Comment to : Uncertainty in the Multielemental Quantification by Total-Reflection X-ray Fluorescence: Theoretical and Empirical Approximation or Generalities on precision and accuracy concepts applied to the propagation of TXRF errors

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Abstract

In this work, basic statistical concepts referred to both precision and accuracy of measurements are described. These concepts are later related to the characterization of the Total Reflection X-Ray Fluorescence technique (TXRF). In the assessment of uncertainties of the TXRF technique, in the case of a confusion between both concepts, errors would be produced in such process, resulting in incomplete mathematical expressions.

1 Generalities on the concepts of accuracy and precision

There is a perfectly balanced coin. When flipping it, two possibilities with equal probability are given: head or tail (H and T). If we increase the amount of flips, we will have a greater number of elements in the sampling space. Then, by using the limit of relative frequencies for the occurrence of H when the experiment is repeated an infinite number of times under the same conditions, we will have:

$$P_H = \lim_{n \to \infty} f(H) = \frac{\text{Cases favourable to } H}{\text{Total possible cases}}$$

Then, by definition it is given:

$$P_H = \lim_{n \to \infty} f(H) = \frac{1}{2} = 0.5$$

It is implicit that after the number 5 there is an infinite number of zeros, that is, this number is perfectly defined. If we consecutively flip 3 times the same coin, which is the probability of getting head? The possible sequences are:

| sequences | 1 | 2 | 3 | f |
|-----------|---|---|---|---|
| A         | H | H | H | 1 |
| B         | H | H | T | 2/3 |
| C         | H | T | H | 2/3 |
| D         | H | T | T | 1/3 |
| E         | T | H | H | 2/3 |
| F         | T | H | T | 1/3 |
| G         | T | T | H | 1/3 |
| H         | T | T | T | 0 |

Table 1: Flipping sequences of a coin with its respective head frequency.

We know that by flipping a perfectly balanced coin, the probability of getting head is $P_H = \frac{1}{2}$. Then, by observing Table 1 we can infer that the probability of getting head is given by:

$$P_H = f(H) \pm \Delta f_H$$

where $f(H)$ is the frequency for every sequence, like A, B, C, etc., and $\Delta f_H$ is an uncertainty associated to every calculated frequency. Even in this kind of experiments where the probability is perfectly known we cannot assure that the uncertainty of the measurements is equal to zero.
A mathematical tool that will be recurrent in the course of this article is the propagation of errors formula, [1] given by:

$$\Delta_c[G_y(x_i)] = \sqrt{\sum_i \left( \frac{\partial G_y}{\partial x_i} \right)^2 \Delta^2(x_i)}$$  \hspace{1cm} (4)

With $\Delta_c$ is the combined uncertainty associated to $G_y$, and $\Delta(x_i)$ is the standard uncertainty of every one of the input parameters $x_i$, which are linearly independent.

It is said that a measurement is exact, as closer it is from the real value. Accuracy is linked to the average of measurements. Precision: is the proximity among the indications or the measured values obtained from repeated measurements of an event, under specific conditions. It can be numerically represented by means of dispersion measurements.

In Figure 1 it can be observed what it is intended to specify in the process of data analysis, the distinction between two concepts, precision and accuracy.

2 Errors propagation in TXRF analysis

TXRF technique is generally used in conditions in which a linear quantification relation can be applied, when enhancement or self-absorption effects are not significant. Then, the intensity as a function of the concentration is expressed:

$$N_y = C_y S_y$$  \hspace{1cm} (5)

Being $N_y$ the intensity of fluorescent radiation of the $y$ element $y$ $S_y$ is the sensitivity and $C_y$ is the concentration of such element in the sample. In TXRF analysis, for quantification purposes, a new element is added to the sample. This reference element should be added in a very well known concentration. The intensity of the reference element would be:

$$N_p = C_p S_p$$  \hspace{1cm} (6)

The relationship between the intensities indicated in Eqs. (5) and (6), produces a relation between the empirical input parameters. This relation, as a function of $C_p$, $N_y$, $N_p$, $S_p$ and $S_y$ in $C_y$ is given by:
\[ C_y(C_p, N_y, S_p, N_p, S_y) = C_p \frac{N_y S_p}{N_p S_y} \] (7)

By applying Eq. (4) on the Eq. (7) the mathematical arrangement of the Eq. (8) is obtained. This corresponds to the uncertainty associated to the parameter \(C_y\) depending from every one of the input parameters.

\[ \Delta^2_{rel}(C_y) = \Delta^2_{rel}(C_p) + \Delta^2_{rel}(N_y) + \Delta^2_{rel}(N_p) + \Delta^2_{rel}(S_p) + \Delta^2_{rel}(S_y) \] (8)

This combined uncertainty presents the precision in our full measurement.

The contribution due to the sensitivities of the uncertainties \(\Delta^2_{rel}(S_p)\) and \(\Delta^2_{rel}(S_y)\) in the TXRF method can be obtained by means of two empirical processes, although we only will be focused in Model based on the use of the TXRF functional relation.

### 2.1 Model based on the use of the TXRF functional relation

Considering the Eq.(7), rearranging and renaming indexes, pattern \((p)\) by reference \((ref)\) we have:

\[ S_y = S'_{ref, y} \frac{N'_y C'_{ref}}{N'_{ref} C'_y} \] (9)

Applying the same procedure provided for the Eq.(4), in the Eq.(9) the relative uncertainties of the sensitivities for the \(y\) and reference \((ref)\) elements are obtained.

\[ \left( \frac{\Delta(S_y)}{S_y} \right)^2 = \left( \frac{\Delta(C'_y)}{C'_y} \right)^2 + \left( \frac{\Delta(C'_{ref})}{C'_{ref}} \right)^2 + \left( \frac{\Delta(N'_y)}{N'_y} \right)^2 + \left( \frac{\Delta(N'_{ref})}{N'_{ref}} \right)^2 + \left( \frac{\Delta(S'_{ref})}{S'_{ref}} \right)^2 \] (10)

The first term of the Eq.(10) is referred to the relative uncertainty corresponding to the concentration of the \(y\) element in the sample. The second term corresponds to the reference concentrations \((ref)\); the third, to the intensity of the \(y\) element in the sample; the fourth, to the intensity of the reference element \((ref)\); and the fifth term, this is to say the element \(\frac{\Delta(S'_{ref})}{S'_{ref}} \) corresponds to the reference sensitivity.

\[ \left( \frac{\Delta(S_p)}{S_p} \right)^2 = \left( \frac{\Delta(C'_p)}{C'_p} \right)^2 + \left( \frac{\Delta(C'_{ref})}{C'_{ref}} \right)^2 + \left( \frac{\Delta(N'_p)}{N'_p} \right)^2 + \left( \frac{\Delta(N'_{ref})}{N'_{ref}} \right)^2 + \left( \frac{\Delta(S'_{ref})}{S'_{ref}} \right)^2 \] (11)

Terms from Eq.(11) correspond to equivalent descriptions of Eq.(10), but referred to the case of the pattern \((p)\) element of the sample.

In Eqs. (10) and (11) uncertainty elements corresponding to the fifth term [1] are not considered, because \(S_{ref}\) is considered unitary, but no mention is given to the uncertainty \(\Delta(S'_{ref})\) which is always different from zero \(\Delta(S'_{ref}) \neq 0\). One way by which the proposed by (11) is fulfilled is:

\[ \Delta(S'_{ref}) = 0 \Rightarrow \left( \frac{\Delta(S'_{ref})}{S'_{ref}} \right)^2 = 0 \] (12)

When we refer to elements of uncertainty in an experiment, we know that every measurement process is not perfect. Therefore, ignoring a term can produce a series of consequences that will affect us in a future. Then, by carrying out an experiment, every measurement must be associated to an element of uncertainty. In the case of the sensitivity, this is

\[ S'_{ref} \pm \Delta(S'_{ref}) \] (13)

We observe that when performing this kind of experiments the term \(S'_{ref}\) is perfectly known, which is equal to 1. Even so, not give us the assurance that the uncertainty of the measurements is zero.

### 3 Conclusions

We showed that, in a error propagation process, both precision and accuracy must be taken into account, because an error may produce an unreal result.
At first case we know that the probability of getting heads when a coin is flipped 0.5, and then evaluating in the experiment from the point of view of frequency, each sequence is associated with an uncertainty, this relationship is given by the Eq.(3). The second case, we know that the sensitivity is 1, now if we follow the case of the coin, the frequency of each sequence or each measurement has associated an uncertainty corresponding to the sensitivity which is given by the equation (13). So, Eq. (12) is incomplete in Ref[1].

References

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