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EFFECTS OF X-RAY ABSORPTION IN THE ANALYSIS OF THICK TARGET SAMPLES BY XRF*

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ABSTRACT. The accuracy of the quantitative analysis of thick targets by XRF is impaired by effects due to the absorption of x-rays in the matrix associated with the non-uniformity of the x-ray beam and the lack of knowledge of the actual distribution of trace elements in the target. The uncertainty in the elemental mass associated to a definite number x-rays detected is discussed in the paper. A correction factor is derived to account specifically for the effect of the absorption of x-rays and the non-uniformity of the x-ray beam.

RESUMO. A ~~acurácia~~ precisão na análise quantitativa de elementos em alvos espessos usando a técnica de XRF é dificultada pelo efeito de absorção de raios X na matriz associado ao desconhecimento da distribuição de elementos traços no alvo. A incerteza na determinação da massa de um elemento associado a um número definido de raios-X característicos detectado é discutida neste trabalho. Um fator de correção é então obtido considerando somente efeitos de absorção de raios-X na matriz e a não uniformidade do feixe de raios-X incidente.

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INTRODUCTION

The quantitative analysis of trace elements, in a diversified type of samples, has in X-Ray Fluorescence (XRF) analysis an outstanding technique(1). The high sensivity of the XRF technique permits, under appropriate conditions, the simultaneous analysis of a large number of elements. However, the accuracy of the analysis of a thick target by XRF is impaired by effects due to the absorption of x-rays in the matrix associated with the lack of knowledge of the actual distribution of trace elements in the target. The corrections due to these effects are generally obtained by assuming a particular elemental distribution for the trace elements in the matrix target. Different corrections for the x-ray self absorption effects can be obtained for different distributions of the trace elements. Since the elemental distribution in the sample is not known for most practical applications of the XRF technique there will be an uncertainty in the elemental quantity associated to a definite number of characteristic x-rays detected. In the present paper this kind of uncertainty will be discussed based upon the assumption that extreme cases of elemental distributions, which will result in maximum or minimum quantities element present in the sample, can be associated to the same definite number of characteristic x-rays detected. This approach has been chosen because, in the XRF technique, the information available is usually the number of characteristic x-rays detected, besides the energy and intensity of the incident x-rays beam and geometrical factors. As a result, a correction factor is derived here to account specifically for the effect of x-rays self absorption and non--uniformity of the x-ray beam. Reliable expressions are also obtained to estimate the error and the uncertainty range in quantitative XRF analysis as a result of the effects mentioned above. The possible enhancement effects were neglected in the theory developed in the present article. However, considerations about the contributions of such effects in the elementar analysis by XRF can be found elsewhere, see for example an article by Sparks(2).

The approach used in this work is somewhat similar to that adopted by the same authors on a previous article(3) about uncertainties in elemental quantitative analysis by Proton Incuced X-ray Emission (PIXE), although there are remarkable differences in the causality of uncertainties in XRF and PIXE.

THEORETICAL FORMULATION

An experimental geommetry commonly used in XRF analysis is obtained by detecting the characteristics x-rays emitted by the target through a 90° angle with respect to the direction of the incident collimated x-ray beam, as shown schematically in figure 1. Under this particular geommetrical configuration the number of characteristic x-rays emitted, N_x, from an element present in a target sample of thickness, t, irradiated by a pure monochromatic x-ray beam of energy, E_s, is given by the equation:

$$N_x = \frac{\Omega}{4\pi} \varepsilon N_s \sigma_{E_s} \int P(x',y')\eta(x,y,z)\exp(-\mu_s z/\cos\theta)\exp(-\mu_c z/\mathrm{sen}\theta)\, dx\, dy\, dz \quad (1)$$

or, after an appropriate change of variables

$$N_x = \frac{\Omega}{4\pi} \varepsilon N_s \sigma_{E_s} \int P(x\cos\theta - z\sin\theta, y)\eta(x,y,z)\exp(-\mu_s z/\cos\theta)\exp(-\mu_c z/\mathrm{sen}\theta)\, dx\, dy\, dz \quad (2)$$

where the coordinate systems are indicated in figure 1;

Ω is the solid angle seen by the detector;

ε is the intrinsic efficiency of the system for x-ray detection:

N_s is the number of monocromatic x-rays with energy E_s irradiating the target sample;

$P(x',y')dx'dy'$ is the probability of an x-ray photon to cross the elemental area $dx'dy'$ in the vicinity of the point $(x'y')$, and is considered constant along the direction of the incident beam before entering the target;

σ_{E_s} is the x-ray fluorescence cross section of photon energy E_s;

$\eta(x,y,z)dxdydz$ is the number of atoms of a particular element in the elemental volume dx dy dz;

μ_S and μ_C are the mass attenuation coefficient for the incident x-ray beam and the emitted x-ray respectively.

It becomes clear from the above relation that the number of characteristic x-rays detected will depend on the number of atoms of a particular element and on its distribution in the target sample. Using the relation for the number of atoms of a particular element in a target sample

$$N = \int \eta(x,y,z)\ dx\ dy\ dz \qquad (3)$$

one may conclude that there are large number of distributions which may satisfy relation (3). Particular distributions which lead to the maximum and the minimum number of atoms of a particular element present in the sample that can be associated to a definite number of characteristic x-rays detected are discussed in the present paper.

The maximum amount of a particular element present in the sample that can be associated to a definite number of characteristic x-rays detected corresponds to the case when that particular element is concentrated in the least intense region of the incident beam and the effects of self-absorption of the X-rays in the target are maximized. This will occur whenever all atoms of a particular element are located in a point (x_0,y_0,t) in the surface opposed to that of the incident beam as illustrated in figure 1. Therefore, we can represent this distribution as:

$$\eta(x,y,z) = N_{MAX}\ \delta(x-x_0\ ,\ y-y_0,\ z-t) \qquad (4)$$

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

The probability that the least intense region of the x-ray beam will strike the target sample at a point $(x_0',y_0',0)$ on the surface facing the incident beam is given by the following expressions:

$$P(x_0', Y_0') = P(x_c \cos\theta, y_0) = P_{MIN} \qquad (5)$$

The probability that the least intense region of the beam will strike the point (x_0, y_0, t) after traversing the thickness t in the target is then given by $P_{MIN}\, e^{-\mu_s t/\cos\theta}$.

Substituting the above result in equation (2) it can be transformed after integration and rearrangement of the terms, as follows:

$$N_{MAX} = \frac{N_s}{\frac{\Omega}{4\pi}\, \varepsilon N_s\, \sigma_{E_s}\, P_{MIN}\, \exp(-\mu_s t/\cos\theta) \exp(-\mu_c t/\mathrm{sen}\,\theta)} \qquad (4)$$

The minimum amount of a particular element that can be associated to a definite number of characteristic x-rays detected will correspond to the case when all atoms of the particular element in the target sample, distributed in such a way that the effect of self absorption is minimum, are irradiated by the most intense region of the x-ray beam. Therefore we can, in accordance with figure 1, represent the elemental distribution by:

$$n(x,y,z) = N_{MIN}\, \delta(x,y,z) \qquad (7)$$

This relation means that all atoms of a particular element are concentrated in a point in the surface of the target sample facing the incident beam.

The probability that the most intense region of the beam will strike at this particular point is given by:

$$P(0,0,0) = P_{MAX} \qquad (8)$$

As before, substituting relation (8) into equation (1) after integration and rearrangement of the terms, N_{MIN} can be expressed as:

$$N_{MIN} = \frac{N_x}{\frac{\Omega}{4\pi}\, \varepsilon N_s\, \sigma_{E_s}\, P_{MAX}} \qquad (9)$$

The maximum and minimum amounts of a particular element that can be associate to a definite number of characteristic x-rays are given by N_{MAX} and N_{MIN} respectively. The true amount of elements present in the target sample should lie between these two extremes. Therefore, we define the average number N of atoms of a particular element that can be associated to a number N_x of characteristic x-rays detected, as follows:

$$N = \frac{(N_{MAX}+N_{MIN})}{2} \pm \frac{N_{MAX}-N_{MIN})}{2} \tag{10}$$

In order to obtain an easier interpreting expression the following parameters are defined:

$$<P> = \frac{1}{2}(P_{MAX}+P_{MIN})$$

$$\Delta = \frac{1}{2}(P_{MAX}-P_{MIn})$$

$$\xi = 1 - \exp(-\mu_s t/\cos\theta)\exp(\mu_c t/\mathrm{sen}\theta)$$

$$N_o = \frac{N_x}{\frac{\Omega}{4\pi}\,\varepsilon N_s\,\sigma_{E_s}<P>} \tag{11}$$

Substituing the results given by relations (6) and (9), in terms of the parameters defined above, into relation (10) we obtain after straighforward algebra:

$$N = N_o\,\frac{<P>}{(1-\xi)}\left\{\frac{<P>+\Delta+(<P>-\Delta)(1-\xi)}{2(<P>^2-\Delta^2)} \pm \frac{<P>-\Delta-(<P>-\Delta)(1-\xi)}{2(<P>^2-\Delta^2)}\right\} \tag{12}$$

The above relation permits to estimate the number of atoms of a particular present in a target sample that can be associated to a definite number of characteristic x-rays detected taking into account effects due to x-ray self absorption and nonuniformity of the incident x-ray beam. One can easily show that if these effects are neglected, that is to make $\xi = \Delta = 0$, N will became equal to N_o. Therefore for practical applications, appropriated exprimental conditions should be chosen to minimize the effects mentioned above. Under such conditions Δ and ξ will become small enough to allow neglecting terms of terms Δ^2, $\Delta\xi$ and $\Delta^2\xi$ in equation (11). The following simplified relation in thus obtained.

$$N = N_0 \left\{ \frac{2-\xi}{2(1-\xi)} \pm \left[\frac{\Delta}{\langle P\rangle(1-\xi)} + \frac{\xi}{2(1-\xi)} \right] \right\} \qquad (13)$$

or

$$N = N\, F(1 \pm \zeta) \qquad (14)$$

where

$$F = \frac{2-\xi}{2(1-\xi)} = \frac{1}{2}\,(1 + \exp(\mu_s t/\cos\Theta)\exp(\mu_c t/\sin\Theta) \qquad (15)$$

$$\zeta = (\varepsilon_f + 1)(\varepsilon_t + 1) - 1 \qquad (16)$$

$$\varepsilon_f = \frac{\Delta}{\langle P\rangle} = \frac{P_{MAX} - P_{MIN}}{2\langle P\rangle} \qquad (17)$$

$$\varepsilon_t = \frac{\xi}{2-\xi} = \frac{F-1}{F} \qquad (18)$$

The correction factor F accounts for the correction due to effects of x-ray self absorption and its dependence with ξ is shown by the dark curve in figure 2.

ζ is the error introduced in the measurement as a result of the lack of knowledge in elemental distribution in the target sample and depends on ε_t, which accounts for the error due to the x-ray self absorption, and on ε_f, which accounts for the error due to the nonuniformity of the incident x-ray beam.

DISCUSSION AND CONCLUSION

The theory developed in the preceding section suggests the importance of the effects of x-ray self absorption and non-uniformity of the x-ray beam in an elementar analysis by XRF technique. To illustrate the results obtained we consider an hypothetical sample constituted by a Carbon matrix with Chromium as trace element. The sample is to be analyzed with a pure monochomatic x-ray beam of 22,1 KeV (Silver K_α line) obtained from a Cadmium 109 source. In this condition the variation with the target thickness of the correction factor due to the effects mentioned above are evaluated for the maximum, average and minimum quantity of Chromium, associated to a definite number of characteristic x-rays detected. The values for the x-rays mass attenuation coefficients were extracted from published tables[4]. The results are presented in figure 3. Figure 4 shows the variation with the target thickness of the error associated with the measurement, as defined by relation (16) in the preceding section. The uncertainty in the measurement is defined by the range between the two dashed curves in figure 3 and reflects the lack of knowledge of trace element distribution in the target. The increase of the correction factor and uncertainty as well the error can be verified easily by inspection of figure 3 and 4 respectively. These results suggests that for a more precise analysis using the XRF technique, the choice of experimental conditions should be such that minimize the effects discussed in the present article.

REFERENCES

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FIGURE CAPTION

Figure 1 - Schematic of the target orientation.

Figure 2 - Relation between the number of atoms N associated to a definite number of observed x-rays and the same number N_0 obtained neglecting all corrections as a function of η. The solid curve is for the averaged value of N obtained from the maximum and minimum values given by the dashed curves. In all cases an uniform incident x-ray beam was assumed

Figure 3 - Relation between the number N of atoms of Chromium in a Carbon matrix associated to a definite number of characteristic x-ray beam with 22,1 keV energy and the same number N_0 obtained neglecting all corrections as function of the target thickness. Solid curve is for the average value of N obtained from the maximum and minimum values given by the dashed curves. In all cases an uniform incident x-ray beam was assumed.

Figure 4 - Variation with the target thickness of the error in the measurement of Chromium homogenously distributed in a Carbon matrix as a result of the x-rays self absorption.

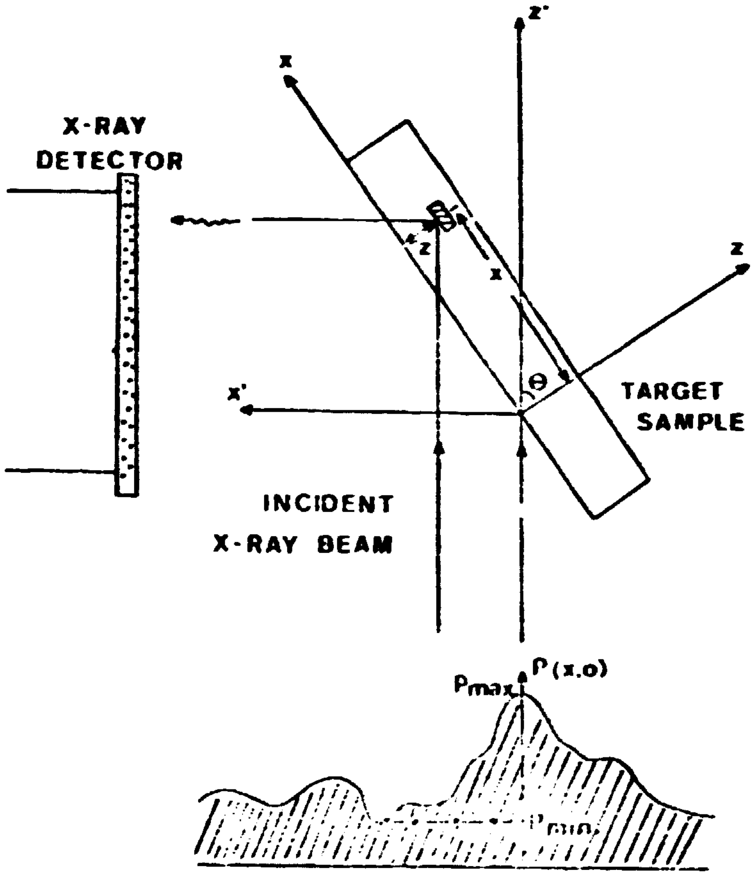

z'
x
X-RAY
DETECTOR
z
x
z
θ
x'
TARGET
SAMPLE
INCIDENT
X-RAY BEAM
P_{max}
$P(x,o)$
P_{min}

Figure 1

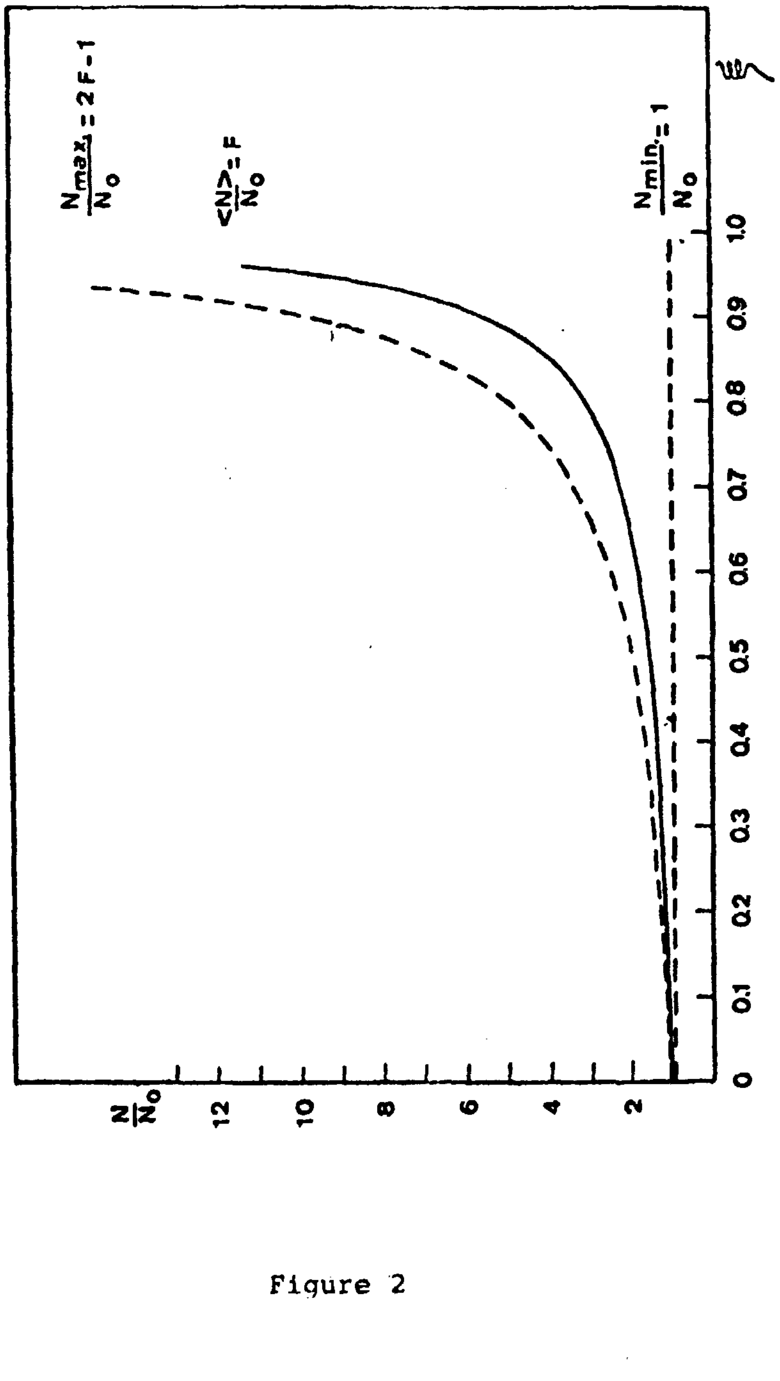
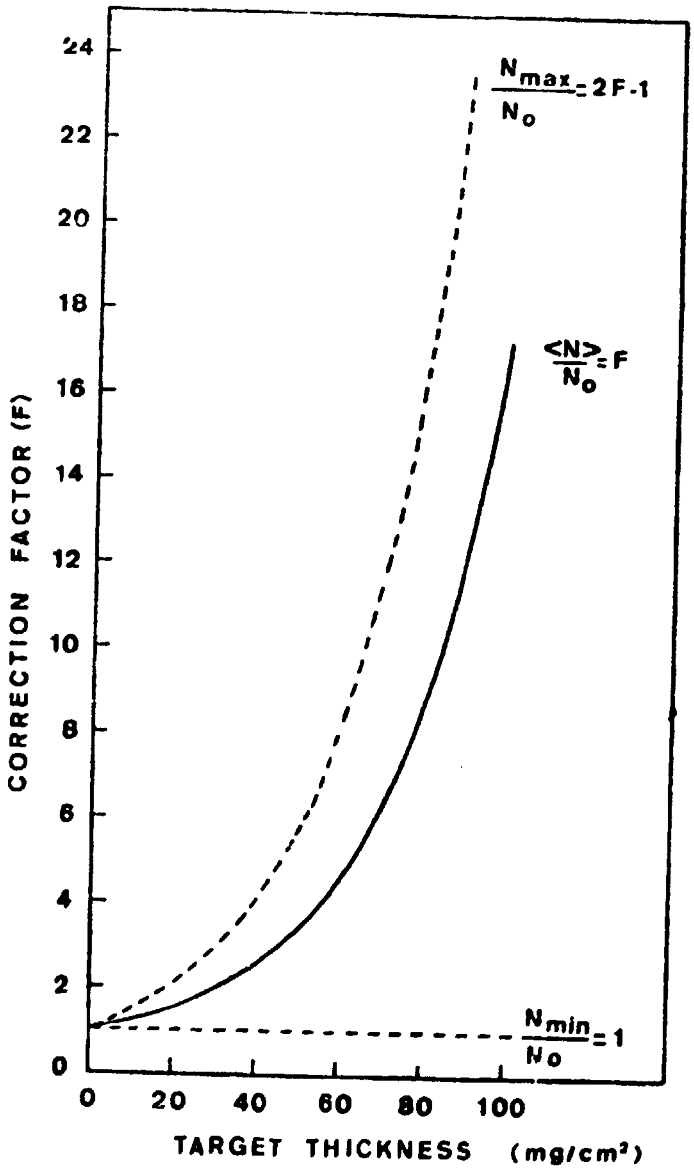

$\frac{N}{N_o}$
12
10
8
6
4
2
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
ξ
$\frac{N_{max.}}{N_o} = 2F-1$
$\frac{<N>}{N_o} = F$
$\frac{N_{min.}}{N_o} = 1$

Figure 2



$\frac{N_{max}}{N_o} = 2F-1$
$\frac{<N>}{N_o} = F$
$\frac{N_{min}}{N_o} = 1$
CORRECTION FACTOR (F)
0
2
4
6
8
10
12
14
16
18
20
22
24
TARGET THICKNESS (mg/cm²)
0
20
40
60
80
100

Figure 3

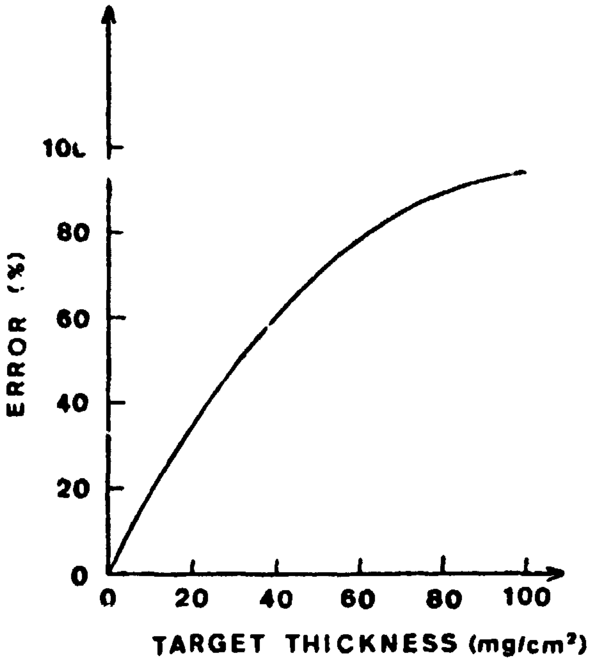


Figure 4