Quantitative Interpretation of X-ray Diffraction Patterns of Mixtures. III. Simultaneous Determination of a Set of Reference Intensities

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A set of reference intensities, k_i, are required for the quantitative interpretation of X-ray diffraction patterns of mixtures. Each k_i was heretofore determined individually from binary mixtures of a one-to-one weight ratio. A procedure for the determination of all k_i's of interest simultaneously is presented. The X-ray diffraction patterns of multicomponent mixtures usually contain overlapping peaks. This overlapping problem can be avoided by choosing an arbitrary reference material already present in the mixture and/or using the strongest *resolved* reflections directly. These concepts are substantiated by ten examples. The maximum standard deviation of the matrix-flushing method has been estimated to be 8% relative.

Introduction

Any practical quantitative X-ray diffraction analysis may be put under one of the two categories: First, all components are crystalline and identified; secondly, some components are non-crystalline and/or unidentified. The former can be analyzed by the application of the 'adiabatic principle' (Chung, 1974a). The latter can be dealt with by the use of the 'matrix-flushing' method (Chung, 1974b). Either case requires the characteristic Reference Intensity, k_i, of the component i concerned. To determine the Reference Intensities individually one by one is simple. Nevertheless, an even simpler way for the determination of a set of k_i's simultaneously is established. It further eases the work of quantitative X-ray diffraction analysis.

Multiple k_i determination

From the adiabatic principle of X-ray diffraction analysis of mixtures, a linear relationship exists between the intensity ratio of diffracted X-rays of any two components in a mixture and the corresponding weight ratio of these two components. This intensity–concentration relationship is independent of the presence or absence of other components. Therefore, n Reference Intensities could be determined simultaneously from a mixture of $(n+1)$ components of *equal weight* including corundum (Chung, 1974a). Moreover, this intensity–concentration relationship is also independent of the amount of each component present. Hence, it is not even necessary to make the mixture of $(n+1)$ components equal in weight (Chung, 1974b). This concept has been verified and is reported herein.

The chemicals used and the procedures of analysis are the same as those described in previous reports (Chung, 1974a,b,c). Sample 1 was made of exactly 0·5000 g of each component. Sample 2 was made of the same set of components but of different amounts.

Sample 3 was made of four of the five components in Samples 1 and 2.

In these three samples, the strongest reflection of each component is resolved. The overlapping problem is taken up later. The intensities of these strongest reflections were counted using constant time (40 s). The composition and intensity data are shown in Table 1. The Reference Intensities were calculated with the following equation:

$$k_i = \left(\frac{X_c}{X_i}\right)\left(\frac{I_i}{I_c}\right) \tag{1}$$

where I and X are the X-ray intensity and weight percentage of component i and corundum c. The calculated k_i's are in good agreement with those obtained individually from 50/50 binary mixtures (Chung, 1974a,c). The intensity data are averages of duplicates.

Overlapping problem

In practical analysis, the sample may contain amorphous components, some components may be unidentified, and the strongest reflections may not be resolved. Samples 5 and 6 are typical examples of this nature. Sample 4 was prepared for the simultaneous determination of k_i's of components of interest in Samples 5 and 6. Note that only components of interest should be included in the sample for multiple k_i determination. Because of overlapping problems, the strongest *resolved* reflections are used directly without converting them to the strongest reflection of each component through the powder pattern of the respective pure compound. In this particular case, the strongest resolved reflections are the strongest reflection (110) of TiO_2, the second-strongest reflection (104) of Al_2O_3, the second-strongest reflection (211) of $BaSO_4$, and the third-strongest reflection (002) of ZnO. Their composition and intensity data are given in Table 2. All data are averages of duplicate determinations. Equation (1) is

used to calculate the k_i's from Sample 4. The following matrix-flushing equation (2) is used to calculate the percentage composition for Samples 5 and 6 with the k_i's obtained from Sample 4:

$$X_i = \left(\frac{X_c}{k_i}\right)\left(\frac{I_i}{I_c}\right). \qquad (2)$$

Arbitrary reference

The X-ray diffraction pattern of a multicomponent sample generally exhibits a large number of diffraction peaks. The introduction of corundum into a sample either for analysis or for multiple k_i determination may cause more overlapping problems. Therefore, it is

Table 1. *Composition and intensity data*

Sample No.	Component	Composition g	% Wt.	Intensity hkl	c.p.s.	k_i Calculated	50/50 Mixture
1.	ZnO	0·5000	20·00	101	1736	4·14	4·35
	CdO	0·5000	20·00	111	3208	7·66	7·62
	LiF	0·5000	20·00	200	533	1·27	1·32
	CaF₂	0·5000	20·00	220	565	1·35	1·41
	Al₂O₃	0·5000	20·00	113	419	1·00	1·00
2.	ZnO	0·4183	16·29	101	1564	4·28	4·35
	CdO	0·3562	13·87	111	2418	7·76	7·62
	LiF	0·6302	24·54	200	729	1·32	1·32
	CaF₂	0·5395	21·01	220	651	1·38	1·41
	Al₂O₃	0·6242	24·30	113	546	1·00	1·00
3.	ZnO	0·5554	32·54	101	4036	4·27	4·35
	CdO	0·2266	13·27	111	3029	7·85	7·62
	LiF	0·3712	21·74	200	778	1·23	1·32
	Al₂O₃	0·5539	32·45	113	943	1·00	1·00

Table 2. *Composition and intensity data*

Sample No.	Component	Composition g	Intensity hkl	c.p.s.	k_i	% Wt. Known	Found
4.	ZnO	0·4133	002	879	2·15	27·45	(Master
	TiO₂ (R)	0·3601	110	1061	2·97	23·92	Reference
	BaSO₄	0·3992	211	820	2·07	26·51	for
	Al₂O₃	0·3330	104	330	1·00	22·12	multiple
							k_i deter-
							mination)
5.	ZnO	0·4655	002	1034	2·15	28·93	28·9
	TiO₂ (R)	0·1961	110	617	2·97	12·19	12·5
	BaSO₄	0·4097	211	860	2·07	25·47	25·0
	SiO₂ Gel	0·2173	—	0	—	13·51	13·7
	Al₂O₃ Flushing	0·3202	104	331	1·00	19·90	—
6.	ZnO	0·2743	002	346	2·15	14·77	14·5
	BaSO₄	0·6894	211	894	2·07	37·13	38·8
	CdO	0·1869	—	—	—	10·07	—
	KBr	0·2620	—	—	—	14·11	—
	Al₂O₃ Flushing	0·4442	104	266	1·00	23·92	—

Table 3. *Composition and intensity data*

Sample No.	Component	Composition g	Intensity hkl	c.p.s.	k_i	% Wt. Known	Found
7.	ZnO	0·4062	002	587	1·00	18·05	(Master
	As₂O₃	0·5669	222	3056	3·73	25·20	Reference
	CdO	0·4192	200	2324	3·84	18·63	for multi-
	NiO	0·6281	200	1907	2·10	27·92	ple k_i
	PbO₂	0·2296	110	1349	4·07	10·20	determination)
8.	ZnO	0·4190	002	468	1·00	17·07	16·7
	As₂O₃	0·4423	222	1978	3·73	18·01	18·9
	CdO	0·4523	200	1984	3·84	18·42	18·4
	NiO	0·6163	200	1455	2·10	25·10	24·7
	PbO₂	0·5252	110	2428	4·07	21·40	21·3
9.	ZnO	0·6001	002	756	1·00	21·06	21·4
	As₂O₃	0·3145	222	1445	3·73	11·04	11·0
	CdO	0·8208	200	3977	3·84	28·81	29·3
	NiO	1·1135	200	2837	2·10	39·09	38·3
10.	ZnO	1·0050	002	985	1·00	35·12	35·4
	As₂O₃	0·6818	222	2413	3·73	23·83	23·2
	CdO	1·1747	200	4431	3·84	41·05	41·4

beneficial and rational to choose an arbitrary reference material already present in the sample rather than always choosing corundum as the fixed reference since any internally consistent set of k_i's should give equally correct results of analysis.

This concept is illustrated by the following examples. The percentage compositions of Samples 8, 9 and 10 are to be determined. Sample 7 was prepared to obtain an internally consistent set of k_i's based on the arbitrary reference chosen. The component ZnO is chosen arbitrarily as the reference material here which means $k_{ZnO} = 1$. Equation (1) is used to calculate the k_i's with reference to ZnO. That is $X_c = X_{ZnO}$ and $I_c = I_{ZnO}$. The following equation (3) from the adiabatic principle is used to calculate the percentage composition X_i's:

$$X_i = \left(\frac{k_i}{I_i} \sum_{i=1}^{n} \frac{I_i}{k_i} \right)^{-1}. \qquad (3)$$

Of course, any other component in the sample such as As_2O_3, CdO, etc., is also eligible for use as the arbitrary reference. The composition and intensity data are listed in Table 3. Note that the intensity of the strongest resolved reflections were measured and used directly.

Precision

The matrix-flushing method has been applied to the analysis of various real samples in our laboratory. In order to establish the precision of this method, a field sample containing aluminum powder, iron oxide and a clay was used for a statistical evaluation. Although the iron oxide (goethite, PDF 17–536) contains impurities and the clay (kaolinite, PDF 6–221) is a metastable mineral; hence not favorable for quantitative X-ray diffraction analysis, the matrix-flushing method can still be used since the original raw materials are available for making the reference.

The results of ten single determinations by the same analyst with the same instrument on different days are

listed in Table 4. Since all the three components in the sample are identified, the adiabatic principle can be applied and the iron oxide is chosen as an arbitrary reference so that $k_{Fe_2O_3} = 1.00$.

These data indicate that the variation in results of analysis is dependent on the content of component sought. The higher the content, the lower the standard deviation. The *maximum* standard deviation of each result of a single determination obtained by the same analyst using the matrix-flushing method on different days would be 8% relative. For duplicate determinations the standard deviations should be reduced by a factor of $1/\sqrt{2}$ (*i.e.* 0.707). Better precision is expected if the component sought has a more defined crystal structure and the reference material has a higher purity.

Note that in this particular application the content of aluminum powder cannot be easily determined by other elemental analyses because the component clay (kaolin, aluminum silicate) also contains aluminum.

Conclusions

In order to obtain a set of reference intensities simultaneously for quantitative multicomponent analysis by the matrix-flushing method, a synthetic reference mixture which contains all the components sought with or without corundum is required. It is convenient to designate this synthetic reference mixture as a 'Master Reference' which dictates what component should be assigned as the reference, specifies what reflection of each component should be chosen for intensity measurement, and eventually prescribes a consistent set of reference intensities.

By the use of Reference Intensities, the standard curves required for conventional quantitative X-ray diffraction analysis are no longer required. By the method of multiple k_i determination the need for preparation of several binary mixtures of an exact one-to-one weight ratio is avoided. By the direct use of the intensity data of the strongest resolved reflections, the overlapping problem is solved. By the choosing of an arbitrary reference material, the need for corundum as a standard and its associated difficulties are eliminated. Therefore, the quantitative interpretation of X-ray diffraction patterns of mixtures seems to be radically simplified without sacrificing accuracy.

Table 4. *Precisions for k_i and X_i*

	Reference Intensity			Composition, %		
	k_{Al}	$k_{Fe_2O_3}$	k_{clay}	X_{Al}	$X_{Fe_2O_3}$	X_{clay}
1	1·97	1	0·549	2·78	36·6	60·7
2	2·09	1	0·551	2·22	37·8	60·0
3	1·90	1	0·477	2·67	33·9	63·5
4	2·05	1	0·521	2·61	37·2	60·2
5	2·06	1	0·545	2·60	36·0	61·4
6	2·11	1	0·511	2·30	33·5	64·2
7	2·01	1	0·528	2·56	37·5	60·1
8	2·08	1	0·550	2·39	34·2	63·5
9	2·13	1	0·546	2·15	37·5	60·4
10	2·14	1	0·576	2·51	37·3	60·3
$\bar{X}$	2·05	1·00	0·535	2·48	36·2	61·4
S	0·07	—	0·026	0·21	1·7	1·7
$S/\bar{X}$	3%	—	5%	8%	5%	3%

$\bar{X}$ = Average value. S = Standard deviation.

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