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*Note*

# Determination of Correction Factor for Preferential Crystallite Orientation in Quantitative X-ray Analysis of Calcium Hydroxide

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In the work of A. Bezjak and I. Jelenić[1] an expression was derived for correcting the intensities of X-ray reflections from samples with preferential crystallite orientation. This expression is:

$$(I_p)_o = I'_p \cdot f \tag{1}$$

where $I'_p$ is the intensity of the analytical reflection which becomes stronger due to preferential orientation of crystallites in a sample of any degree of such an orientation,

$(I_p)_o$ the intensity of analytical reflection which becomes stronger because of preferential orientation of crystallites in a sample with a selected definite degree of preferential orientation

$f =$ correction factor.

In equation (1) the correction factor is

$$f = Aq + B \tag{2}$$

where $q = \frac{I'_{np}}{I'_p}$ *i. e.* the ratio between the intensity of the reflection which becomes weaker and the one which becomes stronger because of preferential orientation of crystallites in a sample of any degree of preferential orientation.

$A$ and $B$ are correction constants.

The factor, $f$, changes with alteration of the degree of preferential orientation (depending upon the change of the ratio, $q$), and makes it possible to deduce the intensity of the analytical reflection $(I_p)_o$ belonging to the sample with a selected degree of preferential orientation from that of the very same reflection obtained from a sample with any degree of preferential orientation ($I'_p$); thus those errors in quantitative X-ray diffraction analysis that arise from preferential crystallite orientation can be minimized. The correction constants $A$ and $B$ are obtained from a series of samples with a different degree of preferential orientation from the equation:

$$\frac{(I_p)_o/I_s}{I'_p/I_s} = Aq + B \tag{3}$$

where $I_s =$ the intensity of standard reflection.

In the mentioned work[1] the experimental determination of constants $A$ and $B$ was carried out on a sample of calcium hydroxide with a strongly pronounced tendency for preferential orientation of crystallites; from which preparates with the low degree of preferential orientation desireable for X-ray quantitative analysis could not be obtained.

In their discussion of X-ray spectrometric technique the authors state that only those crystallites having crystallographic planes parallel to the surface of the sample can contribute to the measured intensity of the corresponding diffraction maximum. As a result many crystallites do not contribute to any measured intensity. It is generally assumed that the statistical distribution between those orientations that can and those that cannot contribute to measured intensity is nearly the same in all samples of one and the same substance. However, in the case of calcium hydroxide crystallites have been noted which differ in morphology and in their tendency to orient preferentially; consequently, it may not be true that the distribution of orientations is always the same for calcium hydroxide. It was, therefore, necessary to determine whether the linear function given in equation (1) is valid for the intensity correction of all types of calcium hydroxide regardless of the differences in size and form of the crystallites; in other words, it was necessary to verify that the constants $A$ and $B$ have the same values for all forms of calcium hydroxide.

In order to check the influence of possible variations in the statistical distribution of crystallites around the most favourable preferential position and to obtain experimental data for the determination of constants $A$ and $B$ in case of both low and high degree of preferential orientation of crystallites, we prepared a series of samples of calcium hydroxide manifesting a different tendency for preferential orientation *i. e.* with different particle size and form of crystallites.

Various methods of preparation served to produce five types of calcium hydroxide. Some of these preparations are described in the work of Copeland and Bragg[2]; the preparations of all five types are presented in detail in the work on influence of particle size of crystallites in quantitative X-ray determination of calcium hydroxide[3]. Calcium hydroxide in hydration of alite pastes had the greatest tendency for preferential orientation; calcium hydroxide precipitated from hot solution showed less tendency to preferential orientation; that produced by hydration in moist atmosphere showed the least preferential orientation.

A number of specimens with a different degree of preferential orientation of crystallites was prepared from each of the mentioned samples of calcium hydroxide. Experimental data for $I'_p/I_s$ and $I'_{np}/I'_p$ served to determine graphically the $(I_p)_o$ for every type of calcium hydroxide separately. $(I_p)_o$ was selected in such a way as to be related to the degree of preferential orientation corresponding to $I'_{np}/I'_p = 1.490$. This ratio was taken as reference because in determining the $(I_p)_o$ on the type of calcium hydroxide which was first used a lower degree of preferential crystallite orientation could not be obtained.

For graphical determination experimental data were entered in the diagram according to the equation

$$\frac{I'_s}{I'_p} = a' \frac{I'_{np}}{I'_p} + b' \tag{4}$$

where $$a' = \frac{A}{(I_p)_o/I_s} \qquad b' = \frac{B}{(I_p)_o/I_s}$$
(from equation 3).

Calcite was used as standard substance in all cases except for calcium hydroxide prepared by hydration of alite where quartz was added. From the linear dependence obtained for every type of calcium hydroxide the $I_s/(I_p)_o$ was read for $I'_{np}/I'_p = 1.490$ and then used in calculating the data needed to find the correction constants $A$ and $B$ from the equation (3).

These data are graphically presented on Fig. 1 for all types of calcium hydroxide. Common correction constants $A$ and $B$ were calculated by the least square method and the values are:

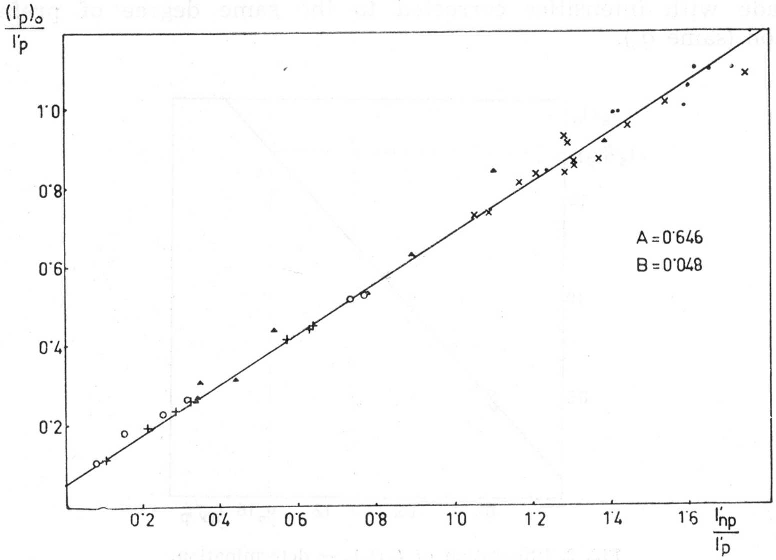

**Fig. 1.** Calibration graph for determining common calibration constants $A$ and $B$ of $Ca(OH)_2$.

$$A = 0.646$$

$$B = 0.048$$

The results suggest that the same linear function applies to all samples regardless of their disposition to orient preferentially, *i. e.* the correction of intensity can be calculated from the same constants $A$ and $B$. However, the dispersion of experimental points round the most likely line is somewhat larger than that around the lines determined for each type of calcium hydroxide separately. The common correction constants $A$ and $B$ are therefore different from those obtained previously when they were calculated for one type of calcium hydroxide only[1].

Although there are differences in value of correction constants $A$ and $B$ for particular types of calcium hydroxide, the correction factor $f = A \cdot I'_{np}/I'_p + B$ does not differ significantly whether calculated from individual or from common correction constants. For very precise correction of preferential orientation it would be best, of course, to determine constants $A$ and $B$ for every type of calcium hydroxide separately. Thus quantitative X-ray determination of calcium hydroxide in an unknown sample consists in mixing the sample with standard substance and making preparates with different degrees of preferential orientation, which are then X-rayed. The most likely line is determined from experimental data for $I'_s/I'_p$ and $I'_{np}/I'_p$ and then used to find out $I_s/(I_p)_o$ for a selected definite degree of preferential orientation (defined by the ratio $I'_{np}/I'_p$). Figure 2 shows how this is done and where we get for $I'_{np}/I'_p = 1.490$ ($q_o$) the value $I_s/(I_p)_o = 1.735$. This $(I_p)_o$ can then be employed for determination of the concentration if the calibration graph has been made with intensities corrected to the same degree of preferential orientation (same $q_o$).

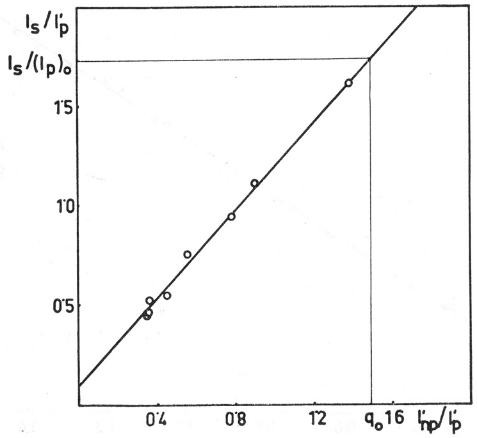

Fig. 2. Illustration of $I_s/(I_p)_o$ — determination.

The work carried out so far makes us conclude that the experimental points on Fig. 1 would be fitted better if the linear function for $f = Aq + B$ was replaced by a parabola with a slight curvature or with the general expression

$$f = Aq^2 + Bq + C$$

This supposition has not yet been theoretically explained but will be taken into consideration in further work on quantitative X-ray determination of calcium hydroxide.

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## REFERENCES

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3. A. Bezjak, T. Gaćeša, and I. Jelenić, *Croat. Chem. Acta* **39** (1967) (in press).

## IZVOD

### Određivanje faktora za korekciju na preferiranu orijentaciju kristalita u kvantitativnoj rendgenskoj analizi $Ca(OH)_2$

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Određene su zajedničke konstante faktora za korekciju na preferiranu orijentaciju kristalita u kvantitativnoj rendgenskoj analizi $Ca(OH)_2$. Određivanje je izvršeno za čitavo područje varijacije intenziteta uzrokovane preferiranom orijentacijom. Upotrebljeno je nekoliko tipova $Ca(OH)_2$ s različitom sposobnošću preferirane orijentacije kristalita. Računanje je provedeno na osnovi eksperimentalnih podataka za odnose intenziteta koji su dobiveni na uzorcima s različitim stupnjem preferirane orijentacije. Prikazan je način najtočnijega korigiranja intenziteta analitičkih refleksa na preferiranu orijentaciju kristalita.

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