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X-Ray-Quantitative Analysis of Multiphase Systems

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The equation by which the X-ray diffracted intensity of one component is related to the concentrations of all components is unsuitable for studying multiphase systems without an internal standard. It is shown that even in such a case the concentration of one component can be expressed as a function of the characteristic X-ray diffracted intensities of all components of a multiphase system. One of them is chosen, at will, as the standard.

INTRODUCTION

A number of authors have treated the quantitative X-ray analysis both in theory and experimentally. The most outstanding work of Alexander and Klug[1,2] deals with the connection between the X-ray diffracted intensity and the concentration of one component in a multiphase system, which is given by the following equation:

$$I_i = K_i \cdot \frac{x_i/\varrho_i}{\sum\limits_i \mu_i^* \cdot x_i} \tag{1}$$

where

- I_i intensity of the X-ray diffracted i-th component
- ϱ_i density of the i-th components
- μ_i^* mass absorption coefficient of the i-th component
- K_i constant depending upon the nature of component i and the geometry of the apparatus
- x_i the weight fraction of the i-th component

This equation may be applied successfully in the quantitative analysis of two-component systems, and also for multicomponent ones if an internal standard is used.

Without the use of an internal standard the above equation is unsuitable for studying multicomponent systems because it relates the intensity of one component to the concentrations of all components:

$$I_i = f_1 (x_1, x_2, \ldots x_i \ldots) \tag{2}$$

A more convenient equation would be such one by which the concentration of one component is expressed as a function of the characteristic X-ray diffracted intensities of all components:

$$x_i = f_2 (I_1, I_2, \ldots I_i \ldots) \tag{3}$$

It is the purpose of the present work to derive such an equation.

THE THEORETICAL PART

One of the components of a multiphase system may be regarded as the standard (s). According to eq. (1) one has for the standard:

$$I_s = K_s \frac{x_s/\varrho_s}{\sum\limits_i \mu_i^* \cdot x_i} \tag{4}$$

It holds by analogy for any other component j ($j \neq s$):

$$I_j = K_j \frac{x_j/\varrho_j}{\sum\limits_i \mu_i^* \cdot x_i} \tag{5}$$

By dividing equation (5) with eq. (4) one obtains

$$\frac{I_j}{I_s} = \frac{K_j \cdot \varrho_s}{K_s \cdot \varrho_j} \cdot \frac{x_j}{x_s}, \tag{6}$$

or

$$\frac{x_j}{x_s} = \alpha_{j,s} \cdot \frac{I_j}{I_s} \tag{7}$$

where

$$\alpha_{j,s} = \frac{K_s}{K_j} \cdot \frac{\varrho_j}{\varrho_s} \tag{8}$$

is a constant that only depends on these two components and on the geometry of the apparatus.

The equation (7) is used in the internal standard method when $x_s = \text{const.}$, with a linear dependence of x_j on I_j/I_s. In our case, there is a linear dependence of the concentration ratio x_j/x_s on the intensity ratio I_j/I_s.

Taking into account all the j components one can write according to eq. (7):

$$1 + \sum_j \frac{x_j}{x_s} = 1 + \sum \alpha_{j,s} \frac{I_j}{I_s} \tag{9}$$

Also, because $x_s + \sum\limits_j x_j = 1$, one obtains

$$\frac{1}{x_s} = 1 + \sum_j \alpha_{j,s} \frac{I_j}{I_s}, \tag{10}$$

or

$$x_s = \frac{1}{1 + \sum\limits_j \alpha_{j,s} \frac{I_j}{I_s}}, \tag{11}$$

which directly connects the concentration of the standard component x_s with the intensities of all components.

In the same way one can relate any concentration x_j to the intensities of the components.

On multiplying eq. (10) by x_j one gets

$$\frac{x_j}{x_s} = x_j \left(1 + \sum_j \alpha_{j,s} \frac{I_j}{I_s}\right) \tag{12}$$

or in respect to (7)

$$\alpha_{j,s} \frac{I_j}{I_s} = x_j \left(1 + \sum_j \alpha_{j,s} \frac{I_j}{I_s}\right) \tag{13}$$

and finally

$$x_j = \frac{\alpha_{j,s} \dfrac{I_j}{I_s}}{1 + \sum_j \alpha_{j,s} \dfrac{I_j}{I_s}} \tag{14}$$

DISCUSSION

The equations (11) and (14) give the required interdependence of the concentration of anyone among the components and the characteristic intensities of all components. One can choose, in general, anyone of the constituents to be the standard component. In doing so one should bear in mind the concentrations of the components and the intensities of their characteristic reflections. It is desirable to take for the standard component the one that would give the strongest intensity taking into account the two above mentioned factors.

As the equations (11) and (14) require the determination of $\alpha_{j,s}$ it is necessary to do calibration measurements in order to obtain the j-straight lines according to eq. (7).

In a definite multicomponent system a change of the standard component can be done. The constants $\alpha_{j,s}$ determined on the basis of one particular standard component can be transformed in the following way:

$$\beta_{j,s_2} = \frac{\alpha_{j,s_1}}{\alpha_{s_2,s_1}} \tag{15}$$

where:

α_{j,s_1} the coefficient of anyone component determined on the basis of the first standard component

α_{s_2,s_1} the coefficient of the component newly chosen as a standard one

β_{j,s_2} the coefficient of anyone component with the newly determined standard component.

An application of eqs. (11) and (14) and the last transformation is shown in the forthcoming paper[3] where a four-component system is dealt with.

REFERENCES

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IZVOD

Rendgenska kvantitativna analiza višekomponentnog sistema

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Izvedene su jednadžbe (11) i (14) koje povezuju koncentraciju bilo koje komponente jednog višekomponentnog sistema s intenzitetima karakterističnih difraktiranih zraka.

Za razliku od metode unutarnjeg standarda, kod primjene ove metode može se kao standardna komponenta uzeti svaka prisutna komponenta. Kako navedene jednadžbe zahtijevaju određivanje α_{js} potrebno je izvesti baždarna mjerenja da se dobije j baždarnih pravaca, koji se izračunavaju na osnovu jednadžbe (7).

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