Quantitative Interpretation of X-ray Diffraction Patterns of Mixtures. II.
Adiabatic Principle of X-ray Diffraction Analysis of Mixtures

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All the information relating to the quantitative composition of a mixture is coded and stored in its X-ray diffraction pattern. It has been the goal of X-ray diffraction analysts since the discovery of X-rays to retrieve and decode this information directly from the X-ray diffraction pattern rather than resort to calibration curves or internal standards. This goal appears to be attained by the application of the 'matrix-flushing theory' and the now-proposed 'adiabatic principle' in applied X-ray diffraction analysis. The matrix-flushing theory offers a simple intensity–concentration equation free from matrix effects which degenerates to 'auto-flushing' for binary systems. The adiabatic principle establishes that the intensity–concentration relationship between each and every pair of components in a multi component system is not perturbed by the presence or absence of other components. A key equation is derived which conducts the decoding process. Both the matrix-flushing theory and the adiabatic principle are experimentally verified.

Introduction

X-ray diffraction analysis has been a very important tool in industrial laboratories for quality control and routine analysis. It stands out from most other techniques since the results are in terms of the materials as they occur in the sample, not in terms of elements, ions, functional groups, fractional species, or spin coupling. However, the X-ray diffraction technique is plagued by the matrix effect which makes quantitative X-ray analysis difficult and time-consuming.

Azaroff & Buerger (1958) wrote: 'Unfortunately, the relations between the intensities of observed reflections and the percentage composition of a mixture are not simple and cannot be expressed by a usable mathematical expression. It is necessary, therefore, to use semi-empirical methods,' which refers to the internal-standard method of Klug & Alexander (1954).

This internal-standard technique is so far the best method for quantitative X-ray diffraction analysis (Kaelble, 1967). It adopts the usual procedure of constructing a calibration curve from standards for each component sought which is rather tedious especially for multicomponent analysis.

In a recent paper (Chung, 1974a) and in Part 1 of this paper (Chung, 1974b) the derivation of a very simple intensity–concentration equation free from matrix effect is described. This theory comprehends and simplifies the three important cases of quantitative X-ray diffraction analysis put forth by Klug & Alexander. For binary systems, it degenerates to an auto-flushing phenomenon. Further development of this theory leads to an 'adiabatic principle' in X-ray diffraction which is presented below. The adiabatic principle eliminates the flushing agent required in the matrix-flushing method. It makes the direct quantitative interpretation of the X-ray diffraction pattern of a mixture possible for the first time.

All information relating to the quantitative composition of a mixture is coded and stored in its X-ray diffraction pattern. The adiabatic principle is the key needed to retrieve and decode this information directly.

Adiabatic principle of auto-flushing

The well-known X-ray diffraction theory gives an expression for intensity of a reflection in a powder diffraction pattern which is well established and described elsewhere (Bunn, 1961; Azaroff, 1968; Nuffield, 1966):

$$I(hkl) = \left(\frac{I_0 \, e^4 \lambda^3 d}{32 \, \pi m^2 c^4 r} \right) \left(N^2 p F^2 \right)$$

$$\times \left(\frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta} \right) TAV, \qquad (1)$$

where:

I = Intensity of X-rays diffracted by (hkl) plane.
I_0 = Intensity of primary X-rays.
e, m = charge and mass of electron.
λ = X-ray wavelength.
d = slit width of detector.
c = Velocity of light.
r = Specimen-to-detector distance.
N = Number of unit cells per unit volume.
p = Multiplicity.
F = Structure factor.
θ = Bragg angle.
T = Temperature factor.
A = Absorption factor.
V = Volume of powder in the beam.

It consists of six factors as shown above, they are (1) a constant factor for a particular diffractometer, (2) a structure factor characteristic of the diffracting

sample, (3) an angle factor known as the Lorentz–polarization factor, (4) a temperature factor to correct for thermal vibration of atoms, (5) an absorption factor which attenuates the diffracted X-rays, and (6) the volume of powder in the primary X-ray beam, in the case of a mixture V indicates the volume fraction.

For quantitative X-ray diffraction analysis of a mixture of n components by use of a diffractometer such as the Philips' unit, the weight fractions of each component are sought. The only unknown variable in the intensity equation (1) is the absorption factor A, all the other factors can be kept constant (K).

Let μ_t and s be the linear absorption coefficient and thickness of the total sample, let V_i and X_i be the volume fraction and weight fraction of component i. Since the absorption of X-rays, just like the absorption of visible light, follows the well-known exponential law, for infinite specimen thickness, we have

$$A = \int_0^\infty \exp\left(-\mu_t s\right) \, ds = \frac{1}{\mu_t} \qquad (2)$$

$$\mu_t = \sum_{i=1}^n V_i \mu_i = \sum_{i=1}^n \frac{X_i}{\varrho_i} \mu_i = \sum_{i=1}^n X_i \left(\frac{\mu_i}{\varrho_i}\right) \qquad (3)$$

where ϱ_i and (μ_i/ϱ_i) are density and mass absorption coefficient of component i.

Therefore the complicated intensity equation (1) is reduced to:

$$I_i = \left(\frac{K_i}{\varrho_i \mu_t}\right) X_i = k_i X_i \qquad (4)$$

where k_i is a factor containing the mass absorption coefficient of the total sample. At this moment, k_i is constant for a very small variation in X_i. Later on, it will be shown that k_i in the ratio k_i/k_j is constant for any X_i.

For the quantitative X-ray diffraction analysis of a mixture of n components, we have n unknowns (X_i, $i = 1$ to n) which must satisfy the following ($n + 1$) equations:

$$\left.\begin{aligned} I_1 &= k_1 X_1 \\ I_2 &= k_2 X_2 \\ &\;\;\vdots \\ &\;\;\vdots \\ I_n &= k_n X_n \\ X_1 + X_2 + &\ldots + X_n = 1 \end{aligned}\right\} \qquad (5)$$

This situation can be most conveniently treated in terms of matrix algebra:

$$\begin{bmatrix} k_1 & 0 & 0 & \ldots & 0 \\ 0 & k_2 & 0 & \ldots & 0 \\ 0 & 0 & k_3 & \ldots & 0 \\ & \cdots\cdots\cdots\cdots \\ 0 & 0 & 0 & \ldots & k_n \\ 1 & 1 & 1 & \ldots & 1 \end{bmatrix} \begin{bmatrix} X_1 \\ X_2 \\ X_3 \\ \cdot \\ \cdot \\ \cdot \\ X_n \end{bmatrix} = \begin{bmatrix} I_1 \\ I_2 \\ I_3 \\ \cdot \\ \cdot \\ \cdot \\ I_n \\ 1 \end{bmatrix} \qquad (6)$$

If the above matrix equation, $KX = I$, has a solution, the solution is unique if and only if the rank of the (K) matrix is equal to the rank of the (K, I) matrix which is also equal to the number of unknowns.

In other words, the necessary and sufficient conditions for the existence of a unique solution of equation (6) is that all its characteristic determinants vanish.

In order to satisfy these conditions, the unique solution of equation (6) has the following simple and symmetrical form:

$$X_i = \left(\frac{k_i}{I_i} \sum_{i=1}^n \frac{I_i}{k_i}\right)^{-1} . \qquad (7)$$

Note that the unusual property of this unique solution is that the weight fraction of any component in a multicomponent system is expressed in terms of ratios like I_i/I_j and k_i/k_j ($i,j = 1,2,\ldots,n$).

From equation (4), each individual k_i contains an absorption factor. However, the ratio k_i/k_j contains no absorption factor, the absorption factor is flushed out. From equation (5):

$$\frac{I_i}{I_j} = \frac{k_i}{k_j} \cdot \frac{X_i}{X_j} \qquad (8)$$

$$\frac{k_i}{k_j} = \frac{I_i}{I_j} \quad \text{at} \quad \frac{X_i}{X_j} = 1 \qquad (9)$$

or

$$\frac{k_i}{k_j} = \left(\frac{I_i}{I_j}\right)_{50/50} = \text{slope} = \text{constant} . \qquad (10)$$

It can be shown easily (Chung, 1974a,b) that the ratio of k_i/k_j is the same ratio of respective Reference Intensities (Berry, 1972). Therefore, the correct solution X_i in equation (7) can be obtained by use of the intensity data directly from the X-ray diffraction pattern of the mixture and the corresponding Reference Intensities ($k_i = I_i/I_c$) of the components.

The foregoing deduction can be summarized in the following theorem:

The plot of intensity ratio (I_i/I_j) to the weight ratio (X_i/X_j) of any two components is a straight line passing through the origin with a slope equal to the ratio of corresponding Reference Intensities (k_i/k_j). This intensity–concentration relationship between each and every pair of components in a multi-component system is not perturbed by the presence or absence of other components. In other words, the auto-flushing phenomenon (Chung, 1974 a,b) of any binary system always holds true regardless of the coexistence of other components.

This theorem can be logically called the 'adiabatic principle of auto-flushing', analogous to the adiabatic principle in molecular spectroscopy and in quantum mechanics.

The unique solution, equation (7), can also be arrived at in reverse by applying the adiabatic principle of auto-flushing to a multicomponent system.

In the matrix-flushing method, the only nuisance variable μ_t in equation (4) is flushed out, the constant

term k_i is obtained through Reference Intensities. Thus a very simple intensity–concentration equation free from matrix effect is accomplished:

$$\frac{I_i}{I_c} = \frac{k_i}{k_c} \cdot \frac{X_i}{X_c} , \qquad (11)$$

where X_c and I_c are the weight fraction and the X-ray intensity of the flushing agent, corundum, k_i and k_c are Reference Intensities of component i and corundum respectively ($k_i = I_i/I_c$, $k_c = 1$). The X-rays do not discriminate between a flushing agent and a component. So the same intensity–concentration relationship should hold true between each and every pair of components in a multicomponent system.

For an n-component system, there are $_nC_2 = n(n-1)/2$ combinations of pairs. There is an equation like equation (11) for each pair of components. However, only $(n-1)$ out of these $n(n-1)/2$ equations are independent. But a normalization equation is available to make up n equations for the n unknowns X_i ($i = 1,2,\ldots,n$). Therefore:

$$\left.\begin{array}{c} \dfrac{I_1}{I_2} = \dfrac{k_1}{k_2} \cdot \dfrac{X_1}{X_2} \\[2mm] \dfrac{I_1}{I_3} = \dfrac{k_1}{k_3} \cdot \dfrac{X_1}{X_3} \\ \cdot \\ \cdot \\ \cdot \\ \dfrac{I_1}{I_n} = \dfrac{k_1}{k_n} \cdot \dfrac{X_1}{X_n} \\[2mm] X_1 + X_2 + \ldots + X_n = 1 \end{array}\right\} . \qquad (12)$$

Solving the n simultaneous equations we obtain n roots identical to that in equation (7).

Equation (7) is an exact deduction, since neither assumption nor approximation is made to derive it from the basic equation (1).

This concise yet precise conclusion has been found to simplify greatly applied X-ray diffraction analysis. It provides the key to retrieving and decoding the quantitative information coded and stored in X-ray diffraction patterns.

Another interesting consequence of the adiabatic principle of auto-flushing is that it offers a unified sensitivity expression. Let S be the unified sensitivity of an X-ray diffraction method for a certain sample. Then

$$S = \frac{I_i}{k_i X_i} = \sum_{i=1}^{n} \frac{I_i}{k_i} = \text{constant} . \qquad (13)$$

The unit of the unified sensitivity S is c.p.s./1% Al_2O_3 no matter whether Al_2O_3 is a component of the sample or not. As indicated in equation (13), the unified sensitivity is a constant for any component in the same sample, but it is different for the same component in a different sample. This is because the unified sensitivity is a means to sense the presence of an absorption

effect. The higher the absorption, the lower the S value. Their quantitative relationship is:

$$\frac{S_I}{S_{II}} = \frac{\mu_{II}}{\mu_I} , \qquad (14)$$

where S_I and S_{II} are the unified sensitivities of two samples I and II and μ_I and μ_{II} are the total mass absorption coefficients of samples I and II respectively.

The sensitivity for a component i in a given sample is defined as the rate of change in net signal output, I_i (c.p.s.), to concentration increment, X_i (%), which is also the slope of a calibration curve. Hence the sensitivity for a component i in a sample by X-ray diffraction is:

$$S_i = \frac{I_i}{X_i} = k_i S . \qquad (15)$$

The unit of S_i is c.p.s./% of component i.

The detection limit for a component i in a given sample is defined as the minimum concentration, X_i (%), required to give an observable signal, I_i (c.p.s.), which is usually taken as three standard deviations of the background intensity, $3\sqrt{N_b}$ (Birks, 1959). Hence the detection limit for component i in a sample by the X-ray diffraction technique is:

$$X_i(\text{d.l.}) = \frac{3}{k_i S} \sqrt{\frac{I_b}{t}} = \frac{3}{S_i} \sqrt{\frac{I_b}{t}} , \qquad (16)$$

where

$S =$ Unified sensitivity for the sample.
$S_i =$ Sensitivity for component i in the sample.
$I_b =$ Background counting rate (c.p.s.).
$t =$ Background counting time (s).
$N_b =$ Background counts accumulated in t seconds.

Note the explicit relationship between sensitivity, S_i, and the detection limit, X_i (d.l.), in quantitative X-ray diffraction analysis.

The soundness and usefulness of this adiabatic principle of auto-flushing are demonstrated in the Experimental section.

Experimental

As discussed earlier in this report, the percentage composition of any mixture is coded and stored in its X-ray diffraction pattern. The adiabatic principle of auto-flushing offers a key to the retrieval and decoding of it. In order to demonstrate this point, four test mixtures of four components each were prepared with six chemical compounds of analytical reagent grade or better, the chemicals used are ZnO (certified A.C.S., Fisher Sci. Co.), KCl (Anal. Reagent, Mallinckrodt Chem. Works), LiF (Baker Anal. Reagent, Baker Chem. Co.), $CaCO_3$ (Baker Anal. Reagent, Baker Chem. Co.), α-Al_2O_3 (Linde semiconductor grade, 1 micron, Union Carbide), and TiO_2 (99·7% rutile). Each test mixture was ground for about 20 min with an automatic mortar grinder (Fisher Scientific Co.) to

achieve optimum particle size and sample homogeneity. The fine powder was introduced into the sample holder in accordance with the method recommended by NBS Monograph 25 (1971) to avoid preferred orientation and induced packing. Then the X-ray diffraction pattern was obtained or specific peaks were counted to collect intensity data. A Norelco diffractometer equipped with a solid-state scintillation counter,

graphite-crystal-monochromatized Cu $K\alpha$ radiation, integrated-circuit panel, and pulse-height analyzer was used for this work. The strongest line of each component is measured if it is resolved; otherwise, the strongest resolved line is measured, which is then converted to the intensity of its strongest line through direct comparison with the X-ray diffraction pattern of the pure compound.

Since the Reference Intensities $(k_i = I_i/I_c)$ given in the Powder Diffraction File (Berry, 1972) have only two digits, the Reference Intensities of these six chemical compounds were determined by a procedure identical to that used for the actual analysis. The more detailed procedures are described in the previous paper (Chung, 1974b). Note that the concentrations of all components including Al_2O_3 are unknown. No flushing agent was used.

All the peaks are resolved in the X-ray diffraction patterns of samples 1 and 2, while some peaks are overlapping in that of samples 3 and 4 as shown in Fig. 1. Only about 1% ZnO and 2% TiO_2 were put into Sample 4 to check the detection limit.

The experimental data obtained are presented in Table 1. Sample 1 is used to present a typical calculation as shown below.

From the key equation (7):

$$X_i = \cfrac{1}{k_i \cfrac{I_i^*}{I_i^*} \sum_{i=1}^{4} \cfrac{I_i}{k_i}},$$

$$X_1 = \cfrac{1}{1 + \cfrac{k_1}{I_1}\left(\cfrac{I_2}{k_2} + \cfrac{I_3}{k_3} + \cfrac{I_4}{k_4}\right)}.$$

$$X_{ZnO} = \cfrac{1}{1 + \cfrac{4 \cdot 35}{5968}\left(\cfrac{2845}{3 \cdot 87} + \cfrac{810}{1 \cdot 32} + \cfrac{599}{1 \cdot 00}\right)} = 41 \cdot 32\%,$$
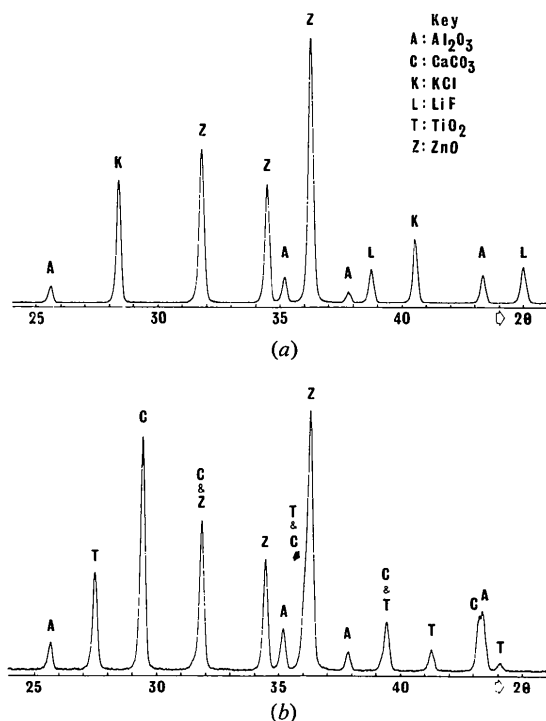

Fig. 1. The X-ray diffraction patterns of (a) Sample 1 where all peaks are resolved, (b) Sample 3 where there are some overlapping peaks.

Table 1. *Intensity and composition data*

These data are the same set used by Chung 1974a,b except that the % Al_2O_3 is counted as unknown here.

Sample	Composition (g)		Intensity I (c.p.s.)	Reference Intensity k_i	% Composition, X_i Known	Found	$\sum X_i$	$S = \dfrac{I_i}{k_iX_i}$
1	ZnO	1·8901	5968	4·35	41·49	41·32		33·2
	KCl	1·0128	2845	3·87	22·23	22·12		33·2
	LiF	0·8348	810	1·32	18·32	18·48		33·2
	Al_2O_3	0·8181	599	1·00	17·96	18·05	99·97	33·2
2	ZnO	0·9532	2856	4·35	18·98	19·42		33·8
	KCl	0·6601	1651	3·87	13·15	12·61		33·8
	LiF	0·8972	765	1·32	17·87	17·15		33·8
	Al_2O_3	2·5114	1719	1·00	50·00	50·84	100·02	33·8
3	ZnO	0·6759	2408	4·35	24·38	25·32		21·9
	TiO_2	0·4317	931	2·62	15·57	16·23		21·9
	$CaCO_3$	1·1309	2558	2·98	40·79	39·22		21·9
	Al_2O_3	0·5341	420	1·00	19·26	19·19	99·96	21·9
4	ZnO	0·0335	120	4·35	1·38	1·36		20·3
	TiO_2	0·0633	139	2·62	2·60	2·61		20·3
	$CaCO_3$	1·9197	4756	2·98	78·96	78·66		20·3
	Al_2O_3	0·4147	352	1·00	17·06	17·36	99·99	20·3

$$X_{KCl} = \cfrac{1}{1 + \cfrac{3 \cdot 87}{2845}\left(\cfrac{5968}{4 \cdot 35} + \cfrac{810}{1 \cdot 32} + \cfrac{599}{1 \cdot 00}\right)} = 22 \cdot 12\%,$$

$$X_{LiF} = \cfrac{1}{1 + \cfrac{1 \cdot 32}{810}\left(\cfrac{5968}{4 \cdot 35} + \cfrac{2845}{3 \cdot 87} + \cfrac{599}{1 \cdot 00}\right)} = 18 \cdot 48\%,$$

$$X_{Al_2O_3} = \cfrac{1}{1 + \cfrac{1 \cdot 00}{599}\left(\cfrac{5968}{4 \cdot 35} + \cfrac{2845}{3 \cdot 87} + \cfrac{810}{1 \cdot 32}\right)} = 18 \cdot 05\%.$$

As shown in Table 1, in each case, very close agreement between experimental data and true values is realized; hence the correctness and authenticity of the adiabatic principle is experimentally verified.

Note that the unified sensitivity $S = I_i/k_i X_i = $ constant for each component in the same sample, as is implied in the adiabatic principle.

The detection limit of the X-ray diffraction analysis depends on the minimum detectable peak intensity above the background. This minimum intensity is usually taken as three standard deviations of the background intensity (Birks, 1959). The backgiound intensities of this set of experiments range from 1000 to 3000 counts in 40 s; hence the standard deviation of the background intensity is $\sqrt{3000} \simeq 55$ counts, or $55/40 \simeq 1 \cdot 5$ c.p.s. Therefore, the required minimum peak intensity is $3 \times 1 \cdot 5 = 4 \cdot 5$ c.p.s.

The detection limit of ZnO in Sample 4 is calculated as follows:

Let ZnO be component 1, Al_2O_3 be component 2, and apply the adiabatic principle:

$$\frac{I_1}{I_2} = \frac{k_1}{k_2} \cdot \frac{X_1}{X_2}.$$

We have $I_1 = 4 \cdot 5$ c.p.s. (minimum peak intensity), $I_2 = 352$ c.p.s. (experimental intensity), $X_2 = 17 \cdot 06\%$ (concentration of Al_2O_3), $k_1 = 4 \cdot 35$, $k_2 = 1 \cdot 00$, thus the detection limit of ZnO is $X_1 = 0 \cdot 05\%$. It is not necessary to choose Al_2O_3 as the second component. Choosing either TiO_2 or $CaCO_3$ would give the same detection limit, which is of course a natural conclusion if the adiabatic principle holds true. Alternatively by substituting the above known quantities into equation (16), the same detection limit for ZnO can be obtained.

Discussion

It has been an ideal, if not a dream, of X-ray diffraction analysts since the discovery of X-rays to determine the quantitative composition of a mixture from its X-ray diffraction pattern directly without resorting to a calibration curve or internal standard. This ideal seems to be fully realized by utilizing the matrix-flushing theory and the adiabatic principle of auto-flushing. The conclusion is simple and the method is straight forward. It broadens the field of application of this well-known technique.

It is not necessary to choose the strongest line of the diffraction pattern for intensity measurement. Any line of the diffraction pattern obeys the adiabatic principle as long as the same line is used consistently, although using the strongest line improves the sensitivity and detection limit of the measurement. For a component of extremely high concentration, it might be beneficial not to use the strongest line in order to avoid the possibility of a flooded counter.

The components sought need not be good crystalline materials. The criterion is that the material used to determine the Reference Intensity must have the same level of crystallinity as the component in the sample. The line width of reflections in an X-ray diffraction pattern is a good indication of the crystallinity of the component.

Corundum has been chosen as the reference material because of its purity, stability and availability. However, many materials have these good qualities, *e.g.* CaF_2, MgO, KCl, *etc.* all of which have cubic symmetry (α-Al_2O_3 has trigonal symmetry), very simple patterns, and low d spacings. They are equally eligible for use as the reference material. By choosing a standard reference material and by standardizing the diffractometer design, the Reference Intensities can be quoted to three significant figures and documented systematically. This would benefit everyone in the field of applied X-ray diffraction analysis.

The emergence of the adiabatic principle of auto-flushing makes the quantitative interpretation of X-ray diffraction patterns of mixtures possible for the first time. However, it will not supersede the matrix-flushing method because of the unique features of the latter:

(1) The matrix-flushing method can predict and determine the presence of amorphous material in a sample while the adiabatic method cannot.

(2) The matrix-flushing method can be applied to samples containing unidentified components by analyzing for only those components of interest. The adiabatic method can be applied to samples where all the components must be fully identified, by analyzing either for all the components or for none of them.

References

AZAROFF, L. V. & BUERGER, M. J. (1958). *The Powder Method in X-Ray Crystallography*, p. 200. New York: McGraw-Hill.

AZAROFF, L. V. (1968). *Elements of X-Ray Crystallography*, p. 202. New York: McGraw-Hill.

BERRY, C. (1972). *Inorganic Index to the Powder Diffraction File*, p. 1421. Joint Committee on Powder Diffraction Standards, Pennsylvania.

BIRKS, L. S. (1959). *X-Ray Spectrochemical Analysis,* p. 54. New York: Interscience.

BUNN, C. W. (1961). *Chemical Crystallography,* p. 223. Oxford: Univ. Press.

CHUNG, F. H. (1974a). *Advanc. X-ray Anal.* **17**, 106–115.

CHUNG, F. H. (1974b). *J. Appl. Cryst.* **7**, 519–525.

KAELBLE, E. F. (1967). *Handbook of X-Rays,* p. 12-1. New York: McGraw-Hill.

KLUG, H. P. & ALEXANDER, L. E. (1954). *X-Ray Diffraction Procedures,* p. 415. New York: John Wiley.

NBS Monograph 25 (1971). *Standard X-Ray Diffraction Powder Patterns,* p. 3. Washington D.C.: U.S. Government Printing Office.

NUFFIELD, E. W. (1966). *X-Ray Diffraction Methods,* p. 107. New York: John Wiley.

Effective Elimination of the Compton Component in Amorphous Scattering by Experimental Means*

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In the X-ray scattering from amorphous materials, the coherent-peak profile overlapped with part of the Compton distribution can be directly obtained at each $(\sin \theta)/\lambda$, with an energy-dispersive detector and multichannel pulse-height analyzer combination adapted to an X-ray diffractometer. For the 'effective' elimination of the Compton component it is useful for one to pick out the half-profile, I_{bh}, on the higher-energy side of the peak maximum of the incident beam (in an energy scan at fixed scattering angle). On the assumption that the Compton scattering occurs within a range of energy lower than that of the incident radiation, the Compton contribution to I_{bh} is negligibly small compared to the strong coherent intensity and I_{bh} can be taken to represent the coherent intensity. As an illustration, the method is applied to the scattering from amorphous selenium. The resulting radial distribution function is in good agreement with the carefully examined result of using a crystal monochromator in the diffracted beam.

Introduction

The X-ray method has been extensively applied to the determination of the structure of liquids and amorphous solids. The results can be portrayed as a radial distribution function which may be derived from a Fourier transform of only the coherent or unmodified component scattered from the sample. Since, as is well known, incoherent, Compton or modified scattering is also produced overlapping the coherent scattering, this Compton component must be subtracted from the total scattered intensity. It is, however, a major problem to assess the intensity of the coherent component at a sufficiently large value of $(\sin \theta)/\lambda$, because the coherent intensity at such a value is considerably weaker than the Compton intensity. It is, therefore, desirable that the Compton component is removed as effectively as possible in experimental measurements.

Of course, one can eliminate the Compton component in some cases; *e.g.,* when a sufficiently high-resolution crystal monochromator is used in the dif-

fracted beam, or when the fluorescence-excitation method of Warren & Mavel (1965) is used. Alternatively, the Compton component can be effectively eliminated by the use of energy-dispersive diffractometry; this is achieved with a solid-state detector (SSD) and multichannel pulse-height analyzer (MPHA) combination with a conventional X-ray goniometer. With this method, the rather strong intensity of the coherent component, from which the Compton component has been effectively eliminated by picking out a half-profile I_{bh} (see Fig. 2), can be obtained. This procedure, as it were, takes the place of an ideal monochromator in the diffracted beam. In this paper, this useful method is explained in detail with reference to the scattering from amorphous selenium.

Experimental and results

Apparatus

Diffraction data were obtained with the experimental arrangement shown in Fig. 1. Radiation from a line-focus tube is filtered by a β-filter and then falls upon the amorphous sample. A conventional goniometer with adjustable slits and $4 \cdot 9°$ lateral Soller slits is used. A