

## Quantitative Interpretation of X-ray Diffraction Patterns of Mixtures. I. Matrix-Flushing Method for Quantitative Multicomponent Analysis

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A matrix-flushing method for quantitative multicomponent analysis by X-ray diffraction is reported. It is simpler and faster than, yet as reliable as, the conventional internal-standard method. In this new method, the calibration-curve procedure is shunted; a more fundamental 'matrix-flushing' concept is introduced. The matrix-flushing theory gives an exact relationship between intensity and concentration free from matrix effect. Contrary to most theoretical methods the working equation is very simple, no complicated calculations are involved. The matrix-flushing theory and the analytical procedure are presented. Eight illustrative examples are drawn to demonstrate how this theory is applied to multicomponent analysis and amorphous-content determination. A novel 'auto-flushing' phenomenon of binary systems was observed which appears to make the analysis of any binary system a simple matter.

### Introduction

Besides broad routine analysis X-ray diffraction is often the only technique available for distinguishing polymorphic structures and analyzing solid solutions. The results obtained are in terms of materials as they occur in the sample, not in terms of elements or ions present. The pigment industry is especially concerned about polymorphic forms and solid solutions. For example, the best red pigment quinacridone (Chung & Scott, 1971) has four polymorphic forms, only two of which have commercial value; the corrosion inhibiting pigment zinc molybdate (Kirkpatrick & Nilles, 1972) is composed of a solid solution of zinc oxide and molybdenum oxide. However, the only analytical technique, X-ray diffraction, dealing with these situations is hampered by a matrix effect. So far, the best method of quantitative X-ray diffraction analysis is still the internal-standard method developed before 1948 (Alexander & Klug, 1948). It involves the usual procedure of constructing a calibration curve from standards, which is rather tedious since each component sought needs a calibration curve, each calibration curve needs at least three standards, and each standard must contain exactly the same percentage of pure reference material chosen.

A new X-ray diffraction method for quantitative multicomponent analysis has been developed. It is much simpler and faster than, yet as reliable as, the conventional internal-standard method.

Since 1970, the Joint Committee on Powder Diffraction Standards has published a set of Reference Intensities ( $I/I_c$ ) (Berry, 1970) of binary mixtures made with a pure material and synthetic corundum ( $\alpha\text{-Al}_2\text{O}_3$ ) by one-to-one weight ratio, where  $I$  and  $I_c$  are the intensities of the strongest lines of the pure material and corundum respectively. These Reference Intensities are intended for 'rough quantitative X-ray diffraction analysis of mixtures'. Occasionally there is a need for

a rapid quantitative X-ray diffraction analysis with moderate accuracy in our industrial analytical laboratories; therefore, attempts were made to utilize these Reference Intensities. This thought led to a new X-ray diffraction method for quantitative multicomponent analysis. In this new method, the conventional calibration-curve procedure is shunted and a more fundamental 'matrix-flushing' concept is introduced. The matrix-flushing concept gives an exact relationship between intensity and concentration since neither assumption nor approximation is made. Contrary to most theoretical methods, the working equation of this matrix-flushing method is very simple, no complicated calculations are involved. It is felt that one can utilize this method without understanding its theoretical basis.

The matrix-flushing theory and the analytical procedure are presented below. Experimental data are collected to demonstrate how this theory is applied to multicomponent analysis and amorphous-content determination. A novel 'auto-flushing' phenomenon of binary systems emerged which makes the analysis of any binary system a simple matter.

### Matrix-flushing theory

In contrast with X-ray emission analysis, X-ray diffraction analysis has two factors favoring a more fundamental approach. Firstly, the primary and the diffracted X-rays are monochromatic and of the same wavelength. Secondly, the matrix effect consists of absorption only, no enhancement.

When the monochromatic primary X-rays impinge on a flat powder specimen, the intensities of diffracted rays are related to the percentage composition by equation (1) as derived by Klug & Alexander (1959),

$$I_i = K_i \frac{X_i/q_i}{\sum \mu_i X_i} = K_i \frac{X_i/q_i}{\mu_i} \quad (1)$$

Hence we have:

$$\frac{I_i}{I_i^0} = X_i \frac{\mu_i}{\mu_t} \quad (2)$$

where:

$I_i$  = Intensity of X-rays diffracted by a selected plane ( $hkl$ ) of component  $i$ .

$I_i^0$  = Intensity of X-rays diffracted by a selected plane ( $hkl$ ) of pure compound  $i$ .

$K_i$  = A constant which depends upon the geometry of the diffractometer and the nature of component  $i$ .

$X_i$  = Weight fraction of component  $i$ .

$\rho_i$  = Density of component  $i$ .

$\mu_i$  = Mass absorption coefficient of pure component  $i$ .

$\mu_t$  = Mass absorption coefficient of the total specimen exposed to primary X-rays, including component  $i$ , internal standard and reference material added, if any.

The  $\mu_i$  and  $\mu_t$  in equation (2) are called the 'absorption effect' which complicates X-ray diffraction analysis. Even  $\mu_i$ , the mass absorption coefficient of pure compound  $i$ , has not been accurately measured. So the best way of approaching this problem is to flush all these  $\mu$  factors out of the intensity-concentration equation. In order to achieve this, a flushing agent, which may be any pure compound *not* present in the sample, is added into a sample of  $n$  components. Let the weight fraction of the flushing agent and original sample be designated  $X_f$  and  $X_o$  respectively, that is

$$X_f + X_o = X_f + \sum_{i=1}^n X_i = 1. \quad (3)$$

Then from equation (2):

$$\left. \begin{aligned} \frac{I_i}{I_i^0} &= X_i \frac{\mu_i}{\mu_t} \\ \frac{I_f}{I_f^0} &= X_f \frac{\mu_f}{\mu_t} \end{aligned} \right\}. \quad (4)$$

We have:

$$\left( \frac{I_i}{I_f} \right) \left( \frac{I_f^0}{I_i^0} \right) = \left( \frac{X_i}{X_f} \right) \left( \frac{\mu_i}{\mu_f} \right). \quad (5)$$

The individual values of  $I_f^0$  and  $I_i^0$  are dependent upon the atomic positions in their respective crystal structures. However, the ratio  $I_f^0/I_i^0$  can be obtained through the Reference Intensities. In the mean time, all the matrix factors in equation (5) can be flushed out completely as shown below.

For a binary mixture of compound  $i$  and corundum  $c$  with one-to-one weight ratio, similar to equation (5), we have

$$\left( \frac{I_i}{I_c} \right) \left( \frac{I_c^0}{I_i^0} \right) = \left( \frac{\mu_i}{\mu_c} \right). \quad (6)$$

For the sake of simplicity, let  $k_i$  stand for the Reference Intensity ratio:

$$\frac{I_i}{I_c} = k_i,$$

then equation (6) becomes

$$\left( \frac{I_c^0}{I_i^0} \right) = \left( \frac{1}{k_i} \right) \left( \frac{\mu_i}{\mu_c} \right) \quad (7)$$

and similarly:

$$\left( \frac{I_c^0}{I_f^0} \right) = \left( \frac{1}{k_f} \right) \left( \frac{\mu_f}{\mu_c} \right). \quad (8)$$

Since  $I_i^0$ ,  $I_c^0$ , and  $I_f^0$  are the intensities of the strongest lines of the X-ray diffraction patterns of respective pure materials, which are constants from the same diffractometer, we get:

$$\left( \frac{I_f^0}{I_i^0} \right) = \left( \frac{k_f}{k_i} \right) \left( \frac{\mu_i}{\mu_f} \right). \quad (9)$$

Substituting equation (9) into equation (5) we have:

$$\left( \frac{I_i}{I_f} \right) \left( \frac{k_f}{k_i} \right) = \left( \frac{X_i}{X_f} \right) \quad (10)$$

$$X_i = X_f \left( \frac{k_f}{k_i} \right) \left( \frac{I_i}{I_f} \right). \quad (11)$$

Equation (11) is a very important conclusion. First, it gives a simple relationship between intensity and concentration. Secondly, it is free from matrix effect; all absorption factors are neatly flushed out. Thirdly, it is an exact deduction; neither assumption nor approximation was made to reach the conclusion. This equation (11) can be used for quantitative multicomponent analysis. Any pure compound which is not a component of the sample can be used as the flushing agent. Yet one more simplification can be realized.

Since corundum ( $\alpha\text{-Al}_2\text{O}_3$ ) has been chosen for Reference Intensities by the Powder Diffraction File for its purity, stability and availability, it is convenient to choose the same corundum as a flushing agent for the same good reasons. Consequently  $k_f = k_c = 1$ , where the subscripts  $f$  and  $c$  stand for flushing agent and for corundum, and we obtain:

$$X_i = \left( \frac{X_c}{k_i} \right) \left( \frac{I_i}{I_c} \right). \quad (12)$$

This is the working equation for quantitative multicomponent analysis. It represents a straight line passing through the origin with a slope equal to  $X_c/k_i$ . It is free from matrix factors. No previous information as to the approximate concentration ranges of various components sought is required. Intensity ratios from the same scan are the experimental data needed. Since it uses intensity ratios of the same scan, the errors due to instrumental drift and sample preparation are minimized. Note that the working equation (12) not only comprehends the internal-standard method (Alexander & Klug, 1948; Klug & Alexander, 1959) but also

prescribes the slope of calibration curve for *every* component in the sample, thus it is not necessary to actually work out these calibration curves. Furthermore, it can be used for amorphous-content determination.

When corundum is chosen as the flushing agent, applying equation (12) to equation (3), we get:

$$X_c + \sum_{i=1}^n X_i = 1, \quad (13)$$

$$X_c + \frac{X_c}{I_c} \sum_{i=1}^n \frac{I_i}{k_i} = 1, \quad (14)$$

$$\sum_{i=1}^n \frac{I_i}{k_i} = \left( \frac{X_o}{X_c} \right) I_c \because 1 - X_c = X_o. \quad (15)$$

Equation (15) affords a means to check experimentally the correctness of the matrix-flushing theory, to appraise the reliability of intensity data, and to predict and assay the presence of amorphous materials in a sample.

As no restriction is imposed by the theory upon the weight fraction of flushing agent  $X_f$  in equation (11) and  $X_c$  in equations (12) and (15), if the specimen is made of exactly 50.00% original sample and 50.00% of corundum, then equations (12) and (15) are reduced to the following rather interesting relations:

$$X_i = \frac{1}{2k_i} \left( \frac{I_i}{I_c} \right) \quad (16)$$

$$\sum_{i=1}^n \frac{I_i}{k_i} = I_c. \quad (17)$$

For a binary system, a novel 'auto-flushing' phenomenon exists. No flushing agent is needed. One component automatically serves as a flushing agent for the other component and *vice versa*, which means quantitative analysis can be done by merely grinding the original sample and scanning it.

Let the weight fraction of the two components of a binary mixture be  $X_1$  and  $X_2$ , similar to the derivation of equation (10) we have:

$$\left. \begin{aligned} X_1 + X_2 &= 1 \\ \frac{I_1}{I_2} &= \frac{k_1}{k_2} \cdot \frac{X_1}{X_2} \end{aligned} \right\}. \quad (18)$$

Solving these two simultaneous equations, we get:

$$X_1 = \frac{1}{1 + \frac{k_1}{k_2} \cdot \frac{I_2}{I_1}}. \quad (19)$$

Therefore, the quantitative composition of a binary system can be easily calculated from the intensity ratio of the strongest diffraction peak from each component in a single diffraction scan.

Mathematically, equation (19) represents a straight line passing through the origin with a slope  $k = k_1/k_2$  when  $I_1/I_2$  is plotted against  $X_1/X_2$ .

Note that this auto-flushing phenomenon is true for any binary system. It is interesting to observe that this linear relationship of binary systems of polymorphic crystals was recognized quite a long time ago. Prime examples are the determination of anatase in rutile  $\text{TiO}_2$  (Spurr & Myers, 1957), quartz in cristobalite  $\text{SiO}_2$  (Alexander & Klug, 1948), calcite in aragonite  $\text{CaCO}_3$  (Azaroff & Buerger, 1958), *etc.* This is because in such special cases  $\mu_1 = \mu_2$  and inherently there are no matrix effects whatsoever in the polymorphic systems. Nevertheless, the slope of the straight line,  $k$ , of each of these systems was acquired through a calibration curve of standards.

The new way of acquiring the slope  $k$  for any binary system and the procedure of quantitative analysis for multicomponent systems are presented in the experimental section below.

### Experimental

Eight synthetic samples were prepared to illustrate the application of the matrix-flushing theory. The chemicals used were certified reagent grade or better. The rutile and anatase titanium dioxide were pigment-grade samples containing 99.7% rutile and 99.8% anatase respectively. The flushing agent, synthetic corundum, was Linde semiconductor-grade  $\alpha\text{-Al}_2\text{O}_3$  (1.0 micron, Union Carbide).

In order to ensure optimum particle size and sample homogeneity, all samples were ground for about 20 min with an automatic mortar grinder (Fisher Scientific Co.). To avoid preferred orientation, the free-falling method of sample preparation recommended by NBS Monograph 25 (1971) was employed.

The intensity data were collected by use of a Norelco diffractometer equipped with a solid-state scintillation counter, graphite-monochromatized  $\text{Cu K}\alpha$  radiation, integrated-circuit control panel, and pulse-height analyzer. A constant-time (40 s) counting technique was used for each peak and each background. The accumulated counts range from 20 000 to 250 000 counts for the period of 40 s after background correction. Duplicate readings were taken for each peak and each background. A strip-chart trace of the X-ray diffraction pattern of each sample was recorded for later reference.

### Reference intensities

The relative intensities of peaks in an X-ray diffraction pattern of a crystalline compound vary slightly depending on the diffractometer design and instrumental conditions. The Reference Intensities ( $I/I_c$ ) obtained from different laboratories hardly agree beyond two significant figures. Consequently, the Reference Intensities in the Powder Diffraction File are quoted to only two digits. If quantitative results are required, it is necessary to determine the Reference Intensities of materials concerned using the same diffractometer under the same instrumental conditions.

Table 1. *Reference intensities by counting*

	PDF card	Intensity (c.p.s.)		Reference intensity, $I_i/I_c$	
		$I_i$	$I_c$	By counting	PDF
ZnO	5-664	8178	1881	4.35	4.5
KCl	4-587	4740	1223	3.87	3.9
LiF	4-857	3283	2487	1.32	1.3
CaCO <sub>3</sub>	5-586	4437	1491	2.98	2.0
TiO <sub>2</sub> rutile	21-1276	2728	1040	2.62	3.4
TiO <sub>2</sub> anatase	21-1272	3573	1054	3.39	4.3

Six chemical compounds were used for the following illustrative examples. Their Reference Intensities ( $I/I_c$ ) and relevant data were determined and are listed in Table 1. The instrumental conditions of the diffractometer are given in Table 2. All subsequent intensity data were collected under the same instrumental conditions.

Table 2. *Diffractometer conditions*

Copper X-ray tube, broad focus	50 kV, 40 mA
Scintillation detector	839 V
Gain	128
Baseline	1.0 V
Window	3.0 V
Constant time	40 s

Multicomponent analysis

Four samples were prepared to demonstrate the application of the matrix-flushing theory to multicomponent analysis. Sample 1 consisted of three components ZnO, KCl and LiF. A known quantity of flushing agent (~16%  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>) was added into this sample

which was then ground to a homogeneous fine powder. All the peaks in the diffraction pattern of this mixture were clearly resolved, and the intensity of the strongest line of each component was measured. The working equation (12) was applied to each component; for example:

$$X_{ZnO} = \frac{17.96}{4.35} \times \frac{5968}{599} = 41.14\% \text{ (Experiment)}$$
$$41.49\% \text{ (True Value) .}$$

The true composition, the intensity data, and the composition found are listed in Table 3. It is found that even the intensities read directly from the pattern on a strip-chart, Fig. 1, give fairly good accuracy.

The correctness of the matrix-flushing theory is further scrutinized by equation (15):

$$\sum \frac{I_i}{k_i} = \frac{5968}{4.35} + \frac{2845}{3.87} + \frac{810}{1.32} = 2721 \text{ (Experiment)}$$
$$\frac{X_o}{X_c} \cdot I_c = \frac{82.04}{17.96} \times 599 = 2736 \text{ (Theory).}$$

Table 3. *Intensity and composition data*

Sample	Composition (g)		Intensity (c.p.s.)	% Composition		$\sum \frac{I_i}{k_i}$	$\frac{X_o}{X_c} \cdot I_c$
				Known	Found		
1	ZnO	1.8901	5968	41.49	41.14	2721	2736
	KCl	1.0128	2845	22.23	22.04		
	LiF	0.8348	810	18.32	18.40		
	Al <sub>2</sub> O <sub>3</sub> Flushing	0.8181	599	17.96	-		
	ZnO	0.9532	2856	18.98	19.10		
2	KCl	0.6601	1651	13.15	12.41	1662	1719
	LiF	0.8972	765	17.87	16.86		
	Al <sub>2</sub> O <sub>3</sub> Flushing	2.5114	1719	50.00	-		
	ZnO	0.6759	2408	24.38	25.36		
3	TiO <sub>2</sub> (R)	0.4317	931	15.57	16.28	1767	1761
	CaCO <sub>3</sub>	1.1309	2558	40.79	39.36		
	Al <sub>2</sub> O <sub>3</sub> Flushing	0.5341	420	19.26	-		
	ZnO	0.0335	120	1.38	1.35		
4	TiO <sub>2</sub> (R)	0.0633	139	2.60	2.57	1677	1711
	CaCO <sub>3</sub>	1.9197	4756	78.96	77.36		
	Al <sub>2</sub> O <sub>3</sub> Flushing	0.4147	352	17.06	-		
	ZnO	0.9037	4661	34.43	36.41		
5	CaCO <sub>3</sub>	0.7351	2298	28.00	26.20	1842	2312
	SiO <sub>2</sub> (Gel)	0.4234	0	16.13	15.95		
	Al <sub>2</sub> O <sub>3</sub> Flushing	0.5629	631	21.44	-		
	ZnO	1.4253	6259	71.22	72.07		
6	TiO <sub>2</sub> (R)	0.5759	1461	28.78	27.93		
	TiO <sub>2</sub> (R)	0.7418	1373	43.80	42.70		
7	TiO <sub>2</sub> (A)	0.9518	2386	56.20	57.30		
	KCl	2.4530	5371	74.90	74.64		
8	LiF	0.8219	604	25.10	25.36		

This proves that the relationship between X-ray intensity and concentration derived from the matrix-flushing theory is real.

Sample 2 is composed of the same three components in different quantities. Exactly 50.00%  $\alpha$ - $\text{Al}_2\text{O}_3$  was incorporated into the sample. Again, a good agreement between experimental values and true values is obtained and the interesting relationship that the sum of  $I_i/k_i$  should be equal to the intensity of corundum  $I_c$  is fulfilled. It also shows that the matrix-flushing effect is independent of the amount of flushing agent used.

Sample 3 is made of ZnO,  $\text{TiO}_2$  and  $\text{CaCO}_3$  with about 20% flushing agent  $\alpha$ - $\text{Al}_2\text{O}_3$ . In this example, not all of the strongest lines are resolved. A  $\text{CaCO}_3$  line interferes with the strongest line of  $\text{Al}_2\text{O}_3$ . The intensity of the next strongest line of  $\text{Al}_2\text{O}_3$  was measured and this is used to calculate the intensity of the strongest line of  $\text{Al}_2\text{O}_3$  with reference to the pattern of pure  $\text{Al}_2\text{O}_3$  obtained by use of the same diffractometer under the same conditions. Two other  $\text{CaCO}_3$  lines overlap the first and second strongest lines of ZnO. The intensity of the third strongest line of ZnO was counted to calculate the intensity of the strongest line of ZnO as

before. Very good agreement between the experimental values and the true values is shown in Table 3.

Sample 4 was prepared to check the sensitivity and detection limit of the method. It contains about 1% ZnO, 2%  $\text{TiO}_2$ , and 80%  $\text{CaCO}_3$  with 17%  $\text{Al}_2\text{O}_3$  as flushing agent. It is apparent that the same working equation (12) can be applied regardless of the concentration range. Note that the scintillation counter might be flooded if the concentration of a strongly diffracting component is extremely high (such as 90%), while the Reference Intensities are obtained at 50% concentration. In such situations, more  $\text{Al}_2\text{O}_3$  should be added to bring the concentration of the major component down. The lower concentration level, however, is limited only by the minimum size of the peak above background which is usually taken as three standard deviations of the background intensity. A sensitivity of 5 c.p.s. or better is typical with the solid-state scintillation counter. The detection limit depends upon the nature of the sample. Generally 0.5% by weight should be detectable.

The precision of intensity measurement is always in our favor. For example, the  $\text{TiO}_2$  peak in this case

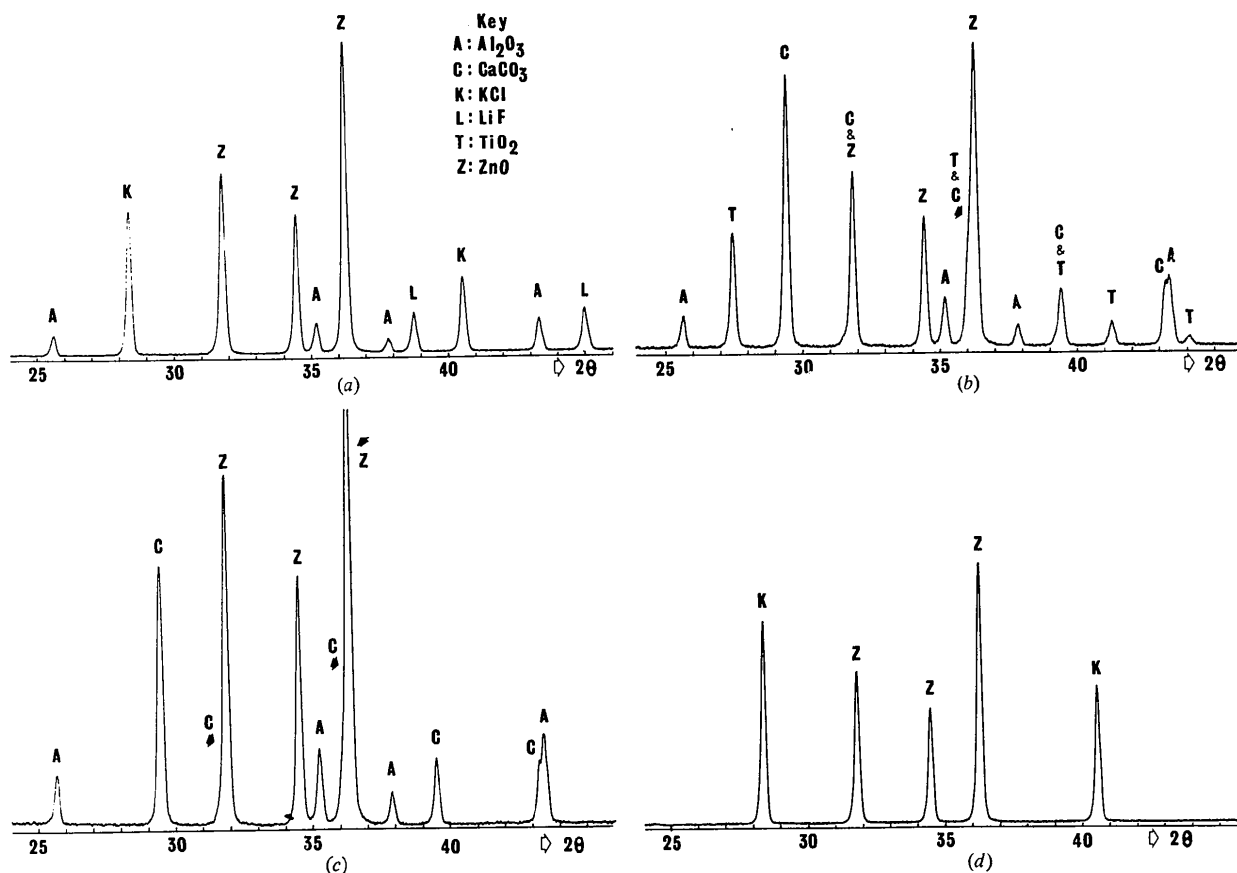


Fig. 1. The X-ray diffraction patterns of (a) Sample 1 where all peaks are resolved, (b) Sample 3 where there are some overlapping peaks, (c) Sample 5 which contains amorphous material, (d) the ZnO-KCl binary system for slope determination.

gives 7394 counts with a background of 1824 counts in a fixed time of 40 s. Since duplicate readings were taken the relative standard deviations (Jenkins & DeVries, 1967) is 1.7%, which is quite good in normal analysis.

$$\varepsilon \% = \frac{100 \sqrt{2}}{\sqrt{T}} \frac{\sqrt{R_p + R_b}}{R_p - R_b} = \frac{100 \sqrt{2}}{\sqrt{2 \times 40}} \frac{\sqrt{185 + 46}}{185 - 46} = 1.7 \%$$

#### Amorphous-content determination

Traditionally, X-ray diffraction analysis provides information about crystalline components in the sample. The presence or absence of amorphous materials is generally ignored.

An interesting feature of this matrix-flushing method is that it can be used to detect and determine the total amorphous material in a sample.

Sample 5 contains three components ZnO, CaCO<sub>3</sub> and SiO<sub>2</sub> (silica gel, amorphous). A normal scan of this sample, Fig. 1, does not indicate the presence of amorphous material. However, the matrix-flushing method shows a large intensity imbalance as shown in Table 3.

In this case

$$\sum \frac{I_i}{k_i} \ll \frac{X_0}{X_c} I_c$$

which indicates the presence of amorphous materials. By the use of equation (12) and material balance, 15.95% amorphous material is found. Comparing this with the 16.13% silica gel actually put in, the recovery is felt to be very good.

#### Auto-flushing

For any binary system, an auto-flushing phenomenon emerges. Each component automatically serves as flushing agent for the other component. No flushing agent is needed. The percentage composition can be obtained from a regular scan of the binary mixture. Three examples are cited to depict the features of the auto-flushing phenomenon.

Sample 6 is a binary system of ZnO and TiO<sub>2</sub> which represents a general case. Substituting the intensity ratio of the strongest line of ZnO to that of TiO<sub>2</sub> into equation (19), we have:

$$X_{\text{ZnO}} = \frac{1}{1 + \frac{4.35}{2.62} \cdot \frac{1461}{6259}} = 72.07 \%$$

$$X_{\text{TiO}_2} = \frac{1}{1 + \frac{2.62}{4.35} \cdot \frac{6259}{1461}} = 27.93 \%$$

These results compare very favorably with the true values as shown in Table 3.

Sample 7 is a special case of a binary system. It is composed of rutile and anatase TiO<sub>2</sub>, a polymorphic binary system. There is no matrix effect whatsoever in such a system, hence a linear relationship between

X-ray intensity and concentration exists for each component:

$$\begin{aligned} I_1 &= k_1^* X_1 \\ I_2 &= k_2^* X_2 \\ \frac{I_1}{I_2} &= \frac{k_1}{k_2} \cdot \frac{X_1}{X_2} \end{aligned} \quad (18)$$

Note that  $k_1^*$  and  $k_2^*$  are *not* the Reference Intensities. They are unknown constants and have to be determined by calibration curves, which is what Alexander & Klug have demonstrated.

Fascinatingly, the  $k_1$  and  $k_2$  in equation (18) derived from the matrix-flushing theory are indeed the Reference Intensities. The difference here is that  $k_1^*$  and  $k_2^*$  do contain absorption factors ( $\mu$ ) while the ratio ( $k_1/k_2$ ) does not. It was previously shown that all  $\mu$  factors are flushed out of the basic intensity-concentration equations (12), (15), (18) and (19).

Other polymorphic binary systems have been discussed in the literature, *e.g.* quartz and cristobalite SiO<sub>2</sub> (Alexander & Klug, 1948), calcite and aragonite CaCO<sub>3</sub> (Azaroff & Buerger, 1958), *etc.* The linear intensity-concentration relationship of all polymorphic systems was recognized and determined by calibration curves. The general nature of this linear relationship and the simplest way to obtain the slope was not discussed in the cited references.

Sample 8 is made of LiF and KCl to illustrate the simpler way to determine the slope  $k = k_1/k_2$  in equation (19) without using the Reference Intensities at all. The slope  $k$  is simply the corresponding intensity ratio of a 50/50 mixture of the same two components.

$$k = \left( \frac{I_{\text{LiF}}}{I_{\text{KCl}}} \right)_{50/50} = \frac{1846}{5583} = 0.331$$

Note that:

$$\frac{k_1}{k_2} = \frac{1.32}{3.87} = 0.341$$

$$X_{\text{LiF}} = \frac{1}{1 + 0.331 \times \frac{5371}{604}} = 25.36 \%$$

Similarly for a ZnO-KCl binary system:

$$k = \left( \frac{I_{\text{ZnO}}}{I_{\text{KCl}}} \right)_{50/50} = \frac{4747}{3956} = 1.20$$

while

$$\frac{k_1}{k_2} = \frac{4.35}{3.87} = 1.13$$

In conclusion, a general rule of auto-flushing for binary systems can be pronounced as follows:

For any binary system, the plot of weight ratio to X-ray intensity ratio is always a straight line passing through the origin. The slope of this line is equal to a singular value which is simply the corresponding intensity ratio of a 50/50 mixture of the two components.

In simple mathematics:

$$\begin{aligned} \frac{I_1}{I_2} &= k \frac{X_1}{X_2} \\ k &= \frac{I_1}{I_2} \text{ at } \frac{X_1}{X_2} = 1 \\ \text{or } k &= \left( \frac{I_1}{I_2} \right)_{50/50} = \text{slope.} \end{aligned} \quad (20)$$

This rule, concise and precise, makes the quantitative X-ray diffraction analysis of any binary system a very simple matter.

It is not necessary to choose the strongest line of the diffraction pattern, any line obeys this rule as long as the same line is used consistently. Therefore, overlapping peaks do not present a problem.

Furthermore, neither component needs to be a good crystalline material as long as the perfection or imperfection in crystal structure of the component sought is of the same order as that of the reference material used to determine the slope  $k$ . The extreme case is the newly developed X-ray diffraction method for the determination of crystallinity of polymers (Chung & Scott, 1973) where one component is amorphous while the other component is a poor crystalline material. It was found that the slope of the straight line in this reference is another proof of equation (20).

The application of this rule of auto-flushing is not confined to strictly binary systems. A case in point is Sample 4 which contains four components when  $\text{Al}_2\text{O}_3$  is counted as an unknown. However, this sample has only two major components  $\text{CaCO}_3$  and  $\text{Al}_2\text{O}_3$ . The minor components contribute only 4% by weight. If it can be regarded as a binary system of  $\text{CaCO}_3$  and  $\text{Al}_2\text{O}_3$ , then

$$X_{\text{Al}_2\text{O}_3} = \frac{1}{1 + \frac{1}{2.98} \frac{4756}{352}} = 18.1\%$$

(True value 17.1%; Note  $18.1 \times 96\% = 17.4\%$ ),

$$X_{\text{CaCO}_3} = \frac{1}{1 + 2.98 \times \frac{352}{4756}} = 81.9\%$$

(True value 79.0%; Note  $81.9 \times 96\% = 78.6\%$ ).

Fairly good results can be obtained this way and thus eliminate the addition of a flushing agent. If the percentage of the minor components is approximately known, closer results could be obtained.

### Discussion

In order to attain high precision and high accuracy of X-ray diffraction analysis by the matrix-flushing method, the following three factors deserve attention:

(1) The material used to determine the Reference Intensity must have the same level of perfection or imperfection in crystal structure as the component sought. The level of perfection or imperfection is revealed by the width of their diffraction lines.

(2) The grinding of the sample must be thorough enough to ensure optimum particle size and sample homogeneity.

(3) The loading of the sample into the sample holder must be free-falling as recommended by NBS Monograph 25 (1971) to avoid preferred orientation and induced packing.

The features of this matrix-flushing method are multifold, the more important ones are:

(1) No calibration curve is needed. All the matrix factors are flushed out of the intensity-concentration equation.

(2) No previous information about the approximate concentration range is required.

(3) All the intensity data are obtained from a single scan, hence the errors due to instrumental drift and sample preparation are eliminated.

(4) It can be used for amorphous-content determination as well as multicomponent analysis.

(5) The general rule of auto-flushing puts the analysis of any binary systems on its shortest route.

(6) It is a most general method in its simplest form embracing the three cases of quantitative analysis put forth by Klug & Alexander (1959).

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