Title	A Correction Procedure for Quantiative Electron Probe Microanalysis of Ternary Systems : Spiral Iteration
Author(s)	Matsubara, K.
Citation	Memoirs of the Faculty of Engineering, Hokkaido University, 13(Suppl), 127-135
Issue Date	1972-05
Doc URL	http://hdl.handle.net/2115/37900
Type	bulletin (article)
File Information	13Suppl_127-136.pdf

A Correction Procedure for Quantitative Electron
Probe Microanalysis of Ternary Systems
------Spiral Iteration------

K. Matsubara, Dept. of Metal. Eng., Faculty of Eng.,
Hokkaido University, Sapporo, Japan

1. Introduction

The correction for quantitative electron probe mi-
croanalysis is to find out the true concentration C,
which follows from $k = C \times \alpha$, where α is the concentration
factor as a function of the concentration and k is the
measured X-ray intensity ratio. With the calculation
required for converting the intensity ratio to the con-
centration, iteration is generally accompanied. But
during the iteration the calculated value is not always
converged and a number of required iteration can not
be predicted. To avoid these difficulties Sanbongi
and Ohomori's approach for binary systems[1] and Toyota-
chuken's approximation[2] have been proposed. But the
accuracy of the latter method is not completely satis-
factory.

Though the procedure of "spiral iteration" proposed
here is valid only for ternary systems, the concentra-
tion within the accuracy of 0.01 may be calculated af-
ter repeating the iteration eight times usually.

The outline of the procedure is as follows:
1. The "normalized relative intensities", which are in
proportion to the measured intensity ratios of three
elements (a, b and c) in a specimen and the sum of

which is unity, are plotted as point O on a regular
triangle diagram (normalized diagram) with coordinates
of normalized relative intensities (Fig. 1).

2. Alternative isoconcentration curves of two elements
(for example, a and b) surround spirally the point O
on the normalized diagram.

3. Finally when the point O is surrounded closely with
1% isoconcentration curves of two elements the concen-
tration corresponding to that point may be determined
by interpolation.

4. So as to draw surely and shortly their isoconcentra-
tion curves surrounding the point O, the concentration
of the first element (a) for two points next to each
other on the diagram are constant and the concentration
of the second element (b) for the latter point may be
decided by assuming that a difference between the con-
centrations of two points near to each other is approx-
imately in proportion to that between the normalized
relative intensities of the twonpoints.

The detailed procedure will be described in the next
section.

2. The procedure
A. Points O and 1

The measured intensity ratios between the standard
for each element in a ternary alloy and the specimen,
$k_0(a)$, $k_0(b)$ and $k_0(c)$, are converted to the normalized
relative intensities $K_0(a)$, $K_0(b)$ and $K_0(c)$ by the
following equation.

$$K_0(a)=k_0(a)/(k_0(a)+k_0(b)+k_0(c))$$
$$K_0(b)=k_0(b)/(k_0(a)+k_0(b)+k_0(c))$$
$$K_0(c)=k_0(c)/(k_0(a)+k_0(b)+k_0(c))$$

So the normalized relative intensities are in proportion to the measured intensity ratios and the sum of them is unity.

The ternary equilibrium diagram can be represented by a regular triangle with coordinates of concentrations of three elements, while in the procedure proposed here it is convenient to use a regular triangle with coordinates of normalized relative intensities (for short, "normalized intensities") of three elements. So that, the normalized intensities $K_0(a)$, $K_0(b)$ and $K_0(c)$ are plotted as point 0 on the normalized diagram (Fig. 1). This point 0 is the target which must be hit by the following "spiral iteration".

If the concentrations of three elements are equivalent to the measured intensity ratios of them respectively, the point 0 will be identical to the point 1 with the concentration of $K_0(a)$, $K_0(b)$ and $K_0(c)$. Generally point 1 is not identical to point 0 and then the distance between both points is the measure for the correction and point 1 is the starting-point in the spiral iteration.

The concentration of every point except point 0 is rounded to two places of decimals because every 1% isoconcentration curve should be drawn through two points next to each other. Therefore, the concentration of point 1 is $C_1(a) \simeq |K_0(a)|$, $C_1(b) \simeq |K_0(b)|$ and $C_1(c)=1-C_1(a)-C_1(b)$, which are all rounded to two places of decimals.

3

From the chosen concentration we obtain the correction factors, the calculated intensity ratios $k_1(a)$, $k_1(b)$ and $k_1(c)$, and the normalized intensities $K_1(a)$, $K_1(b)$ and $K_1(c)$. Point 1 is1plotted on the diagram with coordinates of $K_1(a)$, $K_1(b)$ and $K_1(c)$. It is also the corresponding point with the concentration of $C_1(a)$, $C_1(b)$ and $C_1(c)$.

B. Points 2 and 3

To draw the $C_1(a)$-isoconcentration curve through points 1 and 2, the concentration of point 2 is to be $C_1(a)$, $C_2(b)$ and $C_2(c)=1-C_1(a)-C_2(b)$. Point 2 or the value of $C_2(b)$ will have to be selected to satisfy the requirement that both points 0 and 1 are on the same side against the $C_2(b)$-curve in order that the $C_2(b)$-curve connecting point 2 with the next point 3 may embrace point 0 together with the $C_1(a)$-curve.

When coordinates of point 2 are $K_2(a)$, $K_2(b)$ and $K_2(c)$, $C_2(b)$ must be found to satisfy the following conditions:

$K_0(b)-K_2(b)>0$

$C_2(b)\simeq C_1(b)\times(K_0(b)-0.01\times n)/K_1(b)$,

where $n=1, 2, 3,$ ----------

The value of $C_2(b)$ is also rounded to two places of decimals.

From the chosen concentration $C_1(a)$, $C_2(b)$ and $C_2(c)$ we obtain the normalized intensities $K_2(a)$, $K_2(b)$ and $K_2(c)$ and thus point 2 plotted on the diagram. The tentative line which connects point 1 with point 2 represents the $C_1(a)$-isoconcentration curve as shown in the figure.

4

Now let us find out point 3 with the concentration of $C_3(a)$, known $C_2(b)$ and $C_3(c)=1-C_3(a)-C_2(b)$. When coordinates of point 3 are $K_3(a)$, $K_3(b)$ and $K_3(c)$, $C_3(a)$ must be also found as the case of point 2 to satisfy the following conditions:

$K_3(a)-K_0(a)>0$

$C_3(a) \simeq C_1(a) \times (K_0(a)+0.01 \times n)/K_2(a)$,

      where $n=1, 2, 3, \text{---------}$.

The value of $C_3(a)$ is also rounded to two places of decimals.

Point 3 is plotted on the diagram with coordinates of the normalized intensities calculated from the above chosen concentration. The tentative line which connects point 2 with point 3 also represents the $C_2(b)$-isoconcentration curve.

For the insufficient information on the quantitative relationship between the normalized intensity and the concentration, point 2 and/or 3 is generally several percent away from point 0 on the diagram.

C. Point 4 to point 8

In succession of $C_1(a)$- and $C_2(b)$-isoconcentration curves, $C_3(a)$-, $C_4(b)$-, $C_5(a)$-,------ curves surround the point 0 spirally and finally the point 0 is surrounded with their 1% curves completely and closely. So as to draw their curves, the concentration of every point may be decided by assuming that a difference between the concentrations of two points near to each other is approximately in proportion to that between the normalized intensities of them.

Accordingly, the next point 4 is to lie on the $C_3(a)$-

isoconcentration curve and is desired to be closely
to the point O in less than 1% of normalized intensity
with respect to b component. When the concentration
of point 4 is $C_3(a)$, $C_4(b)$ and $C_4(c)=1-C_3(a)-C_4(b)$ and
its coordinates are $K_4(a)$, $K_4(b)$ and $K_4(c)$, $C_4(b)$ can
be obtained as follows. As the concentrations and
normalized intensities of points 1, 2 and 3 are known,
owing to the proportionality between the difference
of concentrations and that of normalized intensities
of two points, the concentration of b element of point
O, $C_0(b)$ can be expressed approximately by the next
equation:

$$C_0(b) \simeq C_2(b) + (C_1(b)-C_2(b)) \times (K_0(b)-K_3(b))/(K_1(b)-K_2(b)).$$

In order that $C_4(b)$ may be closely to $C_0(b)$ within
1%, $0.01 \geq C_4(b)-C_0(b) \geq 0$.

Hence, $C_4(b)$ may be decided to satisfy the following
conditions:

$$0.01 \geq C_4(b) - \{C_2(b)+(C_1(b)-C_2(b))\times(K_0(b)-K_3(b))/(K_1(b)-K_2(b))\} \geq 0$$

The value of $C_4(b)$ is rounded to two places of dec-
imals.

On the diagram is plotted point 4 with coordinates
of the normalized intensities calculated from the cho-
sen concentration. The tentative line which connects
point 3 with point 4 represents the $C_3(a)$-isoconcentra-
tion curve.

As the process for every point after point 4 being
plotted on the diagram is analogus to that of point 4,
only the summary of the process is shown below.

	Point 5	Point 6	Point 7	Point 8
Coordinate	$K_5(a)$	$K_6(a)$	$K_7(a)$	$K_8(a)$
	$K_5(b)$	$K_6(b)$	$K_7(b)$	$K_8(b)$
	$K_5(c)$	$K_6(c)$	$K_7(c)$	$K_8(c)$
Concentration	$C_5(a)$	$C_5(a)$	$C_7(a)$	$C_7(a)$
	$C_4(b)$	$C_6(b)$	$C_6(b)$	$C_4(b)$
	$C_5(c)$	$C_6(c)$	$C_7(c)$	$C_8(c)$
Isoconcentration curve	$C_4(b)$	$C_5(a)$	$C_6(b)$	$C_7(a)$
Concentration decided	$C_5(a)$	$C_6(b)$	$C_7(a)$	------

Requirement for the decision:

$C_5(a)$: $0.01 \geq \{C_3(a)-(C_3(a)-C_1(a)) \times (K_4(a)-K_0(a))/$
$(K_3(a)-K_2(a))\}-C_5(a) \geq 0$

$C_6(b)$: $0.01 \geq \{C_4(b)-(C_4(b)-C_2(b)) \times (K_5(b)-K_0(b))/$
$(K_4(b)-K_3(b))\}-C_6(b) \geq 0$

$C_7(a)$: $0.01 \geq C_7(a)-\{C_5(a)+(C_3(a)-C_5(a)) \times (K_0(a)-$
$K_6(a))/(K_4(a)-K_5(a))\} \geq 0$

D. Determination of true concentration

As the rusult of the above, point O lies in the
quadrilateral whose vertices are points 5, 6, 7 and
8.   Since $C_7(a)-C_5(a)=C_4(b)-C_6(b)=0.01$, the concen-
tration of point O, that is, the true concentration
of a specimen can be determined by interpolation
within the accuracy of 0.01.

While in the above-described example we have pro-
ceeded counterclockwise to the center of spiral,
point O, in the clockwise case we may also act on the
same procedure.

If the normalized diagram with all 1% isoconcentra-
tion curves for an objective ternary system is pro-

vided, the true concentration can be determined read-
ly with the diagram.   But to do so, all calculations
for 5000 points are required and are tedious tasks.

References

1) K. Sanbongi and Y. Ohomori: Bull. Research Inst.
   of Mineral Dressing and Metallurgy, Tohoku Univer-
   sity, 21, 183 (1965)

2) A. Isogai, Y. Oda and K. Nakajima: Jap. J. Appl.
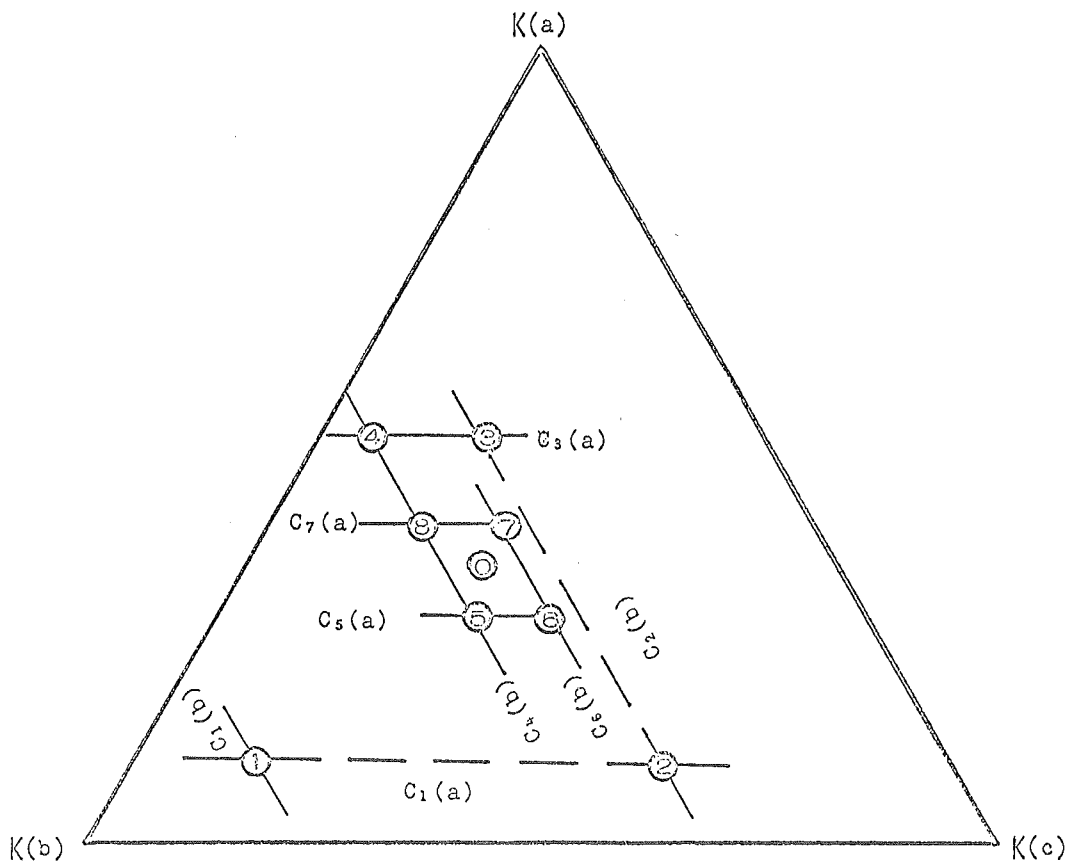   Phys., 40, 49 (1971)

Fig. 1 Schematic illustration of the "spiral iteration" on the
diagram with coordinates of "normalized relative inten-
sities".