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Note

Possible Correction of Preferential Orientation of Crystallites in Quantitative X-ray Determination by Means of Basal Reflections

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In a previously published work¹ we have described a method by which the intensity of an X-ray reflection that has been strengthened by preferential crystallite orientation can be corrected by measuring its ratio to the intensity of a reflection that is weakened by the same effect. In this way the intensity can be corrected to that given by a sample with a selected definite degree of preferential orientation and then applied in quantitative analysis.

With some crystalline compounds, however, the only strong reflections in the X-ray patterns of randomly oriented samples are those resulting from



Fig. 1. X-ray pattern of kaolinite; a) high degree and b) low degree of preferential crystallite orientation. K_1 corresponds to 001 reflection, K_2 corresponds to 002 reflection.

lattice layer parallel to cleavage planes (in most cases these are basal $(00l)$ reflections). These reflections are strengthened by preferential orientation whilst those that become weaker (mostly hkl reflections), are not suitable for X-ray measurement. The correction cannot be made in the previously stated way, and another method has to be applied.

Figure 1 shows the change of intensity of particular reflections caused by the change in degree of preferential orientation of crystallites in kaolinite. In the samples with the lower degree of preferential orientation b both basal reflections are weaker than those in the sample with a high degree of preferential orientation a . Although the intensities of two basal reflections for kaolinite in the sample with the high degree of preferential orientation were not increased in the same proportion, the essential equation for correction of preferential orientation is valid for each of these reflections.

$$\frac{(I_{p1})_o}{I'_{p1}} = A_1 q_1 + B_1 \quad (1)$$

and

$$\frac{(I_{p2})_o}{I'_{p2}} = A_2 q_2 + B_2 \quad (2)$$

where $(I_{p1})_o$ and $(I_{p2})_o$ are the intensities of basal reflections belonging to a definite degree of preferential orientation of crystallites,
 I'_{p1} and I'_{p2} the intensities of basal reflections belonging to any degree of preferential crystallite orientation,
 q_1 and q_2 ratios of intensities of hkl reflections to those of basal reflections in a sample with any degree of preferential orientation of crystallites,
 A_1, B_1, A_2, B_2 correction constants.

Equations (1) and (2) can be written in the form proposed by F. W. Locher² *i. e.*

$$(I_{p1})_o = A_1 I'_{np} + B_1 I'_{p1} \quad (3)$$

$$(I_{p2})_o = A_2 I'_{np} + B_2 I'_{p2} \quad (4)$$

where I'_{np} is the intensity of hkl reflection in a sample with any degree of preferential crystallite orientation.

By eliminating I'_{np} in these equations we get

$$A_2 (I_{p1})_o - A_1 (I_{p2})_o = A_2 B_1 I'_{p1} - A_1 B_2 I'_{p2} \quad (5)$$

and dividing equation (5) by the expression $[A_2 (I_{p1})_o - A_1 (I_{p2})_o] \cdot I'_{p1}$

$$\frac{1}{I'_{p1}} = a_1 \frac{I'_{p2}}{I'_{p1}} + b_1 = a_1 q_{21} + b_1 \quad (6)$$

where:

$$a_1 = \frac{A_1 B_2}{A_2 (I_{p1})_o - A_1 (I_{p2})_o}$$

$$b_1 = \frac{A_2 B_1}{A_2 (I_{p1})_o - A_1 (I_{p2})_o}$$

$$q_{21} = \frac{I'_{p2}}{I'_{p1}}$$

If a definite degree of preferential orientation or a definite ratio of intensities of basal reflections I'_{p2}/I'_{p1} (q_{21}) is taken as referential and all intensities belonging to samples with all other degrees of preferential orientation are then deduced to this referential intensity, *i. e.* if

$$\frac{1}{(I'_{p1})_o} = a_1 (q_{21})_o + b_1 \quad (7)$$

then dividing equation (6) by equation (7) we get the expression

$$\frac{(I'_{p1})_o}{I'_{p1}} = A_{21} q_{21} + B_{21} \quad (8)$$

where

$$A_{21} = \frac{a_1}{a_1 (q_{21})_o + b_1}$$

$$B_{21} = \frac{b_1}{a_1 (q_{21})_o + b_1}$$

Equation (8) makes it possible to correct the intensity of the basal reflection belonging to a sample with any degree of preferential orientation to the intensity of the same reflection belonging to a selected definite degree of preferential crystallite orientation. An analogous equation can be derived for the correction of the second basal reflection, *i. e.*

$$\frac{(I'_{p2})_o}{I'_{p2}} = A_{12} q_{12} + B_{12} \quad (9)$$

where

$$q_{12} = \frac{I'_{p1}}{I'_{p2}}$$

This theory was experimentally verified on kaolinite with two samples of different origin. Calcite was used as standard substance to deduce the intensities of kaolinite reflections to the same scale. Data for ratios of intensities of basal reflections needed in computing the calibration constants a and b from equation (7) were obtained on samples with a different degree of preferential orientation. Figure 2 presents the data from which correction constants were calculated by the least square method. These constants serve to correct the intensity of the first basal reflection for any sample of kaolinite on the intensity belonging to a definite degree of preferential orientation of crystallites (definite I'_{p2}/I'_{p1}) and this intensity is then used for quantitative determination. Somewhat striking variations in experimental data can be explained by the fact that crystallites of the standard substance (calcite) though still succumb slightly to the effect of preferential orientation and that the intensities for kaolinite reflections I'_{p1} and I'_{p2} differ but little one from the other.

Thus the proposed method for correcting intensities supplies the means to determine those compounds that show a pronounced tendency for preferen-

tial crystallite orientation; the use of x-ray quantitative analysis for these substances would be practically impossible without such a correction. The general

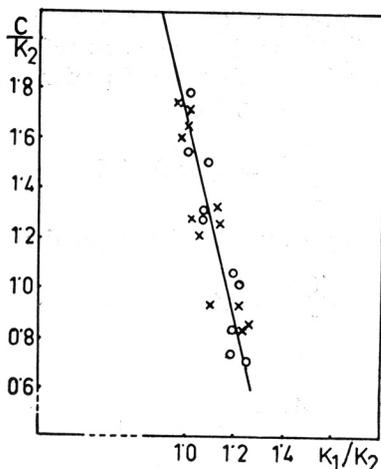


Fig. 2. The calibration graph for determining the constants a_1 and b_1 ; $K_1 = Ip_1$, $K_2 = Ip_2$.

formula for the correction and for that type of preferential orientation follows the expression analogous to the one stated in the earlier work¹ viz.:

$$(I_p)_o = f \cdot I'_p \quad (10)$$

only that here f acquires another form, i. e.:

$$f = A_{21} \frac{I'_{p2}}{I'_{p1}} + B_{21} \quad (11)$$

because I'_{p2}/I'_{p1} expresses the ratio of intensities of two basal reflections become stronger disproportionately owing to the increased degree of preferential orientation of crystallites in the analysed sample.

REFERENCES

1. A. Bezjak and I. Jelenić, *Croat. Chem. Acta* **37** (1965) 255.
2. F. W. Locher, Private communication.

IZVOD

Korekcija na preferiranu orijentaciju kristalita u kvantitativnoj rendgenskoj analizi pomoću bazalnih refleksa

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Izvedene su jednadžbe za korekciju intenziteta analitičkih refleksa u slučaju kvantitativne rendgenske analize supstanci s naglašenom tendencijom preferiranog orijentiranja kristalita. Prema tim jednadžbama korekcija se vrši na osnovi odnosa intenziteta bazalnih refleksa i korekcionih konstanti koje se moraju unaprijed odrediti. Korekzione konstante određuju se iz niza podataka za odnose intenziteta bazalnih refleksa koji se dobiju na uzorcima s različitim stupnjem preferirane orijentacije kristalita. Metoda je demonstrirana na kaolinitu.

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