

# Chemical Analysis by X-Ray Diffraction

## Classification and Use of X-Ray Diffraction Patterns

J. D. Hanawalt, H. W. Rinn, and L. K. Frevel,  
*The Dow Chemical Company, Midland, Mich.*

*Editor's Note: As part of our plan to reprint previously published papers of great historical interest, the editorial board is pleased to reproduce the following paper by Hanawalt, Frevel and Rinn. This paper was originally published in Volume 10 (1938) of the Analytical Edition of "Industrial and Engineering Chemistry" and is considered by most diffractionists to be the classic work in qualitative identification of multiphase polycrystalline material. The original publication carried a foreword written by the editor of Industrial and Engineering Chemistry. This foreword ended with this prophetic statement:*

*"There is reason to believe that this publication, which is made possible in this form by the generous financial assistance of the Dow Chemical Company, will serve to bring this method of analysis into general use in industrial and consulting analytical laboratories."*

This paper supplies tabulated data on the diffraction patterns of 1000 chemical substances and gives a scheme of classification which makes possible a routine and valuable use in the chemical laboratory of the Hull method of X-ray analysis.

In 1919 Hull<sup>9</sup> described a new method of chemical analysis by means of X-ray diffraction. He gave the experimental procedure and pointed out the various interesting and important features of the method, emphasizing the experimental simplicity of obtaining the diffraction pattern of a substance and the fact that it requires only a minute amount of material. He gave illustrations of the important fact that the diffraction method tells the state of chemical combination of the elements present in the unknown, and stated the basis for the method: "That every crystalline substance gives a pattern; that the same substance always gives the same pattern; and that in a mixture of substances, each produces its pattern independently of the other, so that the photograph obtained with a mixture is the superimposed sum of photographs that would be obtained by exposing each of the components separately for the same length of time. This law applies quantitatively to the intensities of the lines [provided absorption is negligible for each of the components], as well as to their positions, so that the method is capable of development as a quantitative analysis."

These unique features would appear to entitle the method to a place of real usefulness in chemical analysis. However, as yet no extensive use has been made of X-ray diffraction in this way. Probably one of the most important circumstances, which at present handicap the general use of the method, is that an adequate file of standard patterns is not available for reference. The method being empirical, standards are necessary. A certain limited amount of work could be done by determining crystal structure, but this is not a practical procedure. For any one person, the assembling of a large library of patterns would be a great task, since it would run into many thousands; also, it is not assured without test that it would be feasible to classify and make use of such a file were it available.

At The Dow Chemical Company it has been found that another useful fact concerning diffraction patterns may be added to those already given by Hull — namely, that the thousands of patterns representing the thousands of different

chemical substances can be classified in such a way that they may be easily used for the identification of an unknown, even when the unknown is a mixture of substances.

The basis for this interesting conclusion and the scheme of classification were described in an earlier publication<sup>8</sup>. Since that time, there have been many requests to make the data available for general use. The Dow Chemical Company has been very willing to do this, but has postponed publication until this time in order to determine a satisfactory form in which to put the data. When the original negatives are on file, the simplest procedure, after locating the standard by means of the classification system, is to compare negatives directly as to position and intensity of the lines. However, for publication, it is not feasible to make a true reproduction of the negatives. Microphotometer traces would give the data accurately, but would involve a more time-consuming technic than is desirable for routine and economical analysis.

The data of the pattern should be recorded as simply as possible and yet sufficiently accurately for analysis. During the past year such a means has been fully demonstrated and it is now possible to present the diffraction data in a form which may be used by a person in another laboratory. If it appears sufficiently interesting, data on more substances could be made available from this laboratory and perhaps from many others. The use of the X-ray method of analysis would be greatly extended if crystal structure workers, after they have taken care to get a pure material, would publish the powder data of the material in the same or in an equivalent form.

For those who are already equipped with X-ray diffraction apparatus, the only step necessary to use the data here presented is to compile the index book as described. For those who are not familiar with the details of what is involved in X-ray diffraction analysis, a survey view is given of the apparatus required, the technic of obtaining the patterns, and the method of interpreting the patterns, as well as some illustrations of the field of application of the general method. The present article is based on experience gained in carrying out several thousand actual analyses during the past five years.

### The Classification System

The diffraction pattern, as commonly obtained, consists of a sequence of lines in certain definite positions (on an A scale giving the spacing of the crystal planes represented) and of certain relative intensities (Figure 1). The method of measuring the negatives is discussed below, but for the purpose of describing the classification system it can be assumed for the moment that the data have been obtained in the form given in the tables of patterns. The lines lie between 20 Å and 0.5 Å, and for indexing purposes are grouped into 77 suitably chosen divisions. The sizes of these divisions are based upon experience and are determined by the consideration that they should be larger than the accuracy of measurement of the position of the lines, and should be no more numerous than is necessary to handle conveniently all the patterns without conflict. Actually the size of a division is 5 to 10 times the error of measurement.

From the data of the patterns, the positions of the three strongest lines are read off in the order of decreasing intensi-



Figure 1. X-ray powder diffraction patterns in calibrated scale. MoK $\alpha$  radiation.

ty. If two lines have the same intensity value, the rule is to list the one with the greater  $\Delta$  spacing first. One thus has as a characteristic of each pattern, three numbers in a certain sequence. The patterns are then listed, at the proper place, in an indexed book which is divided and subdivided into the chosen regions. The first number determines the group, the second number the subgroup, and the third number the location within the subgroup. The index book thus consists of 77 sections or groups, each of which in turn contains 77 subgroups. For illustration, three sections of the index book are shown (Figure 2, 3, 4). The index book as it is actually being used provides 15 spaces in each subgroup, but in the illustration these spaces have been omitted. These sections are typical of the average section of the index book and show that among the 1000 patterns listed, it is hardly necessary to use more than the two strongest lines in order to index patterns.

In the whole index book, there are only 27 subgroups which contain more than 3 patterns and only one which contains more than 5 patterns. The fact that two patterns fall in the same subgroup does not mean that they are identical with respect to their first two lines, since their positions within the divisions may be different and their relative intensities probably will be different. Considering now the coincidences of third lines within a subgroup, there are 11 subgroups in which 2 patterns have the same positions of the third line (within twice the + or - error of measurement) and 4 subgroups in which 3 patterns have the same third line. In seven of these cases, a measurement of the fourth line serves to distinguish the patterns. (A column is included in the book for recording the fourth line.) However, in practice, after a pattern has been located in the index book (which gives its name and number in the file), the pattern data are referred to in the file and compared directly in all their details. When this is done, for the conflicts still remaining there are only three cases left in which the patterns are not immediately distinguishable from each other. In these cases, if there were nothing easier to do, a more accurate determination of planar spacings by a different X-ray technic would be sufficient. Probably, however, some other information would be available to assist in separating these very occasional conflicts.

Taking into account the number of subgroups and the distribution of the lines as they occur in the type of pattern

studied, it is estimated that the index book in its present form, making use of three lines as described, would handle many thousands of patterns. If, for instance, there were 20,000 patterns in the file, there would be a total of only several hundred cases in which one would have to compare his unknown with two patterns from the file, and not more than about twenty cases in which one would have to compare with more than three patterns.

As practiced at The Dow Chemical Company, a second and independent method of listing the patterns is included in the index book. Each of the 77 major groups of the book is followed by a section called the Supplementary Group Index in which (1) all the patterns whose strongest line falls in the major group have their three strongest lines listed in the order 1, 2, 3; (2) all the patterns whose second strongest line falls in the major group have their three strongest lines listed in the order 2, 1, 3; and (3) all the patterns whose third strongest line falls in the major group have their three strongest lines listed in the order 3, 1, 2. An illustration of the use of the Supplementary Group Index will be found among the examples given below.

### Procedure with Unknowns

Suppose that the pattern of an unknown has been obtained and the positions and relative intensities of the lines have been measured and tabulated. One opens the index book at the major group determined by the strongest line, turns to the subgroup determined by the second strongest line, and sees whether any of the lines of the unknown check lines in this subgroup. (This can be done at a glance since, of the subgroups which are occupied, the largest contains only seven patterns and most of them contain only one.) If the unknown is a single substance, the third strongest line will check and the pattern will have been located. However, if the unknown is a mixture of phases and if the second strongest line of the pattern happens to be the strongest line of the second component, the pattern will not have been found and one proceeds by using the third strongest line of the unknown pattern to determine the subgroup, and so on. When a match is found, the lines of the unknown coinciding with the standard are noted, as are also any intensity variations which would indicate superpositions of lines. The remaining unidentified lines of the unknown are then treated in the standard manner.

Group 2.55-2.50

No.	Compound	3rd line	4th line	No.	Compound	3rd line	4th line	No.	Compound	3rd line	4th line	No.	Compound	3rd line	4th line
	20.00-15.00				4.50-4.40				2.75-2.70				1.75-1.70		
	15.00-12.00				4.40-4.30				2.70-2.65				1.70-1.65		
	12.00-10.00				4.30-4.20				2.65-2.60				1.65-1.60		
	10.00- 9.00				4.20-4.10				2.60-2.55				1.60-1.55		
	9.00- 8.50				4.10-4.00				2.55-2.50				1.55-1.50		
	8.50- 8.00				4.00-3.90				2.50-2.45			743	SiC (Cubic)	1.31	
	8.00- 7.50				3.90-3.80				2.45-2.40			426	Fe <sub>3</sub> O <sub>4</sub>	1.62	
	7.50- 7.00				3.80-3.70				2.40-2.35			979	ZnFe <sub>2</sub> O <sub>4</sub>	2.97	
	7.00- 6.50				3.70-3.60			372	CuO	1.86		527	MgFe <sub>2</sub> O <sub>4</sub>	2.95	
	6.50- 6.00				3.60-3.50				2.35-2.30				1.45-1.40		
	6.00- 5.75				3.50-3.40				2.30-2.25				1.40-1.35		
	5.75- 5.50				3.40-3.30				2.25-2.20				1.35-1.30		
	5.50- 5.25				3.30-3.20				2.20-2.15				1.30-1.25		
	5.25- 5.00				3.20-3.10				2.15-2.10				1.25-1.20		
108	Ba(NO <sub>2</sub> ) <sub>2</sub> ·H <sub>2</sub> O	3.48		897	SrO <sub>2</sub>	2.00			2.10-2.05				1.20-1.15		
	5.00- 4.90				3.10-3.00				2.05-2.00				1.15-1.10		
	4.90- 4.80				3.00-2.95				2.00-1.95				1.10-1.05		
	4.80- 4.70				2.95-2.90				1.95-1.90				1.05-1.00		
855	Na <sub>2</sub> SnO <sub>2</sub> ·3H <sub>2</sub> O	1.85			2.90-2.85				1.90-1.85				1.00- .90		
	4.70- 4.60				2.85-2.80				1.85-1.80				.90- .80		
	4.60- 4.50				2.80-2.75				1.80-1.75				.80-		

SUPPLEMENTARY GROUP INDEX 2.55-2.50

No.	Compound	1st line	2nd line	3rd line	No.	Compound	2nd line	1st line	3rd line	No.	Compound	3rd line	1st line	2nd line
108	Ba(NO <sub>2</sub> ) <sub>2</sub> ·H <sub>2</sub> O	2.52	5.1	3.48	127	BeSO <sub>4</sub> ·4H <sub>2</sub> O	2.52	3.90	3.20	362	Cu <sub>2</sub> Fe(CN) <sub>6</sub> ·7H <sub>2</sub> O	2.50	5.0	3.55
855	Na <sub>2</sub> SnO <sub>2</sub> ·3H <sub>2</sub> O	2.51	4.75	1.85	113	Ba <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	2.51	3.58	4.45	848	Na <sub>2</sub> PbO <sub>2</sub> ·3H <sub>2</sub> O	2.53	4.80	4.62
897	SrO <sub>2</sub>	2.52	3.14	2.00	679	KI	2.50	3.53	4.08	95	BaCl <sub>2</sub> ·2H <sub>2</sub> O	2.54	4.48	2.91
372	CuO	2.51	2.31	1.86	683	KNO <sub>3</sub>	2.50	3.31	2.20	165	CdWO <sub>4</sub>	2.53	3.80	3.05
743	SiC	2.51	1.54	1.31	74	SbI <sub>3</sub>	2.54	3.30	2.14	589	Hg(CN) <sub>2</sub>	2.51	3.72	4.85
979	ZnFe <sub>2</sub> O <sub>4</sub>	2.53	1.48	2.97	999	ZrSiO <sub>4</sub>	2.51	3.29	1.71	164	(CdSO <sub>4</sub> ) <sub>2</sub> ·8H <sub>2</sub> O	2.51	3.55	4.90
426	Fe <sub>3</sub> O <sub>4</sub>	2.53	1.48	1.61	918	Th	2.53	2.92	1.79	87	Ba	2.51	3.54	2.04
527	MgFe <sub>2</sub> O <sub>4</sub>	2.51	1.48	2.95	749	Ag <sub>2</sub> AsO <sub>4</sub>	2.50	2.74	1.63	349	2CuCO <sub>3</sub> ·Cu(OH) <sub>2</sub>	2.51	3.51	5.1
					423	Fe <sub>2</sub> O <sub>3</sub>	2.51	2.69	1.84	115	Ba(H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub> ·H <sub>2</sub> O	2.54	3.34	7.8
										84	As <sub>2</sub> O <sub>3</sub>	2.53	3.18	6.3
										726	K <sub>2</sub> WO <sub>4</sub> ·2H <sub>2</sub> O	2.51	3.09	3.92
										724	KCNS	2.51	2.97	2.79

Figure 2

Group 2.70-2.65

No.	Compound	3rd line	4th line	No.	Compound	3rd line	4th line	No.	Compound	3rd line	4th line	No.	Compound	3rd line	4th line
	20.00-15.00				4.40-4.30				2.70-2.65				1.85-1.80		
	15.00-12.00				4.30-4.20				2.65-2.60				1.80-1.75		
	12.00-10.00				4.20-4.10				2.60-2.55				1.75-1.70		
	10.00-9.00				4.10-4.00				2.55-2.50				1.70-1.65		
	9.00-8.50				4.00-3.90			423	Fe <sub>2</sub> O <sub>3</sub>	1.84			1.65-1.60		
	8.50-8.00				3.90-3.80				2.50-2.45				1.60-1.55		
	8.00-7.50				3.80-3.70			765	Ag <sub>3</sub> PO <sub>4</sub>	1.66			1.55-1.50		
	7.50-7.00				3.70-3.60				2.45-2.40				1.50-1.45		
	7.00-6.50				3.60-3.50				2.40-2.35				1.45-1.40		
	6.50-6.00				3.50-3.40				2.35-2.30				1.40-1.35		
	6.00-5.75				3.40-3.30				2.30-2.25				1.35-1.30		
	5.75-5.50				3.30-3.20				2.25-2.20				1.30-1.25		
	5.50-5.25				3.20-3.10			968	ZnCrO <sub>4</sub>	9.50			1.25-1.20		
	5.25-5.00				3.10-3.00				2.20-2.15				1.20-1.15		
	5.00-4.90				3.00-2.95				2.15-2.10				1.15-1.10		
171	5CaO·3Al <sub>2</sub> O <sub>3</sub>	2.44			2.95-2.90			407	FeCl <sub>3</sub>	5.90			1.10-1.05		
	4.90-4.80				2.90-2.85				2.10-2.05				1.05-1.00		
	4.80-4.70			502	Mg <sub>2</sub> Ca	3.14			2.05-2.00				1.00-.90		
	4.70-4.60				2.85-2.80				2.00-1.95				.90-.80		
	4.60-4.50				2.80-2.75			672	KF	3.08		4.23	.80-		
	4.50-4.40				2.75-2.70			846	Na <sub>2</sub> HPO <sub>3</sub> ·5H <sub>2</sub> O	1.54		4.05			
					2.70-2.65			170	3CaO·Al <sub>2</sub> O <sub>3</sub>	1.54					
				752	Ag <sub>2</sub> CO <sub>3</sub>	2.27									

SUPPLEMENTARY GROUP INDEX 2.70-2.65

No.	Compound	1st line	2nd line	3rd line	No.	Compound	2nd line	1st line	3rd line	No.	Compound	3rd line	1st line	2nd line
171	5CaO·3Al <sub>2</sub> O <sub>3</sub>	2.68	4.90	2.44	354	CuCl <sub>2</sub> ·2NH <sub>4</sub> Cl·2H <sub>2</sub> O	2.68	5.5	2.75	138	BiO <sub>2</sub> C <sub>12</sub> H <sub>7</sub>	2.67	20.0	9.9 J
502	Mg <sub>2</sub> Ca	2.65	2.87	3.14	314	Cr <sub>2</sub> (C <sub>2</sub> O <sub>4</sub> ) <sub>2</sub> ·H <sub>2</sub> O	2.68	4.75	9.2	120	Ba(CNS) <sub>2</sub> ·2H <sub>2</sub> O	2.66	7.7	3.4
752	Ag <sub>2</sub> CO <sub>3</sub>	2.65	2.73	2.27	544	MgSO <sub>4</sub> ·7H <sub>2</sub> O	2.66	4.22	5.9	532	Mg <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> ·8H <sub>2</sub> O	2.69	6.7	2.94
423	Fe <sub>2</sub> O <sub>3</sub>	2.69	2.51	1.84	533	MgNH <sub>4</sub> PO <sub>4</sub> ·6H <sub>2</sub> O	2.63	4.28	2.93	566	Mn <sub>2</sub> C <sub>2</sub> O <sub>4</sub> ·2 <sup>1</sup> / <sub>2</sub> H <sub>2</sub> O	2.67	4.80	3.00
765	Ag <sub>3</sub> PO <sub>4</sub>	2.68	2.45	1.66	448	Pb <sub>2</sub> (SbO <sub>4</sub> ) <sub>2</sub>	2.65	3.48	5.8	682	KNO <sub>3</sub>	2.63	3.77	3.03
968	ZnCrO <sub>4</sub>	2.67	2.14	9.5	133	BiOCl	2.67	3.45	7.4	650	K	2.65	3.75	2.16
407	FeCl <sub>3</sub>	2.68	2.08	5.9	111	BaO <sub>2</sub>	2.68	3.37	2.11	829	NaHC <sub>2</sub> O <sub>4</sub> ·H <sub>2</sub> O	2.67	2.97	2.45
846	Na <sub>2</sub> HPO <sub>3</sub> ·5H <sub>2</sub> O	2.67	1.89	1.54	907	TeCl <sub>2</sub>	2.69	3.24	4.29	792	Na <sub>2</sub> CO <sub>3</sub> ·1H <sub>2</sub> O	2.67	2.76	2.37
170	3CaO·Al <sub>2</sub> O <sub>3</sub>	2.68	1.90	1.55	879	Na <sub>2</sub> C <sub>2</sub> H <sub>2</sub> O <sub>2</sub> ·N <sub>4</sub> ·H <sub>2</sub> O	2.66	3.17	4.72	481	LiOH	2.67	2.75	4.35
672	KF	2.66	1.88	3.08	936	SnSO <sub>4</sub>	2.67	3.08	2.10	442	FeS	2.65	2.06	2.98
					48	(NH <sub>4</sub> ) <sub>2</sub> C <sub>2</sub> O <sub>4</sub> ·H <sub>2</sub> O	2.67	3.06	3.81	524	Mg <sub>3</sub> N <sub>2</sub>	2.66	1.76	2.12
					866	Na <sub>2</sub> SO <sub>3</sub> ·7H <sub>2</sub> O	2.66	2.87	4.26					
					315	Cr <sub>2</sub> O <sub>3</sub>	2.67	1.67	2.47					

Figure 3

No.	Compound	3rd line	4th line	No.	Compound	3rd line	4th line	No.	Compound	3rd line	4th line	No.	Compound	3rd line	4th line
	20.00-15.00				4.40-4.30				2.80-2.75				1.90-1.85		
								925	Sn	2.01					
	15.00-12.00				4.30-4.20			178	CaC <sub>2</sub> II	1.95			1.85-1.80		
				818	NaIO <sub>3</sub>	3.19						779	NaN <sub>3</sub>	2.42	
	12.00-10.00								2.75-2.70						
					4.20-4.10			801	Na <sub>2</sub> CrO <sub>4</sub>	4.09			1.80-1.75		
	10.00- 9.00											396	In <sub>2</sub> O <sub>3</sub>	1.52	
					4.10-4.00				2.70-2.65						
	9.00- 8.50			465	Pb <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	3.61							1.75-1.70		
									2.65-2.60						
	8.50- 8.00				4.00-3.90								1.70-1.65		
												303	CsCl	4.11	
	8.00- 7.50				3.90-3.80				2.60-2.55						
								795	NaHCO <sub>3</sub>	3.48			1.65-1.60		
	7.50- 7.00				3.80-3.70				2.55-2.50						
				152	CdCO <sub>3</sub>	1.83		918	Th	1.79			1.60-1.55		
	7.00- 6.50														
640	P <sub>2</sub> S <sub>5</sub>	4.90			3.70-3.60				2.50-2.45				1.55-1.50		
				93	Ba(ClO <sub>4</sub> ) <sub>2</sub> ·3H <sub>2</sub> O	2.14		685	K <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	2.32			1.50-1.45		
	6.50- 6.00														
600	HgSO <sub>4</sub> ·2HgO	5.5			3.60-3.50				2.45-2.40				1.45-1.40		
	6.00- 5.75				3.50-3.40				2.40-2.35				1.40-1.35		
	5.75- 5.50				3.40-3.30				2.35-2.30				1.35-1.30		
				715	C <sub>16</sub> H <sub>8</sub> O <sub>2</sub> N <sub>2</sub> (SO <sub>3</sub> K) <sub>2</sub>	3.00									
	5.50- 5.25								2.30-2.25						
877	Na <sub>2</sub> S <sub>2</sub> O <sub>7</sub> ·5H <sub>2</sub> O	2.84			3.30-3.20								1.30-1.25		
				797	NaClO <sub>3</sub>	1.76			2.25-2.20				1.25-1.20		
	5.25- 5.00														
					3.20-3.10				2.20-2.15						
	5.00- 4.90							782	Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> ·5H <sub>2</sub> O	4.40			1.20-1.15		
					3.10-3.00										
	4.90- 4.80								2.15-2.10				1.15-1.10		
					3.00-2.95										
	4.80- 4.70								2.10-2.05				1.10-1.05		
					2.95-2.90										
	4.70- 4.60								2.05-2.00				1.05-1.00		
					2.90-2.85										
	4.60- 4.50								2.00-1.95				1.00- .90		
					2.85-2.80										
	4.50- 4.40								1.95-1.90				.90- .80		
786	(C <sub>2</sub> H <sub>4</sub> CO <sub>2</sub> ) <sub>2</sub> -BONa	3.45											.80-		

SUPPLEMENTARY GROUP INDEX 2.95-2.90

No.	Compound	1st line	2nd line	3rd line	No.	Compound	2nd line	1st line	3rd line	No.	Compound	3rd line	1st line	2nd line
640	P <sub>2</sub> S <sub>5</sub>	2.90	6.7	4.90	532	Mg <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> ·8H <sub>2</sub> O	2.94	6.7	2.69	697	C <sub>8</sub> H <sub>4</sub> (CO <sub>2</sub> ) <sub>2</sub> NK	2.90	14.5	6.4
600	HgSO <sub>4</sub> ·2HgO	2.92	6.2	5.5	561	MnCl <sub>2</sub> ·1H <sub>2</sub> O	2.93	5.7	2.55	129	Bi(C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ) <sub>3</sub>	2.90	13.5	3.35
877	Na <sub>2</sub> S <sub>2</sub> O <sub>7</sub> ·5H <sub>2</sub> O	2.93	5.4	2.84	95	BaCl <sub>2</sub> ·2H <sub>2</sub> O	2.91	4.48	2.54	748	AgC <sub>2</sub> H <sub>3</sub> O <sub>2</sub>	2.91	10.0	3.04
786	(C <sub>2</sub> H <sub>4</sub> CO <sub>2</sub> ) <sub>2</sub> ·BONa	2.94	4.40	3.45	523	Mg(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	2.93	4.42	3.29	98	Ba(CN) <sub>2</sub>	2.94	9.4	3.37
818	NaIO <sub>3</sub>	2.93	4.25	3.19	543	MgSO <sub>4</sub> ·6H <sub>2</sub> O	2.92	4.40	4.04	927	SnCl <sub>2</sub> ·5H <sub>2</sub> O	2.94	6.2	5.3
465	Pb <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	2.91	4.03	3.61	693	KH <sub>2</sub> PO <sub>4</sub>	2.90	3.72	1.95	326	CoCl <sub>2</sub> ·6H <sub>2</sub> O	2.94	5.6	4.85
152	CdCO <sub>3</sub>	2.94	3.77	1.83	991	α-ZnS	2.91	3.29	1.76	377	CuOH·CuPO <sub>4</sub>	2.91	4.81	2.63
93	Ba(ClO <sub>4</sub> ) <sub>2</sub> ·3H <sub>2</sub> O	2.90	3.65	2.14	462	PbO	2.93	3.06	2.72	533	MgNH <sub>4</sub> PO <sub>4</sub> ·6H <sub>2</sub> O	2.93	4.28	2.69
715	C <sub>16</sub> H <sub>8</sub> O <sub>2</sub> N <sub>2</sub> (SO <sub>3</sub> K) <sub>2</sub>	2.90	3.35	3.00	179	CaC <sub>2</sub> III	2.92	2.86	2.05	586	HgCl <sub>2</sub> ·3HgO	2.92	3.95	2.70
797	NaClO <sub>3</sub>	2.94	3.28	1.76	597	Hg <sub>2</sub> PO <sub>4</sub>	2.94	2.60	3.09	449	PbHAsO <sub>4</sub>	2.93	3.39	3.17
925	Sn	2.91	2.79	2.01						707	K <sub>2</sub> S <sub>2</sub> O <sub>7</sub>	2.90	3.23	3.07
178	CaC <sub>2</sub> II	2.93	2.79	1.95						755	Ag <sub>2</sub> CrO <sub>4</sub>	2.92	3.14	3.02
801	Na <sub>2</sub> CrO <sub>4</sub>	2.91	2.73	4.09						701	K <sub>2</sub> SeO <sub>4</sub>	2.94	3.08	4.35
795	NaHCO <sub>3</sub>	2.94	2.58	3.49						49	(NH <sub>4</sub> )HC <sub>2</sub> O <sub>4</sub> ·H <sub>2</sub> O	2.90	3.00	6.2
918	Th	2.92	2.53	1.79						474	Li <sub>2</sub> CO <sub>3</sub>	2.91	2.80	4.16
685	K <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	2.92	2.46	2.32						853	Na <sub>2</sub> SiO <sub>3</sub> ·9H <sub>2</sub> O	2.92	2.79	3.83
782	Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> ·5H <sub>2</sub> O	2.94	2.19	4.40										
779	NaN <sub>3</sub>	2.91	1.82	2.42										
396	In <sub>2</sub> O <sub>3</sub>	2.91	1.78	1.52										
303	CsCl	2.90	1.68	4.11										

Figure 4

**Table 1.**  
*X-Ray Diffraction Data*

$d^a$	$I^b$	$I/I_1^c$
4.95	8	0.13
4.08	25	0.40
3.89	20	0.32
3.58	17.5	0.28
2.91	62.5	1.00
2.73	40	0.64
2.47	15	0.24
2.16	7	0.11
2.11	5	0.08
2.03	15	0.24
1.94	10	0.16
1.79	15	0.24
1.72	1	0.02
1.68	2	0.03
1.64	6	0.10
1.61	12.5	0.20

<sup>a</sup>  $d$  = interplanar spacing measured in Angstrom units.

<sup>b</sup>  $I$  = intensity of the diffraction line (arbitrary units).

<sup>c</sup>  $I_1$  = intensity of the strongest line.

If the constituent corresponding to the strongest line of the unknown pattern is not contained in the file, or if the strongest line should happen to be so by virtue of the superposition of two lines, neither of which is the strongest line of any component present in a mixture, one will not find a match in the major group determined by the strongest line of the unknown pattern, so he must proceed by using the second strongest line to determine the major group, and so on. One cannot fail to find any or all components of a mixture which exists in the reference file. If the pattern is not found in the file, then even in this case one has obtained considerable negative information about the unknown.

### Use of System in Identifying Unknowns

Probably the easiest way to become acquainted with the details of the system is to follow through the determinations of a few unknowns. For this purpose, three sections of the index book (Figures 2, 3, 4) have been chosen to be reprinted. (The complete index book is not reprinted here because it requires 462 pages, but it can, of course, be easily tabulated from the pattern data given.)

In working with a real unknown, one cannot, in general, tell by simply looking at the pattern whether it represents a single substance or a mixture, nor is it necessary to know this. However, for simplicity the illustrations are picked from different types of cases.

A. A Single Component. Assume that the measurements of the pattern have been recorded as in Table I.

The three strongest lines in order of decreasing intensity are 2.91, 2.73, 4.08. Turn to the index book to group 2.95-2.90 (Figure 4) and look in subgroup 2.75-2.70. One finds that sodium chromate, pattern No. 801, has a third line at 4.09, which is also the third most intense line of the unknown. Then turn to pattern No. 801 and observe that within experimental error all positions and relative intensities check and there are no lines of either pattern not accounted for. The conclusion is that the unknown contains sodium chromate.

B. Mixture of Two Substances (no superposed index lines). The data of such an unknown are reproduced in Table 2.

**Table 2.**  
*X-Ray Diffraction Data*

$d$	$I$	$d$	$I$
4.65	6	1.82	4
3.79	12.5	1.75	30
3.28	30	1.71	2
2.93	50	1.63	1
2.67	20	1.58	10
2.52	50	1.54	1.5
2.32	50	1.50	15
2.18	15	1.465	1.5
2.07	2	1.430	6
1.97	6	1.406	10
1.86	10	1.372	10

Turn to group 2.95-2.90 (Figure 4) and to subgroup 2.55-2.50 and find that there is no compound with a third line corresponding to any of the lines of the unknown. Turn next to subgroup 2.35-2.30 and again find no match. Turn next to subgroup 3.30-3.20 and observe that sodium chlorate, pattern No. 797, has a third line at 1.76. Since there is a line at 1.75 in the unknown pattern, compare the data of sodium chlorate, pattern No. 797, with that of the unknown and list the relative intensities of the identified lines. This gives Table 3 in satisfactory agreement with sodium chlorate, pattern No. 797.

**Table 3.**  
*X-Ray Diffraction Data*

$d$	$I$	$I/I_1$
4.65	6	0.12
3.79	12.5	0.25
3.28	30	0.60
2.93	50	1.00
2.67	20	0.40
2.18	15	0.30
2.07	2	0.04
1.97	6	0.12
1.82	4	0.08
1.75	30	0.60
1.63	1	0.02
1.58	(10)	(0.20)
1.54	1.5	0.03
1.50	(15)	(0.30)
1.465	1.5	0.03
1.430	6	0.12

The identification of one compound of the mixture is thus established. The strongest of the remaining lines is at 2.52; hence turn to group 2.55-2.50 (Figure 2), subgroup 2.35-2.30, and note the compound cupric oxide, pattern No. 372, with a third line at 1.86. Referring to the data of cupric oxide, pattern No. 372, note that all the remaining lines of the unknown are accounted for in position. List the relative intensities, Table 4.

**Table 4.**  
*X-Ray Diffraction Data*

d	I	I/I <sub>1</sub>
2.52	50	1.00
2.32	50	1.00
1.86	10	0.20
1.71	2	0.04
1.58	(10)	(0.20)
1.50	(15)	(0.30)
1.406	10	0.20
1.372	10	0.20

These are seen to be in satisfactory agreement with the cupric oxide data. Since all the diffraction lines of the unknown have been satisfactorily accounted for, the qualitative compound analysis of the mixture is complete.

C. Mixture of Two Components (superposed lines). The data for the unknown are recorded in Table 5.

**Table 5.**  
*X-Ray Diffraction Data*

d	I	d	I
4.90	2	1.309	4
3.68	4	1.274	2
2.96	7	1.256	3
2.69	25	1.220	1
2.52	50	1.189	2
2.43	1	1.160	2
2.21	7	1.140	2
2.08	8	1.120	1
1.84	15	1.103	1
1.69	17.5	1.089	2
1.61	15	1.054	2
1.480	25	1.040	1
1.450	10		

Turn to group 2.55-2.50 (Figure 2), subgroup 2.70-2.65, and find no compound listed with a third line corresponding to any of the lines of the unknown. Turn to subgroup 1.50-1.45 and find iron ferrite (ferrosferric oxide), pattern No. 426, with a third line at 1.62. Compare the data of pattern No. 426 with the data of the unknown. On listing the relative intensities of the identified lines (Table 6), it is seen that the intensity of line 2.52 is decidedly too high, which suggests the possibility of a superposition of lines.

**Table 6.**  
*X-Ray Diffraction Data*

d	I	I/I <sub>1</sub>
4.90	2	0.04
2.96	7	0.14
2.52	50	1.00
2.43	1	0.02
2.08	8	0.16
1.69	17.5	0.35
1.61	15	0.30
1.480	25	0.50
1.274	2	0.04
1.120	1	0.02
1.089	2	0.04
1.054	2	0.04

Therefore include line 2.52 with the remaining unidentified lines. Inspection shows that the intensity of the superposed line on 2.52 of iron ferrite is about as strong as line 2.68. However, group 2.55-2.50, subgroup 2.70-2.65, gives no check, while group 2.70-2.65, subgroup 2.55-2.50, lists ferric oxide, pattern No. 423, with a third line at 1.84.

Comparing the data of ferric oxide, pattern No. 423, with the data of the unknown, it is found that the positions of the ferric oxide lines check with all of those of the remaining unidentified lines of the unknown as well as with three of the lines which had already been checked with the iron ferrite pattern. Thus there are superpositions of lines at three positions in the unknown pattern.

In order to show conclusively that the unknown is a mixture of ferric oxide and iron ferrite, it is necessary to account satisfactorily for the relative intensities of the lines of the unknown pattern. Since line 2.69 is not a superposed line, its intensity is due entirely to ferric oxide, and to get the value of the absolute intensities of all other ferric oxide lines of the unknown, it is only necessary to multiply the intensity of line 2.69 by the known relative intensities of ferric oxide as given in pattern No. 423. This is done in Table 7.

**Table 7.**  
*X-Ray Diffraction Data*

d	I
3.68	0.18 × 25 = 4.5
2.69	1.00 × 25 = 25
2.52	0.75 × 25 = 19
2.21	0.18 × 25 = 4.5
1.84	0.63 × 25 = 16
1.69	0.63 × 25 = 16
1.61	0.13 × 25 = 3
1.480	0.50 × 25 = 12.5
1.450	0.50 × 25 = 12.5
1.309	0.18 × 25 = 4.5
1.256	0.13 × 25 = 3
1.189	0.08 × 25 = 2
1.160	0.05 × 25 = 1
1.140	0.13 × 25 = 3

Then subtract these computed absolute intensities from those of the total unknown pattern (Table 8). The resulting data must agree with those of iron ferrite, if the identification of the unknown is to be considered complete. This is found to be the case.

**Table 8.**  
*X-Ray Diffraction Data*

d	I	I/I <sub>1</sub>
4.90	2	0.07
2.96	7	0.23
2.52	31	1.00
2.43	1	0.03
2.08	8	0.26
1.69	1.5	0.05
1.61	12	0.39
1.480	12.5	0.40
1.274	2	0.07
1.220	1	0.03

The low intensity in the case of line 1.48 can be explained by the fact that this line in the unknown pattern is a partially superposed line, and the intensity as read is not the sum of the intensities of the lines. The case could never exist where this phenomenon would cause the intensity of a line to be calculated too high.

It is worth while to point out an alternative method of identifying a mixture of the above type by making use of the Supplementary Group Index. If one inadvertently fails to recognize the anomalously high intensity of the spacing 2.52 for the identified iron ferrite pattern and proceeds to identify the second phase in the usual manner, he might easily neglect to reconsider the spacing 2.52 (inasmuch as the spacing has already been identified as the most intense line of iron ferrite) and consequently fail to locate the second phase. In that event, upon looking in group 2.70-2.65 in the standard manner, one fails to identify the remaining lines. He then refers to supplementary group 2.70-2.65 and finds listed along with 2.68 and 1.84 the line 2.51 which also occurs in the unknown pattern. The ferric oxide pattern would then be checked. The Supplementary Group Index in general is useful when for any reason the strongest line of a pattern is overlooked and one is attempting to identify a pattern from its second or third strongest lines.

While the illustrations have been limited to mixtures of only two unknowns, no new situation will be encountered in mixtures of three or more components. It has been found from experience in this laboratory that it is practical to use this method of analysis for mixtures with as many as four or five components. However, the ease of analysis becomes less as the number of components increases.

#### Apparatus and Technic

The X-ray literature describes many types of apparatus for diffraction work<sup>1,2,4,6,7,10</sup>. The type to be used in any particular case depends on the kind of data desired and the accuracy necessary. A completely equipped X-ray laboratory which could handle all the X-ray technics for diverse purposes would require a large variety of apparatus. However, for the particular purpose of chemical analysis under discussion in this article, a satisfactory equipment and experimental procedure which is sufficiently accurate and at the same time economical will be described.

The diffraction unit most used in this laboratory is the G. E. multiple diffraction unit, Type VWC, Form E, as described by Davey<sup>3</sup> (Figure 5). (The production of this particular type of X-ray unit has been suspended at the present time, though other powder diffraction units are com-



Figure 5. Diffraction apparatus and central board.



mercially available.) This unit consists of a transformer, X-ray tube with a molybdenum target, and cameras. Twelve slits  $0.05 \times 1.25$  cm. ( $0.02 \times 0.5$  inch), located around the circumference of the cylinder containing the X-ray tube, define the X-ray beams. There is a switchboard holding the operating switches, meters, filament current stabilizer, a water pressure switch, and an overload circuit breaker. In this laboratory there have been added a recording milliammeter, which gives a record of the tube current during the exposure; a time switch, by which an exposure can be stopped at a predetermined time; and a temperature switch, which shuts off the voltage if the temperature of the cooling water reaches about  $38^\circ$  C. ( $100^\circ$  F.).

The G. E. quadrant cassettes of 20.32-cm. (8.00-inch) radius (Figure 6) are used. A slight modification of these cameras makes it possible to record the diffraction lines on both sides of the beam. This produces a symmetrical pattern, which enables an accurate location of the setting of the primary beam on the zero of the measuring scale (Figure 1). In order to obtain a more uniform pattern, the specimen tube is rotated during the exposure. The power for rotating the specimen is supplied by an electric clock motor and is transmitted by a silk fish-line belt. A zirconium dioxide filter about 0.04 cm. (0.016 inch) thick is placed in front of the film to absorb the  $\text{MoK}\beta$  radiation. (These filters are supplied by the Patterson Screen Company, Towanda, Pa.) Double-emulsion X-ray film  $4.76 \times 40$  cm. ( $1.875 \times 16$  inches), costing about 7.5 cents each is used. A fluorazure intensifying screen (also supplied by the Patterson Screen Company) is placed immediately behind the film.

The specimens are loaded in powder form in Pyrex capillary tubes 0.04-cm. (0.016-inch) inside diameter (measured with a No. 78 drill) and 0.06-cm. (0.025-inch) outside diameter (measured with a No. 22 U. S. standard wire gage). These tubes can be readily made in large quantities. A plug of absorbent cotton about 0.1 cm. (0.04 inch) long is placed in the center of the tube. The samples are then loaded on either side of the central plug for a distance of 1 cm. (about 1 mg.) in a manner similar to that used in loading melting point tubes. Piano wire serves well as an aid in packing because it does not buckle and break the tube. After the sample is packed into the tube, another cotton plug is inserted and the ends of the tube are sealed in a flame. Brittle substances can be prepared for loading by grinding in an agate mortar. Samples of metals can be obtained by filing with a clean file. It has been found helpful to have available various dental tools for the purpose of obtaining samples of small inclusions in nonhomogeneous materials. A desiccator box equipped with glass top and rubber sleeves is more convenient for loading hygroscopic substances than loading under a protective liquid. Samples which contain elements of high atomic number should be diluted with an amorphous material such as flour or charcoal to decrease the absorption of the radiation. In general, about 200-mesh is a satisfactory powder size to use. The preparation and loading of a sample can usually be accomplished in 5 minutes or less.

The loaded tube is inserted in the pulley of the camera and secured by Picein wax. The camera is then placed on the diffraction unit and exposed for 6 hours at 30,000 volts and 20 milliamperes. The unit holds twelve cameras, so that



Figure 6. Film cassette with tube and rotating device.

24 specimens may be exposed simultaneously. (When an analysis is desired in the least possible elapsed time, use of copper radiation and a different type of camera would require an exposure time of only about 15 minutes. This technic would not permit the simultaneous exposure of 24 specimens, however.) The exposed films are then developed as a batch in standard X-ray developer for 5 minutes at  $18^\circ$  C. ( $65^\circ$  F.), fixed in X-ray hypo for about 12 minutes, washed in running water for 20 to 30 minutes, and dried in a film dryer. The drying takes about half an hour. The developed film, or pattern, is now ready to be measured.

Table 9.  
Time Study of Operations

	Time Man-minutes
Preparation of specimens and filling of tubes (24 specimens)	120
Loading cameras, mounting specimen (24 specimens)	45
Removing cameras after exposure and filing specimen (24 specimens)	30
Darkroom operation (24 specimens)	20
Labeling and filing negatives (24 specimens)	30
Total	245
Preparation of pattern, average time per specimen	10
Measurement of pattern, average time per specimen	10-15
Identification of pattern, average time per specimen	5-15
Total man-minute time for analysis and permanent record, per specimen	25-40

The pattern is placed symmetrically in the measuring scale (Figure 1) and the positions of the different lines are read off in the order of decreasing  $\lambda$  spacings. The scale division beginning at 20 Å are 20, 15, 12, 10, 9; every 0.5 Å from 9 to 6; every 0.25 Å from 6 to 5; every 0.1 Å from 5 to 3; every 0.05 Å from 3 to 2; and every 0.01 Å from 2 to 0.55.

The next step is to record the intensities of the lines with the aid of an intensity scale. The pattern is placed on top of the intensity scale, and the combination is viewed by eye in transmitted light. A match is then sought between the diffraction line and the standard lines of the intensity scale. The complete data of the diffraction pattern are thus recorded, giving the interplanar spacing and numerical intensity of each line.

The preparation of an intensity scale must be carried out very carefully. However, it need be done only once if the scale is protected from wear by sealing in a Cellophane envelope. (The diffraction patterns themselves can well be filed in Cellophane envelopes.)

While the pattern consists of diffraction lines formed by X-ray beams of very different intensities but of the same exposure time, the intensity scale can, by virtue of the reciprocity relation which holds for X-rays, be constructed by using an X-ray beam of constant intensity and varying the exposure times. The value of the intensity for each step of the intensity scale is therefore proportional to the time of exposure used for that step.

In order to have a beam of  $\text{MoK}\alpha$  radiation of intensity comparable with the powder reflections, a calcite crystal monochromator was used in conjunction with an absorber further to reduce the intensity of the beam. The exposure times were determined to one-third second by a shutter system. The film was mounted on a drum which was turned by a 400-to-1 reduction gear, for the purpose of easily spacing the intensity steps. The secondary voltage was kept constant at about 25 kilovolts to within 0.5 per cent. The tube current was maintained constant by a stabilizer. The shortest exposure to produce a barely visible mark on the film was 10 seconds. This blackness was arbitrarily chosen to represent unit intensity. The longest exposure was 3250 seconds, corresponding to an intensity of 325. The steps of the intensity scale are such that easily observable differences in blackness exist between adjacent intensity marks, and are as follows: 1, 2, 4, 6, 8, 10, 15, 20, 30, 50, 75, 125, 175, 250, 325. The width of the intensity marks is made approximately the same as that of the diffraction lines.

A fair idea of the approximate expense and time involved in carrying out analysis by the X-ray method can be obtained from data based on actual operation in this laboratory.

If only one specimen were run through instead of 24 at a batch, the time for preparation of the pattern would be about 25 minutes instead of 10.

**Table 10.**  
*Cost of Supplies*

	Cents
X-ray tube (\$225 per tube, average life 12,000 hours' operation) per specimen	0.5
Darkroom supplies	0.7
X-ray film	3.7
Specimen tube	2.0
Power	0.3
Total cost of supplies per specimen	7.2

The expense of the analysis is almost entirely due to the labor involved (Table 10).

### Accuracy of the Data

*Spacing Measurements.* In the experimental technic as given, the error of measurement of spacings increases in a smooth curve from + or - 0.001 Å, at 1.0 Å, through + or - 0.01 Å at 3.5 Å to + or - 0.06 Å at 8.0 Å. Higher accuracy than this, of course, could be attained by modern precision X-ray methods, but only at the expense of the ease and speed of making the measurements. The use of  $\text{MoK}\alpha$  radiation and a large camera radius of 20.32 cm. (8.00 inches), as described, makes possible the rapid measurement of the position of the lines on a scale, whereas use of a small precision camera and a comparator is not only tedious but also makes the measurement of weak lines very difficult. In order to secure the accuracy obtained, all cassettes are calibrated with sodium chloride. Since all films are treated under standardized conditions, the effect of film shrinkage is absorbed in the sodium chloride calibration. In 310 cases (the starred compounds) an independent check on the accuracy of the measured spacings was afforded by calculation of the spacings from published data listed by Wyckoff<sup>10</sup> and Ewald and Hermann<sup>5</sup>. The agreement was within the experimental error. Each of the 1000 patterns was measured independently by two different observers.

*Intensity Measurements.* The most objective method of measuring the intensities would be to use the microphotometer or densitometer. However, one year's experience with a direct comparison intensity scale has shown that it is sufficiently accurate for use with the classification system. It has the advantages of being rapid and easy to use. Weak lines can be measured in this way when they would be difficult to record with a microphotometer. The steps of the intensity scale are such that successive differences in blackness can easily be recognized. In use, one decides only whether the intensity of the diffraction line lies closer to one of two adjacent pairs of intensity marks, or lies nearer the mean. To check the accuracy of the intensity data, each of the 1000 patterns was read by two independent observers. The agreement was found to be within the steps of the intensity scale. It has been thoroughly tested that the relative intensities of the lines of a pattern remain essentially unchanged, even though the absolute strength of the pattern be different — for instance, because of different exposure times or amount of diffracting material in the tube. One can obtain on a single film the equivalent of two different exposures by covering half the X-ray film lengthwise with a suitable thickness of aluminum foil.

In order to attach a physical meaning to the seemingly arbitrary intensity values, microphotometer tracings were made of the intensity scale itself and of a number of sodium chloride films, for which the time of exposure and the concentration of sodium chloride were varied. This work showed that the use of the intensity scale eliminates the background and gives intensity values proportional to the peak intensities of the diffraction lines. The relative intensities as listed in the tables of data refer to intensities of the diffraction lines from rotated powdered specimens.

Besides the relative intensities, the values of the intensity of the three strongest lines of each compound are included in the tabulated data in order to have a measure of the absolute strength of the diffraction pattern. This information frequently permits a rough estimate of the sensitivity of detection of a compound in a mixture. In using the intensity data, one should bear in mind that the agreement between the tabulated relative intensities and those determined by the analyst for his film is only a semiquantitative one. While the recorded data for the 1000 compounds were obtained with  $\text{MoK}\alpha$  radiation, it is possible to use the same data for  $\text{CuK}\alpha$  radiation, provided due precautions are taken to reduce the effect of absorption.

### Sources and Reliability of Standards

The majority of the 1000 standards listed in this article have not been subjected to a complete chemical analysis. At The Dow Chemical Company, the patterns of a considerably larger number of substances have been entered in the index book and file. Whenever any one of these patterns is used as a standard, its reliability is invoked and, if questioned, is closely examined. However, to permit testing the usability of the classification system and X-ray method of chemical analysis, 1000 substances were selected whose compositions are thought to be reasonably certain.

The starred patterns are those for which it was possible to check all the lines of the pattern with published crystal structure data. This comprehensive check included the calculation of the spacings, the indexing of the lines, and the application of space group criteria. Since, in general, when a crystal structure investigation is made, the chemical formula of the substance must be definitely known, there is little reason to question the reliability of the starred patterns. There are 310 such patterns. Unfortunately, crystal structure data are lacking for most of the balance of the 1000 patterns. Compounds rated chemically pure were obtained from Eimer & Amend, Merck & Co., Inc., Mallinckrodt Chemical Works, E. H. Sargent and Company, General Chemical Co., Vanadium Corporation of America, G. Frederick Smith Chemical Co., Central Scientific Company, Eastman Kodak Company, and The Dow Chemical Company. When it was not possible to obtain the desired compounds in a C. P. grade, the available grade was used. The less stable hydrates of a sizable group of compounds were prepared in this laboratory, and the degree of hydration was checked gravimetrically. In addition, about 50 compounds not commercially available were synthesized.

It is probable that a small number of cases exist among the unstarred patterns for which the data do not represent the exact formula as given. An idea of the type and extent of the errors to be expected can be obtained from a considera-

tion of the results in those cases where a check with the crystal structure data was possible. Of the 342 cases so investigated, in 14 cases the degree of hydration was incorrectly given by the label on the reagent bottle, the diffraction pattern obtained being that of a different hydrate or of a mixture of hydrates. Seven cases resolved themselves as a mechanical mixture of the labeled substance and an impurity, and four cases as polymorphic mixtures of the same chemical substance. In seven instances, the diffraction pattern experimentally obtained differed completely from the data as published in the crystal structure literature.

### Field of Application of X-Ray Diffraction in Chemical Analysis

It is well known that there are definite limitations to the field of application of the X-ray method of analysis, but the important question is as to the range of usefulness left when these things are taken into account. The method is limited in the first place to solids, and secondly to those solids which are crystalline, meaning by crystalline simply those substances which give a pattern. The only way to determine whether or not a material will give a pattern is to subject the material to X-ray diffraction. It has been found experimentally that about 5 per cent of the solid inorganic chemical substances are essentially amorphous and give no pattern by which they could be identified.

A considerable number of other substances give such weak patterns that, while they could be identified if they were the only constituents present, they might escape detection if they were mixed with something else. Depending to some extent on what the substances are mixed with, some would show if they represented less than 1.0 per cent of the material being examined, but many would not show at less than 10.0 per cent and some would not show plainly even when as much as 50.0 per cent was present. The magnitude of this figure can be estimated after the pattern has been obtained, but cannot be told beforehand. Still another weakness of the method is that appreciable percentages of elements may be present in solid solution without changing the pattern enough to be detected, at least without special technic.

Thus, while certainty of analysis is one of the valuable features of the X-ray method, this certainty applies only to what the pattern does show and not to what it does not show. If, for instance, one obtains the pattern of manganese chloride dihydrate it is certain that manganese chloride dihydrate is present. However, it is not certain that there is not a small amount of a more or less amorphous material mixed with it, nor that there is not in solid solution in the manganese chloride a substance which does not greatly change the characteristics of the manganese chloride pattern.

For these reasons the X-ray method is not independent and cannot, in general, stand alone as a means of chemical analysis. The X-ray data must be combined with other data for complete information. The combination of spectroscopy and X-ray diffraction is very fortunate, since they supplement each other's deficiencies by giving entirely different types of information about the same substance. In the arc or spark, the material is broken up into its elements, so that they show regardless of the state in which they were present, while the X-ray, without so much as changing the temper-

ature of the material, records the existing chemical and physical state. The spectrograph is also sensitive in the region of small percentages, where the X-ray is not.

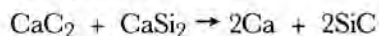
Installation of X-ray diffraction in the laboratory does not, in general, displace other technics, but gives the power to get more information or to obtain information under peculiarly difficult conditions. A practical procedure is to make a survey analysis before other work is attempted. In those cases in which the information obtained is sufficient, it does eliminate other work.

In the field of identification, the merits of X-ray diffraction analysis are sometimes compared with those of microscopic examination. The technics involved and the scientific principles invoked are different. The microscope is much more sensitive than the X-ray to the presence of small percentages of substances, and to amounts of sample of less than 0.1 mg., which is about the practical limit for the X-ray method. It is equally true that the X-ray is much more suited to the general problem of determining the chemical state and composition of the main components of an unknown. The X-rays are less affected by superficial differences, since they analyze the body of the substance. Furthermore, the interpretation of the diffraction pattern is direct. The experimental technic involved can be rapidly acquired. A further advantage of the X-ray method is that no special requirements are imposed upon the form of the specimen. It seems fair to say that, in general, no other single method will yield compound analysis of solids so reliably and economically.

The field of application of X-ray in chemical analysis might be summarized in a general way by saying that, wherever it is necessary to maintain an analytical laboratory, an invaluable supplementary technic will be found in X-ray diffraction. The following are some of the unique features which have been found of practical importance in this laboratory:

1. The substances present show in their true state of chemical combination.

The analysis of reaction mixtures is a good illustration of the application of this feature. The analysis of the residue or slag of a high-temperature reaction in this way shows which components of the charge react, and what the equation of the reaction is. For example, it is desired to determine whether the compounds calcium carbide and calcium silicide will react. About a gram of the two in molecular proportions is mixed and ground, and the mixture is heated to 1500° C. in a small electric vacuum furnace. Before heating, the mixture is a dark powder whose X-ray pattern is the superposition of the calcium carbide and calcium silicide patterns. After heating, the powder looks the same as before, but the X-ray pattern shows only silicon carbide. One concludes with certainty that reaction has taken place according to the equation



The entire experiment is done with a minimum of expense and time.

A problem which resisted the usual chemical methods of attack was that of the chemicals added to molding sand to inhibit the oxidation of magnesium alloys on casting. A single compound such as ammonium fluoride or ammonium

borofluoride may be added to the sand, but reactions begin to take place immediately. The question therefore arises as to what chemicals are actually present in the sand and which ones are actually effective in inhibiting oxidation. The chemical analysis for the ammonium radical present gave no hint as to the various ammonium compounds present; but the X-ray patterns showed that as many as six different ammonium compounds are present in the sand after using it awhile, and, by identifying them separately, showed what reactions were taking place and which agents were stable and which effective in inhibiting oxidation. By setting up standard mixtures with a range of concentrations of the various compounds involved — ammonium fluoride, ammonium acid fluoride, ammonium fluosilicate, ammonium borofluoride, ammonium chloride, ammonium sulfate, boric acid, and sulfur — it was possible to make a semi-quantitative analysis on the basis of the relative intensities of the diffraction lines. The ability of the X-ray to recognize these compounds separately though mixed together was thus very valuable.

A point in connection with this problem which illustrates the fact that the X-ray pattern serves as a unique identification of a substance was that besides the compounds in the sand which were definitely identified, there occurred a substance giving a pattern which could not be identified. The substance was temporarily called X, and it was possible to determine the approximate per cent present in the sand and that it was effective in inhibiting oxidation even before it was isolated and identified by chemical methods. If the file and index of patterns had been available 5 years ago when this problem was investigated, the pattern X would have been identified immediately.

2. The analysis is conclusive, even though only minute amounts of material are available. This is especially valuable for corrosion products from small pits or surface attacks. Identification of small deposits and sediments can also be readily accomplished.

3. Substances are analyzed directly in their "as received" state and are not destroyed.

4. Different crystalline phases, states of oxidation or hydration, and physical state are observable. The ability to determine the degree of graphitization of carbon, or to distinguish quartz and cristobalite, or the high- and low-temperature forms of compounds — e.g., dicalcium silicate, etc. — is frequently important. The patterns of the various oxides of an element — e.g., ferrous oxide, ferric oxide, ferrosferric oxide — are distinct from each other and, of course, from that of the element itself. The state of hydration of calcium chloride as a function of process and also as a function of position in the individual clusters of crystals can be determined, and in other cases the existence of water as water of crystallization can be detected.

5. As has been discussed rather fully in the present article, the process of preparing the specimen and obtaining the X-ray pattern is simple and economical.

6. A permanent record of the original data is always on file in the form of the diffraction pattern.

These features, which have been enumerated, are of obvious importance and would make X-ray diffraction valuable in many analysis problems, even though an easy method of indexing the patterns were not possible.

However, the classification system greatly facilitates the use of X-rays in these cases and extends its field of application to include complete unknowns.

At the present stage of development, X-ray diffraction gives a qualitative or semiquantitative analysis. The accuracy possible varies widely in different cases, but in a favorable case allows a determination to within about 5 per cent of the amount present.

Future technical improvements will undoubtedly greatly increase the accuracy attainable as well as the scope of the X-ray diffraction method of analysis.

### Literature Cited

1. Am. Soc. Testing Materials, "Symposium on Radiography and X-Ray Diffraction Methods," 1937.
2. Clark, G. L., "Applied X-Rays," 2nd ed., New York, McGraw-Hill Book Co., 1932.
3. Davey, W. P., *Gen. Elec. Rev.*, 25, 565 (1922).
4. Davey, W. P., "Study of Crystal Structure and Its Applications," New York, McGraw-Hill Book Co., 1934.
5. Ewald, P. P., and Hermann, C., "Strukturbericht," Leipzig, Akademische Verlagsgesellschaft, 1931.
6. Glocker, R., "Materialprüfung mit Röntgenstrahlen," Berlin, Julius Springer, 1936.
7. Halla, F., and Mark, H., "Röntgenographische Untersuchung von Kristallen," Leipzig, J. A. Barth, 1937.
8. Hanawalt, J. D., and Rinn, H. W., *Ind. Eng. Chem., Anal. Ed.*, 8, 244 (1936).
9. Hull, A. W., *J. Am. Chem. Soc.*, 41, 1168 (1919).
10. Wyckoff, R. W. G., "Structure of Crystals," New York, Reinhold Publishing Corp., 1930-1934.

Editor's Note: The original article concluded with several tables, among them the index to Powder Diffraction Data for 1000 chemical substances.