

Chapter 9

Phase Identification by X-Ray Diffraction

9-1 INTRODUCTION

A given substance always produces a characteristic diffraction pattern, whether that substance is present in the pure state or as one constituent of a mixture of substances. This fact is the basis for the diffraction method of chemical analysis. *Qualitative analysis* for a particular substance is accomplished by identification of the pattern of that substance. *Quantitative analysis* is also possible, because the intensities of the diffraction lines due to one phase of a mixture depend on the proportion of that phase in the specimen.

The particular advantage of diffraction analysis is that it discloses the presence of a substance *as that substance actually exists in the sample*, and not in terms of its constituent chemical elements. For example, if a sample contains the compound A_xB_y , the diffraction method will disclose the presence of A_xB_y as such, whereas ordinary chemical analysis would show only the presence of elements A and B. Furthermore, if the sample contained both A_xB_y and $A_xB_{z_y}$, both of these compounds would be disclosed by the diffraction method, but chemical analysis would again indicate only the presence of A and B.¹ To consider another example, chemical analysis of a plain carbon steel reveals only the amounts of iron, carbon, manganese, etc., which the steel contains, but gives no information regarding the phases present. Is the steel in question wholly martensitic, does it contain both martensite and austenite, or is it composed only of ferrite and cementite? Questions such as these can be answered by the diffraction method. Another rather obvious appli-

¹ Of course, if the sample contains only A and B, and if it can be safely assumed that each of these elements is wholly in a combined form, then the presence of A_xB_y and $A_xB_{z_y}$ can be demonstrated by calculations based on the amounts of A and B in the sample. But this method is not generally applicable, and it usually involves a prior assumption as to the constitution of the sample. For example, a determination of the total amounts of A and B present in a sample composed of A, A_xB_y , and B cannot, in itself, disclose the presence of A_xB_y , either qualitatively or quantitatively.

cation of diffraction analysis is in distinguishing between different allotropic modifications of the same substance: solid silica, for example, exists in one amorphous and six crystalline modifications, and the diffraction patterns of these seven forms are all different.

Diffraction analysis is therefore useful whenever it is necessary to know the state of chemical combination of the elements involved or the particular phases in which they are present. As a result, the diffraction method has been widely applied for the analysis of such materials as ores, clays, refractories, alloys, corrosion products, wear products, industrial dusts, etc. Compared with ordinary chemical analysis, the diffraction method has the additional advantages that it is usually much faster, requires only a very small sample, and is nondestructive. Detailed treatments of chemical analysis by x-ray diffraction are given by Klug and Alexander [G.17] and Jerkins and Snyder [G.25].

9-2 BASIC PRINCIPLES

The powder pattern of a substance is characteristic of that substance and forms a sort of fingerprint by which the substance may be identified. A collection of diffraction patterns for a great many substances, allows identification of an unknown by recording its diffraction pattern and then locating in the file of known patterns one which matches the pattern of the unknown exactly. The collection of known patterns has to be fairly large, if it is to be at all useful, and then pattern-by-pattern comparison in order to find a matching one becomes out of the question.

What is needed is a system of classifying the known patterns so that the one which matches the unknown can be located quickly. Such a system was devised by Hanawalt in 1936 [9.1]. Any one powder pattern is characterized by a set of line positions 2θ and a set of relative line intensities I/I_1 , scaled relative to I_1 , the peak in the pattern with maximum intensity. But the angular positions of the lines depend on the wavelength used, and a more fundamental quantity is the spacing d of the lattice planes forming each line. Hanawalt therefore decided to describe each pattern by listing the d and I values of its diffraction lines, and to arrange the known patterns in decreasing values of d for the strongest line in the pattern. This arrangement made possible a search procedure which would quickly locate the desired pattern. In addition, the problem of solving the pattern was avoided and the method could be used even when the crystal structure of the substance concerned was unknown.

9-3 POWDER DIFFRACTION FILE

The task of building up a collection of known patterns was initiated by Hanawalt, Rinn, and Frevel [9.1] at the Dow Chemical Company; they obtained and classified diffraction data on some 1000 different substances. It soon became apparent that these data were of great potential value to a wide range of industries and, beginning in 1941, several technical societies, including the American Society for Testing and Materials, began to cooperate in acquiring and disseminating diffraction data. From

ores المواد الخام
refractory مادة مقاومة للحرارة
corrosion التآكل

1941 to 1969 the ASTM published and sold an increasing volume of data in the form of 3×5 in. file cards, one card for each pattern. Since 1969 this activity has been carried out by the Joint Committee on Powder Diffraction Standards (JCPDS) which in 1978 was renamed the International Centre for Diffraction Data (ICDD) [9.2]. Approximately three-hundred scientists from around the world participate in the Centre. In 1995 the Powder Diffraction File (PDF) contained nearly 62,000 diffraction patterns in 45 sets, with a new set of about 2000 patterns being added each year. The substances included are elements, alloys, inorganic compounds, minerals, organic compounds, and organometallic compounds.

Hanawalt Method

Since more than one substance can have the same, or nearly the same, d value for its strongest line and even its second strongest line, Hanawalt decided to characterize each substance by the d values of its three strongest lines, namely d_1 , d_2 , and d_3 for the strongest, second-strongest, and third-strongest line, respectively. The values of d_1 , d_2 , and d_3 , together with relative intensities, are usually sufficient to characterize the pattern of an unknown and enable the corresponding pattern in the file to be located. Originally, in each section or set of the ASTM file, the cards were arranged in groups characterized by a certain range of d_1 spacings and identified by a set number and a card number within that set. Within each group, e.g., the group covering d_1 values from 2.29 to 2.25 Å, the cards were arranged in decreasing order of d_2 values, rather than d_1 values. When several substances in the same group had identical d_2 values, the order of decreasing d_3 values was followed. The groups themselves were arranged in decreasing order of their d_1 ranges. However, as the number of cards grew, the direct card search became unwieldy, and it was recognized that it would become more cumbersome as the file became larger. Accordingly, the JCPDS decided to number the cards randomly, or chronologically, in each set, rather than according to the value of d_1 , and to use the Hanawalt Search Manual to replace the group-arranged card sets.

A typical card from the PDF is reproduced in Fig. 9-1. Note that new patterns have superceded older patterns in a number of cases when better data became available, and, for this reason, there are gaps in the older sets of cards. Individual 3×5 in. (8×13 cm) cards are no longer available. Instead, these cards, grouped in inorganic and organic sections, are found in the following forms:

Microfiche. Cards are photographically reduced and printed on 4×6 in. (10×15 cm) sheets of photographic film (microfiche), but this format is fading from use.

Books. Cards from Sets 1 to 45 are reproduced, three to a page, in book form. All cards from these sets, inorganic and organic, are included. The number of sets per volume has decreased as the rate of addition of new patterns have increased.

5-628		1	2	3	4					
d	2.82	1.99	1.63	3.26	NaCl	★				
I/I_1	100	55	15	13	Sodium Chloride	(Halite)				
Rad. $\text{CuK}\alpha_1$	λ 1.5405	Filter Ni	Dia.		d Å	I/I_1	hkl	d Å	i/I_1	hkl
Cut off	I/I_1	Diffraction	I/I cor.		3.258	13	111			
Ref. Swanson and Fuyat, NBS Circular 539, Vol. 2, 41 (1953)					2.821	100	200			
					1.994	55	220			
					1.701	2	311			
					1.628	15	222			
Sys. Cubic		S.G. Fm3m (225)			1.410	6	400			
a 5.6402	b	c	A	C	1.294	1	331			
β	γ	Z 4	Dx	2.164	1.261	11	420			
Ref. Ibid.					1.1515	7	422			
ϵ a	n ω β	1.542	ϵ γ	Sign	1.0855	1	511			
2V	D	mp	Color	Colorless	0.9969	2	440			
Ref. Ibid.					.9533	1	531			
					.9401	3	600			
					.8917	4	620			
An ACS reagent grade sample recrystallized twice from hydrochloric acid.					.8601	1	533			
X-ray pattern at 26°C.					.8503	3	622			
Merck Index, 8th Ed., p. 956.					.8141	2	444			
FORM 2					9					

Figure 9-1 Standard 3 × 5 in. JCDD diffraction data card (card 628 from Set 5) for sodium chloride. Appearing on the card are 1 (file number), 2 (three strongest lines), 3 (lowest-angle line), 4 (chemical formula and name of substance), 5 (data on diffraction method used), 6 (crystallographic data), 7 (optical and other data), 8 (data on specimen), and 9 (diffraction pattern). Intensities are expressed as percentages of I_1 , the intensity of the strongest line on the pattern. Most cards have a symbol in the upper right corner indicating the quality of the data: * (high quality), i (lines indexed, intensities fairly reliable), c (calculated pattern), and o (low reliability). (Courtesy of International Centre for Diffraction Data)

Magnetic Tape. Various formats are available for different tape drives and computer operating systems, but this media has become more or less obsolete since software began to be distributed via CDs.

CD-ROM. These are optical discs read with low-power laser light reflected from a pattern of pits written by the recording laser. Typically 680 Mbytes of data can be stored in a disc, and because the CD technology was originally developed for consumer audio electronics, it is very cost-effective and provides good performance for databases such as the PDF.

Numerous vendors offer software for searching computer-based format of the PDF for a particular pattern, using numerical, alphabetical or other methods.

1. **Alphabetical.** Substances are listed alphabetically by name. After the name are given the chemical formula, the d values and relative intensities (as subscripts) of the three strongest lines and the file number of the card. All entries are fully cross-indexed: i.e., both "sodium chloride" and "chloride"

sodium" are listed. This manual is useful if the investigator has any knowledge of the chemical composition of the sample.

2. *Numerical.* Substances are listed in terms of the d spacings of their three strongest lines, and d spacings and intensities are given for a total of eight lines for each substance. Also included are the chemical formula and file number. Each substance is currently listed twice (d_1, d_2 and d_2, d_1) if $I_2/I_1 > 0.75$ and $I_3/I_1 \leq 0.75$. If $I_3/I_1 > 0.75$ and $I_4/I_1 < 0.75$, the substance is listed three times ($d_1, d_2; d_2, d_1; d_3, d_1$). The pattern appears four times when $I_4/I_1 > 0.75$ ($d_1, d_2; d_2, d_1; d_3, d_1; d_4, d_1$). All entries are divided into groups according to the first spacing listed; the arrangement within each group is in decreasing order of the second spacing listed. The purpose of these additional listings (second-strongest line first and third-strongest line first) is to enable the user to match an unknown with an entry in the search manual even when complicating factors have altered the relative intensities of the three strongest lines of the unknown. These complications are usually due to the presence of more than one phase in the sample. This leads to additional lines and even superimposed lines. Use of the numerical search manual requires no knowledge of the chemical composition of the sample.

Fink Method

The Fink method [9.3] of numerical searching of the data file relies more on d spacings than on intensities. It was originally designed for use with electron diffraction patterns, where observed line intensities are not always directly related to structure and therefore not always a reliable guide to identification. It is sometimes helpful to use the Fink index when there is difficulty identifying an unknown phase using the Hanawalt index; the presence of large amounts of preferred orientation in solid samples is one instance in which intensities may not correspond to those expected from the powder diffraction file.

In the Fink-method search manual, which covers inorganic compounds only, d spacings and intensities are listed for the eight strongest lines of each substance. The order of listing is determined by the four strongest lines. Each substance is listed four times in Set 24 and later (six times in earlier sets), with one of the four strongest lines listed first and the others following in descending order of d values.

9-4 PROCEDURE

- ① Identification of the unknown begins with recording its diffraction pattern. Sample preparation should result in fine grain size and in a minimum of preferred orientation, which can cause relative line intensities to differ markedly from their normal values. Note also that relative line intensities depend to some extent on wavelength; this should be kept in mind if the observed pattern is compared with one in the data

file made with a different wavelength. Most of the patterns in the file were made with $\text{Cu } K\alpha$ radiation, except those for iron-bearing substances.

The pattern may be recorded with a Hull/Debye-Scherrer camera, Guinier camera, or diffractometer. Here again, line intensities depend on the apparatus. In particular, absorption effects cause high-angle lines on a Hull/Debye-Scherrer pattern to be stronger, relative to low-angle lines, than on a diffractometer recording, as shown in Sec. 4-10.

② After the pattern of the unknown is prepared, the d -spacing corresponding to each line on the pattern is calculated. If the diffraction pattern has been obtained on film, relative line intensities are usually estimated by eye, on a scale running from 100 for the strongest line down to 10 or 5 for the weakest. If a densitometer is available, it may be used to provide more accurate values of diffracted intensities. For data recorded with a diffractometer, the background must be subtracted from the peak intensity before computing I_1/I_1 for each peak. In general, the background for a given sample varies with diffraction angle. Modern, computer-integrated diffractometers generally have software to identify peaks positions (angles and d -spacings) and to calculate the relative intensities of peaks.

③ After the experimental values of d and I/I_1 are tabulated, the unknown can be identified by the following procedure:

1. Locate the proper d_1 group in the numerical search manual.
2. Read down the second column of d values to find the closest match to d_1 . (In comparing experimental and tabulated d values, always allow for the possibility that either set of values may differ by $\pm 0.01 \text{ \AA}$.)
3. After the closest match has been found for d_1 , d_2 , and d_3 , compare their relative intensities with the tabulated values.
4. When good agreement has been found for the lines listed in the search manual, locate the proper PDF card and compare the d and I/I_1 values of all the observed lines with those tabulated. When full agreement is obtained, identification is complete.

9-5 IDENTIFICATION OF SINGLE PHASE SAMPLES

When the unknown is a single phase, the search procedure is relatively straight-forward. Consider, for example, the pattern described in Table 9-1. It was obtained with $\text{Cu } K\alpha$ radiation and a Hull/Debye-Scherrer camera: line intensities were estimated. The experimental values of d_1 , d_2 , and d_3 are 2.82, 1.99, and 1.63 \AA , respectively. By examining the numerical search manual, strongest line is found to fall within the 2.84-2.80 \AA group of d_1 values. Inspection of the listed d_2 values in this group discloses twenty-seven substances having $d_2 = 1.99 \text{ \AA}$, but only five of these have $d_1 = 2.82 \text{ \AA}$. The data on these five are shown in Table 9-2 in the form given in the manual. And of these five only NaCl has $d_3 = 1.63 \text{ \AA}$. Note that the intensities listed for the three strongest lines of this substance agree fairly well with the observed intensities; so do the data for the other five lines listed in the

TABLE 9.1 PATTERN OF UNKNOWN

$d(\text{\AA})$	hkl	$d(\text{\AA})$	hkl
3.25	10	1.00	20
2.82	100	0.95	5
2.18	5	0.94	20
1.99	60	0.89	20
1.71	5	0.86	5
1.63	30	0.85	20
1.42	20	0.82	10
1.25	30	0.79	10
1.15	30	0.78	20
1.09	5		

is not listed in card

manual. Turn to PDF card 5-628, reproduced in Fig. 9-1 and compares the complete pattern given there with the observed one. In general the agreement is good, but there are some discrepancies, and these must be resolved before the identification as NaCl is accepted. These discrepancies are:

1. A very weak line with $d = 2.18 \text{ \AA}$, not listed on the file card is observed. Calculation shows that this line is a 220 reflection of Cu $K\beta$ radiation not removed by the filter. Note that the even stronger 200 reflection would also produce a $K\beta$ line, but this $K\beta$ line falls on the 111 $K\alpha$ line and is therefore not seen separately.

TABLE 9.2 PORTION OF THE ICDD HANAWALT SEARCH MANUAL*

QM	Strongest reflections								Chemical formula	Mineral name; common name	PDF #	I/I_c
•	2.82 _x	1.99 ₃	3.99 ₂	1.63 ₂	1.41 ₁	1.26 ₁	1.07 ₁	1.78 ₁	cP5 $\text{Ca}_{0.6}\text{Sr}_{0.4}\text{NbO}_3$	47-35	7.05	
•	2.82 _x	1.99 _y	3.26 ₈	1.63 ₇	1.41 ₁	1.26 ₁	1.15 ₁	1.73 ₁	cF8 PdO	46-1211		
•	2.82 _y	1.99 _x	2.30 ₆	1.41 ₄	1.63 ₂	0.89 ₁	1.20 ₁	1.15 ₁	cP5 KMgF_3	18-1033	0.90	
•	2.82 _x	1.99 ₆	1.63 ₂	3.26 ₁	1.26 ₁	1.15 ₁	0.94 ₁	0.89 ₁	cF8 NaCl	5-628		
C	2.82 _x	1.99 _x	1.99 ₈	1.26 ₃	1.63 ₂	1.15 ₂	0.94 ₁	1.41 ₁	cP2 BiPd	Halite, syn	18-428	

*Extracted from the numerical search manual (Inorganic Compounds, Hanawalt Search Manual, Sets 1-48, 1998). The different quality marks (QM) are explained in Fig. 9-1. The three strongest lines appear in bold-face type. Intensities (rounded) are shown by the suffix $x = 100$ and the subscripts 9, 8, 7 ... = 90, 80, 70 ... The PSC is composed of the Pearson Bravais lattice mnemonic followed by the number of atoms in the unit cell: C denotes cubic, F face-centered and P primitive. The ratio I/I_c gives the ratio of the intensity of the most intense peak of the phase's pattern to that of the most intense peak of corundum hexagonal reflection 113.

2. The 331 line ($d = 1.294 \text{ \AA}$) listed on the file card is not observed. However, its intensity is expected to be very low.
3. Two high-angle lines ($d = 0.79$ and 0.78 \AA) are observed but are not listed on the PDF card. Often the file cards' data do not extend to highest-accessible 2θ values. However, these lines can be indexed as 711-551 and 640 lines, which are the next expected lines after 444 in the FCC sequence.
4. After the fifth observed line, observed intensities on the Hull/Debye-Scherrer pattern are all higher than those on the file pattern, which was obtained with a diffractometer. These differences are due to absorption effects, as mentioned in Sec. 9-4.

Because the discrepancies are now understood, the identification of the specimen as NaCl is complete, or more precisely, the data is consistent with NaCl and not with any other phase in the file. However, not all identifications are as positive as this example. A few unexplained weak lines are often assumed to be due to an unknown impurity; the identification of the main constituent is then somewhat tentative, and its reliability depends on the judgement and experience of the investigator. See also Sec. 9-8.

Because small d spacings correspond to back-reflection lines, they are measurable with greater precision than large d spacings (Sec. 13-1). Spacings smaller than about 1 \AA should therefore be computed to the nearest 0.001 \AA , rather than to 0.01 \AA as in Table 9-1, in order to permit a better match with data in the file.

9.6 IDENTIFICATION OF PHASES IN MIXTURES

The analysis is now more complex, but not impossible. Consider the pattern in Table 9-3, obtained with Cu $K\alpha$ radiation and a diffractometer, for which $d_1 = 2.09 \text{ \AA}$, $d_2 = 2.47 \text{ \AA}$, and $d_3 = 1.80 \text{ \AA}$. Examination of the numerical index in the d_1 group 2.09 to 2.05 \AA reveals several substances having d_2 values near 2.47 \AA , but in no case do the three strongest lines, taken together, agree with those of the unknown. This impasse suggests that the unknown is actually a mixture of phases, and that it is incorrect to assume that the three strongest lines in the pattern of the unknown are all due to the same substance. Suppose the strongest line ($d = 2.09 \text{ \AA}$) and the sec-

TABLE 9.3 PATTERN OF UNKNOWN

$d(\text{\AA})$	I/I_1	$d(\text{\AA})$	I/I_1
3.01	5	1.22	4
2.47	72	1.08*	20
2.13	28	1.04*	3
2.09*	100	0.98	5
1.80*	52	0.91*	4
1.50	20	0.83*	8
1.29	9	0.81*	10
1.28*	18		

impasse
no
2000

TABLE 9.4 PATTERN OF COPPER

$d(\text{\AA})$	I/I_1
2.088	100
1.808	46
1.278	20
1.0900	17
1.0436	5
0.9038	3
0.8293	9
0.8083	8

second-strongest line ($d = 2.47 \text{ \AA}$) are formed by two different phases, and that the third-strongest line ($d = 1.80 \text{ \AA}$) is due to, say, the first phase. In other words, assume that $d_1 = 2.09 \text{ \AA}$ and $d_2 = 1.80 \text{ \AA}$ for one phase. A search of the same group of d_1 values, but now in the vicinity of $d_2 = 1.80 \text{ \AA}$, discloses agreement between the three strongest lines of the pattern of copper, PDF card 4-0836, and three lines in the pattern of our unknown. Turning to PDF card 4-0836, all lines of the copper pattern, described in Table 9-4, agree with the starred lines in Table 9-3, the pattern of the unknown.

One phase of the mixture is thus shown to be copper, providing that the remainder of the lines can be assigned to some other substance. These remaining lines are listed in Table 9-5. By multiplying all the observed intensities by a normalizing factor of 1.39, the intensity of the strongest line is increased to 100. Searching the index and PDF in the usual way reveals that these remaining lines agree with the pattern of cuprous oxide, Cu_2O , which is given at the right of Table 9-5. The unknown is thus shown to be a mixture of copper and cuprous oxide.

The analysis of mixtures becomes still more difficult when a line from one phase is superimposed on a line from another, and when this composite line is one of the three strongest lines in the pattern of the unknown. The usual procedure then leads only to a very tentative identification of one phase, in the sense that agreement is obtained for some d values but not for all the corresponding intensities. This in itself is evidence of line superposition. Such patterns can be untangled by separating lines which agree in d value with those of phase X, the observed intensity of any superimposed lines being divided into two parts. One part is assigned to phase X, and the balance, together with the remaining unidentified lines, is treated as in the previous example.

Analysis of patterns containing multiple overlapping peaks requires careful tracking of how much intensity is from each individual phase. This can be done using a spread sheet, for example, or by the graphical plot-replot method [9.4] which is outlined below. In this subtractive method, the steps are:

1. Make a "stick" plot of I/I_1 vs d for the unknown mixture. Perhaps the most useful plot is I/I_1 vs $\ln d$ which is easily made on semi-log paper; this allows

TABLE 9.5

Remainder of pattern of unknown			Pattern of Cu ₂ O	
$d(\text{\AA})$	I/I_1		$d(\text{\AA})$	I/I_1
	Observed	Normalized		
3.01	5	7	3.020	9
2.47	72	100	2.465	100
2.13	28	39	2.135	37
			1.743	1
		28	1.510	27
1.50	20	13	1.287	17
1.29	9	6	1.233	4
1.22	4		1.0674	2
		7	0.9795	4
0.98	5		0.9548	3
			0.8715	3
			0.8216	3

systematic peak shifts due to various diffractometer errors to be easily recognized. About 10 or 20 increments of I/I_1 are sufficient.

2. Select likely possibilities ("three strongest lines", a priori knowledge, hunches) and make "stick" plots for these knowns based on PDF cards.
3. Solve the "jig-saw" puzzle, allowing for superposition of lines:
 - a. Graphically subtract the relative intensities of the first identified phase of the mixture. Note that the normalization of the identified phase may need to be changed to match the pattern: the mixture's most intense peak may not be the 100% peak of the identified phase.
 - b. Replot the remaining lines (i.e. those with non-zero intensities), renormalizing the maximum peak to 100% intensity. This is done to allow easy comparison of the remainder with another phase from the PDF.
 - c. Repeat a. and b. until all peaks are accounted for.
4. Every line in the pattern must be assigned to some material. All major lines of each component identified (i.e., of each card) must be present. All remainders from subtractions must be zero or higher since negative intensities do not exist. In practise, negative remainders I/I_1 less than 0.05 are acceptable. Preferred orientation is often the cause of less than perfect agreement of intensities.

Completing the steps listed above is sufficient for most analyses. For a complete analysis, however, the following should be done.

5. Prepare mixtures of the identified components until the original diffraction pattern is duplicated. This step adds considerable reliability to the identification.
6. Compare absolute intensities of the peaks in the unknown and duplicating mixtures to see if there is any noncrystalline material in the unknown.

The plot-replot algorithm was developed before the advent of personal computers, and in many cases the same steps, albeit without plotting, can be done using a spreadsheet. A spreadsheet allow rapid sorting of the phases present in a mixture, but the plot-replot or other graphical approaches provide a better over-all view of the hypothetical constituents of the experimental pattern.

The following example illustrates the use of the plot-replot method. Fig. 9-2 shows the diffraction pattern of the unknown mixture, recorded with $\text{Cu } K\alpha$ radiation, a step size of $0.02^\circ 2\theta$ and counting time of 1 sec. The diffractometer used to collect the data was equipped with a post-sample monochromator and with an incident beam slit whose width varied automatically with 2θ so as to irradiate a constant area of the sample. Thus, the measured peak intensities at high 2θ are greater than they would be for a diffractometer with a fixed-width divergence slit (i.e., the

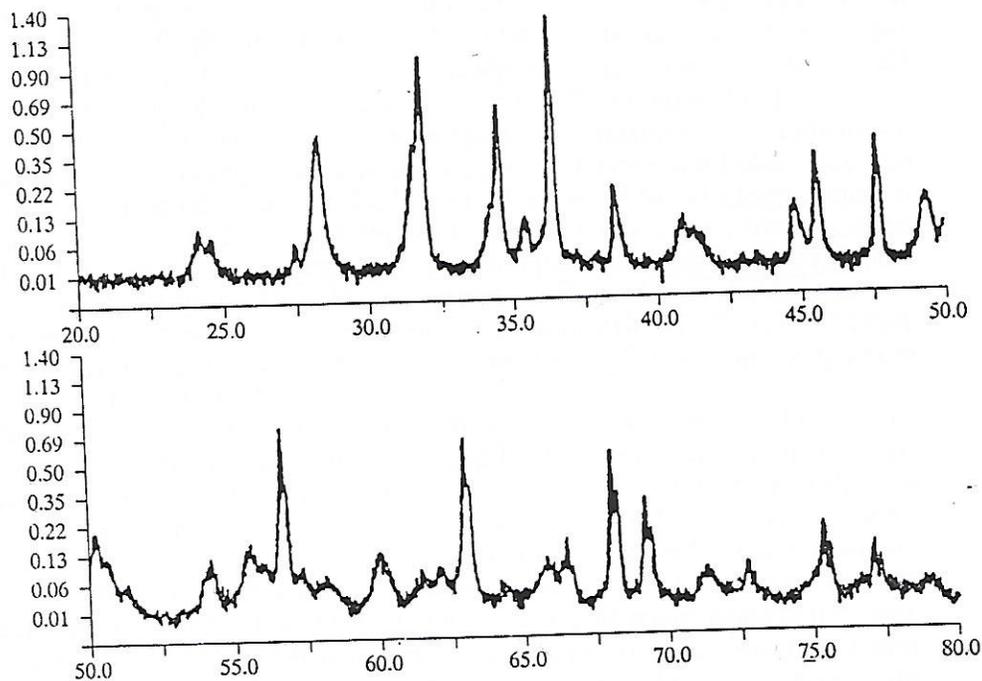


Figure 9-2 Diffraction pattern of a multi-phase sample recorded with a variable slit θ - 2θ diffractometer. The pattern is plotted as the square root of the intensity (in thousands of counts) as a function of 2θ (degrees).

data which appears in the PDF). Note also that the vertical axis plots the square root of intensity in order to show the low intensity peaks more clearly.

Important clues sometimes can be gleaned by examining the entire diffraction pattern, peaks and background. Differences in peak shapes or widths, for example, can suggest which peaks belong to which phase. The pattern in Fig. 9-2 consists of many peaks of different shapes, and several peaks can be resolved from neighboring peaks (e.g., those at $\sim 32^\circ$, 34° , 57°), suggesting that there may be additional peaks which cannot be resolved. The vertical bars on the plot indicate the peaks the diffractometer software has identified, but overmuch reliance on these types of routines is unwise, and their results should always be checked manually (i.e., by comparing the identified peak positions with the diffraction pattern itself). For example, peaks at $\sim 63^\circ$, 68° and 74° in Fig. 9-2 appear to have been missed by the software, whereas similar appearing peaks in the same angular range ($\sim 57^\circ$, 69° and 76°) have been found.

Table 9-6 lists the average d and I/I_1 for the mixture obtained from scans of three repackings of the sample in a powder holder. The average intensities of the peaks identified by the software have been corrected to values which would have been observed were a one degree fixed divergence slit used. The ten most intense peaks appear in bold type in Table 9-6, numerical values of intensities for peaks above 5% are given in normal type and the remaining intensities are represented by "o". For the three repackings, the d -spacings of all peaks were reproducible within ± 0.005 Å, and the relative intensities varied no more than $\pm 3\%$ compared to I_1 .

Table 9-7 lists only the ten most intense peaks of the mixture, and the identification proceeds by checking triplets of peaks against the Hanawalt Index: lines 10, 6 and 8 match zincite (ZnO , card 36-1451) lines 2.48_x, 2.86₆, 2.60₄. The third column of the Table compares zincite's d -spacings and intensities with the experimental data, and Fig. 9-3(a) shows the corresponding I vs. $\ln d$ plots. Multiplying the remainder shown in column four by 2.5 yields the renormalized set of lines shown in column five. Lines 4 and 5 match the Index's entry for baddeleyite (ZrO_2 , card 37-1484), and the remaining lines match halite (NaCl , card 5-628). The corresponding I vs. d plots appear in Fig. 9-3(b) and (c).

The largest remainder from the ten most intense peaks is 4% of the pattern's maximum intensity, and this is not surprising because this peak is primarily from halite, grains of which have a strong cubic morphology. All but three of the very smallest peaks (out of the 43 identified by the software) are from either ZnO , ZrO_2 or NaCl ; examination of the three diffraction patterns recorded of the mixture, one of which is shown in Fig. 9-2, indicates that these three peaks are noise. As all of the expected peaks from the PDF cards are observed, and no major peaks in the experimental pattern have not been assigned to one of the three substances, this identification would be accepted with considerable confidence. In fact, these three phases were combined in the mixture for purposes of this example.

In Fig. 9-4 the diffractometer software is used to compare the experimental pattern with the PDF patterns of the phases identified in the analysis. This type of soft-

TABLE 9.6 LIST OF D-SPACING AND RELATIVE INTENSITIES FOR THE PEAKS IN FIG. 9-2, CONVERTED FROM THE VARIABLE INCIDENT BEAM SLIT DATA TO INTENSITIES WHICH WOULD HAVE BEEN OBSERVED WITH A 1° FIXED INCIDENT SLIT. PEAKS WITH INTENSITIES LESS THAN 5% ARE REPRESENTED BY "0" AND THE INTENSITIES AND D-SPACINGS ARE THE AVERAGE FROM THREE SAMPLE REPACKINGS.

line	$d(\text{Å})$	$I(\%)$	line	$d(\text{Å})$	$I(\%)$
1	3.68	7	26	1.66	6
2	3.62	5	27	1.62	31
3	3.24	0	28	1.60	0
<u>4</u>	<u>3.15</u>	<u>40</u>	29	1.58	0
5	2.84	27	30	1.54	0
<u>6</u>	<u>2.80</u>	<u>83</u>	31	1.51	0
7	2.62	8	32	1.49	0
<u>8</u>	2.60	<u>46</u>	33	1.48	31
9	2.53	6	34	1.45	0
<u>10</u>	2.47	<u>100</u>	35	1.42	0
11	2.40	0	36	1.40	0
12	2.37	0	37	1.38	22
13	2.34	10	38	1.36	12
14	2.21	0	39	1.32	0
15	2.20	5	40	1.30	0
16	2.17	0	41	1.26	6
17	2.08	0	42	1.23	0
18	2.02	6	43	1.21	0
19	1.99	20			
20	1.90	20			
21	1.84	8			
22	1.81	10			
23	1.80	0			
24	1.78	0			
25	1.69	0			

TABLE 9.7 NUMERICAL ILLUSTRATION OF THE GRAPHICAL SUBTRACTIONS IN FIG. 9-3*

Line	Unknown	36-1451	Remain.	Renorm.	37-1484	Remain.	Renorm.	5-628
10	2.47 _x	2.476 _x	0	-	-	-	-	-
6	2.80 ₈₃	2.814 ₅₇	26	2.80 ₆₅	-	65	2.80 _x	2.82 _x
8	2.60 ₄₆	2.603 ₄₄	2	2.60 ₆₅	-	5	2.50 ₀₈	-
4	3.15 ₄₀	-	-	3.15 _x	3.16 _x	0	-	-
27	1.62 ₃₁	1.625 ₃₂	-1	-	-	-	-	-
33	1.48 ₂₉	1.477 ₂₉	0	-	-	-	-	-
5	2.84 ₂₇	-	-	2.84 ₆₈	2.84 ₆₈	0	-	-
37	1.38 ₂₂	1.378 ₂₂	0	-	-	-	-	-
19	1.99 ₂₀	-	-	1.99 ₅₀	-	50	1.99 ₇₇	1.99 ₅₅
20	1.91 ₂₀	1.911 ₂₃	-3	-	-	-	-	-

* Instead of rounding each peak's intensity to the nearest 10% and using the most significant digit in the subscript to indicate intensity, as in the Hanawalt Index, a two digit subscript is used to indicate intensity to the nearest 1%. The peak intensity of 68% is indicated by the subscript "68" instead of "7".

ware is very useful for rapidly confirming the presence of phases suspected to be present but is less useful without this knowledge.

9-7 COMPUTERIZED SEARCH-MATCH

The procedure for searching the PDF for a pattern or patterns matching that of the unknown is essentially one of matching numbers. This task is ideally suited to the computer. As the number of phases in the unknown increases beyond two, manual searching becomes very difficult and time consuming; computer searching is then more efficient. This is especially true since the personal computer revolution of the 1980's has allowed automatic peak intensity and d -spacing measurement to be the rule rather than the exception: data files listing I and d values or even the entire diffraction pattern can be exported into search-match programs without inordinate effort.

At least 17 stand-alone phase identification programs are available in addition to those provided by hardware vendors with their instruments [9.5]. The goal of these programs is to scan the reference data base selecting the phase(s) with highest probability of comprising the unknown sample. Usually the best a program can do is to rank the possibilities based on some figure of merit calculated using a particular algorithm (for example, see Eq. 9-1 below). The different programs' procedures vary widely, and there are often many tricks to getting the best results, tricks which can be learned only from long experience with a specific program.

2.80
(I%) 68 (83)

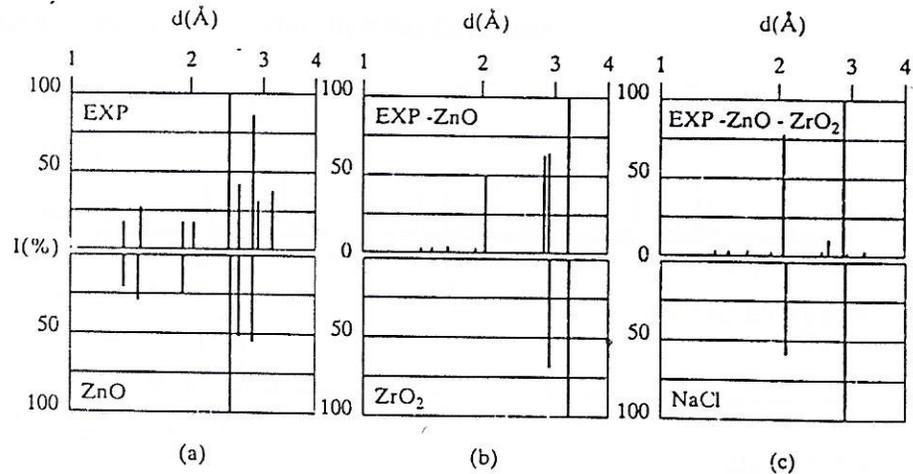


Figure 9-3 Illustration of the plot-replot method for identifying phases in mixtures. Only peaks with intensities greater than or equal to 20% in Fig. 9-2 and the corresponding Table 9-6 are shown. In (a) the top plot shows the experimental peak intensities as a function of $\ln d$ while the bottom plot shows the first phase identified ZnO, zincite, card 36-1451. The top plot of (b) shows the intensities remaining in the experimental pattern after subtracting the zincite peaks' intensities and renormalizing. The bottom plot of pattern (b) shows the peaks of the second phase ZrO₂, zirconia, card 37-1484. The plots in (c) show the same steps as in (b) and show that NaCl, halite, card 5-628, accounts for the remaining peaks of the pattern.

Computer searching is not immune to errors originating in the pattern of the unknown or in the data file. If the unknown contains only one phase, the software may produce from 10 to 50 matching patterns, depending on the width Δd of the "window" selected by the user; this window is the range of d values about a given experimental value within which a match is judged acceptable. The value(s) of d -spacing window(s) in software packages are sometimes not obvious, and considerable caution must be exercised when using search-match software with which one is unfamiliar. In many laboratories more than one researcher will use the search-match software, and the default settings must be checked at the start of every session. From the excessive number of possible matches provided by the computer, the user must select the most probable ones, usually on the basis of some knowledge of the unknown's chemical composition.

Search-match programs are very powerful: an early program successfully identified six phases in a mixture [9.6]. Automatic phase identification, however, is very sensitive to the quality of data in the PDF. In a study of 76 different phosphate minerals (common as well as rare species), 43% were unequivocally identified, 18% were identified with other (absent) phases also being identified, 15% were listed in the output file but were not identified and the remaining 24% did not appear in the output list; and inaccuracies in some of the 275 PDF reference patterns of phosphate minerals in sets 1-31 were found to be the principal origin of the failure of one-in-four identifications of this study [9.7].

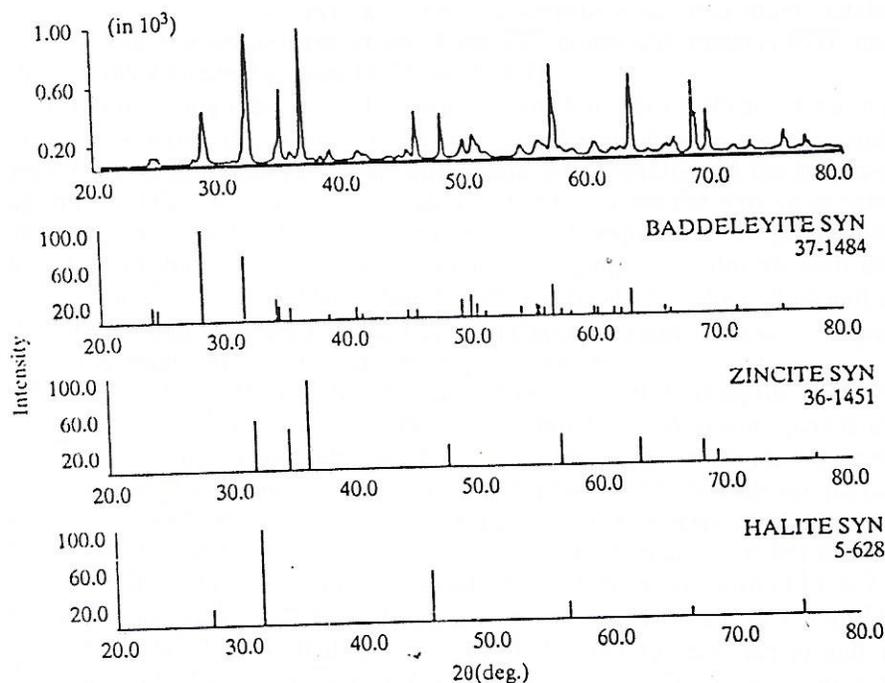


Figure 9-4 Comparison of the experimental diffraction pattern shown in Fig. 9-2 (note the linear intensity scale) with the cards of the phases identified in Fig. 9-3 and Table 9-7.

Fortunately standards are being raised for new additions to the PDF, and considerable effort has gone into replacing inaccurate cards. Routine use of an internal standard² in samples would help to minimize uncertainties in experimental peak positions. Full diffraction patterns and not merely lists of I and d are now being added to the PDF [9.8]; this should lead to major improvements in future phase identification.

One figure of merit which has gained acceptance as a measure of both the accuracy of the diffraction peak positions and the completeness of the pattern is

$$F_N = \frac{1}{|\Delta 2\theta|} \frac{N}{N_{\text{poss}}}, \quad (9-1)$$

where N_{poss} is the number of independent diffraction lines possible up to the N th observed line and $|\Delta 2\theta|$ is the average absolute discrepancy between calculated and observed 2θ values [9.9-9.10]. The units of F_N are reciprocal degrees, and the higher the accuracy or the more complete the pattern, the larger is F_N . Thus, $F_N=100$

² Addition to the unknown of a small amount of a phase with known d -spacings and with peaks which do not interfere with the principle peaks of the unknown. Systematic errors in the peak positions of the unknown(s) can be corrected by observing the shifts in the peaks of the internal standard.

means that the average 2θ difference was $\leq 0.01^\circ$. In the study of phosphate minerals cited earlier in this section, computer identification was quite reliable for $F_{30} \geq 6.0$, and remeasurement of 34 of the 275 phosphate mineral PDF patterns improved the average F_{30} from 11.5 to 49.9 [9.7].

Before discussing the practical difficulties which might be encountered in phase identification work, it is instructive to compare the results of a search-match program on the mixture analyzed manually in Sec. 9-6. SANDMAN, the search-match program provided with the diffractometer used to record the pattern in question, grades the agreement between reference and experimental peaks using a Lorentzian probability distribution instead of relying on a window with definite limits for the "hit/miss" decision. This makes SANDMAN quite robust and allows it to score patterns primarily on the basis of relative line positions and to report the level of systematic errors explicitly for a given match.

The program performs a search through the entire PDF using the eight lines of the Hanawalt Index and checking multiple permutations. A second pass is used to match only the best candidates with the full pattern (generally those lines with $I/I_1 \geq 10\%$ or the 15 most intense lines [9.11]). SANDMAN adds the patterns of the phases identified and compares the result with the experimental pattern; most other search-match programs are subtractive rather than additive. For the mixture analyzed in the previous section, SANDMAN used 15 peaks down to $I/I_1 = 7.9\%$ in the search and matched 126 patterns to the experimental pattern. SANDMAN identified cards 37-1484 (baddeleyite, ZrO_2), 36-1451 (zincite, ZnO) and 17-469 (nadorite) explicitly, with very high match scores for the first two; however, it produced nearly as good a match for halite ($NaCl$, 5-628) as for nadorite.

9-8 PRACTICAL DIFFICULTIES

In theory, the Hanawalt method should lead to the positive identification of any substance whose diffraction pattern is included in the powder diffraction file. In practice, various difficulties arise, and these are usually due either to errors in the diffraction pattern of the unknown or to errors in the PDF.

Errors of the first kind, those affecting the observed positions and intensities of the diffraction lines, have been discussed in various parts of this book and need not be reexamined here. However, the possibility of abnormal intensities due to preferred orientation or graininess needs continuous emphasis. Preferred orientation is particularly common in surface deposits on metals, such as oxide or sulfide layers. If the deposit is very thin, its removal may not yield enough material for examination. The diffractometer is then an ideal instrument for examining the deposit *in situ*, because of the shallow penetration of x-rays. Very thin deposits can yield good diffraction lines, and the analyst can often make a positive identification, even in the presence of pronounced preferred orientation, if he or she has some knowledge of crystal morphology and of the chemical composition of the deposit. Thus, a very thin deposit on sheet steel was identified as graphite by a single strong basal-plane