The Application of the Doping Method in Quantitative X-Ray Diffraction Analysis

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The basic equation relating the intensity of the diffracted X-rays to the weight fraction of respective component and absortive properties of the sample having once been given by Alexander and Klug[1], numerous techniques developed for quantitative X-ray diffraction analysis. Besides the well known, simple internal- and external-standard technique, a simultaneous way of analysis for several components has also been worked out[2-4]. In spite of advantages of the commonly used internal-standard method, there are cases in which this method cannot be successfully applied. For example, for systems containing components with a great number of diffraction maxima it is not easy to find an internal standard whose diffraction maxima will not overlap with diffraction maxima of the components contained in the sample. In their work on the quantitative X-ray diffraction analysis, among other techniques, Copeland and Bragg[2] also described a technique which includes the dilution of the sample. Instead of using an internal standard, the authors diluted the sample with known amounts (x_D) of the unknown component (x_0). After the dilution the weight fraction of the x_0 component is:

$$\frac{x_0 + x_D}{1 + x_D} \tag{1}$$

and the weight fraction of any other component (x_i) is

$$\frac{x_i}{1 + x_D} \tag{2}$$

If we now apply the equation of Alexander and Klug[1], the ratio of X-ray diffraction intensities (I_0/I_i) belonging to the mentioned components will be:

$$\frac{I_{0,m}}{I_{i,n}} = \frac{K_{0,m}}{K_{i,n}} \cdot \frac{x_0 + x_D}{x_i} \tag{2}$$

i. e.

$$\frac{I_{0,m}}{I_{i,n}} = \text{const.} \, (x_0 + x_D) \tag{4}$$

Several $I_{0,m}/I_{i,n}$ ratios belong to several consecutive dilutions, and a graph of $I_{0,m}/I_{i,m}$ plotted as a function of x_D is a straight line from which x_0 can

be read as the intercept on the x-axis. Equation (4) is valid for all possible combinations of diffraction maxima. The result of maltiple-ratio analysis is a group of straight lines having different slopes, with the same absolute value of the x_D-axis intercept, which is in fact the value of x_0.

The technique just described includes several consecutive dilutions of the sample and is therefore rather time-consuming. Our work deals with a technique of X-ray quantitative determination in which a single dilution of the sample, i. e. a single doping of the component to be determined, suffices to get satisfactory results of weight fraction. This technique includes all possible ratios between the intensities belonging to the component to be determined and those belonging to all other components.

Before doping we have the following relation between the weight fractions and intensity ratio[1]:

$$\frac{x_i}{x_0} = \alpha_{m,n} \left(\frac{I_{i,m}}{I_{0,n}} \right) \tag{5}$$

where x_i is weight fraction of i-th component, i. e. of any component except the 0-th

x_0 weight fraction of the 0-th component, i. e. the one to be determined

$I_{i,m}$ intensity of m-th reflection of i-th component

$I_{0,n}$ intensity of n-th reflection of the 0-th component

$\alpha_{m,n}$ coefficients of proportionality depending on the selection of reflections.

After the addition of a known amount (x_D) of the 0-th component of the sample, equation (5) takes the form:

$$\frac{x_i}{x_0 + x_D} = \alpha_{m,n} \left(\frac{I_{i,m}}{I_{0,n}} \right)' \tag{6}$$

where ′ denoted the intensity ratio after doping. Equation (5) divided by equation (6) gives:

$$\frac{x_0 + x_D}{x_0} = \frac{\alpha_{m,n} \left(\dfrac{I_{i,m}}{I_{0,n}} \right)}{\alpha_{m,n} \left(\dfrac{I_{i,m}}{I_{0,n}} \right)'} \tag{7}$$

or:

$$\left(\frac{I_{i,m}}{I_{0,n}} \right) = \frac{x_0 + x_D}{x_0} \left(\frac{I_{i,m}}{I_{0,n}} \right)' \tag{8}$$

Equation (8) represents a straigth line, the slope of which can be determined from experimental data for all possible intensity ratios. From this slope

$$A = \frac{x_0 + x_D}{x_0} \tag{9}$$

and from the known value of x_D we get the initial weight fraction of the 0-th component:

$$x_0 = \frac{x_D}{A-1} \tag{10}$$

Theoretical considerations connected with the doping method were experimentally checked on a mixture containing 30% calcite and 70% magnesite. The mixture was properly homogenized by hand in an agate mortar. The X-ray diffraction pattern of the mixture was recorded on Philips X-ray diffraction equipment PW 1010 using $CuK\alpha$ radiation. The X-ray beam was collimated by means of 1^0 divergent and scatter slits and a 0.2 mm receiving slit. Goniometer speed was $1/4^0$/min and chart paper speed 400 mm/h. Intensities were reduced 32 times at time constant 4.

After the first recording 0.3 g of calcite was added to 1 g of the initial mixture and a new X-ray diffraction pattern taken. For X-ray determination of the weight fraction of calcite in the initial mixture we used reflections listed in Table I.

TABLE I

d-Spacings of Analytical Reflections for Calcite-Magnesite Mixture

Reflections of calcite	d (Å)	Reflections of magnesite	d (Å)
C_1	3.035	M_1	2.74
C_2	2.280	M_2	1.934
C_3	1.917	M_3	1.697
C_4	1.868		

Areas under the diffraction maxima were used as intensities. Table II shows ratios of intensities for combinations of reflections listed in Table I. Data from Table II are graphically represented on Fig. 1. The slope of the

TABLE II

Analytical Intensity Ratios for Calcite-Magnesite Mixture

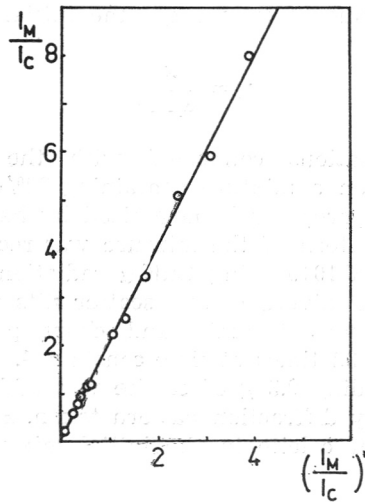| Combination of reflections	Intensity ratios	
	Before doping	After doping
M_1/C_1	1.205	0.616
M_1/C_2	8.000	3.930
M_1/C_3	5.125	2.440
M_1/C_4	5.920	3.090
M_2/C_1	0.177	0.080
M_2/C_2	1.175	0.510
M_2/C_3	0.755	0.318
M_2/C_4	0.870	0.404
M_3/C_1	0.513	0.266
M_3/C_2	3.410	1.710
M_3/C_3	2.190	1.060
M_3/C_4	2.510	1.345

Fig. 1. Interdependence of intensity ratios before doping $[(I_M/I_C)]$ and after doping $[(I_M/I_C)']$ for the system calcite-magnesite.

line was calculated by means of the least square method. The obtained value amounts to 2.005. Introducing this value as well as the value for x_D (0.3) into equation (10) we get x_0 29.8%, which is in a very good agreement with the initial weighed quantity of calcite.

$I_{i,m}$ intensity can also consist of intensities belonging to two or more components whose X-ray diffraction maxima overlap. Such a case is illustrated in weight fraction determination of unreacted quartz in a product of the hydrothermal reaction during the 11.3 Å tobermorite formation. X-ray diffraction effects denoted on Fig. 2a by T_1, T_2, T_3 and T_4 belong not only to the 11.3 Å tobermorite, but also to the intermediate and nearly amorphous phases. The X-ray diffraction chart represented on Fig. 2a has been taken using CuK α radiation, at scanning rate 1/4°/min, with the same slits as in the first example. Intensities were reduced 8 times at TC 4. To determine un-reacted quartz 0.1 g of quartz p. a. with particle size less than 5 μ was added to 1 g of the sample under investigation. Fig. 2b shows the X-ray diffraction chart taken after doping. In this case intensities were reduced 16 times and measured as heights from background to the peak of maxima. $(I_{i,m}/I_{0,n})$ versus $(I_{i,m}/I_{0,n})'$ plotting is represented on Fig. 3. From the slope calculated by the least square method we have determined that the sample contains 6.5% of unreacted quartz, whilst the internal standard method, using aluminium as standard gives 7.0%.

The doping method has already been successfully applied to numerous quantitative X-ray determinations of components in cement raw materials. This method is especially suitable for quick determinations of weight fractions without previous calibration as required in the internal- and external-standard techniques.
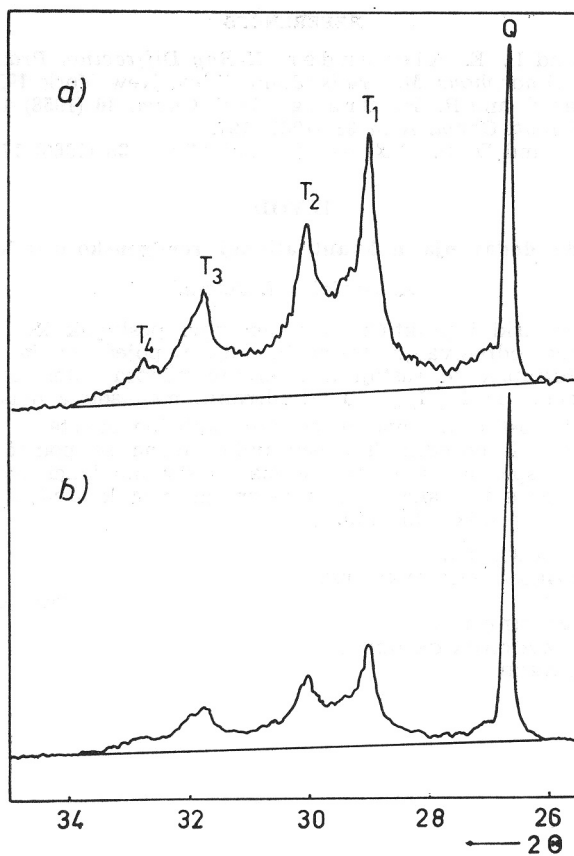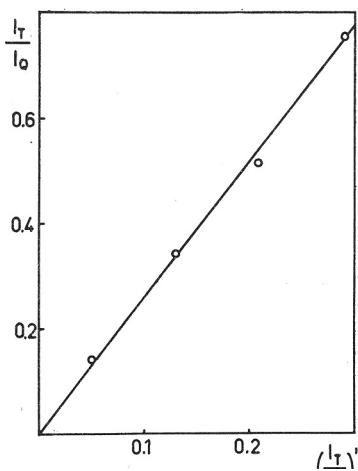
Fig. 2. X-Ray diffraction chart of a product of hydrothermal reaction between CaO and SiO₂
a) before doping
b) after doping

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2. L. E. Copeland and R. H. Bragg, *Anal. Chem.* **30** (1958) 196.
3. A. Bezjak, *Croat. Chem. Acta* **33** (1961) 197.
4. R. F. Karlak and D. S. Burnett, *Anal. Chem.* **38** (1966) 1741.

IZVOD

Primjena metode dodavanja u kvantitativnoj rendgensko-difrakcijskoj analizi

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U radu je teoretski i praktički razrađen novi postupak kvantitativnog rend-gensko-difrakcijskog određivanja težinskih udjela pojedinih konstituenata više-faznih sistema. Postupak se sastoji u mjerenju odnosa intenziteta za veći broj difrakcijskih maksimuma $I_{i,m}/I_{0,n}$ i u određivanju međusobne ovisnosti tih odnosa za uzorak prije i poslije dodavanja poznate količine supstance čiji se težinski udio x_0 u sistemu želi odrediti. Težinski udio računa se pomoću novoizvedenog izraza. Metoda je eksperimentalno provjerena na sistemu kalcit-magnezit, a primi-jenjena na određivanje težinskog udjela neizreagiranog kvarca u produktu hidro-termalne sinteze kalcij silikat hidrata.

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