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A Correction Procedure for Quantitative Electron Probe Microanalysis of Ternary Systems

-----Spiral Iteration-----

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1. Introduction

The correction for quantitative electron probe microanalysis 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 concentration, 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 systems¹⁾ and Toyota-chuken's approximation²⁾ have been proposed. But the accuracy of the latter method is not completely satisfactory.

Though the procedure of "spiral iteration" proposed here is valid only for ternary systems, the concentration within the accuracy of 0.01 may be calculated after 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 0 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 0 on the normalized diagram.

3. Finally when the point 0 is surrounded closely with 1% isoconcentration curves of two elements the concentration corresponding to that point may be determined by interpolation.

4. So as to draw surely and shortly their isoconcentration curves surrounding the point 0, 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 concentrations of two points near to each other is approximately in proportion to that between the normalized relative intensities of the two points.

The detailed procedure will be described in the next section.

2. The procedure

A. Points 0 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 O on the normalized diagram (Fig. 1). This point O 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 O 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 O 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 O 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 $C_1(a) \approx |K_0(a)|$, $C_1(b) \approx |K_0(b)|$ and $C_1(c) = 1 - C_1(a) - C_1(b)$, which are all rounded to two places of decimals.

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 is plotted 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:

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

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

where $n = 1, 2, 3, \dots$

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.

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:

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

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

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 0 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 0, $C_0(b)$ can be expressed approximately by the next equation:

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

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 decimals.

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

As the process for every point after point 4 being plotted on the diagram is analogous 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 result 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 concentration 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 proceeded 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% isoconcentration curves for an objective ternary system is pro-

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

References

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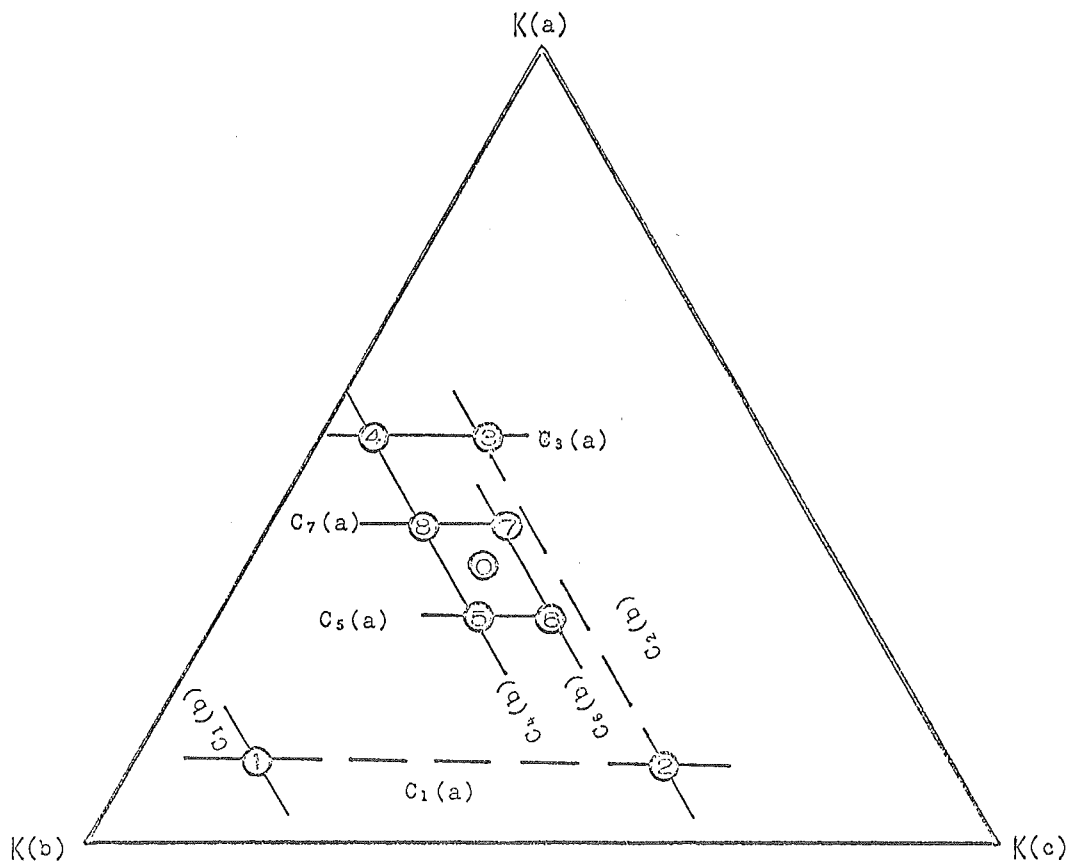


Fig. 1 Schematic illustration of the "spiral iteration" on the diagram with coordinates of "normalized relative intensities".