ANL-7078

ANL-7078

MASTER

Argonne National Laboratory

**CORRECTIONS FOR X-RAY INTENSITY DATA
OBTAINED FROM ELECTRON MICROPROBES**

by

Raymond K. Hart

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IN NUCLEAR SCIENCE ABSTRACTS

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ANL-7078
Chemistry
(TID-4500, 47th Ed.)
AEC Research and
Development Report

ARGONNE NATIONAL LABORATORY
9700 South Cass Avenue
Argonne, Illinois 60439

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Program 10.2.2

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November 1965

Operated by The University of Chicago
under
Contract W-31-109-eng-38
with the
U. S. Atomic Energy Commission

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ABSTRACT

The chemical composition of a specimen can be determined quantitatively by electron microprobe analysis, providing suitable corrections are applied to the instrumental data. Corrections to be made fall into two groups: instrumental, and those associated with the interaction of electrons and X rays with the specimen. The nature and application of these corrections to experimental data are discussed.

I. INTRODUCTION

Chemical analysis by means of microprobes can be put on a quantitative basis by applying suitable corrections to the measured intensities of X rays from both the specimen under investigation and a suitable standard. These corrections can be categorized into two groups. The first group can be called instrumental corrections; the second group is related to the interaction of both electron and X-ray beams with the specimen. Details of these corrections are presented in this report.

II. INSTRUMENTAL CORRECTIONS

Instrumental corrections may be listed as follows:

- a. Correction for instrumental drift.
- b. Precision of intensity measurement.
- c. Background determination.
- d. Correction of counting rates.

A. Correction for Instrumental Drift

During a measurement, either the electron-beam current or the specimen current can be kept constant. If the beam current is kept constant, measurements are made under "fixed-time" conditions. If the specimen current is kept constant, "fixed-charge" conditions are realized. These two conditions are not the same because the electron backscattered component varies.¹

Usually measurements are made under "fixed-time" conditions. The electron-beam current is kept constant, either automatically by means of feedback circuits in conjunction with a beam-monitoring device, or by manual adjustment of the appropriate controls.

If the beam current is manually controlled, it is advisable to make a strip-chart recording of this current while counting is in progress.

B. Precision of Intensity Measurement

When X rays are produced by the impingement of electrons onto a specimen, it is assumed that these X rays are emitted in a random manner. If random, then a certain number of counts will be required to give a certain accuracy in the count rate.

If a considerable number of observations are made on a given count rate, the relative standard deviation, RSD, expressed as a percentage, is determined from

$$\text{RSD \%} = 100/N^{1/2},$$

and the probable error, P, expressed as a percentage, is

$$P \% = 68/N^{1/2}.$$

1. Example

Assume that a certain radioactivity runs about 1000 counts/min. Suppose we count for 10 min. The probable error then is

$$P = 0.68/N^{1/2},$$

where $N = 10,000$ counts. Therefore $P = 0.0068$, or the probable error is 6.8 counts/min. It is therefore seen that one should count long enough to get a small probable error.

Stanley² has published a graph (shown in Fig. 1) which gives the number of counts that have to be made for various peak-to-background ratios in order to obtain a given relative standard deviation.

2. Standard Counting Error

A comparison of the standard deviation, S, with the standard counting error, S_c , indicates the reliability of analytical results. For a given number of counts,

$$S = \left[\sum x^2 / (n - 1) \right]^{1/2},$$

Fig. 1. Various Values of K, the Peak-to-background Ratio, and N, the Number of Counts Measured, Necessary to Obtain a Given Relative Standard Deviation (%); after Stanley²

where x is the deviation of any particular value from the average value, and n is the number of measurements made. Also,

$$S_C = \bar{N}^{1/2},$$

where $\bar{N}$ is the average value of the number of counts. Whenever S far exceeds S_C , operating conditions should be improved immediately.

The precision of an intensity measurement depends not only on the total peak height (i.e., the number of counts for peak plus background) but also on the background. In any given counting time, the relative distribution of the counting between peak

and background has to be considered. Thus one must determine the number of counts to be made on the peak and background in order to obtain a certain required net RSD, Δ_D , which may be expressed (as a percentage) as

$$\Delta_D\% = 100(N_L + N_B)^{1/2} / (N_L - N_B),$$

where N_L = number of counts from peak of diffraction line, and N_B = number of background counts. As the composition decreases, the intensity of the spectral line also decreases until it is no longer distinguishable above the background intensity. The point at which this situation is reached is commonly defined by

$$N_L - N_B = 3N_B^{1/2}.$$

That is, the line must be three times as high as the relative standard deviation of the background.

C. Background Determination

The background intensity can be determined by several methods. A common practice used to derive background intensity is to defocus the spectrometer slightly by moving it off the Bragg angle for the characteristic line being investigated. However, this method can lead to large errors, when the peak-to-background ratios are small, since the total profile of the spectral line is not usually known. Thus the amount of defocusing is questionable.

The usually preferred method³ is to place the beam onto another element that differs by only one or two atomic numbers from the element being determined. It has been found that background intensity varies with composition, but that this variance is usually considered to be linear, especially for binary systems.

D. Correction of Counting Rates

After the counting rate is corrected by taking the mean value of the readings for a particular determination, it is then necessary to make corrections for the dead time in the counting circuits, especially when high counting rates are encountered.

In practice, the resolving time is only slightly larger than the actual dead time of a Geiger tube. Therefore both terms (resolving time and dead time) may be used synonymously.

The true counting rate, N , is given by⁴

$$N = N_0 / (1 - N_0 r),$$

where r is the resolving time and N_0 is the observed counting rate. This formula is good for corrections up to 10% and a reasonable approximation up to at least 20%.

Any counter should be operated only in its linear response range. This range is usually specified by the manufacturer. If it is not readily available, it can be determined experimentally by interposing aluminum foils between a monochromatic X-ray source and the detector. Counting rates are then plotted against number of foils. The theoretical curve is given by

$$\log_{10} N_n = \log_{10} N_0 - (\mu x / 2.303) n,$$

where

n = number of foils,

μ = absorption coefficient of X rays in aluminum,

and

x = thickness of each foil.

Geiger tubes usually deviate from linearity when the counting rate is above approximately 200 counts/sec. Scintillation and proportional counters on the other hand are linear up to about 20,000 counts/sec. These figures are only given as a guide and can vary considerably from counter to counter.

III. CORRECTIONS DUE TO INTERACTION OF BEAMS WITH SPECIMEN

Electrons interact with the specimen in the following ways:

- 1) They are in part backscattered.
- 2) They produce continuous radiation (bremsstrahlung).
- 3) They produce heat.
- 4) They produce characteristic spectral emission.

If it is assumed that the efficiency of electrons for producing X rays in all elements is proportional to the mass density of the elements, then as a first approximation, the relative intensity of characteristic X rays resulting from element A in a mixture of elements is given by

$$I'_A/I_A^{0'} = C_A,$$

where I'_A and $I_A^{0'}$ are the characteristic X-ray intensities from specimen and standard, respectively, and C_A is the concentration (by weight) of element A to the first approximation.

As stressed by Ziebold and Ogilvie,⁵ the relative intensity expressed by the above equation is the intensity produced within the specimen and not that emerging from the surface. The initial intensity of X rays generated within the specimen by the element to be analyzed will be modified by a function f , which varies with μ , (the effective mass-absorption coefficient) and ϕ (the X-ray take-off angle).

Additionally, the continuous radiation generated by the beam will lead to further ionizations. Also, additional ionizations of element A will be produced if the wavelengths of characteristic radiations from other elements present in the specimen fall below the absorption edge of element A. The change in intensity of the line being analyzed by the above two effects is termed secondary fluorescence.

A. Absorption Correction

X rays traversing a layer of substance are reduced in intensity by a constant fraction, μ/cm . The absorption coefficient, μ , is defined as the ratio of the intensity loss by absorption to the total original intensity of radiation. After travelling a distance x in the substance, the X-ray intensity is

$$I = I_0 e^{-\mu x},$$

where I_0 is the initial intensity.

The mass-absorption coefficient is given by μ/ρ , where ρ is the density of the material. The most widely used correction for absorption is that presented by Castaing.⁶

In the case of a binary alloy AB, the weight fraction of A can be calculated from the following equation:

$$C_A = \frac{I_{\text{specimen}}}{I_{\text{standard}}} \times \frac{f(\chi)_{\text{standard}}}{f(\chi)_{\text{specimen}}}$$

The absorption parameter f is a function of χ (see Fig. 2), where

$$\chi = \mu'_A \text{ cosec } \phi,$$

ϕ is the take-off angle of the radiation used, and μ'_A is the total absorption coefficient for A radiation in AB, or

$$\mu'_A = W_A \mu_{AA} + W_B \mu_{BA},$$

where W_A and W_B are the assumed weights of the elements.

Fig. 2

Absorption-correction Parameter. The curves were plotted from values given by Birks.⁷

A correction curve can now be constructed for the binary system containing elements A and B. First, several alloys are prepared with different concentrations of A. These alloys are analyzed and checked for homogeneity. Then the measured relative intensities, corrected for absorption, are plotted against the known concentrations. Figure 3 shows such a plot for uranium-niobium alloys, determined by Peterson.³

B. Atomic-number Correction

With specimens containing major constituents that are greatly separated in atomic number, it is often desirable to correct for variations in electron excitation $\phi(\rho x)$, since these elements will have electron deceleration and backscatter properties that will affect the results obtained by microprobe analysis.

Fig. 3. Measured Intensity Ratio I/I_0 vs Composition for Uranium-Niobium Alloys; after Peterson³

Poole and Thomas¹ have shown that parameter α can be given by the relation

$$\alpha = S\lambda,$$

where S is the retardation effect or stopping power as given by Nelms,⁸ and λ is an empirical backscatter parameter similar to that introduced by Castaing.⁶

In a binary alloy,

$$\alpha = \alpha_A/\alpha_B = S_A\lambda_A/S_B\lambda_B.$$

Values for the electron stopping power, S , are given in Fig. 4, and for the empirical backscatter parameter, λ , in Fig. 5.

Fig. 4. Variation of Electron Stopping Power, S , with Atomic Number; after Nelms⁸

Fig. 5. Variation of Empirical Backscatter Parameter, λ , with Atomic Number; after Poole and Thomas¹

When the atomic-number correction is applied, the value of $\chi(\text{alloy})$ used in calculating the absorption correction is given by

$$\chi(\text{alloy}) = \frac{(W_A\mu_{AA} + W_B\mu_{BA}) \operatorname{cosec} \phi}{C_A + C_B\alpha_B/\alpha_A}.$$

C. Secondary-fluorescence Correction

Secondary fluorescence can be produced by the continuous spectrum or by other characteristic radiation. It is a more difficult correction to apply at present since only very limited data are available. For this reason, secondary fluorescence produced by the continuous spectrum is usually not corrected.

Wittry⁹ has published a fluorescence correction, which corrects some of the shortcomings of Castaing's⁶ original derivation. The correction for the K_α of element A being excited by the K_α of element B in a binary alloy is

$$(I_{sf}/I_{pf})_A = G = G_1(Z_B - Z_A V) G_2(C_A Z_B / Z_A) G_3(Z_B),$$

where I_{pf} is the direct primary intensity (with no absorption), I_{sf} is the measured secondary fluorescence (absorption included), Z_A and Z_B are the atomic numbers of elements A and B, respectively, V is the electron potential, and C_A the mass fraction of element A.

When the correction factor G is applied to the general formula for determining C_A , the result is

$$(I/I^0)_A = (f/f^0)(1 + G/f) C_A.$$

At present, Wittry's correction can only be applied to K_α of element A excited by K_α of element B. The fluorescence parameters, G_1 , G_2 , and G_3 , have been computed for 30-keV incident electrons and spectrometer take-off angles of 15.5 and 52.5°.

Birks⁷ has proposed a simple expression for the fluorescence component K_F , which is introduced into the intensity expression in the following way:

$$(I/I^0)_A = C_A(f/f^0)(1 + K_F).$$

Here, K_F is given by

$$K_F = k E_{AB} W_B (\mu_{AB} / \mu_B^i) (V - V_{OB})^2 / (V - V_{OA})^2,$$

where $k = 0.6$, E_{AB} = excitation efficiency (see Appendix 1 of Birks⁷ for tables), and V_{OA} and V_{OB} = excitation energies of elements A and B, respectively.

Examples in the literature have shown that the above expression provides fair agreement between known and measured concentrations.

IV. SUMMARY

Although the absorption, atomic number, and fluorescence corrections can be computed from the expressions given in this paper and the weight fractions of elements in systems can be determined, it is still advantageous to determine a composition/calibration curve experimentally. The corrections to be applied to experimental data then become a straightforward matter, and many uncertainties can be eliminated from the analysis.

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