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# UNCERTAINTIES IN ELEMENTAL QUANTITATIVE ANALYSIS BY PIXE*

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ABSTRACT. The effects of the degree of non-uniformity of the particle beam, matrix composition and matrix thickness in a quantitative elemental analysis by Particle Induced X-ray Emission (PIXE) are discussed and the criteria to evaluate the resulting degree of uncertainty in the mass determination by this method is established.

RESUMO. Os efeitos do grau de não uniformidade do feixe de partículas, composição e espessura da matriz numa análise quantitativa de elementos através Emissão de Raios-X Induzida por Partículas (PIXE), são discutidos e um critério para avaliar o grau de incerteza na determinação da massa utilizando este método é estabelecido.

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# I. INTRODUCTION

Elemental quantitative analysis by Particle Induced X-ray Emission (PIXE) is based upon the assumption that there is an unambiguous relation between the number of characteristic X-rays of a particular element observed and the amount of this element present in the target sample. Nevertheless, the number of characteristic X-rays observed depends upon the distribution of the element in the sample, the degree of nonuniformity of the particle beam, and the matrix composition.

The distribution of an element in a sample is usually neither known nor modifiable to become homogeneous. Thus if the particle beam is not perfectly uniform the same number of X-rays might be observed for appropriate arrangement of different amounts of an element in the sample.

Since a complete uniformity of the pa ticle beam is not usually achieved under experimental conditions, different points on the target may be reached by a different number of incident particles. Thus, if a quantity of a particular element can be properly arranged to be located in the most intense region of the beam it may result in a different number of characteristic X-rays from an arrangement of the same amount of this element in a less intense region of the beam.

A similar effect will occur for different arrangement of an element in the matrix as a result of the loss of energy of the incident particle beam and X-ray absorption in the sample.

These effects will be discussed and a criteria to evaluate the resulting degree of uncertainty in the mass determination by PIXE will be established hence forth.

## II. THEORY

The amount of a particular element present in a sample associated to a number $N_x$ of characteristic X-rays observed may be different for different arrangements of this element in the matrix and for different particle beam distribution, as stated above. Therefore there are elemental distributions for which number of atoms associated to a definite number of observed characteristic X-rays will be a maximum or a minimum. These two extremes will define the uncertainty in the amount of the element measured. A criterium to associate the number of atoms of an element to a definite number of characteristic X-rays observed may be established from the knowledge of these two limits. The starting point to define this criterium is to discuss the situation in which these limits may occur.

Let us consider that the target sample is arranged in such a way that the normal to its surface is at an angle $\theta$ with respect to the incident particle beam as schematically shown in Figure 1. The x-y plane of the unprimed frame of reference lies on the surface of the target sample. The primed frame of reference has its z'axis coincident with the direction of the incident particle beam, and the origin

and the y axis are common in both frames. The relations between the coordinates in the two frames are given by:

$$x' = x \cos\theta - z \sin\theta \; ; \quad y' = y \; ; \quad z' = x \sin\theta + z \cos\theta$$

An expression for the number $N_x$ of observed characteristics X-rays produced by $N_p$ particles irradiating the target sample and counted within a solid angle $\Omega$ by a system with efficiency $\varepsilon$, can be written as follows[1]:

$$N_x = \frac{\Omega}{4\pi} \varepsilon N_p \int P(x',y') n(x,y,z) \sigma_E\left(\frac{z}{\cos\theta}\right) e^{-\mu z/\sin\theta} \, dxdydz$$

or

$$N_x = \frac{\Omega}{4\pi} \varepsilon N_p \int P(x\cos\theta - z\sin\theta, y) \, n(x,y,z) \, \sigma_E\left(\frac{z}{\cos\theta}\right) e^{-\mu z/\sin\theta} \, dxdydz \quad (1)$$

where

$P(x',y')dx'dy'$ is the probability of a particle of the beam to cross the elemental area dx'dy' in the vicinity of the point (x',y'), and it is considered constant along the direction of the incident beam.

$n(x,y,z)dxdydz$ is the number of atoms of the particular element in the elemental volume dxdydz.

$\sigma_E(z)$ is the cross section for X-ray production by particles with incident energy E penetrating a distance z in the target sample.

The above relation shows that the number of observed characteristic X-ray is not related directly to the number of atoms of a particular element present in the sample, but it will also depend upon the particular distribution.

The number of atoms of the element can be determined by the following relation:

$$N = \int n(x,y,z)\,dx\,dy\,dz$$

It becomes clear from this relation that exists a large number of distribution which will lead to a definite number of atoms in a particular sample.

Let us then choose a particular elemental distribution in the matrix and particle beam configuration in which a definite number $N_x$ of observed characteristic X-ray will be associated to a minimum amount, $N_{min}$, of the element in the sample. This occurs when all the atoms of the element are concentrated in the more intense region of the beam and the loss of energy of the incident particles and the X-ray absorption in the matrix are minimal. This can be obtained if all the atoms of the element are located at a point on the surface toward the incident particle beam. This situation is shown schematically in Figure 1. Taking this point as the origin of the reference frames we may write for the distribution of the atoms of the particular element in the target:

$$n(x,y,z) = N_{min}\,\delta(x,y,z) \qquad (2)$$

where $\delta(x,y,z)$ is Dirac's delta function.

The probability dersity for the particles from the most intense region of the beam to strike at this point is given by:

$$P(x',y') = P(0,0) = P_{max} \qquad (3)$$

and the cross section for X-ray production for particle with energy E at this point is written as $\sigma_E(0)$.

Taking the above results into relation (1) we get, after some manipulations:

$$N_{min} = \frac{N_X}{(\Omega/4\pi) \cdot N_p P_{max} \sigma_E(0)} \qquad (4)$$

For the maximum amount of the element in the sample associated to the number $N_X$ of characteristic X-rays observed, the elemental distribution will be that irradiated by the less intense region of the particle beam and the loss of energy of the incident particles and the X-ray absorption in the sample are maximal. This will be the case if all the atoms of the elemental are concentrated in a point $(x_0,y_0,t)$ on the surface opposed to the incident beam. In this situation, also schematically shown in Figure 1, the distribution of the atoms of the particular element, in the same frames of reference as above, can be written as:

$$n(x,y,z) = N_{max} \delta(x - x_0, y - y_0, z - t) \qquad (5)$$

The probability for the particles of the less intense region of the particle beam to strike at this point is give by:

$$P(x',y') = P(x_0\cos\vartheta - t\sin\vartheta,\ y_0) = P_{min} \qquad (6)$$

Again, taking these results into (1) one gets for the maximum number of atoms of the elements $N_{max}$, associated to the observed number of characteristic X-ray:

$$N_{max} = \frac{N_x}{(\Omega/4\pi)\epsilon N_p P_{min} \sigma_E (t/\cos\vartheta)\ e^{-\mu t/\sin\vartheta}} \qquad (7)$$

Thus, $N_{min}$ and $N_{max}$ are respectively the minimum and the maximum number of atoms of a particular element present in the sample that can be associated to a definite number of observed characteristic X-rays. The true number of atoms for that particular element present in the sample should lie between these two extremes. The range between this two limits can be defined as the uncertainty in the determination of the amount of that particular element in sample.

From the above results we may establish a criterium to associate the number $N_x$ of observed characteristic X-rays to a number N of atoms of the particular element present in the sample. Our choice is

$$N = \frac{N_{max} + N_{min}}{2} \pm \frac{N_{max} - N_{min}}{2} \qquad (8)$$

A easely interpreting relation is obtained in terms of the following parameters:

$$\langle P \rangle = \frac{P_{max} + P_{min}}{2} \qquad (9)$$

$$\delta = \frac{P_{max} - P_{min}}{2} \tag{10}$$

$$\eta = 1 - \frac{\sigma_E(t/\cos\theta)}{\sigma_E(0)} e^{-\mu t/\sin\theta} \tag{11}$$

$$N_0 = \frac{N_x}{(\Omega/4\pi)\varepsilon N_p \sigma_E(0) \langle P \rangle} \tag{12}$$

Substituting the above definitions into (4) and (7) and bringing the results into (8) one get, after straight forward algebra:

$$N = N_0 \langle P \rangle \left[ \frac{\langle P \rangle + \delta + (\langle P \rangle - \delta)(1-\eta)}{2(\langle P \rangle^2 - \delta^2)(1-\eta)} \pm \frac{\langle P \rangle + \delta - (\langle P \rangle - \delta)(1-\eta)}{2(\langle P \rangle^2 - \delta^2)(1-\eta)} \right] \tag{13}$$

This relation will give the number of atoms present in a sample associated to a definite number of observed characteristic X-rays. The second term into the square brackets is related to the uncertainty due to the non-uniformity of the particle beam and the lack of knowledge of the elemental distribution in the matrix. For most of the practical applications this expression may be simplified and for this purpose will explore the meaning of the parameters $\delta$ and $\eta$ defined above. Let us consider an idealized situation by assuming a completely uniform particle beam and that the loss of energy for the incident particles and the X-ray absorption in the matrix are negligible. Taking these assumptions into account, $\delta$ and $\eta$ given in relations (10)

and (11), will be equal to zero. Substituting this results into relation (13) we came to the conclusion that $N = N_0$ and the number of atoms of a particular element can be unambiguously determined. However those assumed conditions can not be achievable in practice, thus we should establish experimental conditions to be as near as possible from the hypothetical situation discussed. In these cases $\delta$ and $\eta$ can be made small enough to allow neglecting terms of order $\delta^2$, $\delta\eta$ and $\delta^2\eta$ in expression (13). The simplifyed expression obtained is therefore:

$$N = N_0\left\{\frac{2-\eta}{2(1-\eta)} \pm \left[\frac{\delta}{\langle P\rangle(1-\eta)} + \frac{\eta}{2(1-\eta)}\right]\right\} \tag{14}$$

or

$$N = N_0 F(1 \pm \xi) \tag{15}$$

where we made

$$F = \frac{2-\eta}{2(1-\eta)} = \frac{1}{2} + \frac{\sigma_E(0)}{2\sigma_E(t/\cos\theta)}\, e^{\mu t/\sin\theta} \tag{16}$$

$$\xi = (\varepsilon_f + 1)(\varepsilon_t + 1) - 1 \tag{17}$$

$$\varepsilon_f = \frac{\delta}{\langle P\rangle} = \frac{P_{max} - P_{min}}{2\langle P\rangle} \tag{18}$$

$$\varepsilon_t = \frac{\eta}{2-\eta} = \frac{F-1}{F} \tag{19}$$

The correction factor F is associated to the loss of energy of the particles of the beam and the characteristic

X-rays absorption in the target sample. $\varepsilon_f$ is the error introduced by the lack of knowledge of the elemental distribution in the matrix.

## III. DISCUSSION

The effects of the nonuniformity of the particle beam, the elemental distribution, and the characteristics of the matrix for a quantitative analysis by PIXE were expressed in terms of the parameter $\delta$ and $\eta$ defined by equations 10 and 11 in the development of the theory.

The parameter $\delta$ may be understood as a measure of the degree of nonuniformity of the particle beam. Its value will permit the evaluation of the error introduced by the degree of nonuniformity of the particle beam in quantitative elemental determination using the PIXE method. The error in the measurement will increase for increasing values of $\delta$ which corresponds to an increase in the degree of nonuniformity of the particle beam. Therefore, in an experimental analysis, the particle beam should be adjusted to be as uniform as possible. An improvement in the uniformity of the beam can be achieved by passing it through a diffuser. In this case the degree of nonuniformity of the particle beam will depend on the characteristics of the diffusing system and the parameter $\delta$ can be estimated from these characteristics. This discussion is presented elsewhere.[9]

The effects of the elemental distribution and matrix characteristics in the mass determination are contained in

the parameter $\eta$. The dependence on the particular element appears in its definition through the X-ray production cross section; the dependence on the elemental distribution is expressed in terms of the layer traversed in the target matrix by the incident particle and by the emitted characteristic X-rays. The dependence on the matrix composition is introduced though the X-ray absorption coefficient and the stopping power. For most of practical applications the matrix composition and the elemental distribution are not controlable and the minimization of the error introduced by the effects discussed above will be constrained to the choice of the appropriate target thickness. Figure 2 illustrate the variation with $\eta$ of the number of atoms that can be associated with a definite number of observed characteristic X-rays. The upper and lower curves correspond respectively to the maximum and minimum number of atoms that can be associated with that definite number of characteristic X-rays. The range between the two curves defines the uncertainty in the determination of the number of atoms of the particular element for each value of $\eta$. It becames clear that the uncertainty will decrease for decreasing values of $\eta$.

## IV. CONCLUSION

The theory developed in this article offers a useful insight into several aspects of the PIXE method for

elemental quantitative analysis. The results obtained permit one to establish the experimental conditions for a more precise elemental trace analysis. The uniformity of the particle beam can be partially controlled as well the thickness of the target sample. The improvement in the particle beam uniformity and the utilization of thin samples will minimize the uncertainty in the amount of the element measured. However the elemental distribution in the matrix is in general unknown for most of the cases of interest and this lack of knowledge will introduce an intrinsic uncertainty in the quantitative elemental determination setting a limit to the precision of the PIXE method.

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FIGURE CAPTIONS

Figure 1 - Schematic particle beam distribution and target orientation.

Figure 2 - Relations between the number of atoms N associated with a definite number of observed characteristic X-rays and the same number $N_i$ obtained in ideal conditions as a function of $\varepsilon$. The dashed curves are for the maximum and minimum values of N, the solid curve is the average between these two extremes. In all cases a uniform particle beam was assumed.

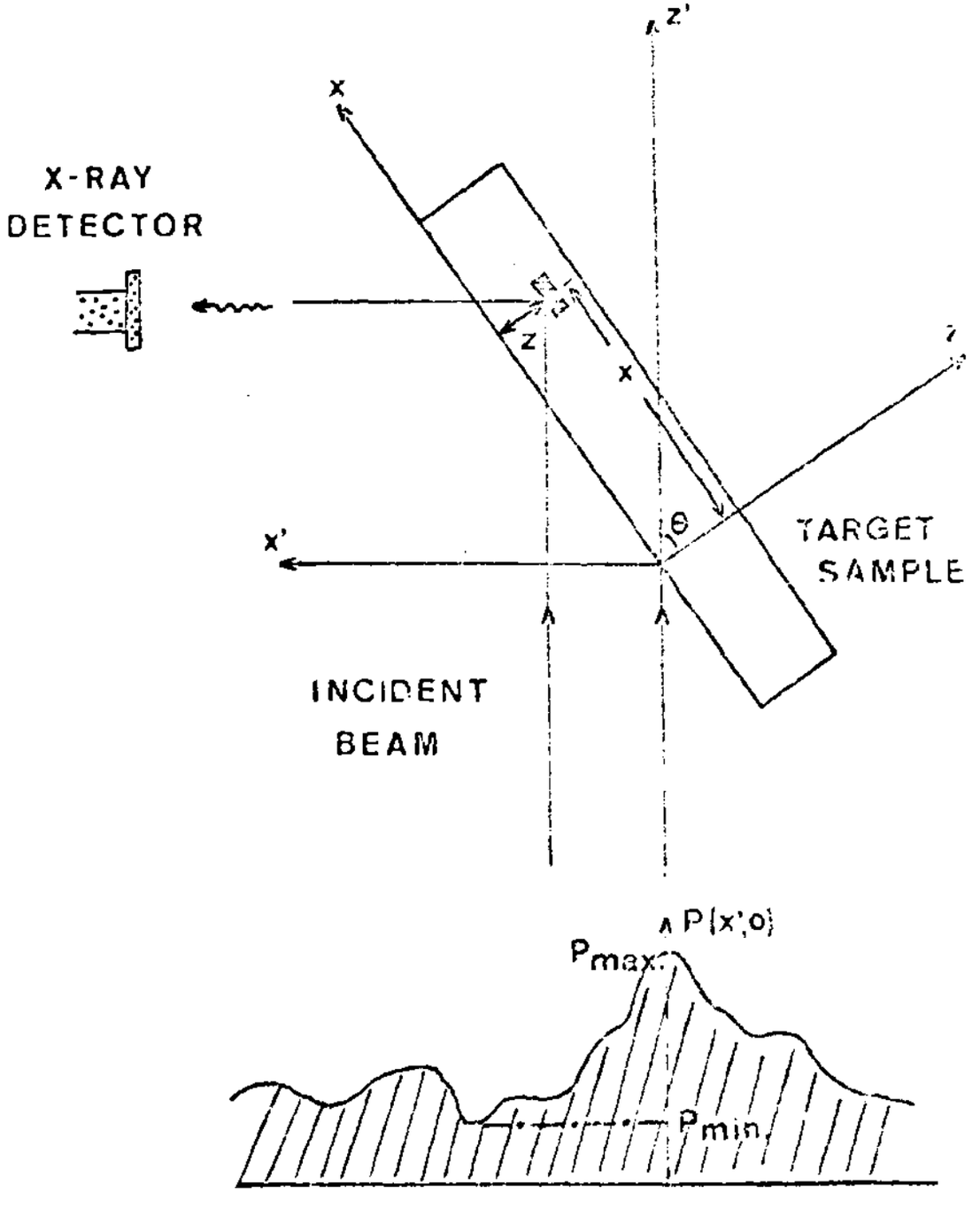
X-RAY
DETECTOR
z'
x
z
x
x'
θ
TARGET
SAMPLE
INCIDENT
BEAM
P(x',o)
Pmax
Pmin

FIGURE 1

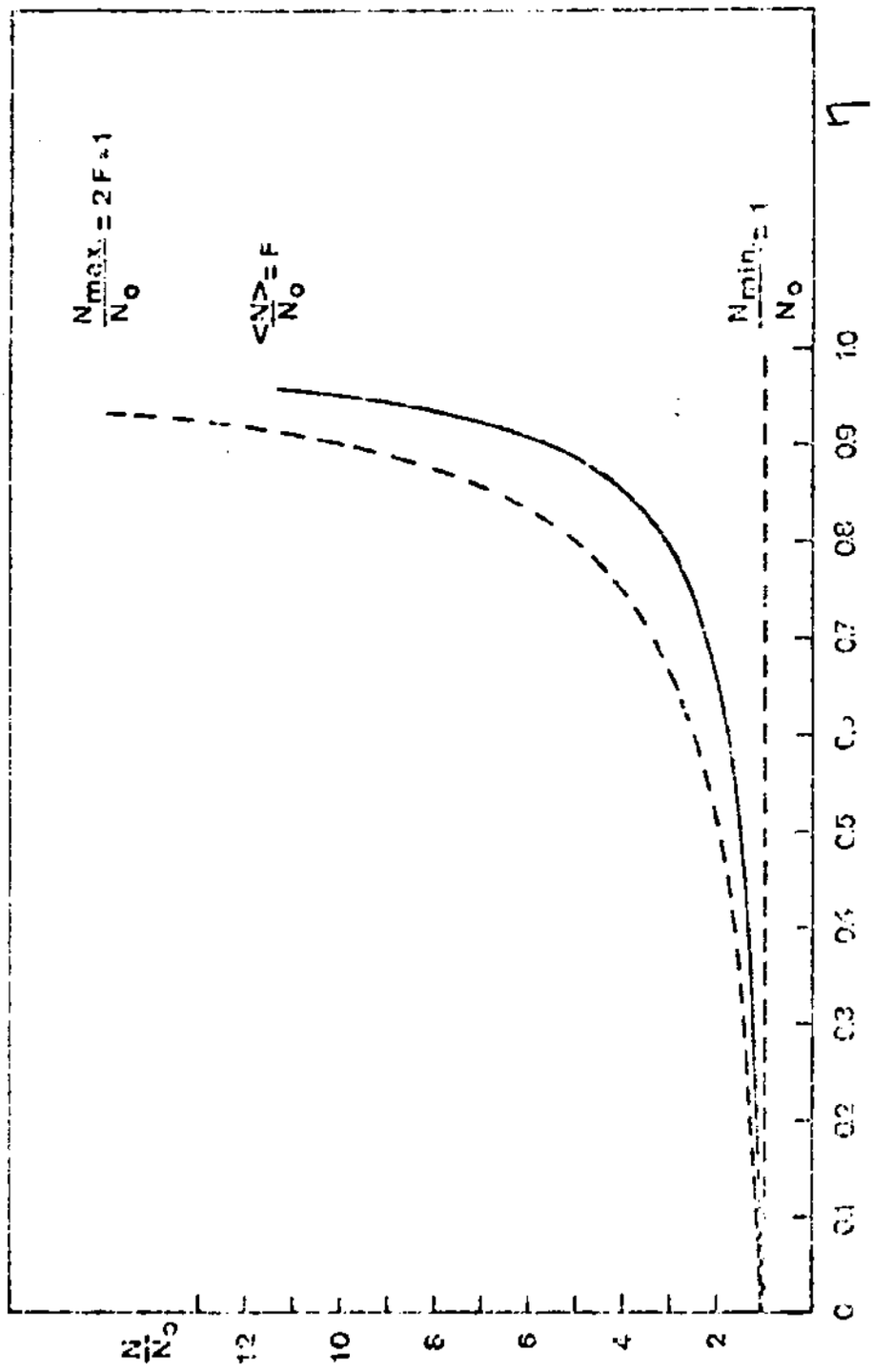
η
$\frac{N_{max}}{N_o} = 2F+1$
$\frac{\langle N \rangle}{N_o} = F$
$\frac{N_{min}}{N_o} = 1$
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
$\frac{N}{N_o}$
12
10
8
6
4
2

FIGURE 2