GEOLOGICAL SURVEY OF CANADA
1842

GEOLOGICAL
SURVEY
OF
CANADA

DEPARTMENT OF MINES
AND TECHNICAL SURVEYS

PAPER 64-50

A SIMPLE METHOD FOR CONVERTING
MEASURED X-RAY INTENSITIES INTO
MASS COMPOSITIONS

(Report and 3 figures)

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1964

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Abstract

In a binary system where the mass absorption coefficients vary from μ_1 to μ_2, if the change is interpreted as being related to $\frac{\mu_2 - \mu_1}{\mu_1}$ rather than $\frac{\mu_2}{\mu_1}$, a simple correction method can be used to convert measured intensities into mass concentrations. The method has been applied to intensity measurements from both x-ray fluorescence and electron microanalyzer data with equally good results. Using this concept and applying the method to microanalyzer data obtained on a series of binary systems (considered to present a significant test of the range of applicability for correction formulas) gave results that were most gratifying. The author concludes that the problem of converting intensity measurements to mass concentration in micro probe analyzers is essentially one of absorption, and proposes a simple method for dealing with this problem. He also concludes that there is some evidence that the absorption of x-radiation is not logarithmic.

A SIMPLE METHOD FOR CONVERTING MEASURED X-RAY INTENSITIES INTO MASS COMPOSITIONS

In a paper presented at the Fourth Ottawa Symposium on Applied Spectroscopy (1)[1], the author described a method whereby variations in the absorption effects on the x-ray fluorescence characteristics line of an element, due to the substitution of one or more other elements in a system, can be compensated for by a simple arithmetic correction. More recently (2), the method was used to determine potassium in micas, where a correction can be applied to compensate for variations in the iron content of the minerals muscovite, phlogopite, and biotite. Data obtained in our laboratory on the electron probe microanalyzer show that this method can also be applied to the ternary system $FeO - SiO_2 - MgO$ when FeO replaces MgO, the SiO_2 remaining essentially constant.

The derivation of the basic equation for the binary system A B:

$$\text{Wt. frac. A} = \frac{\text{Intensity A}}{\text{Intensity A in ref. stand.}} \left(1 + \text{Wt. frac. B x factor}\right) \quad \text{(eqn 1)}$$

from Claisse's equation (3)

$$Im = \frac{kC}{\mu_1 + \mu_2} \quad \text{(eqn 2)}$$

has already been described by Lachance (2) and will not be repeated here.

Because of the limited data available in our own laboratory, data from Ziebold and Ogilvie (4) was used to test the reliability of equation 1 when applied directly to the measured intensities of the ten binary systems where at least two figures for concentration to intensity are given. An example of how the correction factor α can be obtained empirically is shown in Table I below. For this purpose equation 1 for the system Ag/Au is written in the form:

$$\alpha = \frac{\text{Wt. frac. Ag - Ratio} (I/I_o) \text{ Ag}}{\text{Ratio} (I/I_o) \text{ Ag x Wt. frac. Au}} \quad \text{(eqn 3)}$$

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[1] Number of reference listed at end of Paper.

Table I

Calculation of α for Ag/Au System

% Ag*	$\frac{I/I_0*}{C}$	I/I_0	Wt. frac. Ag	Wt. frac. Au	α
80.1	.680	.544	.801	.199	2.38
59.5	.508	.302	.595	.405	2.39

*Data from Ziebold and Ogilvie (4) on two of four alloys in the Ag/Au system.

      If α is now used to compute the weight fraction Ag on all four Ag/Au alloys directly from the measured intensities I/I_0, the results are:

Wt. frac. Ag present	Wt. frac. Ag calculated
.801	.801
.595	.595
.406	.395
.196	.204

i.e., the relation between $\dfrac{I/I_0 \ Ag}{Wt. \ frac. \ Ag}$ is equal to $\dfrac{1}{1+(\alpha \times Wt. \ frac. \ Au)}$.

It was found that α factors could be computed on all ten systems and that the results agreed remarkably well with the true compositions listed.

      An important aspect of equation 1 is that, for a binary system, α can be computed even if I_0 is not known. Actually any two alloys can be used to determine α for the whole system. In this case α is calculated as follows. Select one of the two alloys as a reference standard and express the two measured intensities so that the intensity on the reference standard will be equal to its weight fraction. A "temporary" α can then be calculated from the second alloy provided that the weight fraction Au used in equation 3 is that of the difference between the reference standard and the second alloy. Using this "temporary" α, the intensity that would be obtained on the pure metal Ag. (i.e., I_0 Ag) can be computed, provided that the weight fraction Au is once again expressed as a difference between the reference standard (with proper algebraic signs). From this computed I_0 the "true" I/I_0 ratios can then be computed and α calculated. Since the computation of α from only two alloys cannot be as reliable statistically as that computed from a whole series, the latter method is recommended.

When dealing with a binary system, as Wt. frac. A + Wt. frac. B = 1, equation 1 can be further simplified by substituting (1 - Wt. frac. A) for Wt. frac. B. This gives rise to the general equation

$$C = R \left(1 + \alpha - C \alpha \right) \qquad \text{(eqn 4)}$$

where $\quad C$ = Weight fraction
$\quad R$ = ratio I/I_0
$\quad$ = absorption correction factor (total).

Solving for C, R and α respectively

$$C = \frac{R + R\alpha}{1 + R\alpha} \qquad R = \frac{C}{1 + \alpha - C\alpha} \qquad \alpha = \frac{C - R}{R - CR} \qquad \begin{array}{l}\text{(eqn 5)}\\ \text{(eqn 6)}\\ \text{(eqn 7)}\end{array}$$

The simple relationship between these three variables when α is given a series of fixed values is shown in Table II, and some theoretical curves computed from equation 4 are plotted in Figures 1 and 2.

Table II

Simple expressions relating C to R for fixed values of α .

When $\quad \alpha = 3 \qquad C = \dfrac{4R}{1 + 3R} \qquad\qquad R = \dfrac{C}{4 - 3C}$

$\qquad\qquad = 1 \qquad C = \dfrac{2R}{1 + R} \qquad\qquad R = \dfrac{C}{2 - C}$

$\qquad\qquad = 0 \qquad C = R \qquad\qquad\qquad R = C$

$\qquad\qquad = -.5 \qquad C = \dfrac{.5R}{1 - .5R} \qquad\qquad R = \dfrac{C}{.5 + .5C}$

$\qquad\qquad = n \qquad C = \dfrac{(n + 1) R}{1 + nR} \qquad\qquad R = \dfrac{C}{(n + 1) - nC}$

Note $\qquad$ C being a weight fraction can only have values between 0 and 1.0

$\qquad$ R being the I/I_0 ratio also can only have values between 0 and 1.0

$\qquad$ α being proportional to

$$\frac{\text{total absorption effects due to B - total absorption effects due to A}}{\text{total absorption effects due to A}}$$

will, in practice vary from a value of approx. +5 to approx. -.5.

Figure 1 shows that absorption in x-ray spectrochemical analysis can be considered as falling into five regions.

Region 1. α = 0 (i.e., absorption is constant throughout the system). This is the ideal case where R/C = 1, but is unfortunately rarely encountered.

Region 2. α positive (i.e., the region of net increasing absorption). R/C is less than 1 and some correction must be made, or in the case of x-ray fluorescence, an internal standard must be used.

Region 3. α negative but less than -1 (i.e., the region often called "positive absorption"). Again corrections must be applied because R/C is greater than 1. In x-ray fluorescence, internal standard must be used.

Region 4. α = -1. An unusual system in which absorption is decreasing at the same rate concentration is increasing.

Region 5. α greater than -1. Unusual systems in which absorption is decreasing at a faster rate than concentration is increasing, leading to a negative slope if intensities are plotted against concentrations.

Figure 2 shows the relationship between C and R more clearly. The 45° line represents α = O, a system in which μ is constant or equivalent to region 1 in Figure 1. Curves on the lower side of this line are those of the positive region (Region 2) and curves on the upper side are those with a negative α (Region 3). As the low end members in the Ta/Ru and the W/Rh systems fall remarkably well on a theoretical line computed from α values, and as none of the curves in Figure 2 is logarithmic, the author computed a "theoretical" α factor for a logarithmic series. This was done as follows:

Number	Log	Theoretical "C"
10	1.000	1.0
9	.954	.9
8	.903	.8

etc... for numbers down to 0. By letting log column be equivalent to R, an α factor is computed. Logs of the numbers 9 to 4 yield relatively constant values for α namely -.57. A comparison of the logarithmic curve vs the theoretical curve computed for α -.57 is shown in Figure 3 and the lack of fit at the lower end is apparent. The

author has no experimental data for a system having an α value of -.57 but the Ta/Ru and W/Rh systems mentioned above represent a very high positive absorption, $\alpha = +2.34$ and $+2.05$ respectively, and in both cases the fit between the measured data and its corresponding α curve is excellent. This applies equally for the system computed with the highest negative α factor, -.14 for the Fe/Ni system. The author therefore concludes that the absorption of x-radiation in micro probe and x-ray fluorescence analysis can be explained in much simpler terms if one assumes that the phenomenon is not logarithmic. Further evidence of this can be shown by expanding the series R/C which gives

$$R/C = \frac{1}{\alpha + 1} + \frac{\alpha\,C}{(\alpha+1)^2} + \frac{(\alpha\,C)^2}{(\alpha+1)^3} + \frac{(\alpha\,C)^3}{(\alpha+1)^4} + \frac{(\alpha\,C)^4}{(\alpha+1)^5}$$

The numerator has the characteristics of an exponential series but not the denominator.

In a later paper Ziebold and Ogilvie (5) present further data on binary series. From this data it is evident that α will decrease at higher take-off angles (the x-ray path being shorter) and that α will increase as the excitation voltage is raised (the penetration being deeper the x-ray path longer).

* higher

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(Unpublished)   metallurgical products by x-ray fluorescence.
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(5) Ziebold, T.O., and Ogilvie, R.E.: An empirical method for
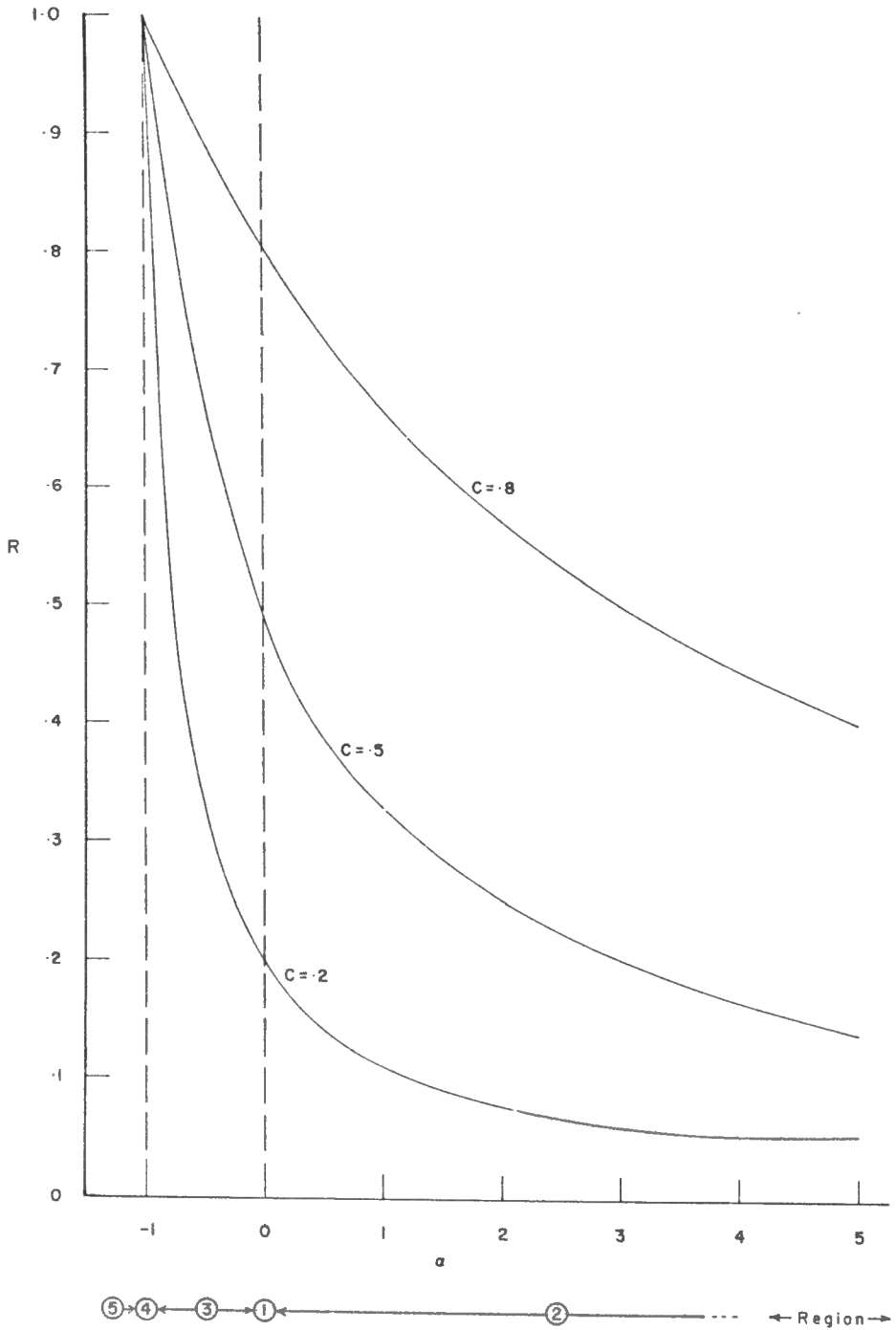electron microanalysis. Anal. Chem. vol. 36,
No. 2, p. 322. (1964).

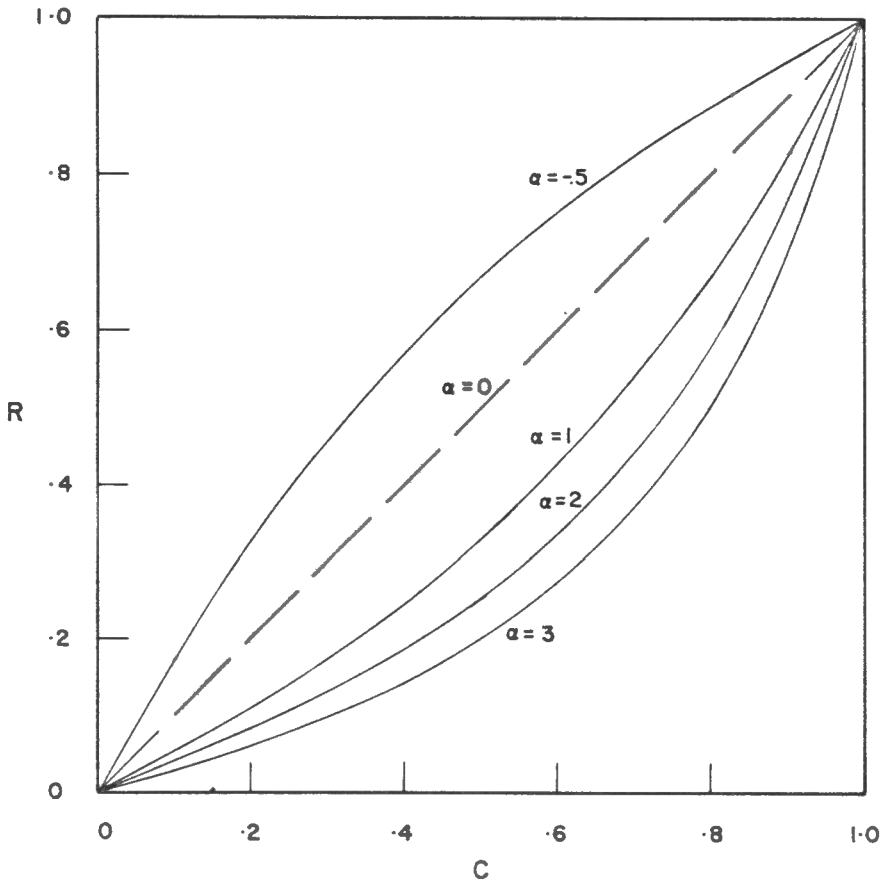Figure 1. Computed R vs. α curves for C = .8, .5 and .2

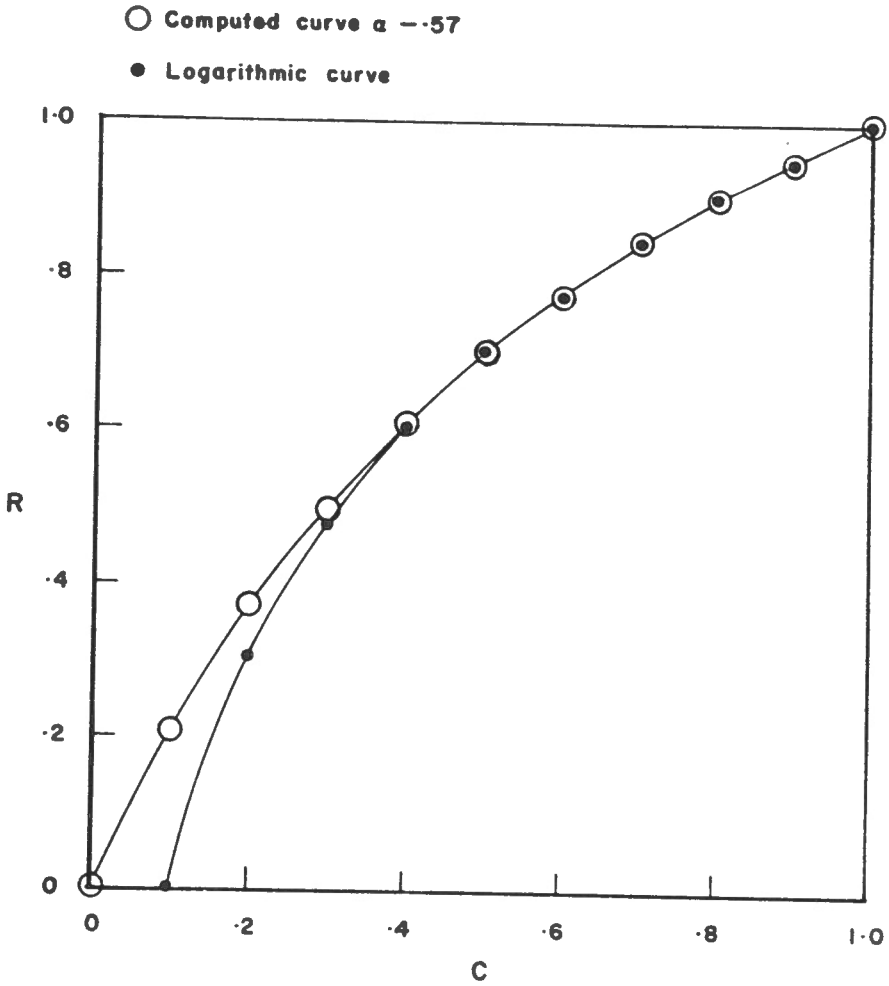Figure 2. Computed R vs. C curves for fixed values of α

Figure 3. Comparison of Logarithmic curve and
a curve computed for $\widehat{\alpha} = -.57$