Ratio of slopes method for quantitative X-ray diffraction analysis

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This method, which employs an internal standard, is both easy to use and accurate. The required weight fraction of a phase in the mixture to be analysed is determined from the ratio of slopes of two linear plots passing through their respective origins, designated as the analysis and reference lines. The analysis line is obtained by plotting the intensity ratio of the required phase to the standard against the weight ratio of the mixture to the standard, for different proportions of mixture and standard. The reference line for the required phase is obtained by plotting the intensity ratio against the weight ratio of the reference material to the standard, using a pure phase or a reference material of known composition. The ease of use comes when weighing out the samples to be X-rayed. The weight of the mixture to be analysed, the reference material and the internal standard need not be any specific values or in any fixed proportions but, of course, require to be determined precisely. The weight ratios can be chosen so that peak intensities can be measured accurately. Precise weighing and the ability to use various weight ratios can give this method greater accuracy than that of the conventional internal standard method.

1. Introduction

The basic relationship between the intensity of an X-ray diffracted peak from a particular set of equivalent planes of a phase in a mixture and the concentration of that phase has been worked out by Alexander and Klug [1]. It can be written as

$$I_{eij} = \frac{K_{ei}x_{ij}}{\rho_i\mu_j^*}$$ (1)

where I_{eij} is the intensity of the diffracted peak from a set of planes e of phase i in sample j which is X-rayed; K_{ei} is a constant which depends on the nature of phase i, the particular peak e considered and the geometry and specifications of the X-ray instrument; ρ_i is the density of phase i; x_{ij} is the weight fraction of phase i in sample j and μ_j^* is the mass absorption coefficient of sample j.

To eliminate the requirement to know the mass absorption coefficient of the sample being X-rayed, Alexander and Klug [1] introduced an internal standard. Their method has been the most widely used since its publication in 1948, and to mark this achievement their original article has recently been republished [2]. In their method a known weight proportion of an internal standard, substance s, is added to the mixture to be analysed. If x_{sj} is the weight fraction of the standard in the X-ray sample j, then according to Equation 1

$$I_{hsj} = \frac{K_{hs}x_{sj}}{\rho_s\mu_j^*}$$ (2)

where I_{hsj} is the diffracted intensity of peak h from the internal standard s in sample j; K_{hs} is a constant which depends on peak h, the standard s and the apparatus; ρ_s is the density of the internal standard.

For Equations 1 and 2 to apply, the sizes of the particles in the powdered sample being X-rayed should be small enough to make extinction and microabsorption effects negligible. Also, the powder mixture should be homogeneous on a scale of size considerably smaller than the amount of material exposed to the X-ray beam and free from preferred orientation. The powder bed which is X-rayed should have a thickness suitable for giving maximum diffracted intensity.

To eliminate μ_j^*, Equation 1 is divided by Equation 2 to give

$$\frac{I_{eij}}{I_{hsj}} = \frac{K_{ei}\rho_s x_{ij}}{\rho_i K_{hs}x_{sj}}$$ (3)

The weight fraction of phase i in the original, undiluted mixture to be analysed, x_{iA}, is related to the concentration in the X-ray sample j, x_{ij}, by

$$x_{iA} = \frac{x_{ij}}{1 - x_{sj}}$$ (4)

By combining Equation 4 with Equation 3 and keeping the proportion of the internal standard at a fixed value,

$$\frac{I_{eij}}{I_{hsj}} = k\,x_{iA}$$ (5)

This is the equation of the calibration line for the

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widely-used internal standard method. The slope k contains the constant values x_{sj} and $(1 - x_{sj})$ and other constants. The calibration line can be constructed by using known amounts of the phase to be analysed, a suitable diluent which allows the fixed ratio of the sample to the standard to be prepared, and a fixed proportion of the internal standard. The diluent should not have peaks too close to those of ei and hs. Then, if a quantity of the mixture to be analysed is blended with the same proportion of the standard and X-rayed, the required weight fraction of phase i in the mixture can be read from the calibration line by measuring the intensity ratio of that phase to the standard.

2. The ratio-of-slopes method

Assume that the mixture to be analysed is composed of phases 1, 2, 3, ... n with unknown weight fractions $x_{1A}, x_{2A}, x_{3A}, \ldots x_{nA}$. The mixture might be a combination of identified and unidentified crystalline phases and amorphous substances.

Suppose that phases 1, 2, 3, ... p $(p \leqslant n)$ are those for which pure phases, or reference materials of known compositions, are available and for which quantitative analysis is required.

A suitable phase, s, other than the n in the mixture is selected as the internal standard. As usual, the standard is preferred to have a crystal structure of high symmetry and a few pronounced X-ray peaks to reduce the possibility of interference with the peaks of the other phases. At least one peak from the standard and one peak from each of the p phases to be analysed should, ideally, not overlap. Care should be taken to avoid using a substance whose particles can be preferentially aligned, because a variable degree of alignment for the standard in different X-ray samples will cause serious errors. Preferably the standard should have a similar mass absorption coefficient at the radiation wavelength being used to that of the mixture to be analysed, since a standard with much higher absorption diminishes the intensities of the other peaks, whilst the peak from a standard with a much lower absorption might be difficult to measure accurately.

For preparation of a sample to be X-rayed, an arbitrary amount of the mixture to be analysed, W_{Aj} g, is weighed to high precision and mixed with an appropriate amount of the standard, W_{sj} g, which is also weighed precisely. The weights should be such that the intensities of the chosen peaks can be measured accurately.

As before, I_{eij} is the diffracted intensity of a set of planes e of phase i in sample j, and according to Equation 1

$$I_{eij} = \frac{K_{ei}}{\rho_i}\left(\frac{W_{ij}}{W_{Aj} + W_{sj}}\right)\frac{1}{\mu_j^*} \qquad (6)$$

where W_{ij} is the weight of phase i in sample j.

In the same way, I_{hsj} is the intensity of peak h of the internal standard in sample j and according to

Equation 2

$$I_{hsj} = \frac{K_{hs}}{\rho_s}\left(\frac{W_{sj}}{W_{Aj} + W_{sj}}\right)\frac{1}{\mu_j^*} \qquad (7)$$

The mass absorption coefficient in sample j is given by

$$\mu_j^* = \frac{1}{W_{Aj} + W_{sj}}\left(\sum_{i=1}^{n} W_{ij}\mu_i^* + W_{sj}\mu_s^*\right) \qquad (8)$$

where μ_i^* are the mass absorption coefficients of the individual phases in the mixture to be analysed and μ_s^* is the mass absorption coefficient of the standard.

Elimination of μ_j^* can be achieved, as before, by division:

$$\frac{I_{eij}}{I_{hsj}} = \frac{K_{ei}\,\rho_s\,W_{ij}}{\rho_i\,K_{hs}\,W_{sj}} \qquad (9)$$

This is equivalent to Equation 3, but from this point onwards a different treatment is employed to that used for the previously described internal standard method.

It is known that the weight of phase i in sample j, W_{ij}, is given by the weight of the mixture in sample j, W_{Aj}, multiplied by the weight fraction of phase i in the mixture, x_{iA}, i.e.

$$W_{ij} = W_{Aj}x_{iA} \qquad (10)$$

By substituting for W_{ij} from Equation 10 into Equation 9 and introducing a constant

$$(M_{eihs})_{\text{analysis}} = \frac{K_{ei}\rho_s}{\rho_i K_{hs}}x_{iA} \qquad (11)$$

the principal equation for the ratio-of-slopes method is obtained. That is

$$\left(\frac{I_{eij}}{I_{hsj}}\right)_{\text{analysis}} = (M_{eihs})_{\text{analysis}}\left(\frac{W_{Aj}}{W_{sj}}\right) \qquad (12)$$

This shows that for any mixture to be analysed, arbitrary amounts of mixture, W_{Aj}, can be blended with appropriate amounts of a suitable standard, W_{sj}, to make different samples j for X-raying. Let the samples be numbered I, II, III, IV, etc. If the intensity ratios for these samples are plotted against the weight ratios, a straight line, the analysis line, which passes through the origin will be obtained as illustrated in Fig. 1.

For each phase in the mixture, a line with a different slope will be obtained. The slope, as shown by Equation 11, depends on the phase, the chosen peak, the concentration of the phase in the mixture and the selected peak of the internal standard.

To carry out the analysis, a reference material is required. The reference material can be a pure phase, a known mixture of two or more pure phases which are in the mixture to be analysed [3], or a material containing a known weight fraction of the required phase. Let the weight fraction of phase i in the reference material be x_{iR}, then the equivalent equation to Equation 11 is

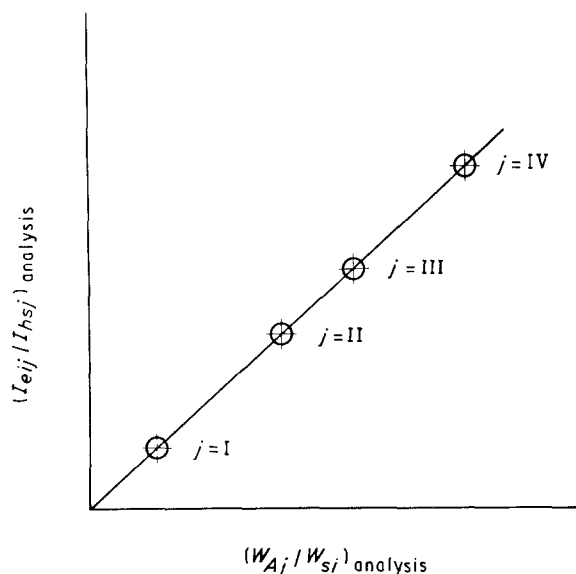$$(M_{eihs})_{\text{reference}} = \frac{K_{ei}\rho_s}{\rho_i K_{hs}}x_{iR} \qquad (13)$$

Figure 1 The analysis line: slope $= (M_{eihs})_{\text{analysis}}$.

The equivalent equation to Equation 12 becomes

$$\left(\frac{I_{eij}}{I_{hsj}}\right)_{\text{reference}} = (M_{eihs})_{\text{reference}}\left(\frac{W_{Rj}}{W_{sj}}\right) \quad (14)$$

Arbitrary amounts of the reference material, W_{Rj}, can be blended with appropriate amounts of the standard, W_{sj}, to make different samples j for X-raying. Again, if the intensity ratios for these samples are plotted against the weight ratios, a straight line passing through the origin will be obtained. This is the reference line.

The weight fraction of phase i in the mixture, x_{iA}, can be determined from the ratio of the slopes of the analysis and reference lines multiplied by the known weight fraction of phase i in the reference material, x_{iR}. That is,

$$x_{iA} = \left(\frac{(M_{eihs})_{\text{analysis}}}{(M_{eihs})_{\text{reference}}}\right)x_{iR} \quad (15)$$

If the reference material is a pure phase, then $x_{iR} = 1$.

To obtain the slopes from the experimental data, the least-squares method can be applied. The weight ratios can be regarded as highly accurate. The uncertainties can be considered to be in the values of the intensity ratios. The uncertainties come mainly from mixing the powders and measuring the intensities of the diffracted peaks. The equation fitted to the points should be of the form

$$Y = MX \quad (16)$$

If Y_j denotes the intensity ratio for the jth point and X_j its related weight ratio value, the least-squares method [4] gives the slope as

$$M = \frac{\Sigma Y_j X_j}{\Sigma X_j^2} \quad (17)$$

3. Experimental illustration of method

The method is illustrated by analysis of a prepared mixture made using 9 g SiO_2 (97.9% α-quartz residue +

TABLE I Weights and weight ratios of the prepared mixture and standard

Sample	Weight (g)		Weight ratio, X_j
	Mixture A	Standard	
$j = I$	0.3069	0.1273	2.411
$j = II$	0.4142	0.1062	3.900
$j = III$	0.5036	0.0878	5.736

2.1% feldspar), 8 g $CaCO_3$ (calcite, 99.5% min. purity) and 3 g CaF_2 (fluorite, 99.0% min. purity). That is, the mixture contained nominally 45 wt % SiO_2, 40 wt % $CaCO_3$ and 15 wt % CaF_2. This mixture was blended for 20 min in an agate mortar with an agate pestle. LiF (98% min. purity) was selected as the internal standard. As the components of the prepared mixture were employed as the reference materials, the effects of the impurities are essentially cancelled out.

The X-ray diffraction was performed at first with a Philips system having a PW 1730 generator with 50 kV tube voltage and 30 mA current. Monochromatic CuK_α radiation, $\lambda = 0.154050$ nm, was employed. A scanning speed of $2°$ min^{-1} for 2θ was used and the X-ray intensity was recorded on a chart with a chart speed of 60 mm min^{-1} and a maximum range of 4000 c.p.s. The peak areas were determined from the chart by multiplying peak heights, after accounting for background, by the peak widths at half the peak heights. The intensity ratios were obtained by dividing the peak areas by the area of the LiF peak.

The selected peaks for $CaCO_3$, CaF_2 and LiF were at 0.2095, 0.3153 and 0.2013 nm, respectively. Two peaks were selected for SiO_2 at 0.4260 and 0.1817 nm. The strongest peaks for $CaCO_3$ and SiO_2 were off the scale of the chart at the selected sensitivity because of the high concentration of these components. Three different samples to be X-rayed were prepared, as shown in Table I.

Two holders were filled with powder from each sample and X-rayed. The average of the two values obtained for the intensity ratios of each phase relative to the standard were plotted against the values of the weight ratios of the mixture to the standard. This is shown in Fig. 2. The intensity ratios for each of the peaks in each sample, together with the slopes of the linear plots calculated using the least-squares method for lines passing through the origin, are given in Table II.

After determining the slopes of the analysis lines, the slopes of the reference lines were established. This was done in a similar way to that used for the analysis lines, but the samples to be X-rayed were mixtures consisting of various proportions of a pure phase and LiF. The reference lines are shown in Fig. 3. The slopes of the reference lines and results of the analysis are given in Table III.

The values, except for $CaCO_3$, are in good agreement with those for the prepared mixture. The more accurate value for SiO_2 was obtained using the

TABLE II Intensity ratios of phases relative to LiF and calculated slopes

Weight ratio, X_j	Intensity ratio, Y_j			
	0.3153 CaF_2	0.4260 SiO_2	0.1817 SiO_2	0.2095 $CaCO_3$
2.411	0.65	0.53	0.31	0.22
3.900	1.07	0.87	0.54	0.38
5.736	1.58	1.28	0.72	0.58
$\Sigma Y_j X_j$	14.803	12.013	6.983	5.339
ΣX_j^2	53.925	53.925	53.925	53.925
$(M_{eihs})_{analysis}$	0.275	0.223	0.129	0.099

TABLE III Slopes of reference lines and results of analysis

	0.3153 CaF_2	0.4260 SiO_2	0.1817 SiO_2	0.2095 $CaCO_3$
$(M_{eihs})_{reference}$	1.852	0.491	0.282	0.260
Result of analysis (wt %)	14.8	45.4	45.7	38.1

TABLE IV Weights, weight ratios and average intensity ratios of prepared mixture and standard

Weight (g)		Weight ratio	Average intensity ratio
Prepared mixture	LiF		
0.4773	0.4015	1.189	0.973
0.5367	0.3249	1.652	1.339
0.7618	0.2026	3.760	3.168

TABLE V Weights, weight ratios and average intensity ratios of calcium carbonate and standard

Weight (g)		Weight ratio	Average intensity ratio
$CaCO_3$	LiF		
0.2477	0.3288	0.753	1.561
0.3524	0.2974	1.185	2.446
0.6954	0.1415	4.914	10.357
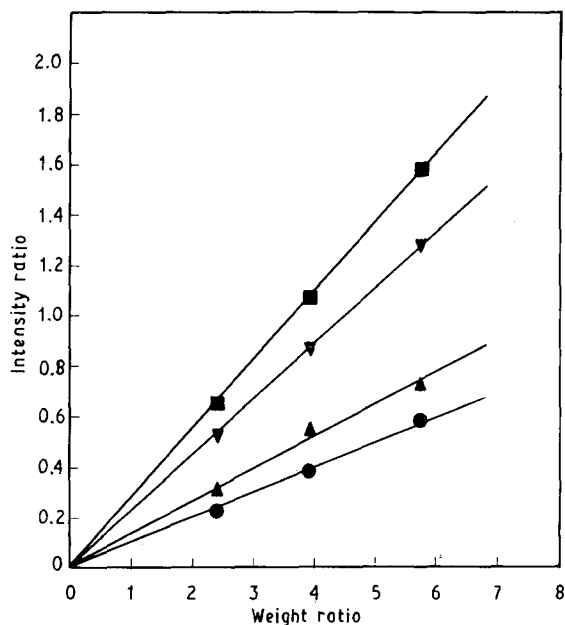
Figure 2 The analysis lines given by the intensity ratios for (▼, ▲) SiO_2, (●) $CaCO_3$ and (■) CaF_2 relative to LiF versus weight ratios of prepared mixture relative to LiF.

Figure 3 The reference lines given by the intensity ratios for (▼, ▲) SiO_2, (●) $CaCO_3$ and (■) CaF_2 relative to LiF versus weight ratios of pure phases to LiF.

stronger of the two quartz peaks. The relatively poor agreement for $CaCO_3$ is considered to result from the use of a peak of low intensity.

The analysis of the amount of $CaCO_3$ in the prepared mixture was carried out again using the major peak at 0.3035 nm and an X-ray set capable of integrating the X-ray intensity over chosen 2θ intervals.
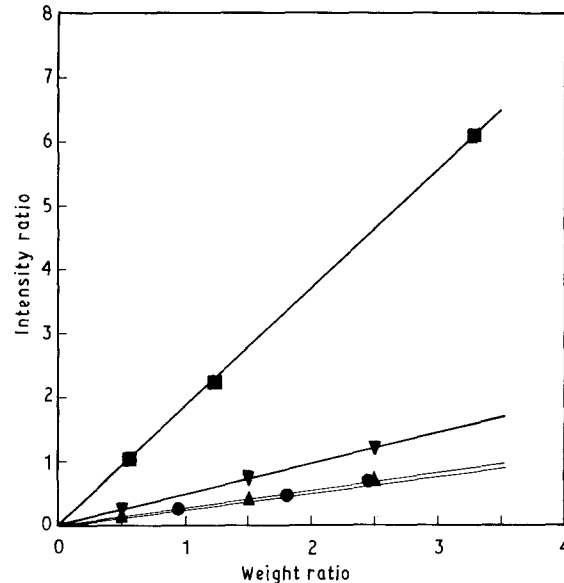
The system was a Philips PW1710, controlled by a computer program. CuK_{α} radiation from a tube operated at 40 kV and 25 mA was employed. The detector was scanned at a speed of $2°$ min^{-1} for 2θ.

The weights of the prepared mixture and LiF in the three samples to be X-rayed are given in Table IV along with the weight ratios. Two holders were again
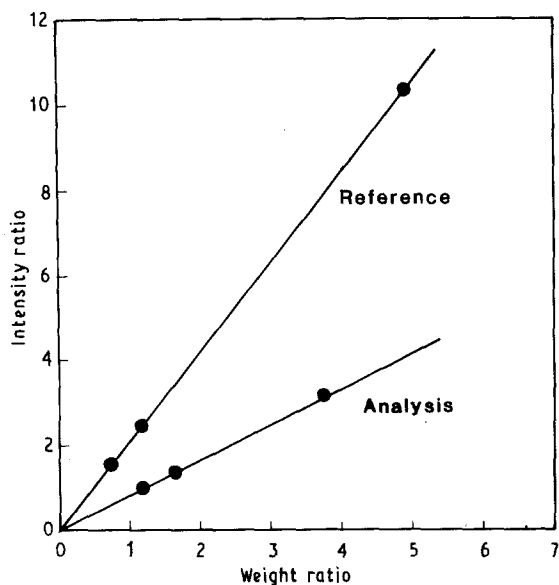
Figure 4 Weight ratios of the prepared mixture and CaCO₃ to LiF.

filled with powder from each of the samples and X-rayed. The averages of the two intensity ratios are also given in Table IV.

A similar procedure was carried out to obtain the data to construct the reference line. The weights used in the mixtures of $CaCO_3$ and LiF are given in Table V along with the weight ratios and average intensity ratios. Both sets of data are plotted in Fig. 4. The slopes of the reference and analysis lines, obtained from least-squares fits, are 2.105 and 0.836, respectively. This yields a value for $CaCO_3$ of 39.7 wt %, which is very close to the value for the prepared mixture of 40 wt %.

4. Discussion
The analysis of the prepared mixture shows that the method can yield accurate results. As with any X-ray method, the use of peaks of high intensity yields more accurate values.

The main advantages of the method are the ease with which the samples can be weighed out precisely, and the ability to choose weight ratios for which the intensities of the required peaks can be measured accurately. Further, no diluent phase is required to establish the reference lines.

The analysis can be carried out using only one prepared X-ray sample, exposed in one or more holders, as in the widely-used internal standard method, but with the advantage of the ease of weighing. However, the use of two or more samples with different weight ratios provides a check on weighing and other experimental errors, since the data should form a linear plot which passes through the origin. It also allows the selection of weight ratios which permit the intensity ratios to be measured accurately.

Performing the analysis with two peaks from a particular phase, e.g. the 0.4260 and 0.1817 nm peaks of SiO_2, can provide an additional check on the data. The ratio of the slopes for the two peaks for the analysis samples and that for the reference samples should be the same. In the example, the slopes for the analysis samples are 0.223 and 0.129, which gives a ratio of 1.73. For the reference samples the slopes are 0.491 and 0.282, which gives a ratio of 1.74. When essentially the same value is obtained, it shows that correction for the background has been carried out correctly and that these peaks in the analysis samples are not superimposed on peaks from another phase.

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