chem 5390

Advanced X-ray Analysis

LECTURE 14

Dr. Teresa D. Golden
University of North Texas
Department of Chemistry

Acquisition of Diffraction Data

C. Use of Databases

Once a reduced pattern is finalized – determination of the crystalline structure can be done through comparison in databases.

Acquisition of Diffraction Data

C. Use of Databases

History

Powder diffraction files: The task of building up a collection of known patterns was initiated by Hanawalt, Rinn, and Fevel at the Dow Chemical Company (1930's). They obtained and classified diffraction data on some 1000 substances. After this point several societies like ASTM (1941-1969) and the JCPS began to take part (1969-1978). In 1978 it was renamed the Int. Center for Diffraction Data (ICDD) with 300 scientists worldwide. In 1995 the powder diffraction file (PDF) contained nearly 62,000 different diffraction patterns with 200 new being added each year. Elements, alloys, inorganic compounds, minerals, organic compounds, organo-metallic compounds.

Acquisition of Diffraction Data

C. Use of Databases

History

Hanawalt: Hanawalt decided that since more than one substance can have the same or nearly the same d value, each substance should be characterized by it's three strongest lines (d1, d2, d3). The values of d1-d3 are usually sufficient to characterize the pattern of an unknown and enable the corresponding pattern in the file to be located.

Acquisition of Diffraction Data

C. Use of Databases

ICCD: JCPDS Files

The International Centre for Diffraction Data (ICDD) maintains a database of powder diffraction patterns, the Powder Diffraction File (PDF).

The database includes:

d-spacings and relative intensities of observable diffraction peaks.

Patterns may be experimentally determined, or computed based on crystal structure and Bragg's law.

The PDF contains more than a million unique material data sets.

Acquisition of Diffraction Data

C. Use of Databases

ICCD: JCPDS Files

The PDF contains more than a million unique material data sets.

Each data set contains diffraction, crystallographic and bibliographic data, as well as experimental, instrument and sampling conditions, and select physical properties in a common standardized format.

https://www.icdd.com/

Acquisition of Diffraction Data

C. Use of Databases

ICCD: JCPDS Files

PDF # 461212, Wavelength = 1.540562 (A)

46-1212 Quality: *

CAS Number:

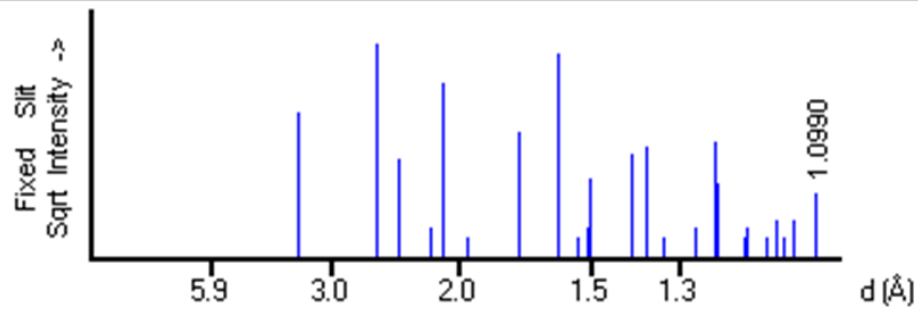
Molecular Weight: 101.96
Volume[CD]: 254.81
Dx: 3.987 Dm:

Sys: Hexagonal
Lattice: Rhomb-centered
S.G.: R$\bar{3}$c (167)
Cell Parameters:
a 4.758 b c 12.99
α β γ

SS/FOM: F25=358(.0028, 25)
I/Icor:
Rad: CuKa1
Lambda: 1.540562
Filter:
d-sp: diffractometer

Mineral Name:
Corundum, syn

α-Al2 O3
Aluminum Oxide
Ref: Huang, T et al., Adv. X-Ray Anal., 33, 295 (1990)

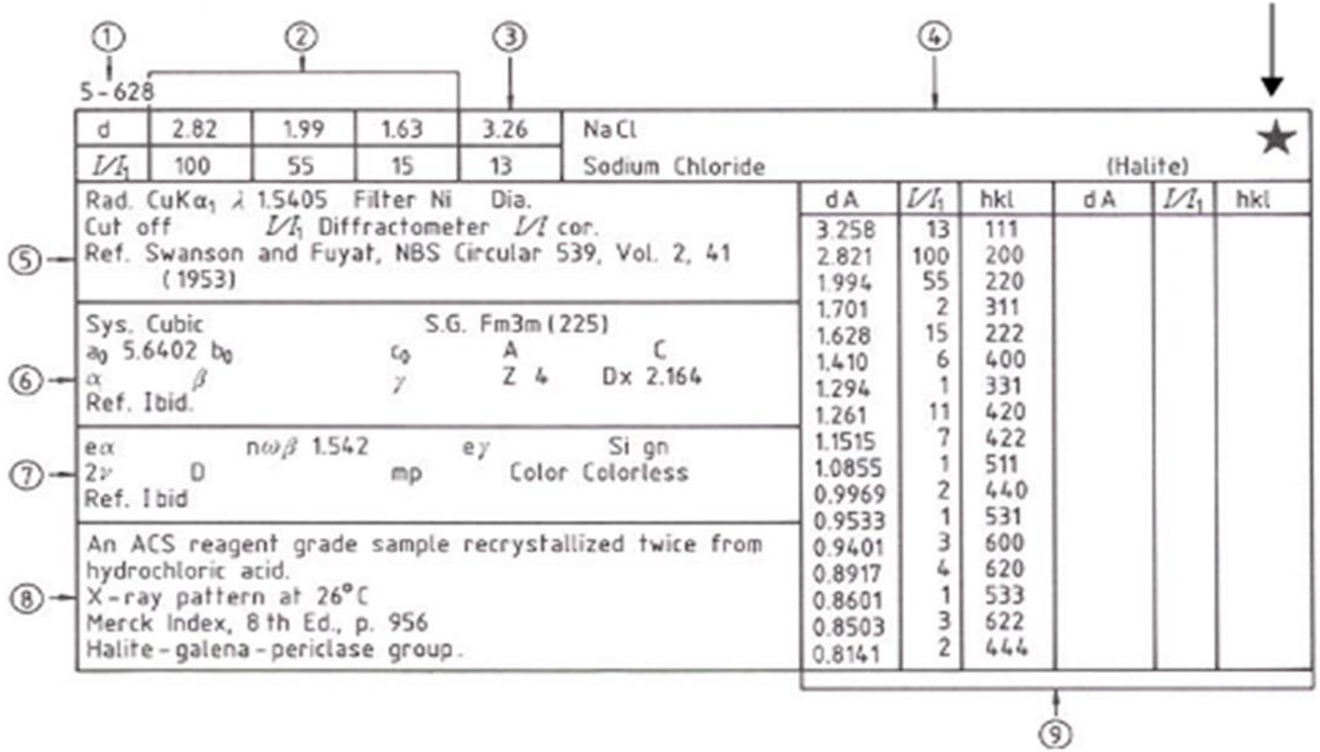


d(A)	Int-f	h	k	l	d(A)	Int-f	h	k	l	d(A)	Int-f	h	k	l
3.4797	45	0	1	2	1.5150	2	1	2	2	1.1897	2	2	2	0
2.5508	100	1	0	4	1.5110	14	0	1	8	1.1600	1	3	0	6
2.3794	21	1	1	0	1.4045	23	2	1	4	1.1472	3	2	2	3
2.1654	2	0	0	6	1.3737	27	3	0	0	1.1386	<1	1	3	1
2.0853	66	1	1	3	1.3359	1	1	2	5	1.1256	2	3	1	2
1.9643	1	2	0	2	1.2755	2	2	0	8	1.1241	3	1	2	8
1.7400	34	0	2	4	1.2391	29	1	0	10	1.0990	9	0	2	10
1.6015	89	1	1	6	1.2343	12	1	1	9					
1.5466	1	2	1	1	1.1931	1	2	1	7					

Acquisition of Diffraction Data

JCPDS Card

Quality of data



1.file number 2.three strongest lines 3.lowest-angle line 4.chemical formula and name 5.data on diffraction method used 6.crystallographic data 7.optical and other data 8.data on specimen 9.data on diffraction pattern.

Qualitative Analysis

A. Evaluation of Data Quality

An ICDD study found that 50% of x-ray labs overestimated the accuracy of their data by an order of magnitude. The problem has increased due to automated diffraction systems.

Automation tends to separate the user from the process. Automate systems use a peak hunting system that tends to find more peaks than manual methods.

Qualitative Analysis

A. Evaluation of Data Quality

Figure of Merit (FOM)

FOM value is an attempt to derive a quantitative measure of data quality.

Qualitative Analysis

A. Evaluation of Data Quality

Table 11.5. Common Figures of Merit and Their Uses

Authors	Use	Basis	Ref.
Jenkins & de Vries	Setting up equipment	Count statistics: peak and background	[23]
Spielberg & Bradenstein	Trace analysis conditions	Count statistics: sensitivity & background	[24]
Jenkins & Schreiner	Diffractometer evaluation	Count statistics: peak, background, & line width	[1]
Smith & Snyder	Quality of data/ success of indexing	$\Delta 2\theta$	[21]
de Wolff	Success of indexing	$\Delta \mathbf{d}^{*2}$	[25]
Snyder	Evaluation of intensities	Intensity	[16]
Lowe-Ma	Evaluation of intensities	Intensity	[26]
Various	Order of hits	Subjective	[27–30]

Qualitative Analysis

A. Evaluation of Data Quality

Figure of Merit (FOM)

Can use FOMs to evaluate instrument performance and data quality evaluation.

Principle application of XRD is qualitative phase identification.

Smith and Synder introduced a FOM based on peak location to evaluate the quality of XRD patterns.

Qualitative Analysis

A. Evaluation of Data Quality

Figure of Merit (FOM)

The American Crystallographic Association, International Union of Crystallography and International Centre for Diffraction Data (ICDD) have adopted Smith & Snyder estimate of FOM which focuses on the d_{hkl} values.

Qualitative Analysis

A. Evaluation of Data Quality

Figure of Merit (FOM)

The Figure of Merit, F_N, is defined as:

$$F_N = \left(\frac{1}{\left| \overline{\Delta 2\theta} \right|} \right) \left(\frac{N}{N_{poss}} \right)$$

Qualitative Analysis

A. Evaluation of Data Quality

The Figure of Merit, F_N

$$F_N = \left(\frac{1}{\left|\overline{\Delta 2\theta}\right|}\right)\left(\frac{N}{N_{poss}}\right)$$

where,

$\left|\overline{\Delta 2\theta}\right|$ is the average absolute discrepancy between observed and calculated 2θ values.

N is the number of independent diffraction reflections possible.

N_{poss} is the number of observed reflections.

Qualitative Analysis

A. Evaluation of Data Quality

The Figure of Merit, F_N

For the computation of N_{poss}, all resolvable reflections allowed by the space group are counted with the following exceptions:

- **systematic absences caused by symmetry elements and lattice type**
- **only one plane from a family is counted**
- **reflections with same spacing treated as a single line, (e.g (333) (511) in cubic system)**

Qualitative Analysis

A. Evaluation of Data Quality

The Figure of Merit, F_N

$$F_N = \left(\frac{1}{\left|\overline{\Delta 2\theta}\right|}\right)\left(\frac{N}{N_{poss}}\right)$$

F_N is given as xx.x(y.yyy,zz)

where

xx.x is the value of F_N

y.yyy is the average $\Delta 2\theta$ error

zz is the number of diffraction lines possible within the 2θ range covered by the first N lines.

Qualitative Analysis

A. Evaluation of Data Quality

Figures of Merit around 80-150 are considered high quality, while those less than 20 are poor quality.

Qualitative Analysis

A. Evaluation of Data Quality

The FOM value varies with the scan range and number of lines observed.

i.e. for a pattern having 50 possible lines, using the first <u>35</u> will give a FOM of <u>104.9</u>

the first <u>42</u> will give a FOM of <u>127.4</u>

and using all <u>50</u> will give a FOM of <u>151.6</u>

Qualitative Analysis

A. Evaluation of Data Quality

F_N is given as xx.x(y.yyy,zz)

33-1161 ★

SiO_2

Silicon Oxide

Quartz, syn

Rad. $CuK\alpha_1$ λ 1.540598 Filter Mono. d-sp Diff.
Cut off Int. Diffractometer $I/I_{cor.}$ 3.6
Ref. *Natl. Bur. Stand. (U.S.) Monogr. 25*, 18 61 (1981)

Sys. Hexagonal S.G. $P3_221$ (154)
a 4.9133(2) b c 5.4053(4) A C 1.1001
α β γ Z 3 mp
Ref. Ibid.

D_x 2.65 D_m 2.66 SS/FOM F_{30}=77(.013,31)

εα nωβ 1.544 εγ 1.553 Sign + 2V
Ref. Swanson, Fuyat, *Natl. Bur. Stand. (U.S.), Circ. 539*, 3 24 (1954)

Color Colorless
Pattern taken at 25 C. Sample from the Glass Section at NBS, Gaithersburg, Maryland, USA, ground single-crystals of optical quality. Pattern reviewed by Holzer, J., McCarthy, G., North Dakota State University, Fargo, North Dakota, USA, *ICDD Grant-in-Aid* (1990). Agrees well with experimental and calculated patterns. O_2Si type. Quartz group. Also called: silica. Also called: low quartz. Silicon used as internal standard. PSC: hP9. To replace 5-490 and validated by calculated pattern. Plus 6 additional reflections to 0.9089.

dÅ	Int	hkℓ	dÅ	Int	hkℓ
4.257	22	100	1.1532	1	311
3.342	100	101	1.1405	<1	204
2.457	8	110	1.1143	<1	303
2.282	8	102	1.0813	2	312
2.237	4	111	1.0635	<1	400
2.127	6	200	1.0476	1	105
1.9792	4	201	1.0438	<1	401
1.8179	14	112	1.0347	<1	214
1.8021	<1	003	1.0150	1	223
1.6719	4	202	0.9898	1	402
1.6591	2	103	0.9873	1	313
1.6082	<1	210	0.9783	<1	304
1.5418	9	211	0.9762	1	320
1.4536	1	113	0.9636	<1	205
1.4189	<1	300			
1.3820	6	212			
1.3752	7	203			
1.3718	8	301			
1.2880	2	104			
1.2558	2	302			
1.2285	1	220			
1.1999	2	213			
1.1978	1	221			
1.1843	3	114			
1.1804	3	310			

Qualitative Analysis

A. Evaluation of Data Quality

PDF#27-1402: QM>Star; d>Diffractometer; I>Diffractometer [JADE - PDF Card]

Silicon, syn
Si

Radiation: CuKa1 Lambda= 1.5405981 Filter=
Calibration: Internal(W) d-Cutoff= I/Ic(RIR)= 4.70
Ref: Natl. Bur. Stand. (U.S.) Monogr. 25, 13 35 (1976)

Cubic (Powder Diffraction), Fd3m(227) Z= 8 mp=
Cell= 5.43088 Pearson: cF8 (C)
Dx= 2.329 Dm= Mwt= 28.09 Vol= 40.05 F(11)=408.8(.0021,13)
Ref: Ibid.

ea= nwB= ey= Sign: 2V=
Ref:

Pattern taken at 25(1) C. This sample is NBS Standard Reference Material No. 640. Reflections calculated from precision measurement of a#0. a#0 uncorrected for refraction. To replace 5-565 and 26-1481.

Color: Gray

11 Reflection(s), Wavelength for Computing Theta = 1.540562<CU>

Strong Line: 3.14/X 1.92/6 1.64/3 1.11/1 1.25/1 0.86/1 0.92/1 1.36/1 1.05/1 0.96/1

#	d(A)	I(f)	h	k	l	2-Theta
1	3.1355	100	1	1	1	28.442
2	1.9201	55	2	2	0	47.302
3	1.6375	30	3	1	1	56.121
4	1.3577	6	4	0	0	69.130
5	1.2459	11	3	3	1	76.377
6	1.1086	12	4	2	2	88.026
7	1.0452	6	5	1	1	94.948
8	0.9600	3	4	4	0	106.715
9	0.9180	7	5	3	1	114.087
10	0.8587	8	6	2	0	127.541
11	0.8282	3	5	3	3	136.890
@	End-Of-List <I%-Type = (Unknown)>					

Qualitative Analysis

B. Phase Identification

Since materials give unique x-ray diffraction patterns, the technique can be used to identify unknowns.

Qualitative Analysis

B. Phase Identification

The history of qualitative analysis in x-ray diffraction has several landmarks that has accumulated to a present day extensive database.

Table 12.1. Major Landmarks in the Use of Powder Diffraction for Qualitative Analysis

1917–1919	P. J. W. Debye and P. Scherrer in Europe and A. W. Hull in the United States point out the potential advantages of powder diffraction as a tool for qualitative analysis.
1927	A. N. Winchell publishes first private collection of diffraction patterns.
1935	A. W. Waldo publishes patterns of 51 copper ores.
1938	J. D. Hanawalt, H. W. Rinn, and L. Frevel publish a file of 1000 patterns with an indexing and search system.
1938	The Institute of Mines in Leningrad tabulates powder data for 142 minerals.
1941	Patterns produced on 3 × 5 cards by the National Research Council (NRC) and Committee American Society for Testing and Materials E4 of the (ASTM).
1941–1945	Other societies join the powder committee of ASTM.
1969	The Joint Committee on Powder Diffraction Standards (JCPDS) is incorporated as an independent nonprofit organization.
1977	JCPDS changes its name to International Centre for Diffraction Data (ICDD).
1994	The ICDD Powder Diffraction File (PDF) grows to 60,000 patterns.

Qualitative Analysis

B. Phase Identification

This database is updated annually by the International Centre for Diffraction Data (ICDD).

42-1849 I

$C_{24}H_{36}O_5$

Lovastatin

Rad. CuKα λ 1.54178 Filter Mono. d-sp Diff.
Cut off 32.7 Int. Diffractometer $I/I_{cor.}$
Ref. Bernstein, J., Zevin, L., Ben-Gurion University of the Negev, Beer-sheva, Israel, *ICDD Grant-in-Aid*, (1991)

Sys. Orthorhombic S.G. $P2_12_12_1$ (19)
a 22.154 b 17.321 c 5.968 A C
α β γ Z mp
Ref. Ibid.

D_x D_m SS/FOM F_{30}=18(.027,61)

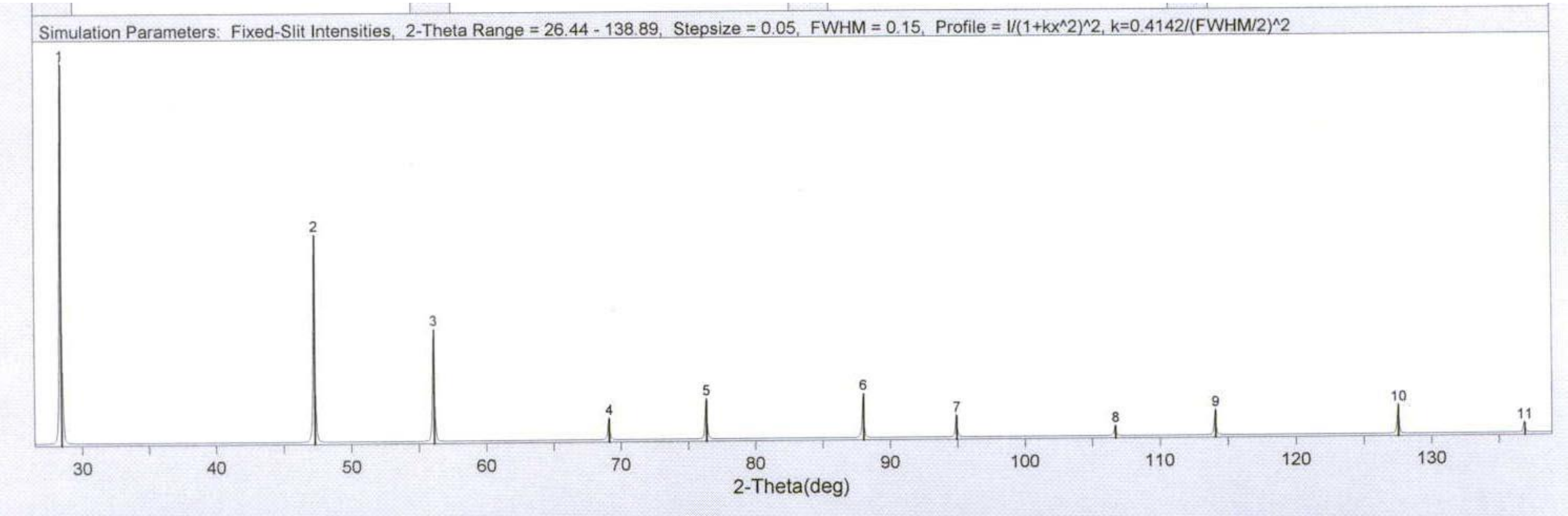
Sample from Merck Sharp and Dohme Research Lab. CAS#: 75330-75-5. C.D. Cell: a=17.321, b=22.154, c=5.968, a/b=0.7818, c/b=0.2694. Mica used as internal standard. PSC: oP?.

dÅ	Int	hkℓ	dÅ	Int	hkℓ
11.06	14	200	3.331	5	241,431
9.32	100	210	3.289	2	521
8.66	33	020	3.137	13	601,350
8.05	37	120	3.095	7	540,611
6.78	3	310	3.029	1	531
5.76	26	101	2.986	1	002
5.61	27	320,130	2.956	6	102,621
5.46	11	111	2.898	1	251
5.27	30	410,201	2.865	5	160
5.11	19	230	2.834	3	212,022
5.02	85	211	2.804	2	122
4.91	57	021			
4.79	3	121			
4.66	39	420,301			
4.55	6	330			
4.49	29	221,311			
4.29	1	510			
4.25	3	140			
4.079	8	321,131			
3.951	27	411,520			
3.887	42	231			
3.616	5	331,610			
3.511	4	530,041			
3.461	6	141			
3.405	8	440,620			

Qualitative Analysis

B. Phase Identification

Traditional methods of storage (cards and books) limited the storage of x-ray diffraction data to reduced forms (d-I values). Line shape and intensity distribution is lost with reduced patterns.



Qualitative Analysis

B. Phase Identification

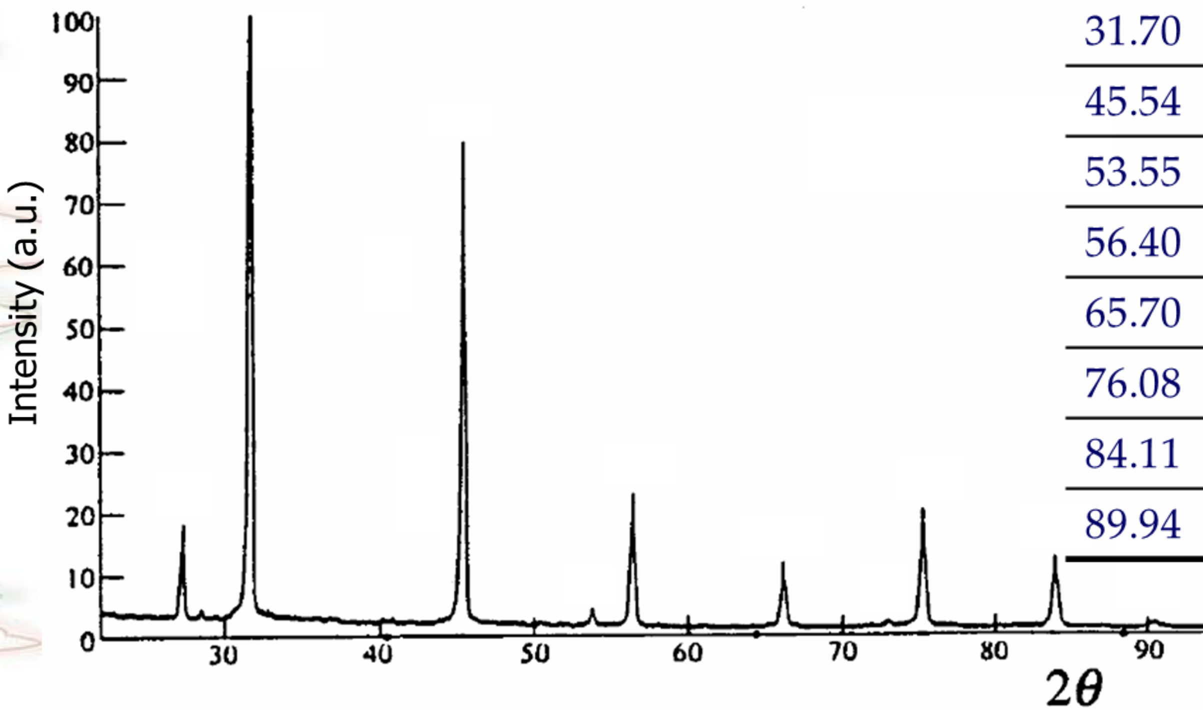
With the development of personal computers using CD ROMS, full diffractograms (fully digitized) are stored in databases.

Qualitative Analysis

B. Phase Identification

Analysis of single phase - example

2θ(°)	d (Å)	(I/I_1)*100
27.42	3.25	10
31.70	2.82	100
45.54	1.99	60
53.55	1.71	5
56.40	1.63	30
65.70	1.42	20
76.08	1.25	30
84.11	1.15	30
89.94	1.09	5



Qualitative Analysis

B. Phase Identification

Analysis of single phase – example

Computer search could give several possibilities:

Specimen and Intensities	Substance	File Number
2.82_9 1.99_9 2.26_x 1.61_9 1.51_9 1.49_9 3.57_8 2.66_8	$(ErSe)_2Q$	19-443
2.82_x 1.99_6 1.63_2 3.26_1 1.26_1 1.15_1 1.41_1 0.89_1	NaCl	5-628
2.82_4 1.99_4 1.54_x 1.20_4 1.19_4 2.44_3 5.62_2 4.89_2	$(NH_4)_2WO_2Cl_4$	22-65
2.82_x 1.99_8 1.26_3 1.63_2 1.15_2 0.94_1 0.89_1 1.41_1	(BePd)2C	18-225

Qualitative Analysis

B. Phase Identification

Analysis of single phase – example

Note from the data – the first three strongest peaks at d1, d2, and d3

In the present case: d1: 2.82; d2: 1.99 and d3: 1.63 Å

Search JCPDS manual to find the d group belonging to the strongest line: between 2.84-2.80 Å

There are 17 substances with approximately similar d2 but only 4 have d1: 2.82 Å

Out of these, only NaCl has d3: 1.63 Å

So probably is NaCl

Qualitative Analysis

B. Phase Identification

Analysis of single phase – example

However more complex samples can make determination difficult.

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

e.g. d1; d2; and d3, the first three strongest lines show have too many alternatives

there are 2 different phases present

Qualitative Analysis

B. Phase Identification

Analysis of single phase – example

However more complex samples can make determination difficult.

The 1st and 3rd strongest lines belong to Cu and peaks for Cu can be separated out

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

Pattern for Cu	
d (Å)	I/I_1
2.088	100
1.808	46
1.278	20
1.09	17
1.0436	5
0.9038	3
0.8293	9
0.8083	8

Qualitative Analysis

B. Phase Identification

This leaves the remaining lines to determine.

The first three lines turn out to belong to Cu_2O.

Remaining Lines		
d (Å)	I/I_1	
	Observed	Normalized
3.01	5	7
2.47	72	100
2.13	28	39
1.50	20	28
1.29	9	13
1.22	4	6
0.98	5	7

Pattern of Cu_2O	
d (Å)	I/I_1
3.020	9
2.465	100
2.135	37
1.743	1
1.510	27
1.287	17
1.233	4
1.0674	2
0.9795	4

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

Qualitative Analysis

B. Phase Identification

Analysis of single phase – example

The more complex a sample – the more difficult it becomes to solve.

Qualitative Analysis

B. Phase Identification

Problems in identification of unknowns include:

- **poor sample preparation**
- **inadequate data treatment**
- **uncertainty of experimental wavelengths**
- **preferred orientation**
- **poor crystallinity**
- **line broadening**

Great improvements have been made in recent years using a technique called profile-fitting to give better measure of integrated peak intensities and profile maxima.

Qualitative Analysis

B. Phase Identification

Improvement of instrumentation and computerization in the last decade has lead to an improvement and update of reference patterns.

For example for patterns before 1980, $\Delta 2\theta$ for the average pattern was 0.10^o

This has improved to 0.01-0.03^o for the newer instruments and 0.0005^o with the use of internal standards.

In the 1980s, the ICDD initiated a critical review of all data in the PDF for sets 1-32.

Qualitative Analysis

B. Phase Identification

1. Databases

There are a number of databases available for x-ray crystallography work.

The majority are designed and maintained by the single-crystal community.

Table 12.3. Databases of Crystallographic and Structural Information

Name	Content	Center
Cambridge Structural Database (CSD)	Organic, organometallic	Cambridge, England
Inorganic Crystal Structure Database (ICSD)	Inorganic materials	Karlsruhe, Germany
NRCC Metals Data File (CRYSTMET)	Metals and alloys	Ottawa, Canada
Protein Data Bank (PDB)	Structure of macromolecules	Brookhaven, New York
NIST Crystal Data [NBS(CDF)]	Inorganic and organic unit cells	Gaithersburg, Maryland

Qualitative Analysis

B. Phase Identification

1. Databases

Databases designed for the powder diffraction community are also available.

Table 12.4. Databases for X-ray Powder Diffraction

Name	Content
Master DB	Master ICDD Database—all known powder data on a single phase, plus editorial marks and comments
PDF-2	User version of the Master DB (does not contain special editorial comments)
PDF-1	Subset of PDF-2, contains *d*'s, *I*'s and names (designed for automated search systems)
PDF-3	Contains raw data as a digitized pattern
CDF	The Crystal Data File (contains cell data, names, and references)
EISI	The Elemental and Interplanar Spacing Index (designed for electron diffraction)

Qualitative Analysis

B. Phase Identification

1. Databases

a. Powder Diffraction File (PDF)

A collection of powder diffraction patterns maintained by ICDD.

Table 12.5. Subfiles of the PDF

Subfile	Entries	Where Available
Inorganic	43,308	Book and computer
Organic	17,661	Book and computer
Metals & Alloys	11,630	Book and computer
Minerals	3,954	Book and computer
Forensic Materials	3,612	Book and computer
Common Phases	3,202	Computer readable
Zeolites	626	Book and computer
Explosives	149	Computer readable
Polymers	248	Computer readable
Cement	360	Computer readable
Superconductors	139	Computer readable
Dyes & Pigments	101	Computer readable
Total as of set 44	59,847	

The PDF is large, so it is organized into subfiles.

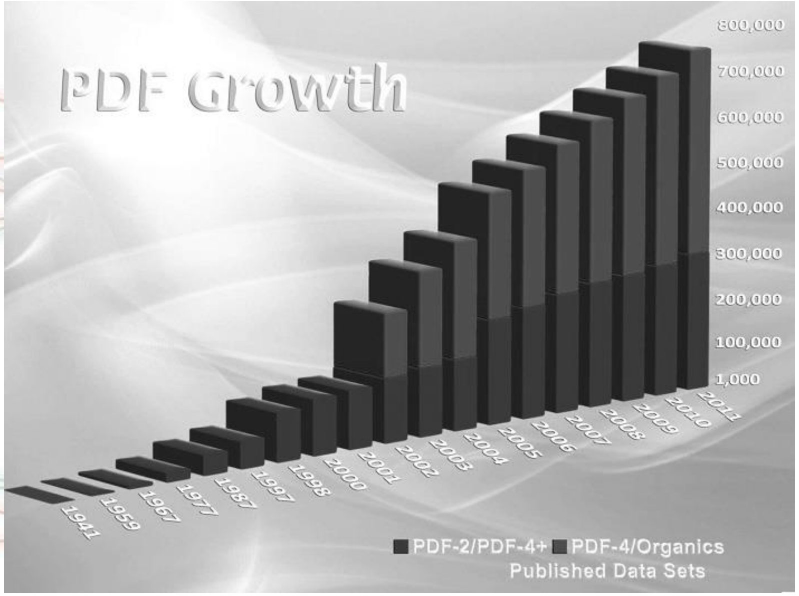
Qualitative Analysis

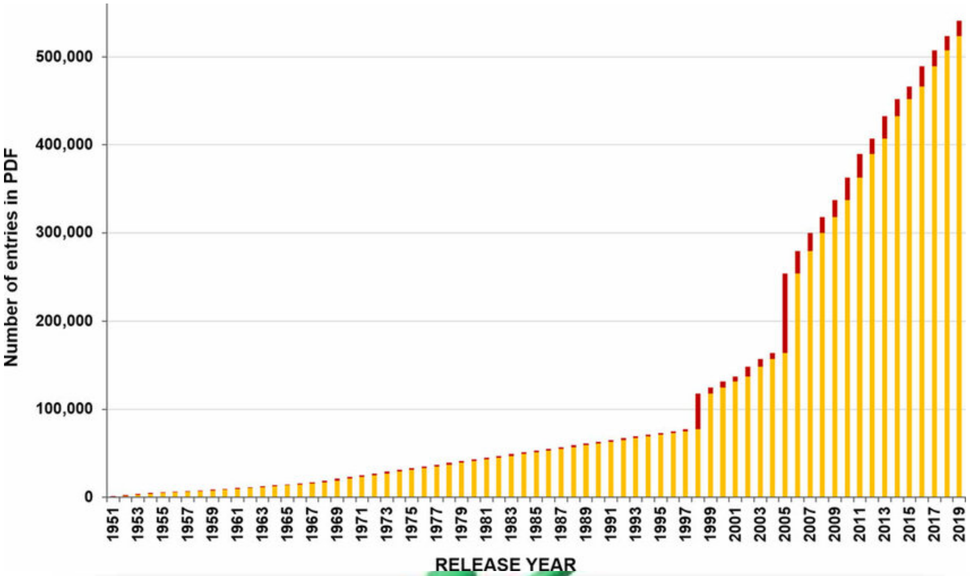
B. Phase Identification

1. Databases

a. Powder Diffraction File (PDF)

A collection of powder diffraction patterns maintained by ICDD.





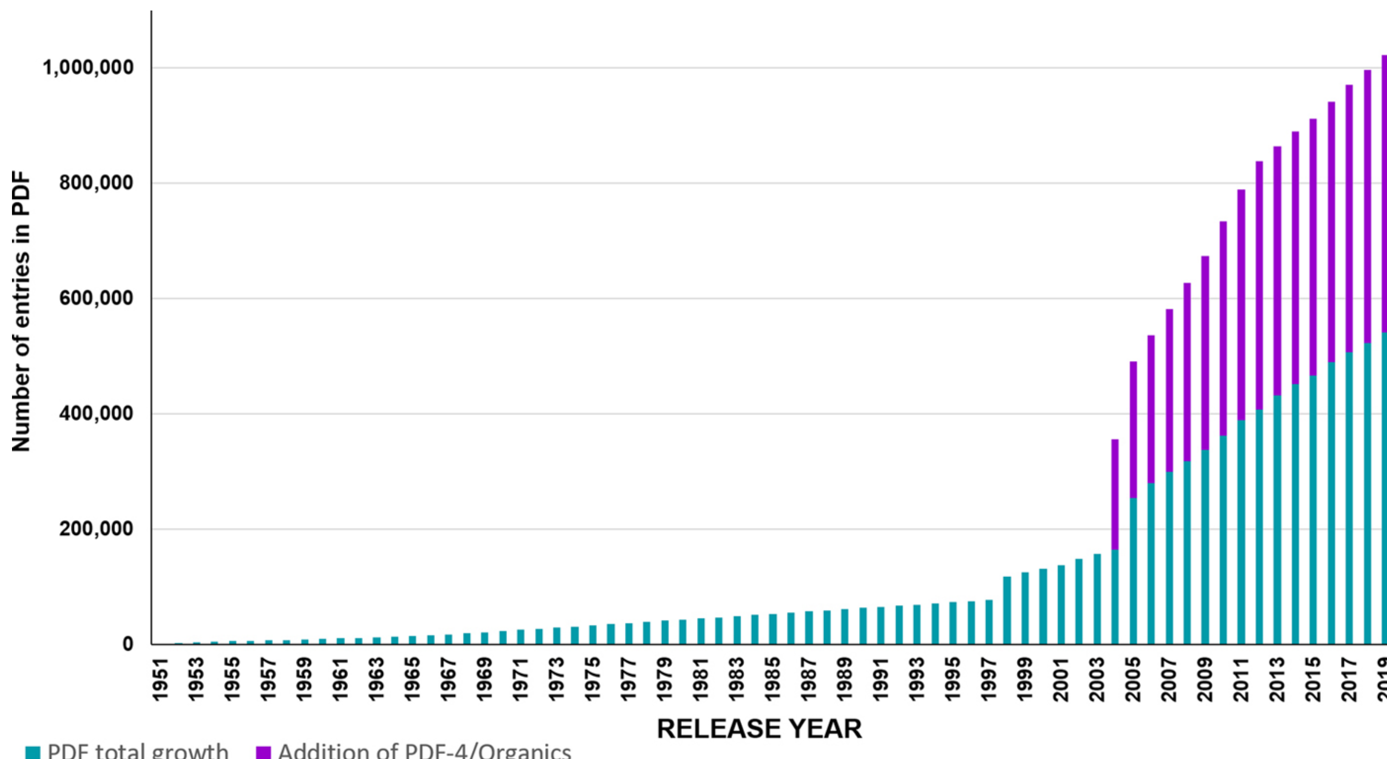
Qualitative Analysis

B. Phase Identification

1. Databases

a. Powder Diffraction File (PDF)

A collection of powder diffraction patterns maintained by ICDD.



Qualitative Analysis

B. Phase Identification

1. Databases

a. Powder Diffraction File (PDF)

Release 2025 of the Powder Diffraction File™ (PDF) contains 1,104,137 material data sets. Each data set contains diffraction, crystallographic, and bibliographic data, as well as experimental, instrument, and sampling conditions, and select physical properties in a common standardized format.

457,800+ inorganic entries

650,200+ organic entries

626,140+ entries with atomic coordinates

997,300+ entries have I/Ic values for quantitative analysis by Reference Intensity Ratio

Combines powder and single crystal data

Includes crystalline, semi-crystalline, and amorphous solid-state materials

Qualitative Analysis

B. Phase Identification

1. Databases

a. Powder Diffraction File (PDF)

Each individual PDF card typically contains:

- » **d-I list**
- » **chemical formula**
- » **chemical name**
- » **PDF number**
- » **reference**
- » **miller indices**
- » **unit cell**
- » **space group**
- » **physical constants**
- » **experimental details**
- » **comments**

Qualitative Analysis

B. Phase Identification

1. Databases

a. Powder Diffraction File (PDF)

The PDF card number is in the form yy-nnnn, where yy represents the year.

PDF#27-1402: QM>Star; d>Diffractometer; I>Diffractometer [JADE - PDF Card]

Silicon, syn
Si

Radiation: CuKa1 Lambda= 1.5405981 Filter=
Calibration: Internal(W) d-Cutoff= I/Ic(RIR)= 4.70
Ref: Natl. Bur. Stand. (U.S.) Monogr. 25, 13 35 (1976)

Cubic (Powder Diffraction), Fd3m(227) Z= 8 mp=
Cell= 5.43088 Pearson: cF8 (C)
Dx= 2.329 Dm= Mwt= 28.09 Vol= 40.05 F(11)=408.8(.0021,13)
Ref: Ibid.

ea= nwB= ey= Sign: 2V=
Ref:

Pattern taken at 25(1) C. This sample is NBS Standard Reference Material No. 640. Reflections calculated from precision measurement of a#0. a#0 uncorrected for refraction. To replace 5-565 and 26-1481.

Color: Gray

11 Reflection(s), Wavelength for Computing Theta = 1.540562<CU>

Strong Line: 3.14/X 1.92/6 1.64/3 1.11/1 1.25/1 0.86/1 0.92/1 1.36/1 1.05/1 0.96/1

Qualitative Analysis

B. Phase Identification

1. Databases

a. Powder Diffraction File (PDF)

For data sets after set 5, the actual year of publication is found by adding 1950 to the value of yy.

i.e. set 27 was published in the year 1950 + 27 = 1977.

The character nnnn represents the number of the pattern published in its appropriate year.

i.e. pattern 41-0001 is the 1st pattern published in 1991.

There are ~2000 patterns added to the database each year.

Qualitative Analysis

B. Phase Identification

1. Databases

a. Powder Diffraction File (PDF)

Table 12.6. Characteristics of Media on Which the PDF Has Been Supplied

Category	Cards	Fiche	Tape	Disk	CD–ROM[a]
Retrieval time	Slow		Moderate	Very fast	Fast
File Stored	All			Part/all	All
File access	Random		Sequential	Random	
Updating	Not retroactive		Retroactive		
Size (cm^2)	200,000	3,000	4,500		20

[a]Compact disk–read-only memory.

Qualitative Analysis

B. Phase Identification

2. Search/Matching Methods

a. Manual Methods

Table 12.7. Types of PDF Data-Searching Indexes

Index	Entry Method	Search Parameters
Alphabetic	Chemistry	Permuted elemental symbols
Hanawalt	*I*/*d*	Three strongest lines
Fink	*d*/*I*	First eight lines
EISI[a]	Chemistry/*d*	Low high *Z* elements; *d*-spacing
Boolean	Various	*d*-Spacings, chemistry, strong lines, CODEN, physical properties, functional groups, etc.

[a]Elemental and Interplanar Spacing Index.

Qualitative Analysis

B. Phase Identification

2. Search/Matching Methods

a. Manual Methods – Most Common

- » Alphabetic Method
- » Hanawalt Method
- » Fink Method

Qualitative Analysis

B. Phase Identification

2. Search/Matching Methods

a. Manual Methods

Problems:

With Hanawalt method, since patterns are indexed based on their strongest lines, it is difficult to match samples with preferred orientation and overlapping lines for complex mixtures.

Qualitative Analysis

B. Phase Identification

2. Search/Matching Methods

a. Manual Methods

Problems:

Fink method is better, since it was based on the 8 largest d values.

However the Fink manual method was not published after 1980s, because of the volume thickness.

Qualitative Analysis

B. Phase Identification

2. Search/Matching Methods

b. Automated Methods

Beginning in the 1980s, programs were written to automate the search/matching process.

Siemens developed some of the 1st software for the D-500 models using the Hanawalt strategy.

Phillips then developed a method of probability searching using least square analysis.

Recently whole pattern including background matches have evolved.

Qualitative Analysis

B. Phase Identification

2. Search/Matching Methods

c. ICDD offers JADE from MDI

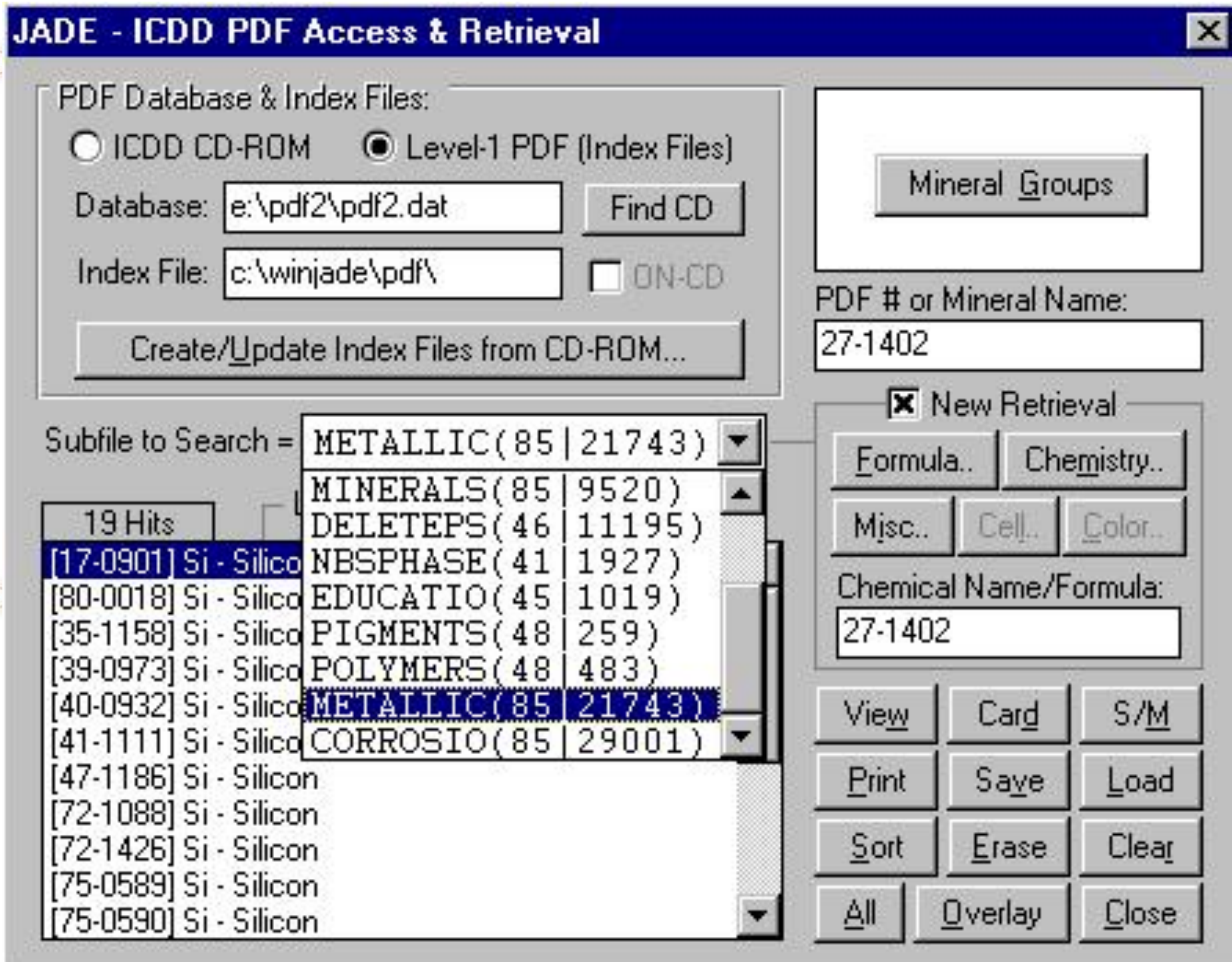
JADE - Extended View of Current Hit List

Close | Print | Save | Clipboard | PDF Card

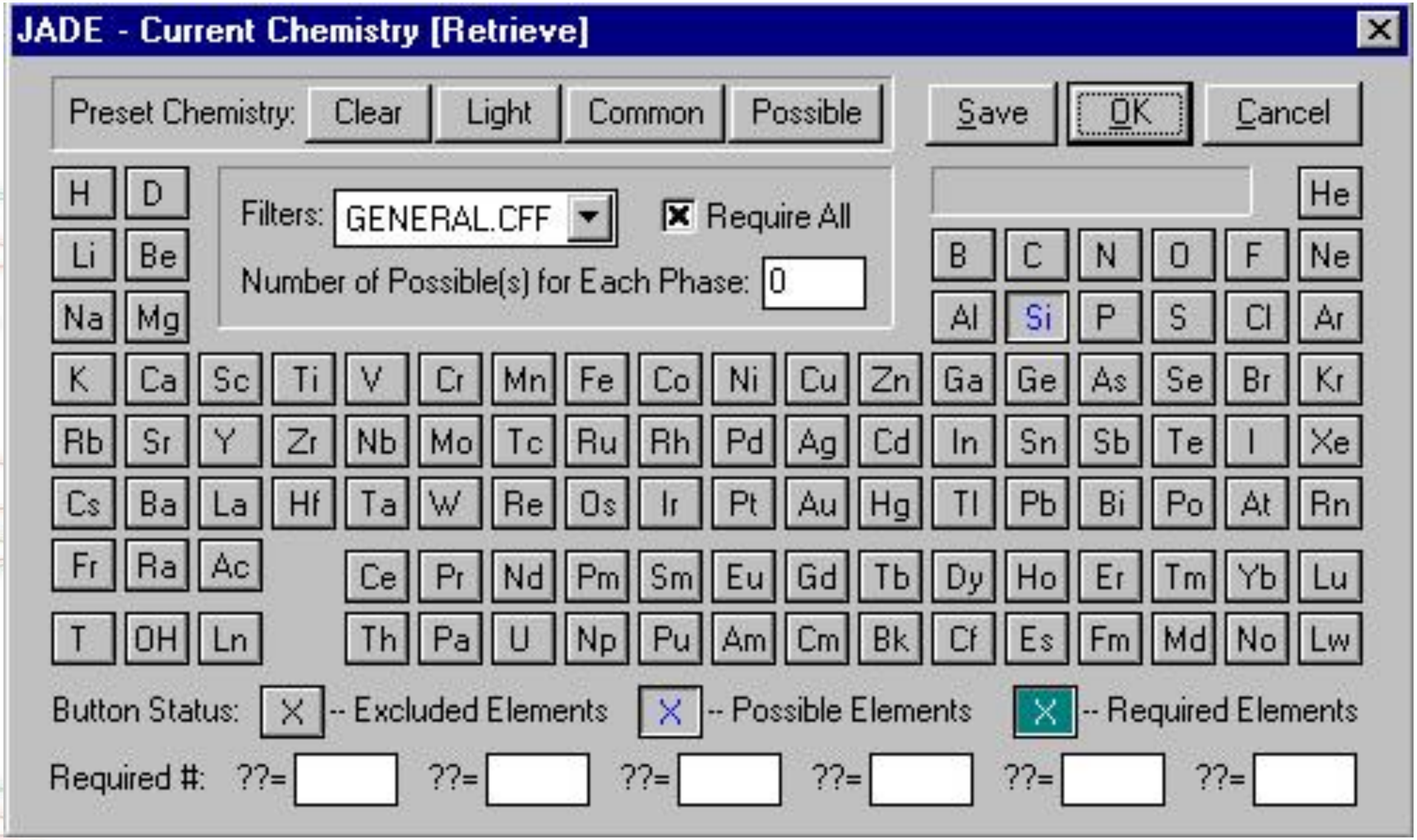
Q - Quality Mark; D - Data Source (Diffractometer etc); S - Crystal Symmetry

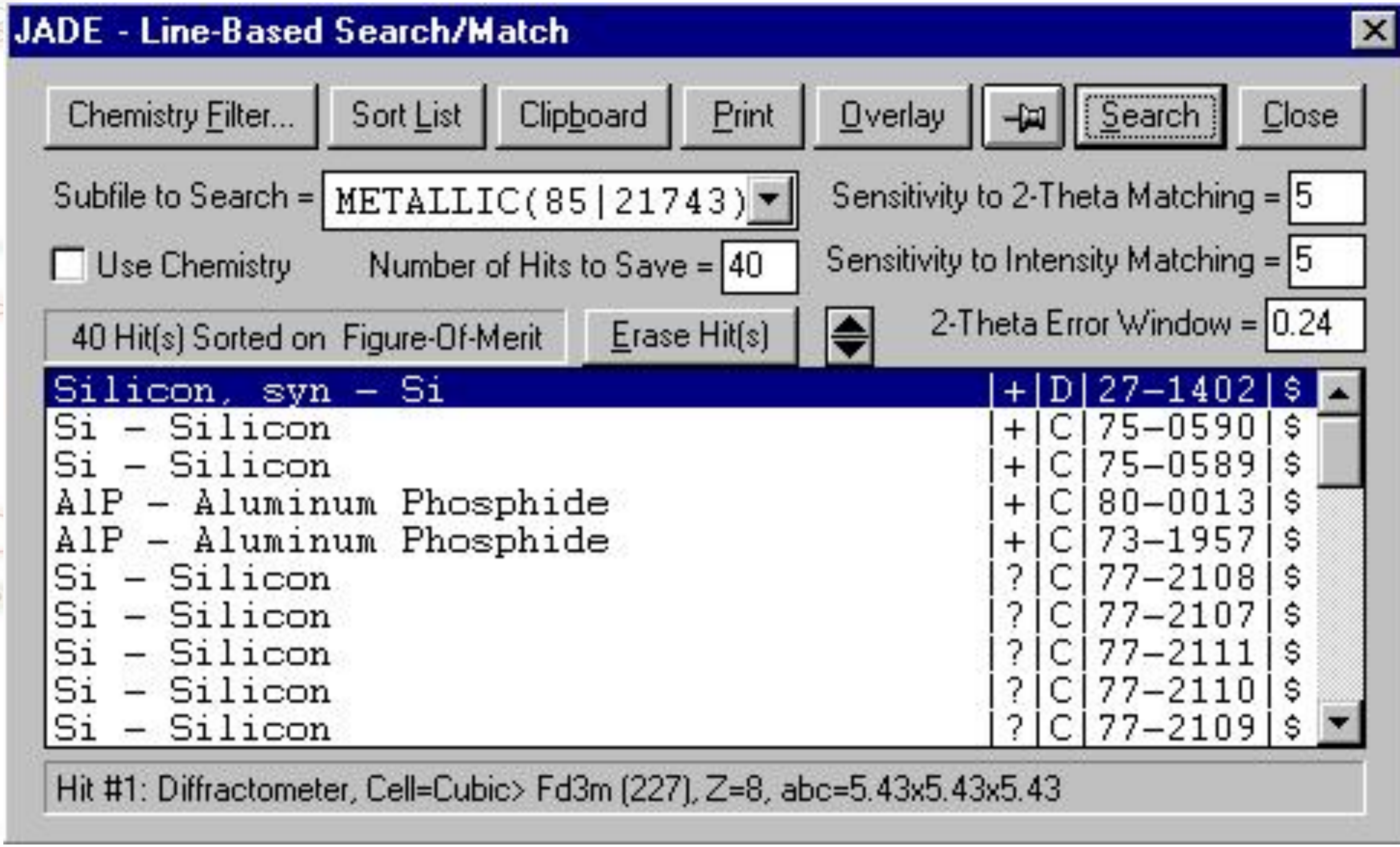
Phase ID	Q	PDF #	D	Dx	S	S.G.	a
Si - Silicon	?	17-0901	F	2.550	C	Ia3	6.64
Si - Silicon	+	80-0018	C	2.380	C	F-43m	5.39
Si - Silicon		35-1158	D	3.125	C	Fm3m	3.90
Si - Silicon		39-0973	V		T	P41212	8.63
Si - Silicon		40-0932	V		T	P422	7.48
Si - Silicon	?	41-1111	X		X		
Si - Silicon	?	47-1186	X		H	P6/mmm	2.46
Si - Silicon	+	72-1088	C	2.553	C	Ia3	6.64
Si - Silicon	+	72-1426	C	2.548	C	Ia3	6.64
Si - Silicon	+	75-0589	C	2.329	C	Fd3m	5.43
Si - Silicon	+	75-0590	C	2.329	C	Fd3m	5.43
Si - Silicon	+	75-0841	C	1.224	H	P63mc	6.60
Si - Silicon	?	77-2107	C	2.343	C	Fd3m	5.42
Si - Silicon	?	77-2108	C	2.343	C	Fd3m	5.42
Si - Silicon	?	77-2109	C	2.345	C	Fd3m	5.42
Si - Silicon	?	77-2110	C	2.345	C	Fd3m	5.42
Si - Silicon	?	77-2111	C	2.343	C	Fd3m	5.42
Si - Silicon	+	80-0005	C	2.379	H	P63mc	3.80
Silicon, syn - Si	+	27-1402	D	2.329	C	Fd3m	5.43

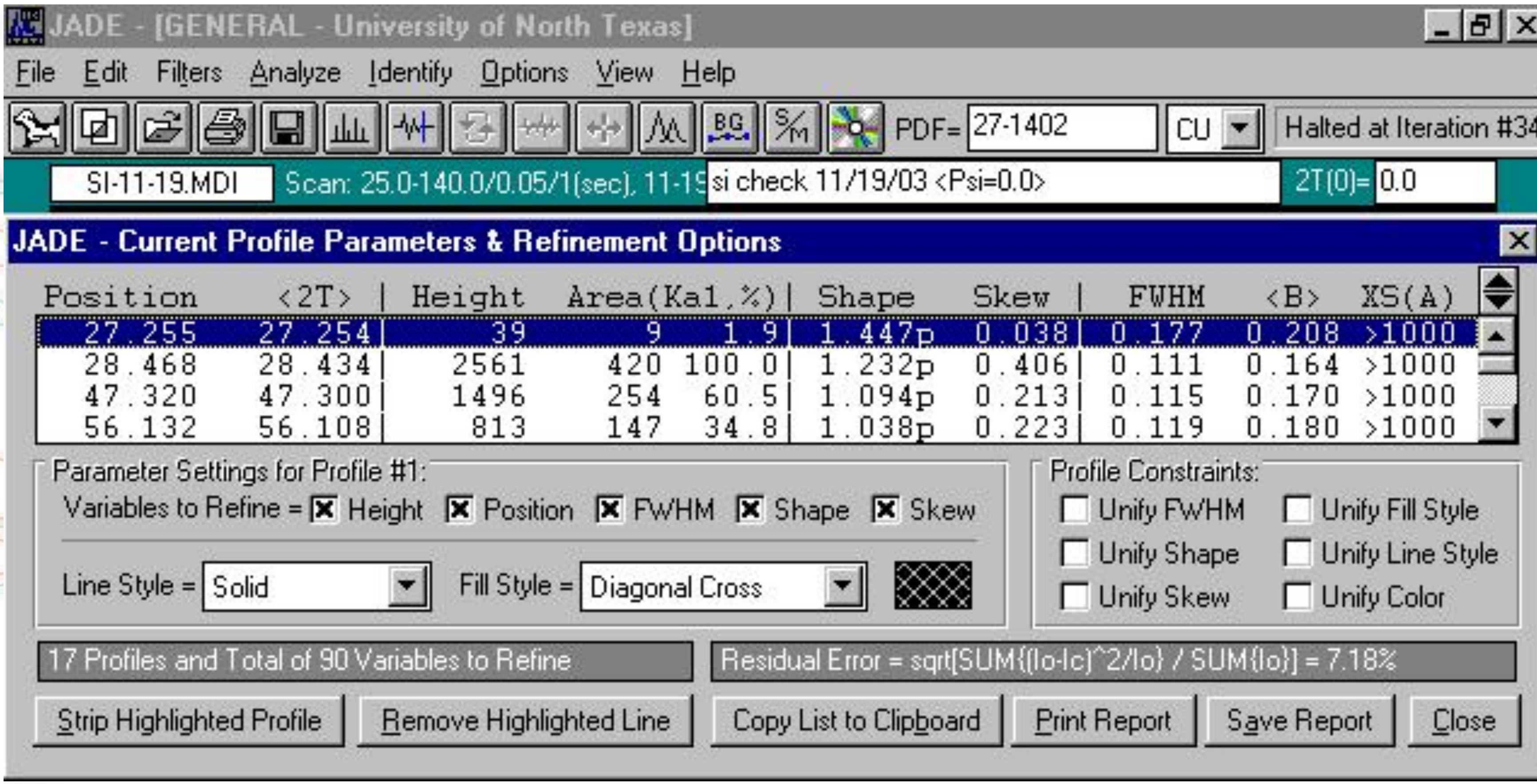
Start | JADE - [GENERAL - Unive... | JADE - ICDD PDF Access & R... | JADE - Extended Vie... | 2:00 PM

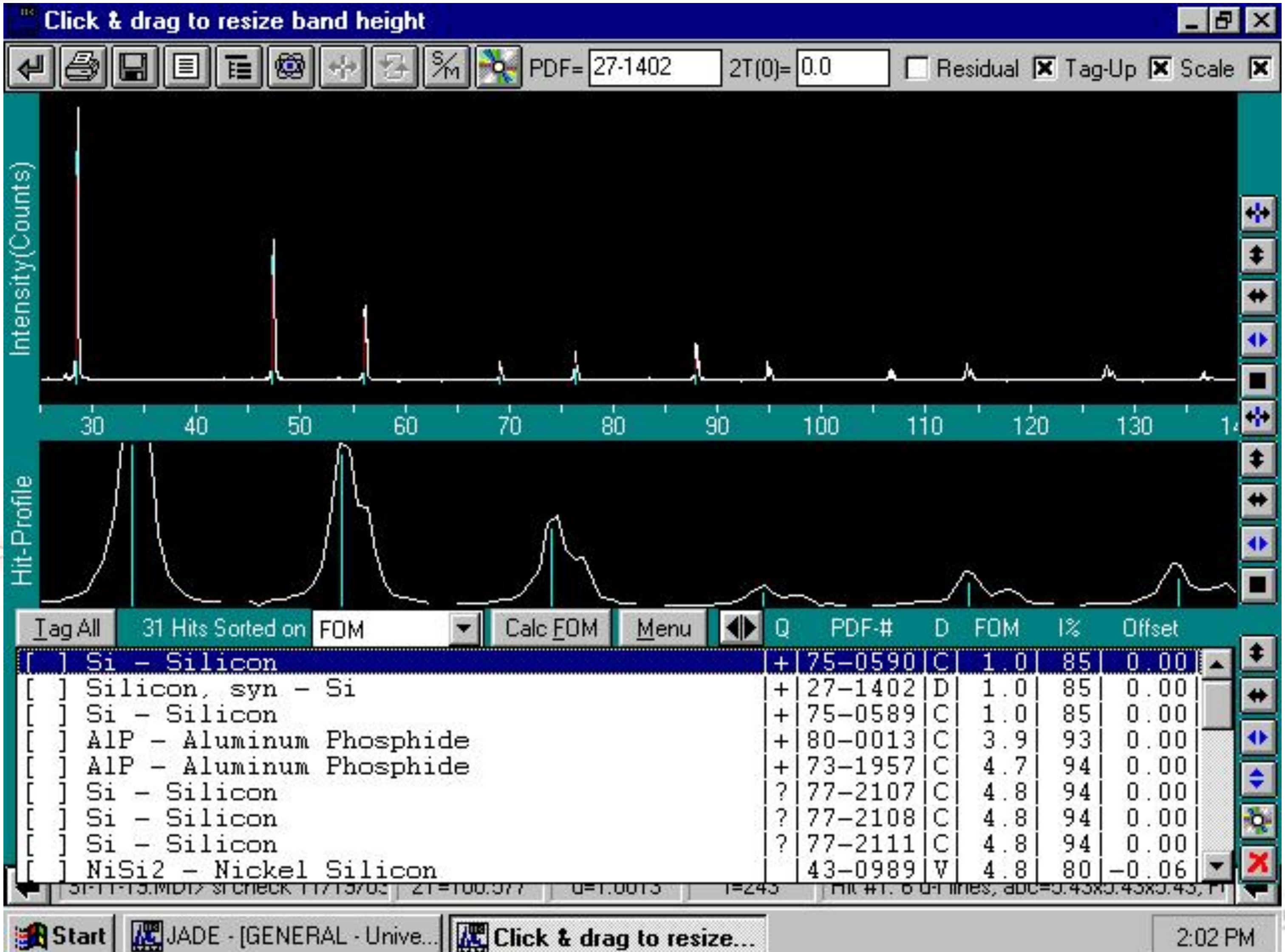


Advanced X-ray Analysis


JADE - Current Chemistry [Retrieve]
Preset Chemistry:
Clear
Light
Common
Possible
Save
OK
Cancel
Filters:
GENERAL.CFF
Require All
Number of Possible(s) for Each Phase:
0
H D He
Li Be B C N O F Ne
Na Mg Al Si P S Cl Ar
K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr
Rb Sr Y Zr Nb Mo Tc Ru Rh Pd Ag Cd In Sn Sb Te I Xe
Cs Ba La Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi Po At Rn
Fr Ra Ac
Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu
T OH Ln
Th Pa U Np Pu Am Cm Bk Cf Es Fm Md No Lw
Button Status:
X -- Excluded Elements
X -- Possible Elements
X -- Required Elements
Required #:
??=
??=
??=
??=
??=
??=

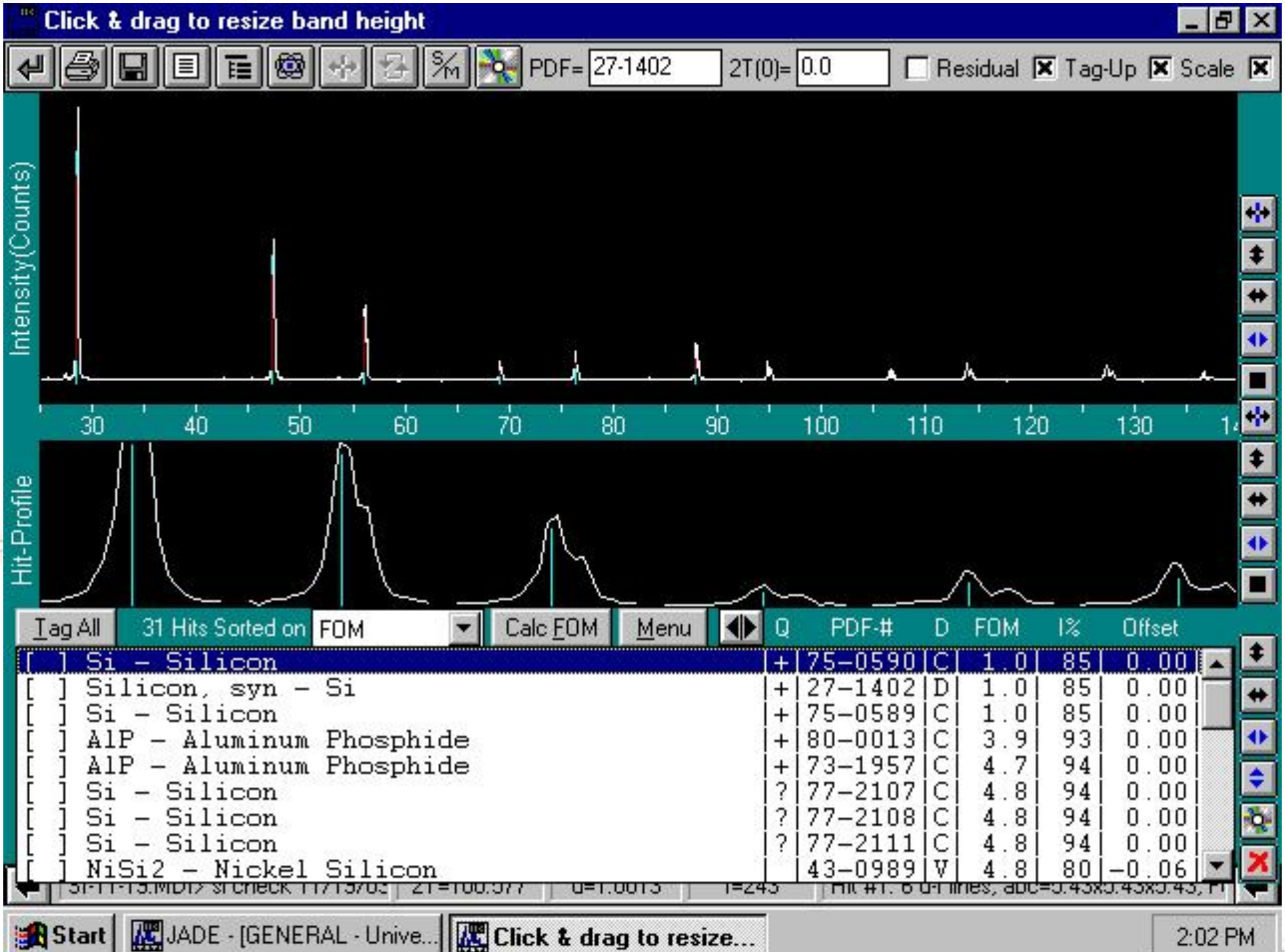

JADE - Line-Based Search/Match
Chemistry Filter...
Sort List
Clipboard
Print
Overlay
Search
Close
Subfile to Search = METALLIC(85|21743)
Sensitivity to 2-Theta Matching = 5
Use Chemistry
Number of Hits to Save = 40
Sensitivity to Intensity Matching = 5
40 Hit(s) Sorted on Figure-Of-Merit
Erase Hit(s)
2-Theta Error Window = 0.24
Silicon, syn - Si | + | D | 27-1402 | $
Si - Silicon | + | C | 75-0590 | $
Si - Silicon | + | C | 75-0589 | $
AlP - Aluminum Phosphide | + | C | 80-0013 | $
AlP - Aluminum Phosphide | + | C | 73-1957 | $
Si - Silicon | ? | C | 77-2108 | $
Si - Silicon | ? | C | 77-2107 | $
Si - Silicon | ? | C | 77-2111 | $
Si - Silicon | ? | C | 77-2110 | $
Si - Silicon | ? | C | 77-2109 | $
Hit #1: Diffractometer, Cell=Cubic> Fd3m (227), Z=8, abc=5.43x5.43x5.43

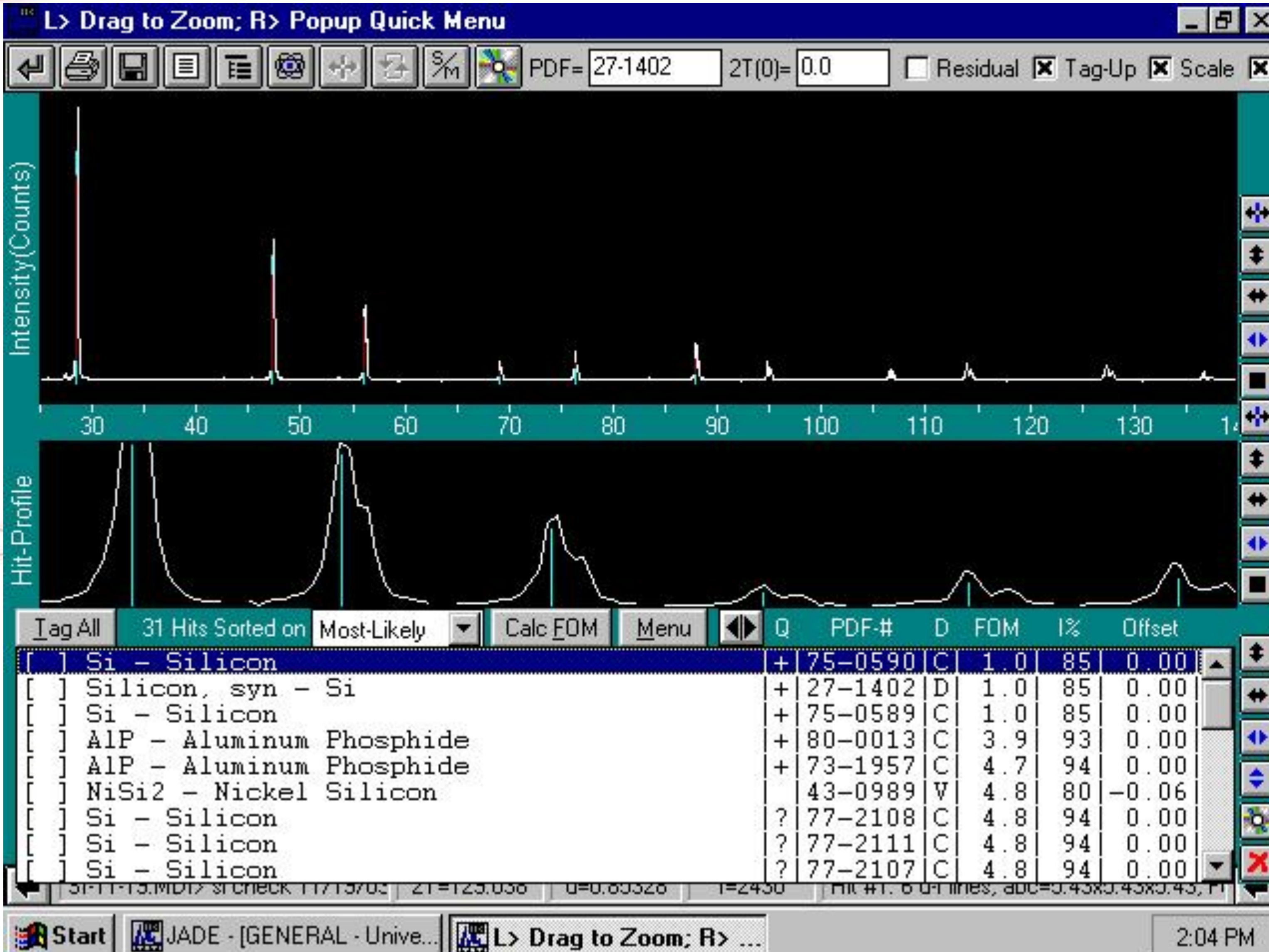

JADE - [GENERAL - University of North Texas]
File Edit Filters Analyze Identify Options View Help
PDF= 27-1402
CU
Halted at Iteration #34
SI-11-19.MDI
Scan: 25.0-140.0/0.05/1(sec), 11-19
si check 11/19/03 <Psi=0.0>
2T(0)= 0.0
JADE - Current Profile Parameters & Refinement Options
Position <2T> | Height Area(Ka1,%) | Shape Skew | FWHM <B> XS(A)
27.255 27.254 | 39 9 1.9 | 1.447p 0.038 | 0.177 0.208 >1000
28.468 28.434 | 2561 420 100.0 | 1.232p 0.406 | 0.111 0.164 >1000
47.320 47.300 | 1496 254 60.5 | 1.094p 0.213 | 0.115 0.170 >1000
56.132 56.108 | 813 147 34.8 | 1.038p 0.223 | 0.119 0.180 >1000
Parameter Settings for Profile #1:
Variables to Refine = Height Position FWHM Shape Skew
Line Style = Solid
Fill Style = Diagonal Cross
Profile Constraints:
Unify FWHM
Unify Fill Style
Unify Shape
Unify Line Style
Unify Skew
Unify Color
17 Profiles and Total of 90 Variables to Refine
Residual Error = sqrt[SUM{(Io-Ic)^2/Io} / SUM{Io}] = 7.18%
Strip Highlighted Profile
Remove Highlighted Line
Copy List to Clipboard
Print Report
Save Report
Close



5390

Advanced X-ray Analysis


Click & drag to resize band height
PDF= 27-1402
2T(0)= 0.0
Residual
Tag-Up
Scale
Intensity(Counts)
30
40
50
60
70
80
90
100
110
120
130
Hit-Profile
Tag All
31 Hits Sorted on FOM
Calc FOM
Menu
Q
PDF-#
D
FOM
I%
Offset
[ ] Si - Silicon + 75-0590 C 1.0 85 0.00
[ ] Silicon, syn - Si + 27-1402 D 1.0 85 0.00
[ ] Si - Silicon + 75-0589 C 1.0 85 0.00
[ ] AlP - Aluminum Phosphide + 80-0013 C 3.9 93 0.00
[ ] AlP - Aluminum Phosphide + 73-1957 C 4.7 94 0.00
[ ] Si - Silicon ? 77-2107 C 4.8 94 0.00
[ ] Si - Silicon ? 77-2108 C 4.8 94 0.00
[ ] Si - Silicon ? 77-2111 C 4.8 94 0.00
[ ] NiSi2 - Nickel Silicon 43-0989 V 4.8 80 -0.06
Start
JADE - [GENERAL - Unive...
Click & drag to resize...
2:02 PM



Advanced X-ray Analysis

Reading Assignment:

Read Chapter 3-7, 9-13 from:

- **-Introduction to X-ray powder Diffractometry by Jenkins and Synder**

Read Chapter 3, 4, 6, 13, and 14 from

- **-Elements of X-ray Diffraction by Cullity and Stock**

Read Chapter 2 from Norton