



J. Donald Hanawalt

Manual Search/Match Methods for Powder Diffraction in 1986

By J. D. Hanawalt, Prof. Emeritus, *The University of Michigan*

The objectives of this paper are: 1. to up-date the manual search system and index book described in 1936⁵ and 1938⁶; 2. to introduce a "work form" which serves to guide the analyst through the procedural steps involved in using the manual search index book and 3. to review briefly the literature on manual search/match systems.

Design of the 1986 Search Manual

Two of the basic features of the 1936⁵ design of the search index book were first, to divide the "d" range into arbitrarily sized "groups" and "subgroups" rather than using a scale of continuously decreasing "d" values, and second, to use the "d" values of the strongest lines of the diffraction pattern in order of decreasing intensity in making the entries of the standard patterns in the search index book. These two features are still the basis of the design of the 1986 Hanawalt Search Manual published by the JCPDS International Centre for Diffraction Data.

The original use of the search index book at Dow Chemical was to lead the analyst to corresponding patterns among the thousands of Debye films which had been produced and placed on file. The "d" values and intensities of only the three or four strongest lines of the pattern were measured. Comparisons and indentifications were then made visually simply by holding the concerned films together in juxtaposition. Unfortunately, attempts to reproduce usable copies of such Debye films for general reference have not been satisfactory. Therefore, for general usage the diffraction data carried by the film negative or also the data from a diffractometer trace are recorded using the *numerical* values of the "d" spacings and intensities. These tables of numerical data are then used to represent the diffraction patterns. The search index book for general usage must therefore deal entirely with these numerical values.

The present 1986 design of Hanawalt search index book divides the "d" range from 999.99 Å down to 1.00 Å into forty intervals or "groups" into which the standard patterns are entered according to the "d" value of the strongest line of the pattern. The "d" value of the second strongest line

determines the sub-group. The entries are ordered within the sub-group according to decreasing values of the strongest line (though early manuals used decreasing values of the third strongest line). The entry lists the next six strongest lines of the pattern in order of decreasing intensity. Intensities are difficult to measure reproducibly and because intensity values are subject to various factors not necessarily constant from case to case. A line of intensity 75, for example, in a given case, may measure 100 in another case and vice versa. In practice the analyst enters the search index book with line-pairs formed by a "prime" line paired with succeeding lines of decreasing intensity. Because of the possibility of intensity variations just mentioned above, multiple entries are made for the diffraction pattern depending upon the number of strong lines. If the reference pattern has just one strong line then it will have just one entry. If the pattern has two strong lines it will have two entries, etc. In the 1986 Hanawalt Search Manual "strong" means any lines with an intensity ≥ 75 . This value of 75 is an arbitrary choice based upon experience and may be increased or decreased in later editions. The lower the value, the more allowance for errors in the data. But if this value is lowered too much, there would be so many entries that the search index book would be too voluminous to use efficiently. The 1986 Hanawalt Search Manual averages less than three entries per pattern.

The use of the "group" format requires some explanation. The merit of the "group" system is that all entries which should be considered because of falling within the \pm error range are conveniently located together for the necessary comparisons for determining the best "fit" with the unknown pattern. This fact is illustrated in Figure 1 which shows that all of the entries qualifying for line-pair 3.04–2.95 fall on one page of the search manual. It is seen that there are twenty-five cases of the nine combinations of $3.04 \pm .01$ with $2.95 \pm .01$. In a non-group format these same twenty-five entries would be present but scattered through-out about 688 entries, that is, over about eight pages of a non-group search manual. All twenty-five entries could still be compared but obviously not nearly so conveniently. Often the analyst must examine all eight lines of the entry to make the correct choice.

The "group" format also provides a secondary benefit in that the groups can be over-lapped by a $\pm \Delta d$ error value. Thus when a line-pair falls at the boundary between two groups the search does not have to be carried out in both groups. While the total size of the search manual is increased about 25% by over-lapping, the number of entries which the eye must scan is not increased. The reason is because the additional entries introduced are not interspersed with the previous entries but only appear as extensions of the sub-groups. Thus, while neither the "group" format nor the over-lapping of groups are necessary features of a search manual, both have been found to be of very practical advantage.

These changes in entry specifications and modifications of the design of the original search book are the result of many trial indexes tested experimentally in the last twenty-four years at the University of Michigan. These numerous trial indexes were produced in computer print-out form at the Pennsylvania State University by Prof.

Gerald G. Johnson, Jr. The work would not have been possible without the enthusiastic cooperation and efforts of Prof. Johnson in programming sometimes seemingly impossible specifications for entries, groups, etc.

A "Work Form" for Manual Search Procedure

If the unknown powder diffraction pattern happens to be that of a single phase, the retrieval process can be quite simple. But in the more general case in which the pattern is that of a mixture of two or more phases the process of examining and comparing the many numbers involved is obviously a candidate for a job using a computer. The job can also be done successfully manually with the guidance of a "Work Form" on which a record can be kept of the necessary sequence of steps. The merit of such a "Work Form" will be better appreciated by a demonstration of its use in the solution of a real problem. The problem was published by L. K. Frevel⁸ in 1965 and is selected for this illustration because it is representative of the high quality of diffraction data by the techniques introduced and developed by Frevel in the early 1960's. The diffraction data was automatically processed by a computer programmed to handle the microphotometer readings of an internal-standard calibrated film from a Guinier camera. The resulting d,I diffraction data is given in Figure 2. For high quality data an allowance for errors of $\pm .01$ is sufficient over the range of "d" values encountered in this particular problem. The search manual used for purposes of this illustration is that for "Common Phases" published by the JCPDS – International Centre for Diffraction Data. The analyst chooses from the table of diffraction data pairs of lines with which to enter the search manual. The analyst then examines the remainder of the eight lines of any qualifying entry to check whether these lines also match lines in the unknown. The analyst need follow just one rule, namely, begin with the strongest line available for the "prime" line and form the line-pairs with the remaining lines chosen in order of decreasing intensity. This procedure is continued to locate all qualifying entries.

Referring to Figure 2, line 3.061, being the strongest, is indicated by a \checkmark and will be the "prime" line of the pairs. The first line-pair the analyst will try will be $3.06 \pm .01 - 3.20 \pm .01$. There are no qualifying entries for this line-pair, so a zero is placed in the "e" column which lists the number of entries examined. The next line-pair would be $3.06 \pm .01 - 2.74 \pm .01$. Again there are no qualifying entries. With the fourth line-pair $3.06 \pm .01 - 2.98 \pm .01$ there are three qualifying entries each of which must therefore be examined further for matching lines with those of the unknown. The analyst finds none of these three entries satisfactory and therefore continues the procedure until finally on the sixth try he arrives at line-pair $3.06 \pm .01 - 1.88 \pm .01$. Here there are two qualifying entries, one of which, Y_2O_3 , 25–1200, matches all eight lines of the entry with lines of the unknown. The analyst then checks the complete pattern 25–1200 and finds that it accounts for twelve lines of the unknown. With six line-pairs and five examinations of entries, the analyst has identified Y_2O_3 as one of the phases of the unknown mixture. Carefully comparing intensities of these twelve lines of the standard with those of the unknown, the analyst eliminates some lines, partially eliminates others and is ready to begin the process over

3.04 - 3.00 (± 0.1)

										File No.	l/c
	3.03x	2.96 _a	2.92 _z	1.97 _z	4.18 _z	3.66 _a	2.25 _z	2.08 _z	(Pb,Ca) ₃ (As ₂ P) ₃ O ₁₂ Cl	14- 213	2.11
	3.03 _a	2.96x	2.91 _z	2.12 _a	6.06 _a	2.08 _z	4.15 _z	2.10 _z	AsNaSe ₂	32- 50	
	3.03 _a	2.96x	1.95 _b	3.33 _z	3.39 _z	2.11 _z	1.78 _z	3.61 _z	TiTa ₃ O ₉	28-1334	
	3.03x	2.96 _b	1.85 _b	3.39 _z	2.65 _z	2.56 _z	1.88 _z	1.84 _z	Ga ₂ Y ₂ O ₇	22- 306	
	3.03x	2.96 _a	1.82 _b	5.21 _z	3.66 _a	2.36 _z	1.58 _z	2.36 _z	Na ₂ MgFeF ₇	22- 895	
	3.02 _a	2.96x	2.09 _z	1.72 _z	1.48 _z	1.33 _z	1.75 _z	1.51 _z	Ba ₃ Zr ₂ O ₇	24- 131	
	3.02x	2.96 _a	1.83 _z	5.19 _a	3.66 _a	2.36 _z	1.58 _z	6.04 _z	Na ₂ MgVF ₇	22- 896	
	3.02x	2.96x	1.83 _z	6.05 _a	5.19 _a	3.66 _a	3.12 _z	3.11 _z	Na ₂ NiFeF ₇	24-1115	
	3.01x	2.96 _a	4.15 _z	2.97 _z	2.10 _z	2.52 _z	1.58 _z	1.85 _z	α -Mg ₂ P ₂ O ₇	32- 626	
	3.01x	2.96x	2.92x	6.50 _a	1.74 _a	1.71 _a	1.69 _a	4.00 _a	Cl ₂ O ₂ SO ₄	26-1174	
	3.01x	2.96x	2.92x	2.17 _z	6.53 _a	2.03 _z	3.99 _z	2.19 _z	Gd ₂ O ₂ bO ₄	29- 613	
	3.01 _a	2.96x	2.89 _z	3.34 _a	2.18 _z	3.20 _z	2.42 _z	2.31 _z	SrBe ₂ Si ₂ O ₇	26- 979	
	3.01x	2.96 _a	2.54 _z	2.11 _z	2.55 _z	1.58 _z	1.62 _z	2.15 _z	α -Co ₂ (P ₂ O ₇) ₂	34-1378	
	3.01x	2.96 _a	2.44 _z	2.09 _z	1.72 _z	1.50 _z	4.89 _z	2.16 _z	NaRb ₂ MnF ₆	27- 554	
	3.01x	2.96 _a	1.72 _z	2.10 _z	1.75 _z	2.17 _z	2.29 _z	1.51 _z	Ba ₃ In ₂ O ₆	29- 167	
	3.00 _a	2.96x	9.13 _a	5.71 _z	4.02 _z	7.01 _a	3.12 _z	2.73 _z	(NH ₄) ₂ Co ₂ (SO ₄) ₂ (OH) ₂ ·2H ₂ O	23- 779	
	3.00x	2.96x	3.67 _z	2.50 _z	1.78 _z	1.73 _z	2.57 _z	2.38 _z	MnTa ₂ O ₇	34- 54	
	3.00 _a	2.96x	3.27 _z	2.83 _z	2.75 _z	2.80 _z	2.69 _z	2.47 _z	K ₂ Mg ₆ Al ₂ B ₃ P ₂ O ₂₀ F ₄	15- 352	
	3.00x	2.96 _b	2.90 _z	3.29 _z	1.87 _z	4.14 _z	3.38 _z	2.07 _z	AgPb ₄ (As ₂ O ₄) ₃	32-1014	
	3.00x	2.96 _a	2.90 _z	1.96 _z	3.66 _z	1.92 _z	4.14 _z	2.07 _z	NaPb ₄ (As ₂ O ₄) ₃	29-1222	
	3.00 _a	2.96x	2.11 _z	4.22 _z	1.72 _z	2.42 _z	1.71 _z	1.74 _z	BaCaTiO ₄	13- 323	
	2.99x	2.96x	3.56 _z	2.18 _z	1.95 _z	2.84 _z	4.10 _z	2.69 _z	Ce ₂ Ti ₂ Si ₂ O ₁₁	19- 302	
	2.99x	2.96 _a	2.94 _z	7.85 _a	4.46 _z	3.91 _z	2.37 _z	1.95 _z	K ₂ Na ₂ Ta ₂ Si ₄ O ₄₇	33-1042	
	2.99x	2.96x	2.89 _z	4.13 _z	3.27 _z	2.06 _z	3.38 _z	1.92 _z	Pb ₂ (PO ₄) ₃ Cl	19- 701	
	2.99 _a	2.96x	2.70 _z	2.84 _z	3.57 _z	2.75 _z	1.95 _z	3.06 _z	Co ₂ La ₂ Ti ₂ Si ₄ O ₂₂	20- 546	
	2.99x	2.96 _a	1.89 _z	3.12 _z	5.92 _z	3.30 _z	3.17 _z	1.97 _z	Sr ₂ B ₂ O ₅	19-1268	
	3.05 _a	2.95x	5.91 _a	4.47 _z	2.71 _z	2.61 _z	2.07 _z	5.57 _z	K ₂ SrGe ₃ O ₆	26-1333	
	3.05x	2.95x	3.16 _z	2.32 _z	2.18 _z	2.04 _z	1.86 _z	1.83 _z	Rb ₄ As ₂ O ₇ ·2Rb ₂ MA ₃ O ₄	28- 904	
	3.04 _a	2.95x	1.52 _z	1.73 _z	1.25 _z	2.25 _z	1.96 _z	1.30 _z	(CrTe)M	2- 722	
	3.03 _a	2.95x	3.16 _z	3.59 _z	2.97 _z	2.62 _z	3.70 _z	3.98 _z	Y ₂ GeO ₃	23-1484	
	3.03x	2.95x	2.90x	1.74x	1.71x	1.68 _z	1.37 _z	2.19 _z	Sm ₂ O ₇ SO ₄	30-1105	
	3.03x	2.95x	2.88 _z	2.43 _z	3.65 _z	2.36 _z	2.24 _z	2.14 _z	SrMn ₂ O _{6-x}	28-1233	
	3.03x	2.95x	2.11x	1.75 _z	1.73 _z	2.04 _z	1.69 _z	1.51 _z	Ba ₃ Tm ₂ O ₆	23- 59	
	3.02 _a	2.95x	4.04 _z	4.42 _z	3.08 _z	2.68 _z	1.59 _z	5.49 _z	PrYVO ₆	26-1354	
	3.02x	2.95x	3.09 _z	5.50 _z	2.97 _z	2.66 _z	4.43 _z	2.80 _z	(YCeNdTh)(NbTiTa) ₃ O ₆	18- 765	
	3.02x	2.95x	2.98 _z	3.60 _z	1.73 _z	1.54 _z	1.93 _z	1.80 _z	C ₅ TiGe ₃ O ₉	27-1073	
	3.01x	2.95x	3.79 _z	3.66 _z	4.80 _z	2.48 _z	2.56 _z	2.19 _z	ScTaO ₄	24-1017	5.10
	3.01 _a	2.95x	3.10 _z	2.65 _z	2.01 _z	1.59 _z	2.80 _z	1.87 _z	SmNbTiO ₆	20-1470	
	3.01x	2.95x	2.88x	3.33x	3.20 _z	2.42 _z	2.30 _z	2.18 _z	Be ₂ SrSi ₂ O ₇	20-1188	
	3.01x	2.95 _a	2.74 _z	2.76 _z	2.98 _z	2.47 _z	3.57 _z	2.60 _z	SnPSe ₃	28-1396	
	3.01x	2.95x	2.31x	2.12x	1.74x	2.99 _a	2.26 _a	1.96 _a	NbSe ₂ SnS ₂	34-1374	
	3.01x	2.95x	1.73 _z	2.11 _z	2.63 _z	4.70 _z	1.74 _z	1.54 _z	(K ₂ Sb)8H	4- 643	
	3.00x	2.95x	4.84 _z	3.78 _z	3.70 _z	2.50 _z	2.88 _z	1.73 _z	MnWO ₄	13- 434	
	3.00x	2.95 _a	3.67 _z	4.82 _z	1.76 _z	1.83 _z	1.77 _z	1.74 _z	ScNbO ₄	24-1013	2.30
	3.00 _a	2.95x	3.55 _z	2.64 _z	3.10 _z	3.86 _z	3.63 _z	2.86 _z	BaZnP ₂ O ₇	16- 558	
	3.00x	2.95 _a	3.05 _z	2.12 _z	1.71 _z	1.75 _z	1.75 _z	2.13 _z	LaYO ₂	28- 518	
	3.00x	2.95x	2.90x	3.11 _z	6.46 _z	2.16 _z	2.02 _z	2.18 _z	Gd ₂ O ₂ SO ₄	31- 531	
	3.00x	2.95x	1.64x	3.39 _z	3.11 _z	2.31 _z	2.03 _z	1.93 _z	Th ₂ N ₂ (NH)	21-1417	
	2.99 _a	2.95x	2.85x	3.78 _z	2.89 _z	2.44 _z	1.83 _z	1.82 _z	(Ti ₂ Te ₂)20N	23- 928	
	2.99x	2.95 _a	2.70 _z	5.68 _z	4.00 _z	3.08 _z	2.44 _z	8.99 _z	K ₂ CO ₃ (SO ₄) ₂ (OH) ₂ ·2H ₂ O	23-1322	
	2.99x	2.95x	1.72 _z	1.73 _z	1.49 _z	2.26 _z	5.92 _z	5.40 _z	NaUV ₃ O ₁₀	30-1255	
	3.05x	2.94 _a	2.98 _z	2.86 _z	2.33 _z	2.23 _z	2.75 _z	4.65 _z	Sb ₂ Sr ₂	33- 116	2.14
	3.05x	2.94x	2.70 _z	2.56 _z	1.77 _z	1.65 _z	1.60 _z	3.19 _z	Ag(NSO ₃) ₃	16- 836	
	3.04x	2.94x	2.12 _z	1.80 _z	5.05 _z	2.33 _z	2.55 _z	3.81 _z	Ti ₂ VO ₄	30-1337	
	3.03 _a	2.94x	3.15 _z	1.59 _z	2.63 _z	3.57 _z	2.22 _z	1.88 _z	GeY ₂ O ₅	23- 270	
	3.03 _a	2.94x	2.91 _z	4.22 _z	4.20 _z	2.44 _z	3.78 _z	2.10 _z	K ₂ (SO ₄) _{0.67} (CrO ₄) _{0.33}	25-1236	1.10
	3.03x	2.94 _a	2.44 _z	2.97 _z	3.77 _z	2.12 _z	1.89 _z	3.18 _z	K ₂ PO ₃ F	18-1015	
	3.02 _a	2.94x	4.42 _z	4.03 _z	3.08 _z	2.66 _z	1.58 _z	2.80 _z	NdVWO ₆	26-1279	
	3.02x	2.94x	3.42 _z	2.91 _z	2.43 _z	1.71 _z	2.10 _z	4.20 _z	Ba ₂ SiO ₄	26-1403	
	3.02x	2.94x	3.15 _z	4.55 _z	2.27 _z	3.81 _z	4.82 _z	4.72 _z	K ₈ H ₂ As ₄ O ₁₅	23- 481	1.80
	3.01x	2.94x	6.02 _a	5.19 _a	3.63 _a	2.59 _a	1.81 _a	1.58 _a	Na _{0.3} Ca _{1.3} Fe _{0.5} Te _{1.5} O ₇	32-1054	
	3.01x	2.94 _a	2.87 _z	2.51 _z	3.78 _z	3.70 _z	1.78 _z	5.75 _z	Mn ₃ TeMo ₂ O ₁₂	33- 912	
	3.01x	2.94x	2.81x	1.75 _z	2.25 _z	1.98 _z	1.66 _z	1.63 _z	Pb ₃ (As ₂ O ₄) ₂ O ₈ Cl ₄	22- 664	
	3.00 _a	2.94x	3.10 _z	3.20 _z	2.88 _z	2.53 _z	2.20 _z	2.11 _z	Ca ₇ Pb ₂ (SO ₄) ₂ Si ₆ O ₁₈ (OH) ₁₀	18- 292	
	3.00x	2.94x	2.78 _z	2.88 _z	2.85 _z	5.07 _z	3.40 _z	2.75 _z	Cd ₃ V ₂ O ₈	28- 203	
	3.00x	2.94x	1.58 _z	2.65 _z	1.70 _z	1.86 _z	3.71 _z	2.21 _z	(Y,Ce,Co)(Ta,Ti,Nb) ₂ O ₆	26- 1	
	2.99x	2.94 _a	7.10 _z	3.67 _z	3.57 _z	7.60 _z	3.97 _z	3.41 _z	RbCrP ₃ O ₇	24- 930	
	2.99x	2.94 _a	2.90 _z	3.28 _z	1.95 _z	3.35 _z	2.06 _z	4.34 _z	Pb ₃ Bi ₂ (GeO ₄) ₃	34-1021	
	2.99x	2.94 _a	2.82 _z	3.40 _z	2.04 _z	1.87 _z	2.30 _z	2.03 _z	Ca ₃ (VO ₄) ₃ Cl	2	

		25-1200			4-566		
l/l-	d	l-p	e	Y ₂ O ₃	l-p	e	As ₂ O ₃
10	7.07						
9	6.79						
66	6.397	3	0		2	2	6.394 ₆₃
24	5.258						
24	5.224						
9	5.001						
7	4.816						
12	4.477						
12	4.430						
12	4.330			4.34 ₁₆			
10	4.146						
30	3.814						
17	3.482						
17	3.382						
26	3.269						
19	3.212						
78	3.198	1	0		✓		3.195 ₁₀₀
17	3.152						
21	3.079						
100[30]	3.061	✓		3.060 ₁₀₀			
59	2.984	4	3				
14	2.852						
19	2.767						2.768 ₂₈
73	2.741	2	0		1	0	
7	2.696						
17	2.650			2.652 ₃₀			
7	2.622						
7	2.587						
23	2.540						2.541 ₃₈
48	2.502	5	0	2.500 ₇			
14[8]	2.259			2.261 ₈			2.262 ₁₂
14	2.131						2.132 ₁₇
10	2.100						
9	2.078			2.080 ₁₂			
21	2.000						
9	1.988						
17	1.958						1.957 ₂₇
31	1.874	6	2	1.874 ₄₆			
7	1.852						
19	1.704						
19	1.700						
10	1.668						1.670 ₂₁
23	1.638			1.636 ₄			
7	1.620						
22	1.598			1.599 ₃₁			1.599 ₁₀
7	1.563			1.563 ₇			
9	1.549						1.551 ₂₂
10[6]	1.532			1.531 ₅			
7	1.491						
9	1.442			1.443 ₃			1.442 ₁₂
line-pairs		6			2		
entries			5			2	

Figure 2. Example of "work form" for the manual search procedure. The form helps the diffractonist to keep track of the necessary analytical steps.

		25-1200		
l/l-	d	l-p	e	Y ₂ O ₃
10	7.07			
9	6.79			
66	6.397	3	0	
24	5.258			
24	5.224			
9	5.001			
7	4.816			
12	4.477			
12	4.430			
12	4.330			4.34 ₁₆
10	4.146			
30	3.814			
17	3.482			
17	3.382			
26	3.269			
19	3.212			
78	3.198	1	0	
17	3.152			
21	3.079			
100	3.061	✓		3.060 ₁₀₀
59	2.984	4	3	
14	2.852			
19	2.767			
73	2.741	2	0	
7	2.696			
17	2.650			2.652 ₃₀
7	2.622			
7	2.587			
23	2.540			2.541 ₃₈
48	2.502	5	0	2.500 ₇
14	2.259			2.261 ₈
14	2.131			2.132 ₁₇
10	2.100			
9	2.078			2.080 ₁₂
21	2.000			
9	1.988			
17	1.958			1.957 ₂₇
31	1.874	6	2	1.874 ₄₆
7	1.852			
19	1.704			
19	1.700			
10	1.668			1.670 ₂₁
23	1.638			1.636 ₄
7	1.620			
22	1.598			1.599 ₃₁
7	1.563			1.563 ₇
9	1.549			1.551 ₂₂
10	1.532			1.531 ₅
7	1.491			
9	1.442			1.443 ₃
line-pairs		6		
entries			5	

Figure 3. Interim stage in the elimination of line pairs.

l/l-	d	25-1200			4-566			6-493			12-767			15-375		
		l-p	e	Y_2O_3	l-p	e	As_2O_3	l-p	e	Ag_3O_4	l-p	e	KH_2AsO_4	l-p	e	$PbSeO_4$
10	7.07															
9	6.79															
66(20)	6.397	3	0		2	2	6.394 ₆₃									
24	5.258													1	0	
24	5.224											5.2165				
9	5.001															5.00 ₃₀
7	4.816															
12	4.477															
12	4.430															4.43 ₃₅
12	4.330			4.34 _[16]												4.38 ₁₂
10	4.146															
30	3.814									1	1	3.81 ₁₀₀				
17	3.482												4	1	3.483 ₈₀	
17	3.382															3.384 ₁₀
26	3.269													✓		3.270 ₁₀₀
19	3.212													2	2	
78	3.198	1	0		✓		3.195 ₁₀₀									
17	3.152															3.150 ₄₀
21	3.079											3.078 ₃₀				3.075 ₇₀
100 30	3.061	✓		3.060 ₁₀₀					3.066 ₂₅							
58	2.984	4	3					1	1		✓	2.980 ₈₅				
14	2.852															
18	2.767						2.768 ₂₈	✓								2.765 ₃₀
73	2.741	2	0		1	0				2.743 ₁₀₀						
7	2.696											2.697 ₃₀				
17	2.650			2.652 ₃₀												
7	2.622															2.621 ₂₅
7	2.587															2.589 ₂₅
23	2.540						2.541 ₃₈									
48	2.502	5	0	2.500 ₇				2	2	2.504 ₅₅						
14 8	2.259			2.261 ₈			2.262 ₁₂									2.255 ₃₅
14	2.131						2.132 ₁₇									
10	2.100															2.099 ₄₀
8	2.078			2.080 ₁₂												
21	2.000											2.000 ₇₀				2.003 ₁₄
9	1.988															1.989 ₃₅
17	1.958						1.957 ₂₇					1.956 ₄				1.966 ₂₅
31	1.874	6	2	1.874 ₄₆												
7	1.852															1.852 ₄₀
18	1.704									1.701 ₂₁		1.707 ₁₈				
19	1.700															
18	1.668						1.670 ₂₁									
23 5	1.638			1.636 ₄						1.639 ₂₈						
7	1.620											1.622 ₁₄				
22	1.598			1.599 ₃₁			1.599 ₁₀									
7	1.563			1.563 ₇												
8	1.549						1.551 ₂₂									
18 8	1.532			1.531 ₅						1.533 ₉						
7	1.491											1.492 ₅₁₄				
8	1.442			1.443 ₃			1.442 ₁₃									
line-pairs		6			2			2			1			4		15
entries			5			2			3		1				3	14

Figure 4. Identification of five of seven phases in the unknown with 15 line pairs and 14 examination entries.

again as seen in Figure 3. This time the strongest line available 3.198 is indicated with a ✓ and used as the "prime" line of the sequence of line-pairs which lead to As_2O_3 , 4-566. It will be noted that to retrieve the phase As_2O_3 required trying two line-pairs and examining two entries. Referring to Figure 4, it will be seen that five phases are identified by continuing the specified procedure. It will be noted that there are still lines remaining unaccounted for in the unknown. If the search procedure were continued, two additional phases contained in the unknown mixture would be identified.

The above search procedure made use of powder diffraction data only. If other information about the unknown sample is available use should naturally be made of it. For example, if the analyst knows what elements are present or not present, this knowledge can be very helpful. It is much easier for most people to check a name than a series of numbers.

With the "Work Form" record the analyst can look back to make sure that he has not overlooked any necessary steps. The "Work Form" is equally helpful whether the analyst is using the Fink Search Manual or the Hanawalt Search Manual or probably even some other design of search manual.

This illustration of the use of the "Work Form" retrieved five of the seven phases as seen in Figure 4 with 15 line-pairs and 14 examinations of entries in the special Search Manual which contains entries for 2500 commonly occurring phases. If the phases present in the Frevel problem had not been included in this special small file but instead required a larger search manual for a file of 25,000 or 50,000 standards, the number of line-pairs required for solution would have remained at 15 but the number of entries requiring examination would have been several hundred instead of only 14.

Obviously, it is a great advantage if knowledge of the unknown allows the search to be limited to a special field such as minerals, metals and alloys, forensics, etc. Such special files and corresponding search manuals are available from the JCPDS - International Centre for Diffraction Data.

Literature on Manual Search/Match Methods

While this paper is concerned only with the manual retrieval of patterns from a file of standard reference patterns, it will not be out of place to note briefly the initial literature on X-ray diffraction in chemical phase analysis. The contribution to crystal analysis of the Debye Scherrer type X-ray powder diffraction camera in 1917¹ is universally acknowledged. Not so well known is A. W. Hull's independent paper in 1919² on the same subject and in particular Hull's recognition and emphasis on the unique contribution of the method for analytical chemistry. Hull's paper showed the X-ray powder patterns of NaCl, KCl, NaF and KF. He made up two mixtures each of which analyzed 19.7% Na, 33.5% K, 16.3% F and 30.5% Cl. By X-ray powder diffraction he showed easily and positively that neither contained any phase present in the other. One sample consisted of 36.0% NaF and 74% KCl, while the other sample consisted of 50.2% NaCl and 49.8% KF. Obviously the unique power of X-ray powder diffraction to identify phases

is of great importance and can be used independently of the existence of large files of standard reference patterns. It is also of importance that it is possible and practical by both computer and manual search methods to retrieve any pattern contained in a file of standards using X-ray diffraction data alone.

The first paper proposing collection of standard patterns and noting his own file of 170 minerals was by Winchell³ in 1927. In 1935 Waldo⁴ published the patterns of 51 copper ore minerals. In one table he listed the patterns in order of decreasing "d" values of the strongest line of each pattern. In another table the patterns were listed in decreasing "d" values of the largest "d" value of each pattern. Beginning in 1938 a series of papers⁷ of diffraction data for minerals appeared from Leningrad.

1938	142 minerals
1957	905 minerals
1965	300 minerals
1969	232 minerals with boron
1974	225 phosphate minerals

Originally the five strongest lines of each pattern were listed according to the "d" value of the strongest line of each pattern. In the 1957 publication each pattern was given five entries in the list according to the "d" value of the five strongest lines. In the later publications this number was reduced to the three strongest lines of each pattern. In more recent years diffraction data for minerals from Leningrad has been made available to JCPDS-International Centre for Diffraction Data through the cooperation of Prof. Frank-Kamenetsky.

In 1965 a new and creative approach to the problem of retrieval was proposed by W. C. Bigelow and J. V. Smith⁹. Because electron powder diffraction intensities may differ widely from the corresponding X-ray diffraction intensities it was proposed to design a search manual which could be used effectively for both techniques. In the Bigelow-Smith design each entry in the search manual consisted of the "d" values of the eight strongest lines of the pattern in order of decreasing "d" values but with no notation of the intensity values of each line. Each pattern was entered in the search manual of continuously decreasing "d" values eight times as each of the eight lines was rotated into first position in the entry. This search manual was named by the authors the Fink Index in honour of Wm. L. Fink, long time chairman of the JCPDS. The index book was first produced in 1965 in computer print-out form by F. W. Matthews and G. G. Johnson, Jr. Later editions made just six entries corresponding to the first six lines of the eight line entry. In 1968 major modifications of the Fink Index were introduced by Julian Messick¹¹; the "group" design was adopted, intensity values of each line were included and the number of entries for each pattern was reduced to four, corresponding to the four strongest lines of the pattern.

It is perhaps just a matter of choice or habit whether the analyst prefers to work with lines of decreasing intensity or lines of decreasing "d" values. Characteristically the larger "d" values are from the low index planes of the crystal structure which are usually the stronger diffraction lines as well. The problem is to design a successful search index book with as few entries per pattern as possible. The difficulty with

more entries per pattern is the increase in size of the index book and the eyestrain involved in scanning more entries. Obviously this consideration is of less importance for files of limited size such as the mineral file. The advantage associated with over-lapping of "groups" does not come free. It results in about a 25% increase in the size of the index book and for this reason over-lapping is not employed in the various models of "Fink" type manuals. One of the advantages of the system using the strongest lines in decreasing intensity is that these may be the only lines which will be observable in a weak pattern, for example, of a minor phase in a mixture of phases.

Further experience on the part of many analysts around the world will no doubt serve to improve the systems of search/match presently employed by both manual and computer methods. These methods are presently very successful when the diffraction data is of high quality. If a problem exists in the solution of an unknown pattern it may help to repeat the experimental diffraction data with techniques for better resolution and accuracy of "d's" and "I's".

The difficulty in retrieval when there is a solid solution of two phases has not as yet been successfully overcome. The "d" value of the intermediate compositions may be enough different from those of the end members to avoid retrieval. One idea is to make enough entries with in-

termediate "d" values. Hopefully, a more promising idea is that of B. D. Sturman¹² who proposes to plot the second and third strongest lines as coordinates on a series of charts, one for each of the "groups" determined by the strongest line. The intermediate compositions should then land on a line connecting the two points of the end members.

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