, Table 3 compares the results of the measurement on 10 different fused disc specimens to 10 measurements on the same fused disc.

The uncertainty due only to sample preparation can be calculated as follows. The total uncertainty due to sample preparation, instrument and counting statistics is given by the relative standard deviation of the first test:

$$(E\%)_{Total} = \frac{585}{213,110} \cdot 100 = 0.27\%$$

The uncertainty due to the instrument and counting statistics is given by the relative standard deviation of the second test:

$$(E\%)_{Test\#2} = \frac{185}{212,996} \cdot 100 = 0.09\%$$

The total uncertainty of the first test is due to sample preparation, instrument and counting statistics and can be calculated from

$$(E\%)_{Total} = \sqrt{(e\%)_{Counting\ Statistics}^2 + (E\%)_{Instrument}^2 + (E\%)_{Sample\ Preparation}^2} \quad (16)$$

where the uncertainty due to the instrument and counting statistics is given by the relative standard deviation of the second test. Thus, we can write

$$(E\%)_{Test\#2} = \sqrt{(e\%)_{Counting\ Statistics}^2 + (E\%)_{Instrument}^2} \quad (17)$$

Combination of the last two equations leads to

$$(E\%)_{Total} = \sqrt{(E\%)_{Test\#2}^2 + (E\%)_{Sample\ Preparation}^2}$$

or

$$(E\%)_{Sample\ Preparation} = \sqrt{(E\%)_{Total}^2 - (E\%)_{Test\#2}^2}$$

Replacing the different uncertainties by their respective numerical values, one gets

$$(E\%)_{Sample\ Preparation} = \sqrt{(0.27\%)^2 - (0.09\%)^2} = 0.26\%$$

Another way to calculate the uncertainty due to sample preparation is as follows. The relative counting error due to counting statistics only (essentially random errors) is calculated from the measurements of the second test:

$$(e\%)_{Counting\ Statistics} = \frac{100}{\sqrt{I \cdot T}} = \frac{100}{\sqrt{212,996 \times 12}} = 0.06\%$$

The uncertainty of the second test is due to the instrument and counting statistics and can be calculated from equation (17). Thus, the uncertainty due to the instrument only is:

$$0.09\% = \sqrt{(0.06\%)^2 + (E\%)_{Instrument}^2}$$

or

$$(E\%)_{Instrument} = \sqrt{(0.06\%)^2 + (0.09\%)^2} = 0.07\%$$

Thus, using the equation (16), the uncertainty due to the sample preparation only is

$$0.27\% = \sqrt{(0.06\%)^2 + (0.07\%)^2 + (E\%)_{Sample\ Preparation}^2}$$

Thus,

$$(E\%)_{Sample\ Preparation} = \sqrt{(0.27\%)^2 - (0.06\%)^2 - 0.07\%} = 0.26\%$$

which means, in this case, that the total uncertainty is mainly due to sample preparation. It is not due to the errors of instrument or counting statistics, which is what it should be! Note that in the actual analytical context of fused discs, the uncertainty associated with sampling is relatively low. In other real applications (especially environmental), it is often substantially larger than any of the uncertainties considered here.

7. Reporting of Analytical Results

As the conclusion to this paper, a few comments on the way of reporting analytical results are presented. The following example clearly shows the problems associated with the incorrect reporting of results. A simple numerical result, such as 30.35% Cu for example, may give a wrong impression to the reader if all analytical errors (which include precision and accuracy) of the result are not given. All these different types of information should always be supplied on the front page of any report of analyses. Otherwise, the mere fact that the result (30.35% Cu) is written with two digits after the decimal point does not assure the reader that such accuracy is obtainable nor does it reassure the reader that a subsequent measurement (repeatability) will produce the same result.

Often, examination of the analytical results leads to a number of questions related to their experimental uncertainty. That is why the analysts must absolutely employ an explicit way, and a preferably accepted one, of reporting results and assessing the capabilities and limits of the analytical method. It is absolutely vital that those who use the results know exactly the limit of determination of the method (LDM), the global analytical uncertainty (precision and accuracy) associated with each result and for which concentration range these two parameters are valid. They must also know whether the given LDM parameter was derived from only counting statistical error calculations or from replicate determinations. Finally, the LDM is more meaningful if the degree of confidence for it is included.

The LDM of an analytical result, which is a measure of the repeatability or precision, describes the magnitude of the deviation, which occurs after

repeatedly measuring different specimens of the same sample in the same analytical context. In other words, repeating the same measurement on different specimens prepared from the same sample enables experimental estimation of the uncertainty of analytical results. It can be adequately estimated by the absolute value, in % or ppm, of the LDM (Eqn 12). It can be derived from n (where $n=10$) replicate determinations with a 95.4% confidence level. This information is very important since it enables to estimate the minimum uncertainty value associated with an analytical result. It is usually reported as a "plus-or-minus" absolute value, in % or ppm, aside a group of results (for example, $0.022\% \pm 0.002\%$).

The other component of analytical errors, i.e. systematic errors, is present when a certain bias exists in the results, as could happen if a badly determined calibration line is used. This bias is a measure of the difference between the given and the calculated concentration value. Systematic errors not only depends upon errors that arise from the conversion of intensities into concentrations (calibration), but also from those produced by the sample preparation, the instrument and the analytical method used for the correction of matrix effects.

In quantitative XRF analysis, the calibration procedure, with the aid of reference materials, transforms the measured X-ray fluorescence intensity of a particular analyte to concentration [1]. An example of such a calibration line is given in Figure 2. It is desirable to use several reference materials so that the error due to calibration is held as small as possible. However, the calibration transformation is usually subject to errors depending on the reliability of the reference materials used and on the accuracy of the analytical method [12] for the matrix effect corrections. If certified reference materials are used, the reliability is quantifiable by the uncertainty that is always associated with a certified value. Although the reference materials may well be in agreement among themselves, they nevertheless may be the cause of systematically erroneous analyses. The relative standard deviation calculated from the regression analysis of data of the calibration line is therefore not a reliable criterion to estimate the global uncertainty over a given range of concentrations for an analytical method. However, the global uncertainty of the analytical results may be very well estimated by comparing

Table 4. Global relative uncertainty (%) and determination limit of the method (%) over a given concentration range of analytes in rock samples analyzed by XRF and prepared as fused discs.

Component	Calibration range (%)	Estimate of global and relative uncertainty	Limit of determination (%)
Na ₂ O	0-10	1	0.03
MgO	0-50	1	0.04
Al ₂ O ₃	0-60	1	0.20
SiO ₂	0-100	1	0.50
P ₂ O ₅	0-1	1	0.01
K ₂ O	0-15	1	0.05
CaO	0-35	1	0.01
TiO ₂	0-3	1	0.02
Cr ₂ O ₃	0-4	1	0.01
MnO	0-1	1	0.01
Fe ₂ O ₃	0-90	1	0.06
Rb	0-0.0600	2	0.001
Sr	0-0.2000	10	0.002
Y	0-0.0200	10	0.001
Zr	0-0.2000	10	0.001
Nb	0-0.0400	10	0.001
Ba	0-0.3000	10	0.003

the results obtained from reference materials that have **not** participated to the calibration, to their given (or certified) concentration values. The global relative uncertainty (in %) over a given concentration range of a series of results for an analyte can be estimated from

$$(E\%)_{global} = \frac{\sum_{m=1}^n \left(\frac{\sqrt{(C_{i\ given} - C_{i\ calculated})^2}}{C_{i\ given}} \right)_m}{n} \cdot 100 \quad (18)$$

where

- (E%)_{global} Average relative analytical uncertainty value in %
- n Total number of calibration reference materials
- m Suffix for identifying each calibration reference material
- i Element to be determined or analyte
- $C_{i\ given}$ Given or certified concentration value of element i in calibration reference materials
- $C_{i\ calculated}$ Calculated concentration value of element i in calibration reference materials

The global analytical uncertainty is a combination of all sources of random and systematic er-

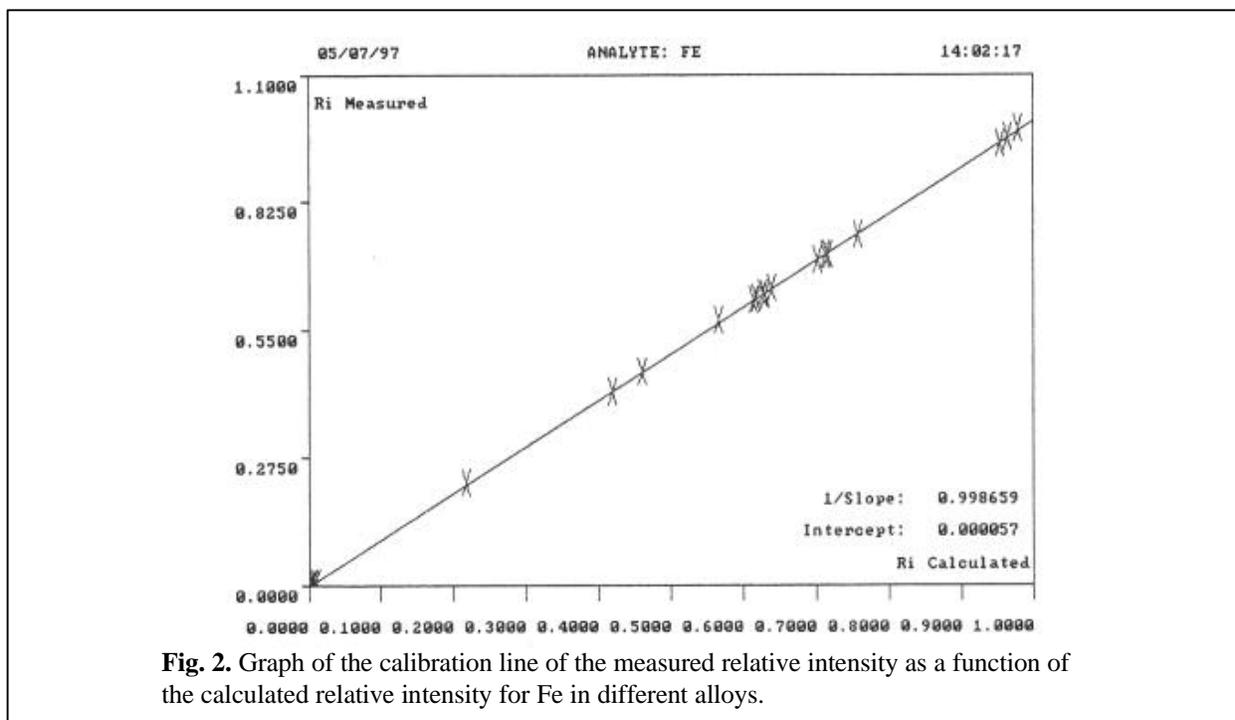


Fig. 2. Graph of the calibration line of the measured relative intensity as a function of the calculated relative intensity for Fe in different alloys.

Table 5. Calculation of the average relative uncertainty from the data of the calibration line of Figure 2 for typical alloys. Only the reference materials D807A and C1119 have been used to calculate the slope and the intercept of the line. Because the calibration range is very large (0-100%), only results > 1% have been considered. The last two digits of each result are meaningless for any value > 0.10% (or 1000 ppm)

Reference material	Concentration (%)		Uncertainty (%)	
	Given	Calculated	Absolute	Relative
NBS-628	0.0660	0.0855	0.0195	
NBS-629	0.0170	0.0297	0.0127	
NBS-644	1.3600	1.3316	-0.0284	2.08
NBS-646	2.1400	2.1202	-0.0198	0.92
D805A	97.6350	98.1277	0.4927	0.50
D807A *	97.5830	97.5949	0.0119	0.01
D809B	95.7560	95.9046	0.1486	0.16
D836	80.2450	80.8630	0.6180	0.77
D837	80.9600	81.4751	0.5151	0.64
D838	78.7700	79.1955	0.4255	0.54
D840	70.5500	71.5141	0.9641	1.37
D845	83.5230	82.9450	-0.5780	0.69
D847	62.0290	61.9952	-0.0338	0.05
D848	85.5640	85.4016	-0.1624	0.19
D849	84.5190	84.3856	-0.1334	0.16
D850	71.3220	70.8900	-0.4320	0.61
C1101	0.0370	0.0374	0.0004	
C1103	0.2600	0.2787	0.0187	
C1110	0.0330	0.0361	0.0031	
C1113	0.0430	0.0398	-0.0032	
C1116	0.0460	0.0457	-0.0003	
C1119 *	0.0300	0.0306	0.0006	
1154	65.0600	65.2628	0.2028	0.31
1156	69.6700	69.7695	0.0995	0.14
1159	51.0000	51.3395	0.3395	0.67
1160	14.3000	14.6420	.3420	2.39
			Average:	0.68

rors, or precision and accuracy respectively, which can affect the final value of a result. This uncertainty is usually reported as a relative value in %. For major elements, the global uncertainty is usually within 0.5 to 1%. However, it has to be kept in mind that the given concentration values of reference materials are also subject to errors just as the results determined by X-ray spectrometry. Table 4 gives an example of the global analytical uncertainty of the XRF analysis of rock samples prepared as fused discs.

A good strategy for calculating the global relative uncertainty for the type of calibration plot of Figure 2, when several reference materials are available, is to use only the lowest and the highest points of the analyte calibration range to calculate the slope and the intercept of the line. The concentrations of all the other intermediary points are then calculated from this calibration line and compared to the given concentration values. As an example, Table 5 gives all the data [13] necessary to calculate the global (or average) relative uncertainty of the calibration line of Figure 2 for typical alloys.

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