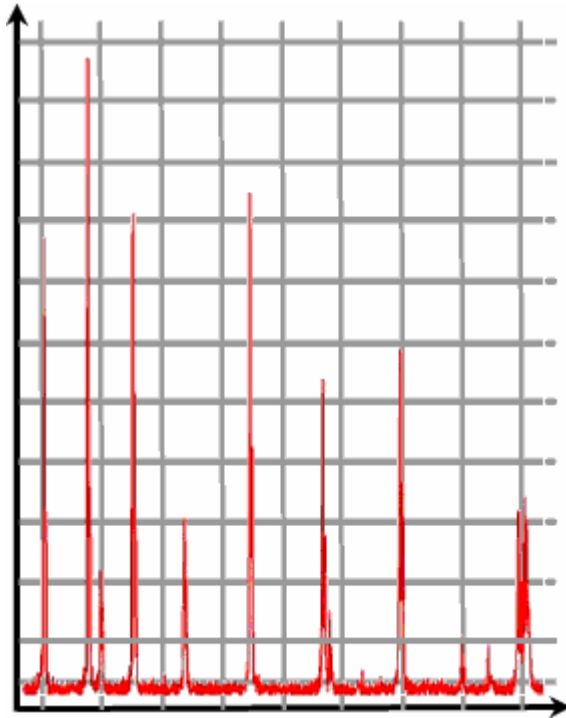


Siroquant Version 3

Technical & Clay Manuals



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Siroquant Version 3.0

Technical & Clay Manuals

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0. FOREWARD

This Technical Manual has been adapted to Siroquant Version 3 from the Technical Manual of earlier versions written by Dr. John Taylor while he was part of what is now CSIRO Division of Energy Technology. After his retirement John took a very active part in the further development of Siroquant until his sudden death in September 2002. After John's death it was not possible to add further refinement features but effort was made in putting in features suggested by various Siroquant users and updating the interface.

As the main purpose of the manual was and is to provide technical information on the Rietveld method and how Siroquant uses the manual has been retained with appropriate modifications to reflect the new interface.

1. General Overview

1.1 Siroquant Version 3.0 – Program overview

Siroquant is a personal computer software package that gives standardless quantitative phase analysis of any mineral, including preferred orientation, amorphicity, anomalous dispersion and absorption contrast corrections. It uses the full-profile Rietveld method of refining the shape of a calculated XRD pattern against the profile of a measured pattern. The total calculated pattern is the sum of the individual phase calculated patterns.

The core functions of Siroquant have been tested over the last ten years on many applications and with many standard mixtures. With version 3.0 TRACSCAL has been integrated with the main application and this has resulted in improved performance as this part of the program no longer needs to transfer data by means of disk files. The TRACSCAL code has been transliterated from the original FORTRAN into Delphi with the elimination of disk input/output during refinement. TRACSCAL is retained as the name for the refinement part of Siroquant.

1.2 Crystal Structure Databank

Siroquant computes standard phase profiles using crystallographic data with access information stored in the Standard Database. At present, the database contains approx 1800 common mineral phases, 17 minerals with no crystal structure data and the Claypack phases. If a mineral is not in the database, please contact Sietronics and it will be added (with a fee, to cover costs). Users may generate their own databanks using the instructions in Chapter 5.

1.3 Refinement Overview

Refinement of Rietveld parameters leading to a successful fit of the total calculated pattern to the measured pattern is usually done in a certain sequence, refining the more robust (stable) parameters first. The stages of a Siroquant analysis can be summarised as follows:

- (a) An automatic pre-scaling routine is used to compute approximately correct Rietveld scales with no user input required. This involves 13 cycles of least-squares refinement of the phase scales and instrument zero.
- (b) The calculated pattern now shows some resemblance to the measured pattern; fine-tuning with the least squares routine can be then done. For each phase, refinements of the unit cell dimensions and linewidths, the next most important parameters are made. Refine the instrument zero with each operation if it is not correlating with the unit cell parameters. In linewidth refinement, refine W only at first, with $U=V=0$. Then refine U and V later if they are stable.
- (c) Preferred orientation can be checked at this stage also. Siroquant allows refinement of a March orientation parameter for each phase. Scales and zero are still usually adjusted as well.
- (d) The Pearson- m line shape parameter, which is about 1 for Lorentzian and ∞ for Gaussian can also be refined. For Bragg-Brentano diffractometers, this parameter is usually 1.3-1.5 and can be safely left fixed at 1.4 except for the most precise analyses. Alternatively a pseudo-Voigt shape parameter (starting value usually about 0.8 for an 80% Lorentzian/Gaussian ratio) can be refined.
- (e) The asymmetry parameter, as defined in the Rietveld (1969) paper can also be safely left fixed at a small value, say 0.01, except when very low angle lines are encountered. These are more asymmetric, with a tail towards lower angles, and then the asymmetry parameter can be refined. This is a less robust parameter, and should only be refined near the end of the analysis, and then with a damping factor. The use of this type of asymmetry parameter is now discouraged, as the new Split Peak Shape Parameter gives a better asymmetry correction. Use the latter asymmetry correction if at all possible when asymmetry is evident.
- (f) If parameters prove to be unstable, e.g. U and W , or if a parameter is started a long way from the 'true' value (e.g. the preferred orientation parameter could well be 0.5 instead of the

default of 1.0) then successful convergence can usually be obtained with a shift damping factor under Parameters - Stage Control and Refinement. Use a damp factor of 0.2 to 0.3 if the parameter is unstable.

For a new sample, manual operation of the type described in (a) to (f) above could take 10 to 30 minutes, depending on the speed of the computer and the complexity of the sample; automatic production runs can also be pre-programmed with the different variables refined in different "Stages" on the one run.

In summary, we can define the parameters refined in a Rietveld run as Robust, R, and Soft, S. The soft ones are refined last, if at all, as in the case of the U and V halfwidth parameters. Also, for any phase, those parameters to be switched on are dictated by the phase concentration. The lower limit of detection of a phase with Siroquant will be about 0.5% to 1%.

We also have the two global parameters Instrument Zero and Pattern Background. The zero parameter is robust and must be refined at or near the start. The background parameter is usually robust, but can sometimes be unstable, if too many polynomial coefficients are refined at once, or the background curve is not smooth.

The following table can be used as a guide to phase concentration and parameters switched on for refinement:

Global Parameter	Stability	Comment
Instrument zero, ZERO	R	Switched on, refine immediately
Pattern background, BACK	R	Only refine necessary coefficients. Too many coefficients may cause false minimum.

The following table can be used as a guide to phase concentration and parameters switched on for refinement:

Phase Parameters, Phase i	Stability	Concentration Limit (%) for refinement
Scales SCALE _i	R	0.3
Unit cell, CELL _i	R	2
Single lineshape, SHAPE _i	R	15 (program defaults usually O.K.)
Split shape, SPLITSHAPE _i	R or S	25
Linewidth W _i	R	2
Linewidths U _i , V _i	S	20
Preferred orientation , P _i	R or S	5
Extinction, E _i	S	15 (not often invoked; it can correlate with systematic errors)

A typical refinement sequence would be like the following:

Stage	Parameters On or Off	Cycles	Damp Factor
1	On: ZERO, SCALE _i	8	0.5
2	Off: ZERO. On: SCALE _i , CELL _i , W _i	5	1
4	On: SCALE _i , CELL _i , P _i . Off: W _i	8	0.5
5	On: SCALE _i , CELL _i , P _i , W _i	8	0.5
6	On: ZERO, SCALE _i , CELL _i , P _i , W _i , (and U _i , V _i , SHAPE _i , SPLITSHAPE _i if needed).	8	0.5

1.4 Particle Size and Absorption Contrast Corrections

Siroquant includes the Brindley absorption contrast correction to correct the results for the varying absorptive power of the minerals for the radiation. This correction is particle size dependent, and the only input required is an estimated average particle thickness for each phase. According to the Brindley (1945) theory, the particles are aggregates, so the Brindley particle sizes are larger by a factor of about 50 than the particle sizes calculated from the Scherrer equation. They can be found from, say, SEM measurements, or from knowledge of the mode of sample preparation.

Micronisers are commercially available which can grind a sample to a 1-micron average radius, while hand grinding in an agate mortar gives an average radius of about 5 microns. When the component phases in a mineral have greatly different radiation absorptive powers, then it is advisable to carefully standardise the method of sample preparation. This correction can be considerable for very contrasting phases, e.g. $\text{Pb}(\text{NO}_3)_2$ and LiF , (see Taylor and Matulis, "Absorption Contrast Effects in the Quantitative XRD Analysis of Powders by Full Multiphase Profile Refinement", J. Appl. Cryst., Vol 24, p.14-17, 1990). Brindley correction parameters are input through the menus.

1.5 Choice Of Radiation for a Siroquant Quantification

1.5.1 Phase Absorption Considerations (Absorption Contrast)

This is a very important point, and often overlooked until standard mixtures fail to quantify successfully with Rietveld programs. The X-ray absorption in a sample should be considered if some elements in the sample are high absorbers of the X-ray tube wavelength used. Table 1, from Henry, Lipson and Wooster, "The Interpretation of X-Ray Diffraction Photographs", 1953, p.236 is useful. The information in Table 1 shows, for example, that elements with atomic numbers between 21 and 27, i.e. Sc to Co, absorb $\text{CuK}\alpha$ strongly, while Cl to Mn are strong absorbers of $\text{CoK}\alpha$. Samples containing strongly absorbing elements should be ground finely, in order to minimise absorption contrast. In Table 1, the absorption coefficients are expressed as (μ/ρ) values,

independent of the degree of dilution, or density of the elements. For a phase, the $\left(\frac{\mu}{\rho}\right)$ value is the weighted average of the atoms in the crystal structure, i.e.

$$\left(\frac{\mu}{\rho}\right)_{\text{SiO}_2} = X_{\text{Si}}\left(\frac{\mu}{\rho}\right)_{\text{Si}} + X_{\text{O}}\left(\frac{\mu}{\rho}\right)_{\text{O}}$$

where X is the weight fraction. Thus, for $\text{CuK}\alpha$, we have from the Table:

$$\left(\frac{\mu}{\rho}\right)_{\text{SiO}_2} = \frac{28}{60} \times 60.3 + \frac{32}{60} \times 12.7 = 34.9$$

Since the density of quartz is 2.649, $\mu_{\text{SiO}_2} = 93 \text{ cm}^{-1}$ for $\text{CuK}\alpha$.

Quantitative analysis by the Rietveld method is interfered with when the phases have absorption contrast i.e. when a phase absorbs more or less than the surrounding matrix. Brindley (Phil. Mag., 36, 347-369 (1945)) has given a correction factor for phase A based on the product $\left(\mu_A - \bar{\mu}\right)D_A$

where $\bar{\mu}$ is the mean linear absorption coefficient of the matrix (no voids) and D is the mean particle diameter of phase A, the particle being an aggregate of ultimate diffracting single crystallites.

He states that the theory of absorption contrast corrections is only valid when $\mu_A D_A$ is less than 0.1.

Let us take a hypothetical Rietveld quantification of quartz and iron minerals with a $\text{CuK}\alpha$ tube.

Assuming all D_A values are 5μ we have:

Phase A	$\mu_A(\text{CuK}\alpha)(\text{cm}^{-1})$	$\mu_A D_A$
Quartz	93	.05
Hematite	1200	.60
Pyrite	1012	.51
Chalcopyrite	623	.31

From the above table we can see that compounds containing iron have much higher absorption for $\text{CuK}\alpha$ than quartz, giving an “absorption contrast”. The $\mu_A D_A$ values are as high as 0.6, six times the limit recommended by Brindley. Therefore Rietveld quantifications will not be reliable if the particles are as large as $5\mu\text{m}$ for the iron compounds. In fact, if Brindley corrections are attempted with Siroquant and all D values set at $5\mu\text{m}$, the Rietveld quantifications for each iron-containing mineral will be about 25% too low and consequently quartz will assay about 50% too high. The situation is also complicated by beam losses due to fluorescence (something like an extinction effect), as the $\text{CuK}\alpha$ wavelength (1.54\AA) is just less than the K-absorption edge of Fe, 1.74\AA .

The diffractionist has two choices in such a situation. Either the sample is ground until the $\mu_A D_A$ values are less than 0.1 or a different X-ray radiation can be used. The sample in this case would have to be ground to $D < 1\mu\text{m}$, giving a risk that the softer phases, quartz and chalcopyrite, could have their crystal structures damaged. It would appear better to change the wavelength.

With $\text{CoK}\alpha$ the situation looks much better for quantifying iron minerals. We have, for a D_A of $2.5\mu\text{m}$:

Phase A	$\mu_A(\text{CoK}\alpha)(\text{cm}^{-1})$	$\mu_A D_A$
Quartz	146	.04
Hematite	253	.06
Pyrite	516	.13
Chalcopyrite	393	.10

The Siroquant analysis thus becomes workable if the sample is ground to a D_A of $2.5\mu\text{m}$ or less, several times more than can be tolerated with a Cu tube.

The Siroquant long results file* for $D_A = 2.5\mu\text{m}$, gives the following absorption contrast correction factors for $\text{CuK}\alpha$ and $\text{CoK}\alpha$ for a quartz, magnetite, hematite, pyrite and chalcopyrite mixture in roughly equal amounts:

Phase	Contrast Correction Factor	
	$\text{CuK}\alpha$	$\text{CoK}\alpha$
Quartz	0.85	0.96
Magnetite	1.15	0.99
Hematite	1.15	0.099
Pyrite	1.09	1.06
Chalcopyrite	0.97	1.03

Thus even though the contrast situation is not ideal for this mixture with $\text{CoK}\alpha$ the correction factors

* In version 3 the long results file is no longer used. To obtain these values you will need to use the Calculate/Contrast Correction form after a refinement.

for contrast are much closer to 1 with $\text{CoK}\alpha$, than with $\text{CuK}\alpha$.

The above considerations suggest that both Selection of wavelength and Sample preparation can be of paramount importance in Rietveld phase quantification. One should not push a correction algorithm such as the Brindley contrast formula outside the limit below which it was meant to be used ($\mu_A D_A > 0.1$), otherwise severe problems may be encountered. In the above case, absorption contrast is a much greater effect than anomalous dispersion. (see section **1.7**)

Table 1: Mass Absorption Coefficients, $\frac{\mu}{\rho}$, for $K\alpha$ -Radiations

Atomic No	Element	Mo λ 0.711 A.	Zn 1.436 A.	Cu 1.542 A.	Ni 1.659 A.	Co 1.790 A.	Fe 1.937 A.	Mn 2.103 A.	Cr 2.291 A.
2	He	0.18	0.31	0.37	0.43	0.52	0.64	0.74	0.86
3	Li	0.22	0.54	0.68	0.87	1.13	1.48	1.76	2.11
4	Be	0.30	1.02	1.35	1.80	2.42	3.24	3.90	4.74
5	B	0.45	2.51	3.06	3.79	4.67	5.80	7.36	9.37
6	C	0.70	4.43	5.50	6.76	8.50	10.7	13.8	17.9
7	N	1.10	6.85	8.51	10.7	13.6	17.3	21.8	27.7
8	O	1.50	11.4	12.7	16.2	20.2	25.2	32.2	40.1
9	F	1.93	14.4	17.5	21.5	26.6	33.0	41.1	51.6
10	Ne	2.67	20.2	24.6	30.2	37.2	46.0	57.6	72.7
11	Na	3.36	25.6	30.9	37.9	46.2	56.9	72.3	92.5
12	Mg	4.38	33.0	40.6	47.9	60.0	75.7	95.2	120
13	Al	5.30	40.0	48.7	58.4	73.4	92.8	117	149
14	Si	6.70	49.5	60.3	75.8	94.1	116	146	192
15	P	7.98	59.4	73.0	90.5	113	141	177	223
16	S	10.0	75.0	91.3	112	139	175	217	273
17	Cl	11.6	85.0	103	126	158	199	245	308
18	A	12.6	93.0	113	141	174	217	270	341
19	K	16.7	119	143	179	218	269	330	425
20	Ca	19.8	142	172	210	257	317	400	508
21	Sc	21.1	153	185	222	273	338	428	545
22	Ti	23.7	167	204	247	304	377	475	603

Table 1: Mass Absorption Coefficients, $\frac{\mu}{\rho}$, for $K\alpha$ -Radiations

Atomic No	Element	Mo λ 0.711 A.	Zn 1.436 A.	Cu 1.542 A.	Ni 1.659 A.	Co 1.790 A.	Fe 1.937 A.	Mn 2.103 A.	Cr 2.291 A.
23	V	26.5	186	227	275	339	422	530	77.3
24	Cr	30.4	213	259	316	392	490	70.5	89.9
25	Mn	33.5	234	284	348	431	63.6	79.6	99.4
26	Fe	38.3	270	324	397	59.5	72.8	90.9	115
27	Co	41.6	292	354	54.4	65.9	80.6	102	126
28	Ni	47.4	325	49.3	61.0	75.1	93.1	116	145
29	Cu	49.7	42.0	52.7	65.0	79.8	98.8	123	154
30	Zn	54.8	49.3	59.0	72.1	88.5	109	135	169
31	Ga	57.3	52.4	63.3	76.9	94.3	116	144	179
32	Ge	63.4	57.6	69.4	84.2	104	128	158	196
33	As	69.5	63.5	76.5	93.8	115	142	175	218
34	Se	74.0	69.4	82.8	101	125	152	188	235
35	Br	82.2	77.0	92.6	112	137	169	206	264
36	Kr	88.1	83.0	100	122	148	182	226	285
37	Rb	94.4	91.5	109	133	161	197	246	309
38	Sr	101.2	100	119	145	176	214	266	334
39	Y	108.9	107	129	158	192	235	289	360
40	Zr	17.2	118	143	173	211	260	317	391

Table 1: Mass Absorption Coefficients, $\frac{\mu}{\rho}$, for $K\alpha$ -Radiations

Atomic No	Element	Mo λ 0.711 A.	Zn 1.436 A.	Cu 1.542 A.	Ni 1.659 A.	Co 1.790 A.	Fe 1.937 A.	Mn 2.103 A.	Cr 2.291 A.
41	Nb	18.7	126	153	183	225	279	338	415
42	Mo	20.2	136	164	197	242	299	360	439
44	Ru	23.4	153	185	221	272	337	404	488
45	Rh	25.3	165	198	240	293	361	432	522
46	Pd	26.7	173	207	254	308	376	450	545
47	Ag	28.6	192	223	276	332	402	483	585
48	Cd	29.9	202	234	289	352	417	500	608
49	In	31.8	214	252	307	366	440	531	648
50	Sn	33.3	230	265	322	382	457	555	681
51	Sb	35.3	245	284	342	404	482	589	727
52	Te	36.1	248	289	347	410	488	598	742
53	I	39.2	269	314	375	442	527	650	808
54	Xe	41.3	283	330	392	463	552	680	852
55	Cs	43.3	298	347	410	486	579	715	844
56	Ba	45.2	307	359	423	501	599	677	819
58	Ce	52.0	358	407	476	549	636	670	235
73	Ta	101	136	164	200	246	305	364	440
74	W	105	143	171	209	258	320	380	456

Table 1: Mass Absorption Coefficients, $\frac{\mu}{\rho}$, for $K\alpha$ -Radiations

Atomic No	Element	Mo λ 0.711 A.	Zn 1.436 A.	Cu 1.542 A.	Ni 1.659 A.	Co 1.790 A.	Fe 1.937 A.	Mn 2.103 A.	Cr 2.291 A.
76	Os	113	152	186	226	278	346	406	480
77	Ir	118	160	194	237	292	362	422	498
78	Pt	123	172	205	248	304	376	436	518
79	Au	128	179	214	260	317	390	456	537
80	Hg	132	186	223	272	330	404	471	552
81	Tl	136	194	231	282	341	416	484	568
82	Pb	141	202	241	294	354	429	499	585
83	Bi	145	214	253	310	372	448	522	612
88	Ra	172	258	304	371	433	509	598	708
90	Th	143	286	327	399	460	536	633	755
92	U	153	310	352	423	488	566	672	805

1.6 Preferred Orientation Corrections

Siroquant allows correction of the profile intensities for preferred orientation of the crystallites of the various phases in the sample. The method is that of Dollase (J. Appl. Cryst., 19, 267 (1986)), which uses the March function. The refinable orientation parameter, r , is less than 1 for plates and greater than 1 for rod morphology. The (hkl) orienting plane, usually a reflection that is abnormally strong (the "plate" reflection) or weak (the "rod" reflection) must be selected. It is always better to prepare patterns with minimal orientation present, but mostly a correction is unavoidable and the inclusion of this correction adds to the power of Siroquant. The only user input is the orientation plane (hkl) indices, input in the menus when the (hkl) file is calculated.

For the convenience of the user, a default orientation plane has been selected for each phase in the Siroquant mineral database. Where the dominant morphology of the crystal is well known, this has been entered as the default. Thus, for example, it is relatively simple to select the following default planes, and these appear as Siroquant defaults:

Mineral Family	Default Orientation Plane	Comment
Clays	001	plates
Carbonates (calcite, dolomite, etc)	104	dominating line
Feldspars	010 or 001	prominent cleavage planes
Cubic materials	100 or 111	cubic or octahedral faces usually prominent
Amphiboles	110	Chains
Micas	001	sheet plane

Table 2: Default Orientation Planes for Mineral Families

The book "Crystal Structures of Minerals", the Crystalline State, Vol. IV, by Bragg and Claringbull (1965) was also consulted, as it gave good indications of structural features likely to result in cleavage planes.

For most minerals, however, orientation planes were not readily obvious. In these cases, the XRD powder pattern of the mineral was examined, in the form of the phase (hkl) file, and the phase entry in the PLOTGR file after a dummy task was run with the mineral included (see Section 4.16). The first candidate for orientation for these phases was then selected as a prominent plane in these files.

The user may find the default orientation plane may not be suitable for their refinement. In this case, examine features in your difference plot for the phase with PREF (i.e. the March r -parameter) set at 1.0 for the phase. A strongly positive peak at a (hkl) position indicates a likely plate orientation, while a strongly negative peak in the difference profile suggests the (hkl) plane is perpendicular to a needle-axis. In either case make the (hkl) line with a strong feature in the difference plot your orientation plane, and try the refinement again.

1.7 Anomalous Dispersion Corrections

This effect has been known for at least 71 years (see de Broglie, "X-Rays, Methuen, London, 1925, p.192). In general, tabulated x-ray atomic scattering factors are practically independent of the incident wavelength (e.g. $\text{CuK}\alpha$, $\text{CoK}\alpha$ and so on) and these are to be found in the form of polynomial coefficients in the International Tables, Volume IV, page 99 (1974). These are used to calculate Structure Factors, $F(\text{hkl})$, and therefore Rietveld pattern intensities, in the Siroquant program.

However, the scattering factor for x-rays becomes dependent on the radiation used if its wavelength is near an absorption edge of the scattering atom. The scattering factor is then

given by:

$$f = (f_o + \Delta f') + i\Delta f''$$

where f_o is the uncorrected (International Tables) scattering factor and $\Delta f'$ and $\Delta f''$ are real and imaginary correction terms. Tables of $\Delta f'$ and $\Delta f''$ have been given for selected tube wavelengths by Dauben and Templeton (Acta Cryst., 8, 841 (1955)) and Cromer and Liberman (J. Chem. Phys. 53, 1891 (1970)).

The effect is serious for samples containing Co, Ni and Cu with $\text{CuK}\alpha$ radiation, Mn, Fe and Co with $\text{CoK}\alpha$ radiation and Cr, Mn, Fe and Co with $\text{FeK}\alpha$ radiation. Rare earth elements can also have large dispersion corrections with common tube wavelengths.

With $\text{CoK}\alpha$ radiation, the biggest dispersion correction for a transition element is for the iron atom ($\Delta f' = -3.349\text{e}$, $\Delta f'' = 0.491\text{e}$). This will give, at $\sin\theta = 0^\circ$, an actual scattering factor of $[(26-3.35)^2 + 0.49^2]^{1/2} = 22.7\text{e}$, instead of the uncorrected value of 26.0e . The depression of the Fe scattering factor with $\text{CoK}\alpha$ at higher angles of 2θ is proportionately a little greater than at $0^\circ 2\theta$. Thus, one should not use $\text{CoK}\alpha$ when quantifying compounds containing iron, unless anomalous dispersion corrections are applied.

An application note has been written on the effect of anomalous dispersion on the Siroquant analysis of phases containing iron with $\text{CoK}\alpha$ radiation. For a mixture of 55% Fe_2O_3 and 45% Al_2O_3 (corundum) it was shown in the Application Note that:

Dispersion Correction	Wt % Fe_2O_3		Wt % Al_2O_3	
	Siroquant	Weighed	Siroquant	Weighed
On	54.2±0.3	55.0	45.8±0.3	45.0
Off	40.9±0.3	55.0	59.1±0.3	45.0

The anomalous dispersion correction is large for Fe compounds with $\text{CoK}\alpha$, as the wavelength of $\text{CoK}\alpha$ (1.79026) is near the FeK-absorption edge (1.74334Å). The dispersion correction "on" scenario must be used here.

In the present version of Siroquant, anomalous dispersion corrections can be applied for the common wavelengths ($\text{MoK}\alpha$, $\text{CuK}\alpha$, $\text{FeK}\alpha$, $\text{CoK}\alpha$, $\text{NiK}\alpha$ and $\text{CrK}\alpha$). The atomic numbers of the elements in the crystalline phases are recorded in the Siroquant database Quantlib V3.mdb for this purpose and $\Delta f'$ and $\Delta f''$ looked up in a Table. The anomalous dispersion correction can be switched on or off as desired. If wavelengths other than given above are used in Siroquant, then the appropriate $\Delta f'$ and $\Delta f''$ values for the elements in the phases can be inserted through the menus. The variation of anomalous dispersion corrections with wavelength and over the Periodic Table is given in Table 3. These corrections in Siroquant are not made with this table. They are instead made with values computed by the method of Cromer and Liberman (1970). Table 3 is for illustration purposes only. Remember: (hkl) files corrected for dispersion must be used only for data from the corresponding X-ray tube. In Siroquant v3 for the standard tubes (Mo, Cu, Fe, Co, Ni or Cr) the values for $\Delta f'$ and $\Delta f''$ coefficients are stored in a binary table in the database. For other wavelengths the values are now calculated when needed.

Table 3: Variation of Anomalous Dispersion Over the Periodic Table

Atomic Number		Cr K α		Cu K α		Mo K α	
		$\Delta f''$	$-\Delta f'$	$\Delta f''$	$-\Delta f'$	$\Delta f''$	$-\Delta f'$
20	Ca	2.7	0.2	1.4	-0.2	0.2	-0.2
21	Sc	3.2	0.7	1.6	-0.2	0.3	-0.2
22	Ti	3.8	1.7	1.9	-0.2	0.4	-0.3
23	V	0.6	4.4*	2.3	-0.2	0.5	-0.3
24	Cr	0.7	2.2	2.6	0.1	0.6	-0.4
25	Mn	0.8	1.8	3.0	0.5	0.8	-0.4
26	Fe	0.9	1.6	3.4	1.1	1.0	-0.4
27	Co	1.0	1.4	3.9	2.2	1.1	-0.4
28	Ni	1.2	1.2	0.6	3.1*	1.2	-0.4
29	Cu	1.3	1.1	0.7	2.1	1.4	-0.4
30	Zn	1.5	1.0	0.8	1.7	1.6	-0.3
31	Ga	1.7	0.9	0.9	1.5	1.7	-0.2
32	Ge	1.9	0.8	1.1	1.3	1.9	-0.2
33	As	2.2	0.7	1.2	1.2	2.2	-0.1
34	Se	2.4	0.7	1.3	1.0	2.4	0.1
35	Br	2.7	0.6	1.5	0.9	2.6	0.3
36	Kr	3.0	0.6	1.7	0.9	2.9	0.6
37	Rb	3.4	0.6	1.9	0.8	3.2	0.9
38	Sr	3.8	0.6	2.1	0.7	3.6	1.4
39	Y	4.2	0.6	2.3	0.7	3.9	2.3
40	Zr	4.6	0.7	2.5	0.6	0.8	2.8
41	Nb	5.1	0.8	2.8	0.6	0.9	2.1
42	Mo	5.6	0.9	3.0	0.5	0.9	1.7
43	Tc	6.2	1.0	3.3	0.5	1.0	1.4
44	Ru	6.7	1.2	3.6	0.5	1.1	1.2
45	Rh	7.3	1.3	4.0	0.5	1.2	1.1
46	Pd	7.9	1.6	4.3	0.5	1.3	1.0
47	Ag	8.6	1.9	4.7	0.5	1.4	0.9
48	Cd	9.2	2.2	5.0	0.6	1.6	0.8
49	In	10	2.7	5.4	0.6	1.7	0.7
50	Sn	11	3.2	5.8	0.7	1.9	0.6
51	Sb	12	4.0	6.3	0.8	2.0	0.6
52	Te	12	5.0	6.7	0.9	2.2	0.5
53	I	14	7.2*	7.2	1.1	2.4	0.5
54	Xe	11	+	7.8	1.4	2.5	0.4
55	Cs	12	12*	8.3	1.7	2.7	0.4
56	Ba	8	11*	8.9	2.1	2.9	0.4
57	La	3	14*	9.6	2.5	3.1	0.3

Atomic Number		Cr K α		Cu K α		Mo K α	
		$\Delta f''$	$-\Delta f'$	$\Delta f''$	$-\Delta f'$	$\Delta f''$	$-\Delta f'$
58	Ce	3	10	10	3.0	3.3	0.3
59	Pr	4	9	11	3.5	3.6	0.3
60	Nd	4	8	12	4.3	3.8	0.3
61	Pm	4	7	12	5.2	4.0	0.3
62	Sm	5	7	13	6.7	4.2	0.3
63	Eu	5	6	11	+	4.5	0.3
64	Gd	5	6	12	12*	4.7	0.3
65	Tb	6	6	8	11*	5.0	0.4
66	Dy	6	6	8	10	5.2	0.4
67	Ho	7	6	4	13*	5.5	0.4
68	Er	7	5	4	9*	5.8	0.5
69	Tm	8	5	4	8	6.2	0.5
70	Yb	9	5	4	8	6.4	0.6
71	Lu	8	5	5	7	6.8	0.7
72	Hf	9	5	5	7	7.1	0.8
73	Ta	10	5	5	6	7.4	0.9
74	W	11	5	6	6	7.8	1.1
75	Re	11	5	6	6	8.1	1.3
76	Os	12	5	6	6	8.5	1.5
77	Ir	13	5	7	5	8.9	1.8
78	Pt	13	5	7	5	9.3	2.0
79	Au	14	6	8	5	9.8	2.4
80	Hg	15	6	8	5	10	2.8
81	Tl	16	6	8	5	11	3.4
82	Pb	16	7	9	5	11	4.0
83	Bi	17	7	9	5	12	4.8
84	Po	18	8	10	5	12	5.6
85	At	20	9	10	5	10	+
86	Rn	20	9	11	5	10	8*
87	Fr	21	10	11	5	7	8*
88	Ra	23	11	12	5	7	7
89	Ac	24	13	12	5	8	7
90	Th	25	15	13	5	8	7
91	Pa	26	17*	14	5	8	7
92	U	19	19*	15	5	8	8*
93	Np	+	+	15	5	5	+
94	Pu	+	+	16	5	5	+
95	Am	+	+	17	6	5	+
96	Cm	+	+	18	6	5	+

+ Not calculated

* These values are uncertain because of proximity to absorption edges.

1.8 Extinction Corrections

If the crystals in the powder are too large and perfect, the intensities of lines of simple phases with large $F(hkl)$'s and low 2θ angles can sometimes be reduced by "extinction". There is a tendency in modern powder work towards the use of actual rocks in an un-ground state and many-pattern batches of XRD patterns over the rock to see trends in phase abundance. Thus, correction of phase patterns for primary extinction, where multiple reflections weakens the main beam, and thus the diffracted intensities, may assume greater importance than previously.

The new extinction correction factor in Siroquant is $SQ/\tanh(SQ)$ where SQ is given by:

$$0.5632 * D(\text{microns}) * d(hkl)(\text{Angstroms}) * p^{0.5} * F(hkl)^2 * / V(\text{cell})(\text{A}^3)$$

and D is a refineable phase crystal thickness, p the X-ray polarisation factor (1 for neutrons), $F(hkl)$ the structure factor of the line, and V the phase unit cell volume.

Crystals with large thickness D and small V , and lines with large d -spacing $d(hkl)$, and large $F(hkl)$ are thus more prone to extinction effects.

D is input in the task file in microns (units of 10^{-4} cm.). In the Long Results File, the refined crystal thickness is given in cm.

For theoretical details, see M.J. Buerger, *Crystal Structure Analysis*, Chapter 8, page 200, K. Lonsdale, *Min. Mag.*, **28** 14-25 (1947), W.H. Zachariasen, *Theory of X-Ray Diffraction in Crystals*, Wiley, NY, (1945) and T.M. Sabine, Chapter 3 in *The Rietveld Method*, Ed. R.A. Young, Oxford University Press, (1993).

1.9 Refineable Phase Overall Temperature Factor

Here, the phase calculated intensities are corrected for an exponential drift over and above that given by the phase temperature factors in the Siroquant Standard Library. This drift may be caused by systematic errors rather than the temperature factor. The correction is of the form $\exp(-\Delta B * \sin^2\theta/\lambda^2)$, where B is in the form of a Debye-Waller "temperature factor" correction.

Note the temperature factors in the Standard Library are in units of $u = 8 * \pi^2 * B.$, i.e. $u = B / 79$.

The starting value for ΔB is entered in the Phase Dependent Parameter dialog. It can be a value near zero. Use of this correction can sometimes reduce residuals by compensating for systematic errors such as absorption or inaccurate diffractometer calibrations.

1.10 Background Level Refinement

The XRD pattern background is fitted to one of the two following polynomials:

$$\text{Function I. } a_0 + a_1(2\theta) + a_2(2\theta)^2 + a_3(2\theta)^3 + a_4(2\theta)^4 + a_5(2\theta)^5$$

$$\text{Function II. } a_{-1} / (2\theta) + a_0 + a_1(2\theta) + a_2(2\theta)^2 + a_3(2\theta)^3 + a_4(2\theta)^4$$

The "a" coefficients can be refined or held constant by clicking a 1 or 0 in the respective columns of the task menu "Parameters, Refinement" screen. In version 3 if you switch between equations the values of the previous equivalent power are retained.

Use of the new background refinement feature is illustrated in the examples below for Quartz/ZnO and cement clinker patterns.

1.10.1 Background Refinement of Demo1.cpi

Visual inspection of the pattern under the Menu "Fit background" screen shows this pattern to have a nearly constant background level of 50 ± 10 counts over the range 23° to 90° of the peaks. Since the background is flat, only the first one or two of the coefficients should be refined.

When the visual circle-clicking background selection procedure of the menus is used, the best refinements give $\chi^2 = 3.4$ and profile $R = \sum | (y_0 - y_c)_i | / \sum (y_0)_i = .22$.

When the background is refined with either of the above functions, on the other hand, $\chi^2 = 2.4$ and profile $R = \sum | (y_0 - y_c)_i | / \sum (y_0)_i = .15$, quite a sizeable reduction in residuals. Further background refinement details for this pattern are given in Table 4.

Table 4: Background Refinement for Demo1.cpi

2θ	Visually Estimated Background	Refined Background Level			
		Background Function I		Background Function II	
		a ₀ refined	(a ₀ +a ₁) refined	a ₋₁ refined	(a ₋₁ +a ₀) refined
23	50±10	58	51	58	44
26	50±10	58	51	58	46
40	50±10	58	55	58	52
45	50±10	58	55	58	53
53	50±10	58	57	58	55
67	50±10	58	60	58	57
74	50±10	58	62	58	57
86	50±10	58	64	58	58
a ₀ (a ₋₁)		58±1	46±3	58±1	-460±116
a ₁ (a ₀)			.22±.05		65±3

It is not advisable to refine more than the first two coefficients for a pattern that has a level background.

1.10.2 Background Refinement of a Cement Clinker pattern

In this pattern, the background is not constant, but drops from 277 counts (visually estimated) at $2\theta=5^\circ$ to 43 counts at $2\theta=70^\circ$. Here, all 6 coefficients can be refined. The cement pattern results are given in Table 5:

Table 5: Background Refinement for Cement pattern

2θ	Visually Estimated Background	Program Background	
		Function I	Function II
5	277	251	279
6	242	231	244
7	180	184	179
18	53	45	49
23	47	39	42
29	50	43	41
36	50	50	45
40	50	50	47
45	50	46	46
49	43	43	44
55	43	37	39
65	43	38	35
70	43	41	40

Table 6: Background Refinement Coefficients for Cement pattern

Coefficient	Function I	Function II
a ₀ or a ₋₁	476(6)	1427(71)
a ₁ or a ₀	-59(1)	20(19)
a ₂ or a ₁	3.1(1)	-9(2)
a ₃ or a ₂	-.071(3)	.5(1)
a ₄ or a ₃	.00078(4)	-.009(1)
a ₅ or a ₄	-.0000033(2)	.000057(6)

The above coefficients have low associated errors and the calculated backgrounds agree well with the observed background levels using the 6 coefficients in either function.

The use of the refineable backgrounds also halves the cement pattern residuals; χ^2 is reduced from 3.4 to 1.7 and the profile R-factor from .22 to .11. Use of refineable backgrounds is recommended here. The background level refinement is robust and converges quickly.

1.11 Rietveld Parameters

In Siroquant the following parameters can be adjusted by least squares:

- (a) Global parameters - line asymmetry and instrument zero.
- (b) Phase parameters - scale, preferred orientation, two sets of halfwidth parameters (U_1 V_1 W_1) and (U_2 V_2 W_2) for the sharp and diffuse lines if present. Pearson-m or Pseudo-Voigt line shape (single or split), and unit cell dimensions for each phase.

See Section 1.3 for a description of the refinement strategies with these parameters.

1.12 Siroquant Flow Diagram

In version 3 PREP, STRUCT and TRACSCAL represent the functions of the original Fortran programs. This and other documents retain them as terms for their original functions. PREP and STRUCT are used to calculate hkl data for each phase whether this be disk files or in memory.

The structure in which PREP, STRUCT and TRACSCAL work together in the Siroquant system to produce a quantitative mineral analysis is shown in Figure 1.

PREP generates (hkl) reflection information and STRUCT attaches structure factors, F(hkl), to this reflection data. The resulting "(hkl) file" for a mineral forms the basis for calculation of its X-ray power diffraction profile in the main program, TRACSCAL, which adjusts the Rietveld parameters.

NOTE: In version 3 the information that would normally be stored in a hkl file for a phase can be calculated when a task is opened provided that the phase is in the Standard Database. User databases still require that a hkl file be generated before the task is set up.

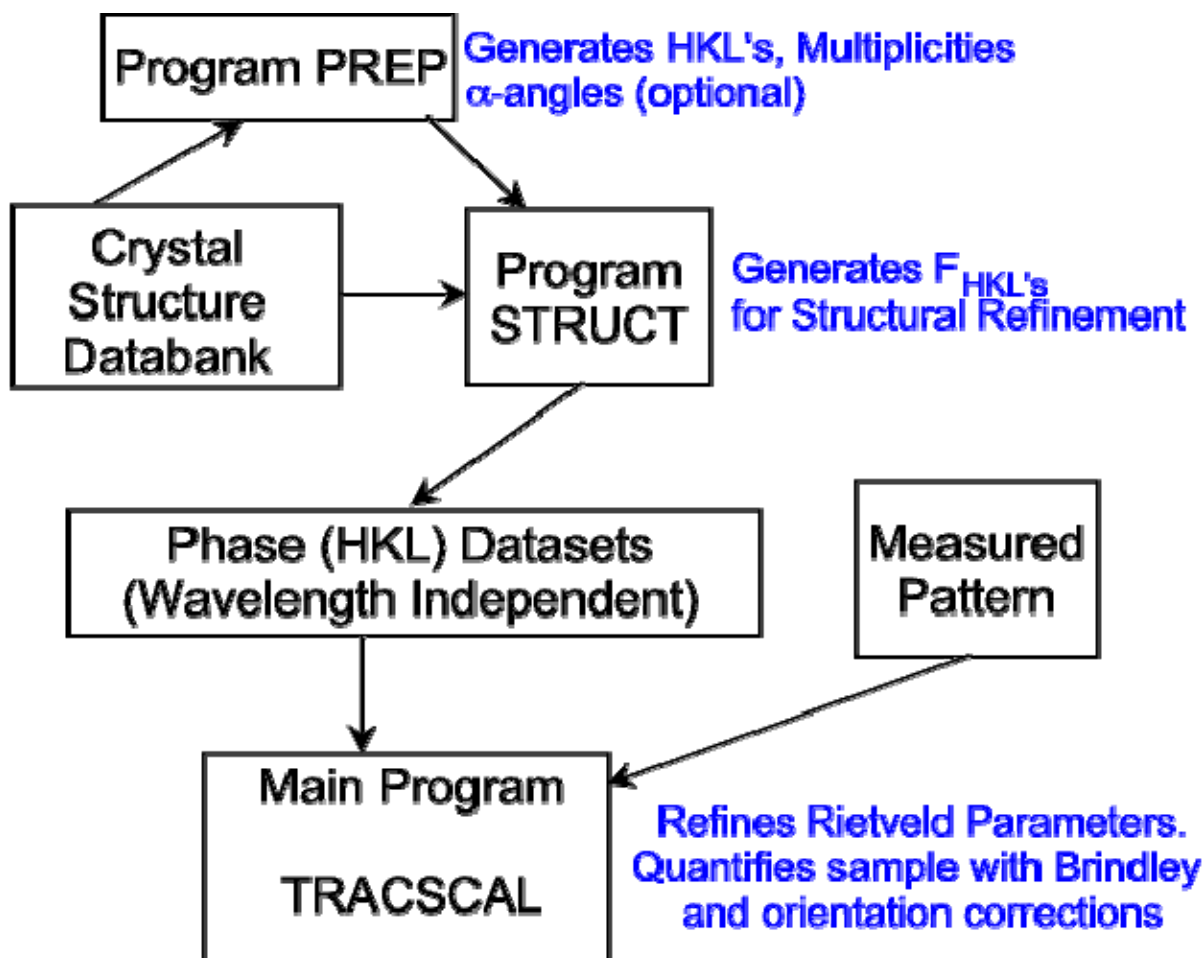


Figure 1: Siroquant System – Quantitative Analysis Program Structure

1.13 Errors and Residuals in a Siroquant Quantification

The Short Results form (menu item **Results/Quantification**) lists the phase names, computed weight percentages and errors associated with the weight percentages. The errors are the square roots of the diagonal elements of the least-squares variance-covariance matrix, and are the “estimated standard deviations”, or e.s.d.’s of the weight percentages. These errors are first given precisely as they come out of the least-squares process, (not multiplied by any factor in an attempt to correct for systematic errors in the least-squares model). It should be kept in mind however, that the least-squares e.s.d.’s could be underestimated because of factors not considered in the model.

Prince (The Rietveld method, e.d. R.A. Young, Oxford University Press 1993, p.51) suggests the ratio of the pattern R-factor to the expected pattern R-factor could be used as an estimate of the factor which could be applied to the computed e.s.d.’s to make them ‘true’ e.s.d.’s. This idea is used as the basis of giving an estimate of the factor to apply. Examination of a number of task results showed that the ratio R(actual) to R(expected) for the patterns was close to χ , the square root of χ^2 where:

$$R(\text{actual}) = \frac{\sum |Y_o - Y_c|}{\sum |Y_o|}$$

$$R(\text{expected}) = \left(\frac{NO - NV}{\sum Y_o^2} \right)^{\frac{1}{2}}, \text{ and}$$

$$\chi^2 = \left(\frac{\sum \left(\frac{(Y_o - Y_c)^2}{Y_o} \right)}{NO - NV} \right)^{\frac{1}{2}}$$

The Siroquant Short Results file lists phase, weight percent, and computed and actual errors, e.g.

Phase	Weight %	Computed Error, e	Actual Error, e*CHI
Hematite, etc	54.1	0.12	0.23

In the above example, chi squared was 3.66, and chi 1.91. In most examples, it was found that the necessary factor to convert computed to real e.s.d's was about 2. The errors are \pm the values given.

1.14 Phases with no Published Crystal Structure in the Siroquant Databank

Because Siroquant has the very desirable feature of being able to substitute $F_o(hkl)$ for $F_c(hkl)$ in the Rietveld calculation (the (hkl) file is then an "observed" instead of a "calculated" (hkl) file) one can quantify phases for which there is no published crystal structure available. Clays are an important mineral group having very disordered and ill-defined structures - many common clays have been included in the databank and these are specified in the Clay Package Manual (see chapter 3). The Siroquant user does not prepare (hkl) files for these structurally disordered mineral phases; these are already supplied for use with Siroquant. The content of the Clay Pack hkl files is stored in the Standard Database rather than disk hkl files.

From time to time Siroquant users have encountered non-clay phases for which no crystal structure data could be found. Observed (hkl) files were prepared for these phases and supplied to the users.

These phases are specified in Table 7. Note as from Version 2.5 observed hkl files will have serial numbers 5001 or greater. The observed hkl files with version 3 are stored in the Standard Database. They are also provided as disk hkl files and are located, for the standard setup, in the directory "C:\Program Files\Siroquant\v3\Observed". Note that (hkl) files cannot be prepared for these entries.

Table 7: Observed HKL files provided with Siroquant

Special Phase (No Crystal Structure Data)	Database Serial #	Name of "Observed" (hkl) File
para-Spurrite	5197	pspurr1.hkl
Pyrrhotite-5c	5199	pyrr5c_1.hkl
CaSiF ₆	5235	CaSiF61.hkl
Theta-alumina	5299	thal1.hkl
Talc, disordered	5320	talb1.hkl

1.15 Program Language


Unless otherwise acknowledged Siroquant executable code is completely original and has been written specifically for the purpose of XRD quantitative analysis. It is not a modification of any public domain program previously written with other purposes in mind.

Siroquant version 3 is entirely written in Delphi 6 with the previous FORTRAN code converted to DELPHI code, the program is no longer reliant on spawning any other program in a DOS box or otherwise. TeeChart is used as the graphics control and some LMD components are used. The program, as developed, may use a lot of computer memory especially if many task windows are open.

Delphi is a product of Borland Software Corporation (www.borland.com)

TeeChart is a product of Steema Software (www.Steema.com).

LMD components are from LMD Innovative (www.lmdinnovative.com)



2. Literature on the Rietveld method & Siroquant

2.1 Recommended Text On Rietveld Analysis

The Rietveld (1969) refinement method of least squares fitting of measured to calculated XRD profiles and extracting various parameters is complex and can be somewhat daunting to the beginner.

For those starting with the Siroquant Manuals, the text "The Rietveld Method", edited by R.A. Young, (Oxford University Press, 1993) is recommended. This textbook tends to cater for the XRD specialist, rather than the beginner or laboratory technician, but contains useful overviews of many aspects of the subject of Rietveld analysis, except quantification.

A comprehensive text "Industrial Applications of X-ray Diffraction" (ed. D.K. Smith and F.H. Chung, Marcel Dekker, N.Y., 2000) has very recently appeared and covers basic descriptions of XRD, many developments since 1993 and lists many industrial applications of Rietveld analysis including quantitative analysis.

The Monograph "Modern Powder Diffraction" (Reviews in Mineralogy, Volume 20, Mineralogical Society of America, 1989) has some excellent reviews of the subject of XRD for those entering the field, while of course, the book of Klug and Alexander, "X-ray Diffraction Procedures for Polycrystalline and Amorphous Materials" (2nd Edition, 1974, Wiley) is still the classic XRD text. Cullity (1978) "Elements of X-ray Diffraction" (Addison-Wesley) is a very readable introductory text, while more recently, Jenkins and Snyder (1996) "Introduction to Powder Diffractometry" have produced another very useful up-to-date basic text for X-ray analysis laboratories.

A textbook titled "Rietveld Made Easy" was published in December 2001 written by Dr John Taylor and Dr Ihor Hinczak. This book is intended to give the user a grounding in the crystallographic theory behind Rietveld analysis and its application by the Siroquant software. This book is available from Sietronics (email: spl@sietronics.com.au).

In addition to these basic texts, an introduction to non-Rietveld and Rietveld XRD analysis has been written illustrating use of the method with the difficult but important application of Portland cement. This occurs as Chapter 1 entitled "X-Ray Powder Diffraction of Cements", by J.C. Taylor, L.P. Aldridge, C.E. Matulis, and I. Hinczak, in the Monograph "Structure and Performance of Cements", 2nd Edition, Eds P. Barnes, J. Bensted, Spon Books, U.K. which was published in 2002. This chapter describes how Rietveld refinement has revolutionised the field of XRD phase quantification of cements since its introduction in 1990. In pioneering papers in this field, the present program, Siroquant has featured significantly, and the papers of Taylor, Aldridge, Matulis and Hinczak, using Siroquant, listed in section 2.3 below, are now frequently cited by other authors. This chapter on cement XRD Rietveld phase analysis has 30 pages and 103 references to the end of 2000.

2.2 Benchmark Paper on Siroquant

A description of the Siroquant system has been given in the paper "Computer Programs for the Standardless Quantitative Analysis of Minerals Using the Full Powder Diffraction Profile", by J.C. Taylor, in the journal "Powder Diffraction", Volume 6, pages 2-9 (1991).

This paper gives:

- Mathematical theory of Siroquant.
- Descriptions of absorption contrast, preferred orientation and amorphicity correction factors.
- Descriptions of the programs in the system.
- Crystal Structure Databank contents.
- Performance of Siroquant on various applications.

2.3 Siroquant and Rietveld Analysis References

In addition to the basic XRD references given in section 2.1, the following references, mainly associated with the development of Siroquant, are given.

- Taylor, J.C. (1991). Computer Programs for Standardless Quantitative Analysis of Minerals Using the Full Powder Diffraction Profile. *Powder Diffraction*, **6**, 2-9.
- Taylor, J.C. and Clapp, R.A. (1992). New Features and Advanced Applications of Siroquant: a Personal Computer XRD Full Profile Quantitative Analysis Software Package. *Advances in X-Ray Analysis*. **35**, page 49.
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- Rietveld, H.M. (1969). A Profile Refinement Method for Nuclear and Magnetic Structures. *J. Appl. Cryst.* **2**, 65 (1969).
- Taylor, J.C. (1985). Technique and Performance of Powder Diffraction in Crystal Structure Studies. *Aust. J. Phys.*, **38**, 519-538.
- Taylor, J.C., Miller, S.A. and Bibby, D.M. (1986). A Study of Decomposition Methods for Refinement of H⁺-ZSM5 Zeolite with Powder Diffraction Data. *Z. Krist*, **176**, 183-192.
- Taylor, J.C. (1987). A Comparison of Profile Decomposition and Rietveld Methods for Structural Refinement with Powder Diffraction Data. *Z. Krist*, **181**, 151-160.
- Taylor, J.C. (1987). Locations of Deuterobenzene Molecules in the Synthetic Zeolite ZSM-5 at 77 K by Powder Neutron Diffraction. *Zeolites*, **7**, 311-318.
[Because the structure refinement feature is DOS-based, this is not supported from Siroquant, Version 2 onwards].
- Dollase, W.A. (1986). Correction of Intensities for Preferred Orientation in Powder Diffractometry: Application of the March Model. *J. Appl. Cryst*, **19**, 267-272.
- Taylor, J.C. and Aldridge, L.P. (1993). Full-Profile Quantitative XRD Analysis of Portland Cement: Testing of Possible Standard XRD Profiles for the Major Phase Tricalcium Silicate. *Powder Diffraction*, **8**, 138-144.
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3.0 Siroquant Clay Package Manual

3.1 Introduction to the Siroquant Clay XRD Quantification Method

Traditional XRD methods for clay quantification typically involve physical separation of the clay material and analysis of the (00l) reflection profiles on traces prepared from fully oriented samples. This analysis can be done with programs such as NEWMOD (Reynolds, R.C. (1980), in "Crystal Structures of Clay Minerals and their X-Ray Identification", ed. Brindley and Brown 1980), but is not suitable for use by a non-specialist, as detailed input on layer stacking sequences in the clay is required.

The disadvantages of this approach can be summarised as follows:

1. The special sample treatment is labour intensive.
2. The sample is altered by the treatment.
3. Layer stacking input details are required.
4. Clay and non-clay minerals are treated separately.
5. The fundamental premise of powder diffraction, namely that the crystallites should be randomly oriented, is ignored. The aim of powder diffraction should be to reduce preferred orientation effects, not maximise them. Although the (00l) reflections from a fully oriented clay specimen are strong, their absolute scaling is difficult because theories of preferred orientation correction, e.g. the March model (Dollase, 1986), break down with perfect orientation.
6. Because of the strong orientation in the traditional method, the great bulk of clay XRD data, namely the (hkl) reflections, is lost, as these planes are never in diffracting Bragg angle positions.

The traditional one-dimensional XRD analysis method for the clays is thus not only time consuming, but is also flawed in its approach.

A completely new method was developed for Siroquant allowing the Rietveld quantification of minerals, e.g. clays, with unknown or imperfectly known crystal structures. The Siroquant Clay Package is extremely easy to use and disordered clays are refined just like any normal mineral. All clay parameters (linewidth, preferred orientation, unit cells, etc) are refinable, as for the non-clay minerals.

This method was developed to coincide with the release of Siroquant Version 2, and is called the Siroquant Clay Package. This consisted of a collection of demonstration (template) tasks for the common disordered clays, including montmorillonite, halloysite, disordered kaolins, and so on. Each task was provided an "observed (hkl) file" for the particular clay, which was fully standardised and generated a Rietveld XRD profile that matches a measured clay pattern.

With Siroquant Version 3, the Clay Pack hkl files are now stored in the Standard Database and used like any other phase in the database. Use the Select from Standard Database page when specifying a Clay Pack file. For a quick view of all the clays in the claypack, uncheck the Normal and Observed options on the Search tab. Clay Pack phases have reference numbers greater than 8000.

Important: In Version 3 do not attempt to use the previous version disk hkl files whether directly or modified. The program will not accept any disk hkl files with a reference ID greater than 8000. When converting tasks from earlier version the program will automatically reference the appropriate hkl file in the database. If you have parameters that must be permanently changed then change them in a newly set up task or use suitably set up template files. Existing tasks can be used as templates but remember the initial value of refinable parameters will be as either last refined (and saved) or otherwise altered.

The new Siroquant Clay Package has many advantages over conventional clay XRD quantification using separated, oriented clays. These advantages are summarized below:

- No knowledge of the crystal structure of the clay is required. The $F_0(hkl)$ in the observed (hkl) file bypass the need for detailed structural analysis. Preparation of these files can be tedious and requires knowledge of chemical crystallography but, once prepared, the observed (hkl) file for a particular type of clay is universal, i.e. it can be used to quantify any other clay of that type. The “observed (hkl) file” concept is therefore a new and powerful Rietveld analysis tool.
- Clay and non-clay minerals are quantified in the one Siroquant run.
- The sample is not altered and lengthy sample treatments are avoided.
- The dual halfwidth feature allows modelling of sharp and diffuse reflections in the diffraction bands.
- Preferred orientation, unit cells, lineshapes and linewidths are fully refinable.
- Calibration curves for loss of intensity at low angles are used.
- Clays are treated like any other mineral, except the clay “observed” (hkl) files are supplied in the Standard Database.
- Random orientation of the crystallites is more in harmony with the conventional theory of powder diffraction, rather than the complete clay orientation of the traditional clay XRD methods.

3.2 Clay Minerals in the Siroquant Clay Package

The following clay minerals have reasonably good descriptions in terms of (x, y, z) coordinates and have been entered into the Siroquant Crystal Structure Database, Quantlib V3.mdb. The second halfwidth feature can be used for these clays. Compute your (hkl) file for these clays in the usual way through the menus; use of the two-halfwidth feature may be necessary:

Ordered kaolin, dickite, nacrite, chlorite, chamosite, sepiolite, palygorskite, vermiculite, lizardite, talc, pyrophyllite, phlogopite, celadonite and clay-like minerals (9 micas and 9 amphiboles).

The following clays have imperfectly known or unknown crystal structures and are included in the Clay Package as observed (hkl) files:

Montmorillonite, illite, kaolins with varying degrees of disorder, halloysites, palygorskites (attapulgites), mixed layer mica-montmorillonite and clay-like minerals chrysotile and antigorite.

Clays of both types (well-known and unknown structures) can be given broad and sharp (hkl) reflections using the dual-halfwidth feature, and these halfwidths are refinable.

3.2.1 Inclusion of New Clay Minerals

Clay varieties may be encountered which do not fall into the above groups entered into the Siroquant Clay Package. If this happens we suggest you forward a sample (as phase-pure as possible) to Sietronics Pty Ltd, and an “observed (hkl) file” for your clay will be prepared for you (for a fee to cover costs). Once prepared, this file is universal and can be used to quantify all further clays of that type. As the observed (hkl) file preparation can be tedious, involving assessment of available crystal structure data, line indexing, determination of (hkl) population density over the broad (hkl) bands, and final standardisation of the file absolute scaling, we recommend you contact us for addition of these minerals.

Experienced crystallographers may wish to create their own “observed (hkl) file” for the clay. The references (Section 2.3) outline the general approach needed. This could take you some time in collection of long-exposure XRD patterns of standard mixtures and “observed (hkl) file” creation and scaling. If you do make your own “observed” (hkl) file, we would appreciate a copy of the file for checking and possible inclusion in later versions of the

Siroquant Clay Package, which would allow others to quantify the same type of clay.

However, you will probably find it easier to send a sample of the clay to Sietronics as it only takes us approx 3 weeks to prepare an observed (hkl) file with certain utilities that have been prepared for rapid file preparation.

3.3 Using the Siroquant Clay package:

The clays in your sample must first be identified. Traditional methods, such as addition of ethylene glycol to check whether the clay has swelling properties, can be useful here. The present Siroquant method, however, differs from the traditional clay-separation, one-dimensional oriented refinement approach outlined above.

Instead of using limited (ool) XRD data with physically separated clays, as in the traditional approach, it is considered better to use the powerful Rietveld (1969) method on the original, ground, but otherwise untreated sample, with the full three-dimensional XRD profile collected from a sample in which the crystallites are randomly oriented. In effect, the clays are treated in exactly the same manner as the non-clay phases in the new Siroquant method, avoiding an artificial distinction between clay and non-clay minerals. This is possible because of the unique program structure of the Siroquant system (Taylor, 1991).

Figure 2 shows how phase (hkl) files play a pivotal role in the program structure. From crystal structure data for a mineral in the Siroquant Crystal Structure Databank, a (hkl) file is created, containing a calculated structure factor, $F_c(\text{hkl})$ for each reflection. This defines the intensity of the (hkl) reflection.

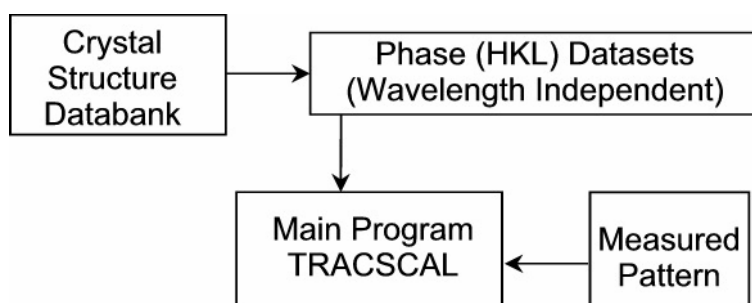


Figure 2. Siroquant Modified Rietveld Method: Pivotal Role of the (hkl) File in the Program Structure

At first sight, it would seem impossible to quantify disordered clays in Rietveld analysis, because precise crystal structure data are not available for these clays, e.g. illites, montmorillonites, and mixed-layer clays. The solution to this problem is simple and is shown in Figure 2. If we substitute the calculated $F_c(\text{hkl})$ in the (hkl) file with *measured* $F_o(\text{hkl})$ taken from the XRD pattern of the clay, suitably scaled, then the problem of the flawed crystal structure data for the clay is overcome. In summary:

- (a) (hkl) Files contain $F(\text{hkl})$ values which define the pattern line intensities:
- (b) Normal Rietveld: $F_{\text{calc}}(\text{hkl})$ values are calculated from a crystal structure - "calculated (hkl) file".
- (c) Modified Rietveld: $F_{\text{obs}}(\text{hkl})$ values are derived from the measured phase XRD pattern. This "observed (hkl) file" is used for clays with ill-defined crystal structures.

Note that although the new Siroquant program has integrated the previous version's TRACSCAL program the refinement part of the program is still referred to as 'TRACSCAL'.

3.4 Historical: Development of the Siroquant Observed HKL Method

3.4.1 The first application of the observed HKL method:

The observed (hkl) file technique was first used to quantify structurally disordered pseudorutile in beach sands (Taylor and Zhu Rui, 1992). It was then applied to the major phase in Portland cement, alite (Taylor and Aldridge, 1993; Taylor, Zhu Rui and Aldridge, 1993). Preparation of observed (hkl) files and use of this new Rietveld method is described in these publications. An obvious extension is in quantification of clays, where ill-defined crystallinity is common.

3.4.2 First clay application: Montmorillonite (1993)

The first application of the “observed (hkl) file” method of clay XRD quantification was with the swelling clay, montmorillonite. The standard montmorillonite selected was an Algerian bentonite, which contained 1% quartz as an impurity. In the literature, no attempts at defining its crystal structure in terms of (x, y, z) coordinates were made after 1935. The model of Magdefrau and Hofmann (1935) was flawed, but sufficient for indexing and calculation of a rough XRD profile, which was then adjusted to fit the measured XRD profile by changing the F_c (hkl) values given by their model. A multiple cell was necessary to provide sufficient (hkl), especially near the leading edges of the diffraction bands. Absolute scaling of the montmorillonite observed (hkl) file was achieved by Siroquant refinement of XRD patterns of eight bentonite-quartz mixtures. The normalised observed (hkl) file was then found to successfully quantify six other natural montmorillonites, confirming the validity of the new method. The fact that the same observed (hkl) file could be used to quantify all other natural montmorillonites suggested the amorphous content did not vary greatly over the specimens studied. Differences in interlayer cations in different montmorillonites were probably unimportant in quantification, as these did not contribute to the diffraction, being strongly disordered. Different degrees of hydration could be corrected for by varying the c-axis length (making sure the minimum angle for unit cell refinement in the global parameters (Menu) was set at a low angle, e.g. $3^\circ 2\theta$), to include the first (001) reflection in any cell refinement. The orientation parameters and linewidths also varied significantly from one montmorillonite to another, as shown in Table 1. Despite the large variations in W_1 and W_2 in the natural montmorillonites (the sharp line W_2 values varied from 0.13(3) to 0.31(4) and the broad W_1 values from 1.27(1) to 6.7(1)), the program quantified these montmorillonites successfully, as shown in Table 2. The dual halfwidth function gave good profile fits for the other montmorillonites also.

A paper on the montmorillonite quantification study has appeared in the journal “Powder Diffraction” (Taylor and Matulis, 1994a). Approximately 20 XRD patterns were analysed with Siroquant in the creation, standardisation and testing of the montmorillonite observed (hkl) file.

Table 1: Orientation Parameters and “Sharp” and “Broad” Linewidth Parameters for Standard Montmorillonites

Standard Montmorillonite	March Function Orientation Parameters	W_1 (Broad)	W_2 (Sharp)
Chambers	0.94(1)	1.36(1)	0.13(3)
SWA-1	0.88(1)	2.25(1)	0.16(5)
SAZ-1	0.97(1)	1.27(1)	0.17(3)
SM-23	1.02(1)	3.83(4)	0.26(5)
Osage	1.01(1)	6.7(1)	0.31(4)
SCA-2	0.89(1)	2.83(2)	0.21(3)

Table 2: Some Standard Quartz - Montmorillonite Mixtures[†]

Montmorillonite Standard	Wt % Montmorillonite	Method
Chambers (Ariz.) #23	70.5	Weighed
	67.2±0.4	Siroquant
Ferruginous Smectite SWA-1	73.7	Weighed
	72.8±0.4	Siroquant
Osage (Wards)	65.9	Weighed
	70.5±0.5	Siroquant
SCA-2 (Calif.)	68.0	Weighed
	66.8±0.4	Siroquant
Bentonite, SM-23	69.9	Weighed
	68.5±0.4	Siroquant
Cheto (Ariz.) SAZ-1	70.6	Weighed
	67.5±0.7	Siroquant

3.5 Bragg-Brentano Intensity Calibration Curves

After the background has been removed from the XRD pattern of a sample containing clay, the background-corrected pattern (.CPB) needs to be corrected for the significant loss of intensity at low angles found in the Bragg-Brentano geometry. This is important for clays, which have strong peaks at low 2θ angles (sometimes $5-10^\circ 2\theta$, where the correction factor may be as much as 5). If you do not calibration-correct your patterns, the clay assay will be low relative to the non-clay minerals.

Refer to the User Manual for details of Calibration Corrections.

3.6 Clay Minerals Included In The Siroquant Version 3, Clay Package

3.6.1 *Clays with Reasonably Well-Determined Ordered Crystal Structures*

The following clay minerals (Table 3) have reasonably well-described crystal structures, and have been entered into the Siroquant Crystal Structure Standard Database. The second-halfwidth feature can, of course, be used for these clays if necessary. The (hkl) files for these clays are computed in the normal way through the menus (see File - "prepare (hkl) file"). Calculated (hkl) files for these clays, computed in the normal manner, are supplied on the distribution disc, and will work for any radiation wavelength. These are all oriented on the c-axis.

[†] Impurity phases in quartz and standards were also quantified.

Table 3: Ordered Clay Minerals in the Siroquant Standard Database

Clay Mineral	QUANTLIB V3.MDB Database	
	Serial Number	Header
Celadonite	85	Celadonite
Chamosite	174	Chamosite
Chlorite	84	Chlorite
	175	Chlorite, Chromium
Dickite	171	Dickite
Kaolin, ordered	28	Kaolin (Wyckoff)
	58	Kaolin (Young)
	185	Kaolin (Bish)
Nacrite	179	Nacrite
Lizardite	167	Lizardite, 1T
Palygorskite (Attapulgitite)	122	Palygorskite
Phlogopite	83	Phlogopite
Pyrophyllite	87	Pyrophyllite, (Rayner & Brown 1965)
	95	Pyrophyllite, 1T _c dehydroxylate
	218	Pyrophyllite, 1T _c
Sepiolite	177	Sepiolite
Talc	86	Talc
	206	Talc
Vermiculite	23	Vermiculite

3.6.2 Clay-like Micas and Amphiboles (Ordered) in the Standard Database

The following clay-like mica and amphibole minerals (Tables 4 and 5) are included in the Standard Database. Their (hkl) files are calculated in the normal way. If their lines are broadened, or if some of their lines are made sharp and others diffuse, then their patterns may be similar to some clay profiles (e.g. an illite pattern may be similar to broadened muscovite). These minerals are listed here for reference purposes. Calculated (hkl) files for these clay-like minerals and precursors are supplied on the distribution package, and can be used with any wavelength.

Table 4: Micas in the Standard Database

Mica Mineral	Serial Number	Header
Biotite	153	Biotite (manganophyllite)
	225	Biotite, 1M
	226	Biotite, 2M ₁
Chloritoid	103	Chloritoid (triclinic)
	104	Chloritoid (monoclinic)
Clintonite	176	Clintonite, 1M
Margarite	227	Margarite, brittle mica
Muscovite	82	Muscovite

Table 5: Amphiboles in the Standard Database

Amphibole Mineral	QUANTLIB V3.MDB	
	Serial Number	Header
Actinolite	220	Actinolite
Anthophyllite	222	Anthophyllite
Crocidolite	217	Crocidolite
Cummingtonite	219	Cummingtonite
Glaucophane	223	Glaucophane
Grunerite	224	Grunerite
Hornblende	152	Hornblende
Tremolite	178	Tremolite

3.6.3 Clays With Imperfect (Defect) or Unknown Crystal Structures

The clays listed below have either very disordered or unknown crystal structures (Table 6). For the first time, these common disorder clays can now be included in full Rietveld refinements together with the non-clay minerals, using the present Siroquant Clay Package with unaltered samples. For these clays, an “observed” (hkl) file is supplied for use with Siroquant and stored as an hkl file image in the Standard Database.

Included are montmorillonite, illite, halloysite, palygorskite, a mixed-layer illite-smectite, antigorite, and a tridymite-based file which can be used to quantify opaline amorphous humps. 1T_c kaolin is represented by two moderately ordered kaolins and two highly disordered kaolins. Another form of kaolin is 1Md kaolin (disordered). These examples cover most of the common disorder clays. See Table 6 for details.

Table 6: Clays With Imperfect or Unknown Crystal Structures in the Clay Package.[‡]

Clay Mineral in Siroquant Clay Package	Crystal Structure Status	Ref. ID Number
Antigorite	Modulated structure (unknown)	8237
Halloysite	Curved lattice (unknown)	8161
Illite	Mica-like (unknown)	8146
Moderately Ordered 1T _c Kaolin, No 1.	Unknown	8240
Moderately Ordered 1T _c Kaolin No 2	Unknown	8440
Disordered 1T _c Kaolin produced by grinding Kaolin No 2	Unknown	8441
Highly Disordered 1T _c Kaolin	Unknown	8442
Highly Disordered 1Md Kaolin	Unknown	8239
Montmorillonite	Poorly Known	8137
Amorphous Opal,	Amorphous, Tridymite-like	8101

[‡] When a file name of the Demonstration task contains a number, this denotes the weight percentage of the standard, e.g. quartz, which has been added.

Clay Mineral in Siroquant Clay Package	Crystal Structure Status	Ref. ID Number
Tridymite-based Palygorskite (Attapulgitite)	regions Poorly Known	8237
Mixed-Layer Illite-Smectite	Unknown	8236
Meta-Kaolin	Unknown	8274

The sources of the standard clays used in preparing the “observed” (hkl) files for the Siroquant Clay Package are as follows:

Table 7: Sources of Standard Disordered Clays

Clay Mineral in Siroquant Clay Package	Source of Standard Clay(s)
Antigorite	Western Australian antigorite
Halloysite	API #12 clay standard for the observed (hkl) file then checked with seven natural halloysites
Illite	Standard Clay IMT-1
Moderately Ordered 1T _c Kaolin, No 1	New Mexico Kaolin Standard
Moderately Ordered 1T _c Kaolin, No 2 (SWK)	Industrial source
Disordered 1T _c Kaolin, produced by grinding of SWK Kaolin	Industrial source
Highly Disordered 1T _c Kaolin	Kalgoorlie (WA) Kaolin
Highly Disordered 1Md Kaolin	North Queensland Kaolin
Montmorillonite	Algerian Bentonite
Amorphous Opal, Tridymite based	Silica Fume
Palygorskite	Attapulgitite, Attapulgitus, Georgia
Mixed-Layer Illite-smectite	Standard Clay SYN-1

3.7 Using the Clay Package in Siroquant Version 3

3.7.1 Introduction

The Clay Package will be set up when you set up Siroquant Version 3. Earlier versions of Siroquant must continue to access the Clay Pack files as supplied with their respective versions. The default setup gives:

C:\Program Files\Siroquant\v3\EXAMPLES - the examples in Table 6. Some examples have an internal standard added to the clay.

C:\Program Files\Siroquant\v3\CLAYS - the (hkl) files listed in Tables 3, 4 and 5 for clays with “normal” crystal structures.

The clay (hkl) files supplied in the database are not corrected for anomalous dispersion and

work with any tube. They are standardised to absolute intensities and an aberration-free diffractometer.

All the Clay Pack (hkl) files stored in the Standard Database have ID numbers greater than 8000 on their headers (numbers greater than 8000 are for supplied observed (hkl) files). The Clay Pack (hkl) file names appear in the menu boxes just like any normal (hkl) file and are set up into a task in the usual way (File/New Task or File/Edit Current Task).

3.7.2 *Setting Up a task to include an Observed HKL File*

Set up your task clay mineral in the task in exactly the same way as you would for a normal non-clay mineral. The only difference here is that the (hkl) file is a binary image of an hkl file and does not have to be generated on-the-fly. The (hkl) file name for the clay will appear in the menus for preparing the task.

Do not forget to subtract your background and apply the calibration correction curve with the menus. If the pattern is not calibrated, errors in the clay weight percentages will result, giving a clay weight percentage that is too low.

After your task has been prepared perform the Siroquant refinement in the normal way, refining the special clay parameters just like those for any other mineral.

Golden Rule 1: Use the observed (hkl) file for the clay as supplied, unchanged. These special observed (hkl) files should never be edited.

Golden Rule 2: Do not change the list of (hkl) having the second halfwidth W_2 given on the template task in Parameters/Halfwidth Parameters, as this defines the sharp reflections for the clay diffraction bands for the standard clay of that type. These (hkl) are listed (IWIDTH =2, Sect 5.4) after the values of $(U_2V_2W_2)$ for the clay phase. You can, however, refine W_2 ($U_2 = V_2 = 0$ usually), the second halfwidth for the sharp lines of the clay.

3.7.3 *Summary of Clay Package Operation*

It is very easy to use the Siroquant Clay Package. The only difference from normal refinement is that clay (hkl) files are supplied and never changed, or generated from the menus, like ordinary (hkl) files. Load a clay (hkl) file into a task just as you would a non-clay mineral. The two halfwidth parameters W_1 and W_2 , orientation and cell dimensions are also refined for the clay.

3.8 Clay References

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4. Technical Descriptions

4.1 HKL Files

At the heart of Siroquant operation is the concept of a "(hkl) file". A (hkl) file of a mineral contains data that allows the main program TRACSCAL to calculate a synthetic XRD pattern for that mineral. For example, a (hkl) file for rutile to a d-spacing of 1.423Å is shown below (a-axis oriented, some decimal places deleted for simplicity).

In Version 3 the values that would have been stored in an hkl file can be calculated when a task is loaded as long as the phase is from the Standard Database. HKL files are still required if a phase is from a user database and databank combination. They can also be generated from the Standard Database if the user wishes.

Version 2 and 2.5 hkl files are still valid in Version 3 and can be generated if necessary.

The format for all types of hkl files can be found in file formats.

From Version 2.0 onwards, TRACSCAL (the refinement program) no longer directly accesses the mineral databank. All phase-dependent defaults are now in the header, and there is a version number for future compatibility.

4.2 Program PREP

PREP.PAR is not used in version 3.

4.3 Program STRUCT

STRUCT.PAR is not used in version 3.

4.4 The Two-Halfwidth Feature

4.4.1 General Description

Each mineral, clay or non-clay, is allowed two halfwidth functions for its (hkl) reflections, namely $(U_1V_1W_1)$ and $(U_2V_2W_2)$. For the definition of U, V and W, the so-called halfwidth parameters for a parabolic linewidth function, see Rietveld (1969), in the References Section 2.3. Each (hkl) line in the profile of a phase is assigned either to the (U_1, V_1, W_1) or (U_2, V_2, W_2) halfwidth function.

This assignment is done in the menus under "HALFWIDTH PARAMETERS" in one of two ways:

- (a) The second halfwidth function can be assigned to a certain "zone" of reflections e.g. the (hkl) zone.
- (b) Certain reflections of the phase can be selected by double-clicking on the (hkl) triplet and passed over to the (U_2, V_2, W_2) box. This is the recommended approach and is perfectly general. For example, the (001) reflection can be left in the $(U_1V_1W_1)$ box and the (002) reflection placed in the $(U_2V_2W_2)$ box.

This feature allows modelling of the sharp leading edges of clay (hkl) bands. The d-spacing of the leading-edge reflections are measured on the graphics, and the sharp (hkl) reflections identified. They are then moved into the $(U_2V_2W_2)$ box. This feature was used in preparing the observed clay (hkl) files provided in the Siroquant Clay Package.

4.4.2 Details of the 2-Width Feature in the TRACSCAL Program .TSK File

See the task file format to see how the changes are saved in the task file.

The halfwidths [UVW] screen displays $(U_1V_1W_1)$ and $(U_2V_2W_2)$ and indicates which (hkl) reflections are in the "sharp" and "broad" boxes. The "Zone" option allows selection of the zone, e.g. hk0, with the second halfwidth. The "All" option allows transference of reflections from the $(U_1V_1W_1)$ box to the $(U_2V_2W_2)$ box or vice-versa by double clicking.

The “Two-Width Functions per Phase” option is essential for use of the Siroquant Clay Package and useful for quantification of any disordered material with anomalies in the line halfwidths.

4.5 Line Shape Functions used in Siroquant

To allow for fine differences in the line-shape function for different diffractometers, a second line shape function, the pseudo-Voigt, has been included in Siroquant. Like the Pearson VII function, a single parameter, the mixing parameter η , is refined. η is a measure of the Lorentzian-Gaussian ratio in the peak shape. A typical value of η is 0.8 (80% Lorentzian character).

In the .TSK file the key **ISHAPE** in the **[Globals]** section determines which shape function will be used. If **ISHAPE** = 1, the Pearson VII function applies. If **ISHAPE** = 2, then the shape function is pseudo-Voigt. The selection of peak shape (Pearson VII or pseudo-Voigt) is made in the Global Parameters in the Menus, and all phases have either Pearson VII or Pseudo-Voigt shape functions.

In the Siroquant Clay Package the template tasks have been set up with the Pearson VII shape function. With tasks containing clay minerals it is thus advisable to choose the Pearson VII function for the phase lineshapes.

4.6 Split Shape Function

Siroquant includes the Rietveld (1969) overall line asymmetry correction. This function is not entirely satisfactory, so it is recommended that the former asymmetry function be left at the default, and the new split Pearson “m” or split Pseudo-Voigt phase asymmetry correction functions be used instead. The split functions can be applied to any particular phase, and any chosen pattern 2θ ranges for the phase. When using split peak-shapes, we use two Pearson “m” or Pseudo-Voigt shape parameters for the phase instead of one, one for the low side, and one for the high side of the peaks.

Line asymmetry may arise from machine geometry or crystal deformities. The more deformities there are in a phase, the more symmetric and broader their lineshapes become, i.e. the diffractometer line asymmetry becomes less important for the phase. However, phases with a higher degree of perfection, e.g. quartz, show less broadening and more asymmetry as defined by the machine and tube dimensions (“fundamental parameters”). Use of the split functions then tends to correct for the machine shape aberrations, and reduce the need for knowledge of the machine fundamental parameters in Rietveld quantitative analysis work.

In some mineral patterns where there is a lot of quartz present the strong line of quartz at $2\theta=31.07^\circ$ ($\text{CoK}\alpha$) can show a large asymmetry that may interfere with the identification of minor minerals having peaks near the strong quartz peak. It may be sufficient in this case to use the split peak function for quartz over the strong peak only, i.e. between say 30.5° and 31.5° . In other cases, the split function may be needed over a larger angular range. Accordingly, there is a provision for the split function to be applicable over a specified range of the pattern, i.e. between $2\theta_1^\circ$ and $2\theta_2^\circ$. The angular limits $2\theta_1^\circ$ and $2\theta_2^\circ$ are input in the Phase Dependent Parameters dialog.

Each peak of a phase has a low side and a high side with respect to the peak centre. In the “Split Peak Shape” feature, a separate Pearson-‘m’ or Pseudo-Voigt parameter is used for the two sides of the split peak. If Split Peak functions are not specified, or a peak is outside the range specified in a split function mode, then only one shape parameter is used for the whole phase line as was done previously.

It is important to refine the machine zero properly before utilising a split peak-shape function, as the program needs to work with a good calculated value of the peak centre.

4.7 Task Files

Task files are loaded into Siroquant when they are opened and are no longer automatically saved at refinement time as optioned otherwise. Task files have the extension '**.tsk**'. Long file names can be used. Template tasks have the same format but have a version number of 20005 and an extension of '**.tmk**'. It is not permitted to have a task and template task with the same name in the same directory.

Previous version task files will be automatically converted to Version 3 task files when they are loaded. They are resaved to disk with 'v3' added to the name part of the filename in the same directory as the original. Otherwise previous task file formats are not supported.

4.7.1 Ancillary Task File Types and Extensions

Ancillary files allow a task to be saved and then restored state it was when it was last closed.

Ancillary files with the same name and path but different extensions. They also include the calculated pattern which, therefore, has the name of the task file rather than the pattern file.

Extension	Replaces	Function	Comment
.cps	<i>pattern.cps</i>	Calculated pattern	Avoids confusion if two tasks refer to the same pattern file.
.cpd	New	Difference pattern	Resultant trace when the calculated pattern is subtracted from the active pattern.
.cpk	<i>Pattern.cpk</i>	Background trace	From background refinement.
.000	New	Map file	Maps the phases used in a refinement from the list of all phases.
.003	Plotgr.	hkl lines	A version number inserted on a new first line
.004	Result.par	Results file	A version number inserted on a new first line
.005	New	New long results file	List the parameter values and shifts for the last saved refinement.
.006	New	TRACSCAL Object	The variables related to the last refinement. Its saving is optional and only useful for post refinement calculations.
.999	New	Parameter History	History of changes to the parameters over previous refinements.
.998	New	Task INI file	Saves configuration type information related to the task.
.997	New	Non-parameter history	Saves other information about a refinement e.g. refinement times.
.996	New	Annotations	Saves information about annotations on a task's display.
.995	New	Oxide information	Saves user supplied oxide analysis information

4.8 Automatic Prescaling

At the beginning of a Siroquant analysis of a new type of sample, the Rietveld scales of the minerals in the sample will not be precisely known. The default instrument zero of 0.0° may also be out by up to $0.1^\circ 2\theta$. To commence Siroquant, approximately correct scales and zero are needed before the other parameters, which are less robust, can be varied. Approximate Rietveld phase scales have been computed from crystallographic data, assuming a 20% concentration. These computed scales, correct to within a factor of about three, are used as default phase scales on the (hkl) file header.

A method has been developed in Siroquant for automatically homing in on the correct scales and zero, by overwriting STAGE parameters with a fixed PRESCALE STAGE procedure. It is only necessary to click the automatic prescale box with the mouse and start Siroquant. The procedure runs in three hard-coded STAGES:

1. 6 cycles, full pattern, refining all scales with a 0.4 damping factor.

2. 4 cycles, 0.4 damping factor, refining the instrument zero, full pattern.
3. 3 cycles, 0.8 shifts, full pattern, refining all phase scales again.

Automatic writeback will then place good starting Rietveld scales and zero in the parameter dataset. This procedure should be suitable for any sample. In the unlikely event of any trouble occurring, then you can do your own prescaling through the stage menus, with a similar system to the above, only with stronger damping factors or other variations.

Any stage information can be present in the stage parameters (no of cycles, damp and maximum two theta), and corresponding parameter refinement selections in the menu boxes before the automatic prescale starts. The program simply ignores these and sets up the above pre-programmed stages when automatic prescaling is selected.

4.9 Amorphous Content Determination

4.9.1 Introduction

Siroquant permits entry of an "overall amorphous content" and a "phase amorphous content". The overall amorphous content is entered in the global parameter menus. For example, if a sample is known to have 40% by weight of non-diffracting material, then Siroquant quantifies the diffracting phase, i.e., those phases that give powder lines, then normalises the weight percentages to include the amorphous material. Because the amorphous material gives no diffraction lines, it may not be possible to identify the amorphous phase.

The "phase amorphous content" can be entered in the Phase Parameter menus for any phase in the phase list. If, for example, quartz gives some diffraction lines, and occurs in the phase list, then an entry of 10% amorphicity for quartz means that there is actually more quartz than accounted for in its diffraction lines. Some of the quartz may be so finely divided that sharp lines are impossible for this fraction, or there may be "glassy quartz" present with an ill-defined crystal structure. The quartz percentage is adjusted upwards according to the entered "quartz amorphicity" percentage.

As well as allowing entered estimated amorphous percentages, Siroquant can be used to measure an overall amorphicity for a mineral. For this purpose, a spike phase such as SiO₂ or ZnO is added in a known weight percentage (10-15% by weight is usually sufficient as the spike lines will probably dominate the pattern of the mixture). The spike must be the last phase in the phase list. A normal Siroquant analysis is then performed on the spiked mineral pattern.

If amorphous material is present, then the weight percentage of the spike found by Siroquant will be larger than that actually weighed out. Siroquant then works out the amount of amorphous material that causes this difference in the spike weight percentages, and normalises all weight percentages to include the amorphous content.

To run in this mode, specify amorphous content calculation in the Process menu, and Siroquant will assume the last phase is an internal standard (spike). The weighed weight percentage of the spike (in the mixture of sample and spike) is entered in the Process menu also.

One can use the spiked pattern completely, or combine the run with a previous unspiked pattern result. This choice is given because the weight percentages from an unspiked pattern are more accurate since the intensities are not diluted by the spike addition. If you choose to use a previous run, then weight percentages and errors found in the previous run are entered in the menus, and these percentages are normalised to the amorphous content found with the spiked sample pattern.

Siroquant can be used to determine the amorphous content in any mineral sample. In this context, "amorphous content" means non-diffracting material or material present in the sample but not modelled. This is done by mixing the sample with an internal standard such

as quartz or corundum, collecting an XRD pattern for the spiked mixture, and performing a Siroquant analysis on this pattern. If there is any non-diffracting material in the sample, the internal standard weight percentage found by the program, (x), will be larger than the weighed amount, (y). This is because the non-diffracting material affects the weighed amount, but is invisible to Siroquant.

The weight fraction of an amorphous phase (in the spike sample), W_{AMORPH} , is

$$W_{AMORPH} = 1 - y/x$$

Where: y = the weighed weight percentage of the spike phase, and

x = the Siroquant weight percentage for the spike phase.

We define the sensitivity of the amorphous content calculation for a particular value of W_{AMORPH} as (y-x).

For $W_{AMORPH} = 0.20$, the above equation gives the following result:

Wt% Spike (Weighed)	Wt% Spike (Siroquant)	Difference
0	0	0
10	12.2	2.2
20	23.8	3.8
30	35.0	5.0
40	45.5	5.5
50	55.5	5.5
60	65.2	5.2
70	74.5	4.5
80	83.3	3.3
90	91.8	1.8
100	100.0	0.0

For 20% amorphous content in the spiked sample, the table shows the maximum sensitivity is practically reached with 30% of spike, in the spiked sample. In practice, half of this, say 15% of added spike in the spiked sample, could be desirable, as the spike phase profile usually dominates the spiked sample pattern, reducing the intensity of the non-spike diffraction lines.

4.10 Crystallite Size Calculations

The Scherrer equation (see Klug, H.P. and Alexander, L.E., X-Ray Diffraction Procedures for Polycrystalline and Amorphous Materials, 2nd Ed., New York: Wiley (1974)) is as follows:

$$\varepsilon_i = \frac{1.04 \lambda}{(B_i - b) \cos \theta}$$

Where ε_i is an average crystallite thickness in Å for phase i , B_i is an observed linewidth, b is the instrumental linewidth (both in radians) and θ is taken as 15° .

Assume a well-crystallised material has a crystallite thickness of $10,000 \text{ \AA}$. Then if the sharpest line observed on your diffractometer gives $U = 0$, $V = 0$, $W = 0.011$, then the halfwidth = $\sqrt{W} = 0.105^\circ 2\theta$. The Scherrer equation then gives $b = 0.00164$ radians or $0.094^\circ 2\theta$. If you choose crystallite size calculations in Siroquant, under "Process", then you need to input in the menus the instrumental width, 0.094 in this example.

To get errors on the crystallite thicknesses computed by Siroquant, W should be refined (results are generally better with $U = V = 0$) for each phase. The errors in W are generally less also if other parameters, e.g. unit cells or orientation parameters, are not refined. You have the choice of entering your own U , V and W values, e.g. more accurate numbers from

an unspiked run, or using the U, V, W computed in the present Siroquant run.

For example, with $b = 0.094$ the following U, V, W values from a Siroquant run give the following results:

Phase	U	V	W	Particle Thickness (Å)
Tridymite	0	0	0.73±0.15	140±16
Hematite	0.13±0.29	-0.04±0.30	0.246±0.072	266±74
Boehmite	0.58±0.16	-0.30±0.10	0.131±0.013	515±132
Quartz	0	0	0.021±0.003	2094±426
Anatase	0	0	0.015±0.001	3744±537

Note, that as the lines become sharper, the error becomes larger and less well defined because $(B-b)$ approaches zero on the denominator of the Scherrer equation. For broad lines, the crystallite sizes are computed with lower errors.

The crystallite sizes found in this way are useful in determining micro-absorption correction Brindley particle sizes. The latter are, however, aggregates and not individual crystallite sizes, as given by the Scherrer formula. An aggregation factor of about 50 is needed to convert the Scherrer crystallite thicknesses to Brindley particle sizes for use in absorption contrast correction calculations. The Scherrer equation gives the ultimate diffracting crystallite size rather than the aggregate particle size.

4.11 Useful Hints for Siroquant Rietveld Analysis

1. Having 2θ (max) low in the initial stages saves run time.
2. Start with sharper rather than broader linewidths; the run time increases as the reflections get broader.
3. Orienting a phase increases the number of reflections with higher symmetry structures especially (but not for triclinic) and thus the run time. When a phase is unoriented, the orientation angles on the (hkl) dataset are all zero.
4. It is usually a good idea to start preferred orientation refinements with PREF different from 1.0 (0.9 or 1.1) especially in high symmetry refinements e.g. cubic. Starting with 1.0 in high symmetry situations may cause a program stop. PREF may behave better if refined by itself in non-robust refinements and a damping factor is often useful in the first cycles.
5. Refine the more significant variables (scales, zero) first. Full U, V, W refinements may be impossible for weaker phases. Then try V, W (linear $\tan \theta$ dependence) or W (constant width).
6. Use the default 10- μm particle diameter in the Brindley calculation for hand-ground samples and about 1 micron for micronised samples.
7. Asymmetry may be from say 0.1 - 1.0 (only use below 45 deg - see global parameters). Do not use ASYM = 0, but default at 0.005. Asymmetry is only relevant for patterns with strong low-angle lines. It can be a non-robust parameter.
8. Amorphous minerals give no lines. Qualitative analysis programs will not detect these, but a combination of Siroquant spiked runs and chemical analysis (e.g. XRF) may reveal the amorphous weight percentages and chemistry of the amorphous

phase(s).

9. In initial stages, or with weak patterns, use of the least squares damping factor is advisable. A low value, say 0.3 to 0.5 allows convergence from parameters far away from the real values, without program stops.
10. Calculations can be speeded up, sometimes considerably, by removing the weak reflections (those with small $F(hkl)$ values) from the (hkl) datasets with an editor. (Remember $I(hkl) = m F^2$, an angular factor). Remove reflections, say $1/20$ of the strongest line if needed. The intensity ratio of the strongest line to the weakest line will be then 400. It is best to keep all data in the calculations if possible.
11. Siroquant results, with amorphicity corrections if applicable, should agree with chemical analysis data if the program is used properly. Sometimes agreement will never be obtained if your phases are solid solutions. The phases in the Crystal Structure Databank are not chemically the same as the phases in the sample.

4.12 Limits on Siroquant Parameters

Some limitations have been imposed in Siroquant on the values of input parameters, in order to reduce the possibility of faulty parameters causing a run failure. If a parameter is out of range, then the Windows menus will refuse to accept the parameter, and it should be reconsidered. The limitations imposed on input parameters are:

Number of phases	1 to 50
Wavelengths	0 to 10 Å
Zero	-1.0° to 1.0°
Asymmetry	0 to 10
$\left(\frac{\mu}{\rho}\right)$ of overall amorphous phase	0 to 5000
Density of overall amorphous phase	0 to 20
Halfwidth of sharpest line on diffractometer	0 to 1.0°
Halfwidth parameters U, V, W and their errors	-1000 to 1000
Lower 2θ angles for cell and zero 0 to 30° refinement	0 to 30°
Upper angle for asymmetry refinement	0 to 180°
Termination factor on chi squared	0 to 2000
Monochromator 2θ angle	to 100°
Peak ranges in halfwidths	0 to 20
Background values	0 to 20,000
Two theta (max) for stage	0 to 180°
Diffractometer calibration curve point	0 to 1000
Number of cycles/stage	1 to 10
Damp factor in stage	0 to 1
Unit cell edge	0 to 100 Å
Rietveld Scaling factor on phase	-0.1 to 1.0
Preferred orientation parameter	-1 to 10
Pearson m parameter	0 to 50
Particle diameter in Brindley correction	0 to 100 microns

The limits on the programs in the Siroquant system are shown in Table 8. Note: 'No prescribed limit' indicates that the limits are determined by the factors related to the computer and far exceed anything that will occur in practice.

Table 8: Program Dimension Limits

Program	Quantity	Maximum Number Allowed
PREP	Symmetry cards	48
	(h, k, l) reflections before merging	No prescribed limit
STRUCT	Scattering factor types	10
	Atoms in asymmetric unit	500
	Merged (hkl) in pattern range	No prescribed limit
TRACSCAL	Number of mineral phases	No prescribed limit
	Points in a pattern	No prescribed limit
	Excluded regions	No prescribed limit
	(hkl) reflections for a mineral phase	No prescribed limit
	Background points	No prescribed limit
	Calibration curve points	No prescribed limit
	Least-squares variables in a run	100 [§]
	Number of Brindley Trials	No prescribed limit
Number of stages	No prescribed limit	

4.14 Refinement Progress

After you have finished a Siroquant run, a display in graphical form is given of the changes in residuals during the cycles of the run. This enables you to see whether the least squares is converging (ideally) or diverging (not so ideal). The quantities plotted are:

1. The value of the chi squared residual at each cycle. Chi squared is a residual that, for a perfect fit, should approach 1. In practice, a value of 4 or 5 is usually a visually good fit. In an automatic prescale, starting from computer-generated estimated scaling factors, chi squared can typically drop from, say, 300 to 5 over that preset series of stages.

Remember, the first chi squared is for the input parameters, the second for parameters after cycle 1, etc. The final cycle chi squared is never calculated.

2. The mean percentage shift per phase. When parameters are being varied for a phase, Siroquant calculates the percentage shifts on all the phase variables and then averages them. After the run, these mean "phase shifts" are plotted over the cycles to enable the user to see if a particular phase is diverging in the least-squares instead of converging.

4.15 .CPx Scan File Format

Scan data files used by Siroquant are based on the CPI (Counts Per Interval) file format, a

[§] If you try and enter more than 100 refined variables, the program stops entry with a beep.

simple ASCII format used by Sietronics XRD automation systems. This format is used by the raw file (.CPI), calibration corrected file (.CPC) and the background corrected file (.CPB).

The scan data is stored with the scan parameters and tube anode and wavelength data, in the ASCII text format, as shown below.

SIETRONICS XRD SCAN	<i>File identification marker (copy exactly)</i>
20	<i>Start angle</i>
40	<i>End angle</i>
.02	<i>Step size</i>
Cu	<i>Tube anode</i>
1.541838	<i>Wavelength</i>
01-03-1992	<i>Date of scan</i>
2	<i>Scan speed</i>
Demonstration sample	<i>Comment</i>
SCANDATA	<i>Start of scan data marker (upper case)</i>
28	<i>Counts collected on the first interval</i>
26	<i>data</i>
.	
.	
17	<i>Counts collected on the last interval</i>

Note that after the comment field, and before the SCANDATA marker, there is reserved space for extra comment or information lines. If you create a utility to read or write .CPI files, ensure that you search for the SCANDATA item to mark the start of scan data.

The SIE122D collects data in a continuous scan of the scan range, (as continuous as the stepper motor will allow). Counts are accumulated and integrated over the step size width, which may be several motor steps wide. (The motor step is the minimum resolution and scan step size). Although the Rietveld equation is based on a step-scan, rather than continuous, this approximation should be sufficient for most purposes.

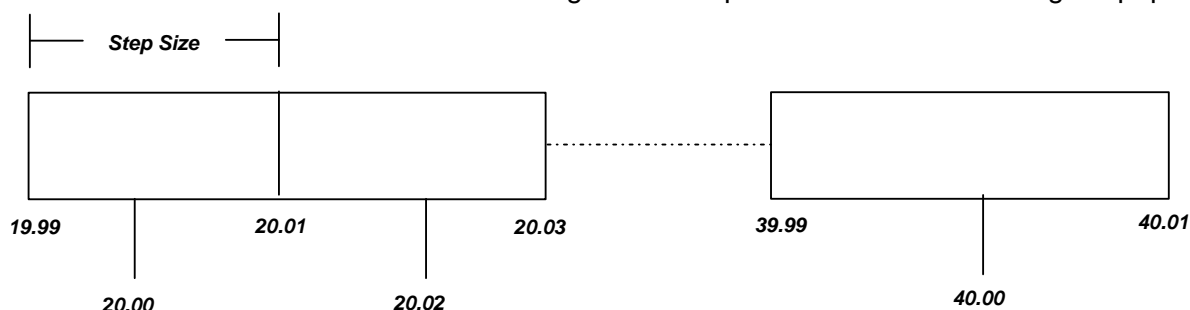
The first step is centered around the start angle - i.e. the leading edge of the first step starts at the specified start angle, less half the step size, and the trailing edge is at the specified start angle, plus half the step size. The same situation occurs for all other steps. In this fashion, the number of steps in a scan can be calculated as:

$$n = (\text{range} / \text{step size}) + 1$$

where range = (end - start).

The diagram below illustrates the method: Scan start: 20°, Scan end : 40°, Step size: 0.02°

Note that this "continuous" mode of scanning is not compatible with Rietveld's original paper,



where a strict "step-scan" is specified, and therefore preferable.

Note: SIROQUANT version 3 can read and write cpi files with non integral values for readings. These files may not be compatible with earlier versions of SIROQUANT and other programs.

4.16 The Plotgr File (for Graphics Display)

For users of earlier versions of Siroquant the *plotgr* file that was present in earlier versions of Siroquant is replaced by a file *taskname.003*. This allows *plotgr* type information to be retained for each task after refinement. Also the *plotgr* file is now retained for the last saved refinement of each task rather than just for the last refinement. The contents for the last refinement can be viewed in the **Long Results** form. For further information see Siroquant File Formats.

4.17 Diffractometer Calibration

The reference in Section 2.3 should be consulted. Calibration curves for different Bragg-Brentano configurations can be supplied on request. Curves for clays with $\text{CuK}\alpha$ and $\text{CoK}\alpha$ radiation are supplied with this release of Siroquant and should be adequate for most applications.

A file *default.cal* is supplied in the Program Files/Siroquant/V3 folder. The format consists of a title line, a line with the number of calibration points, N, and then N pairs of (2θ , calibration factor). This default file is loaded by default. Make sure the start and end 2θ angles on the calibration curve agree with those on your pattern.

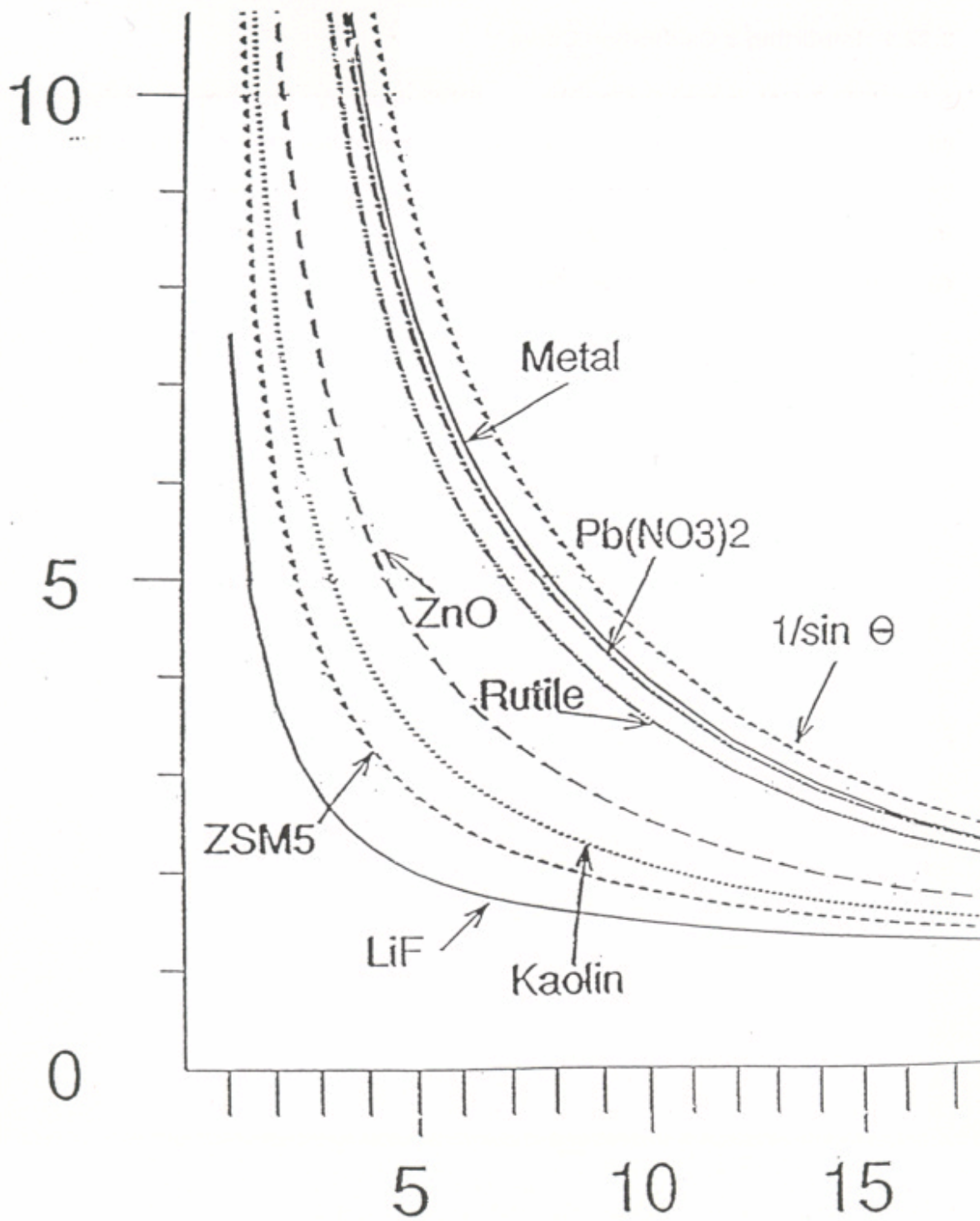


Figure 3. Some CoKa Bragg-Brentano Calibration Curves

5. The Siroquant Crystal Structure Databank

5.1 Introduction

The Siroquant Crystal Structure Databank contains a summary of the crystal structure, atomic scattering factors and unit cell data, needed for calculating its XRD powder pattern and quantifying the mineral for approx 1800 common minerals and other phases in the Version 2.5 distribution. As of version 2.5, the crystal data bank has been reorganized into binary files some of which may be encoded. There are approx 1800 minerals in this databank and the phase information for this standard databank is in .

The previous text based format (as used in quant.dat) is still fully supported in version 2.5 and the Version 2 quant.dat and its accompanying files are still provided. Users who require the text based entry for a phase in Quantlib V3.mdb should contact Sietronics. Users who have phase entries specially made up will be supplied the phases in the format below. Users should note that all scattering factors in the standard library are based on the atomic number of the atom concerned and represent the neutral atom. Users who have constructed or have had constructed for them phases with scattering factors based on other than the neutral atom should use a .DAT databank.

As there are thousands of known minerals, you may occasionally find that a mineral or other phase you wish to include in a quantification is missing. A new mineral entry in your Structure Databank will then be needed. As quant.dat is an ASCII text file, it is easily read and it is also possible to add new minerals with an editor.

The Version 2.0 quant.dat database contains 291 minerals. Observed (hkl) files for minerals with no crystal structure data (mainly disordered clays) are supplied separately.

The Prepare (hkl) file dialog box has an alphabetical list of the minerals is present in the MDB file. The minerals' listing is prepared so that the common mineral name, or chemical formula in some cases, is presented, for the most efficient way of locating your mineral in the list. A database Quant.MDB has been prepared, listing alternative mineral names.

Listings of this database with minerals arranged (a) alphabetically and (b) mineral families, are available. Thus for example, "beta-alumina" is given under "alumina, beta", as the alumina part is more significant. Double salts may be under alternative ionic names. quant.mdb also appears under File | Prepare HKL file in Siroquant for easier selection of minerals in a category e.g. cements, to prepare their (hkl) files. Just click on the category you want and the selected minerals will appear ready for hkl file preparation.

5.2 Format of a quant.dat Entry

Allow this quant.dat is no longer used for the supplied databank a .dat file in the same format is required for user databanks. A quant.dat of the first 300 phases or so is provided for demonstration purposes (it was part of version 2.0) .

View your Databank ASCII text file with a viewing program such as WordPad or Notepad. You will see entries for many minerals, with sequential mineral serial numbers. These do not really need to be sequential; the program searches until the required serial number is found. The only requirement is that each serial number be unique within one Structure Databank.

The entry for quartz, phase number 1 in the quant.dat Structure Databank, is shown below (Line Type numbers are added here for help in discussing the various groups of lines). Each entry is preceded by a phase serial number; for quartz the serial number is 1. Free format is used; i.e. the numbers are separated by one or more blanks. A few more blanks than necessary have been added here for easier reading of the entry for quartz.

The lines are of 9 types:

Line Type 1: 1
Line Type 2: 1 180.26 112.98 2.649 3.9 34.9 67.6 54.74 44.1 111.1
Line Type 3: 1 "quartz P3sub121,#152."
Line Type 4: 1 4.913 4.913 5.404 90. 90. 120.
Line Type 5: 1 6 0 2 2 7 2
Lines Type 6: 1 1. 0. 0. 0. 0. 1. 0. 0. 0. 0. 1. 0.
1 0. -1. 0. 0. 1. -1. 0. 0. 0. 0. 1. .6666666666666667
1 -1. 1. 0. 0. -1. 0. 0. 0. 0. 0. 1. .3333333333333333
1 0. 1. 0. 0. 1. 0. 0. 0. 0. 0. -1. .6666666666666667
1 -1. 0. 0. 0. -1. 1. 0. 0. 0. 0. -1. .3333333333333333
1 1. -1. 0. 0. 0. -1. 0. 0. 0. 0. -1. .0
Lines Type 7: 1 'Si' 1 0.465 10. 10. 10.5 1 14
1 'O' 2 0.415 0.272 0.120 11. 2 8
Lines Type 8: 1 6.2915 2.4386 3.0353 32.3337
1 1.9891 .6785 1.541 81.6937 1.1407 .4149
1 3.0485 13.2771 2.2868 5.7011
1 1.5463 .3239 .867 32.9089 .2508 .5805
Line Type 9: 1 0.012 .019

The details of each line type are as follows:

Line Type 1:

The first line is blank except for the phase number.

Line Type 2:

This line can be filled in with simple calculations on a hand calculator. There are nine numbers to calculate:

Number 1: The unit cell mass. Use the table of atomic weights given with this Note. With quartz there are three Si and six O atoms in the unit cell of. The total cell mass is then:

$$(3*28.086)+(6*16.00) = 180.26.$$

Number 2: The unit cell volume. If the unit cell dimensions in the paper are called a, b, c, α , β , γ , where a, b, c, are the edges in A and α , β , γ are the angles (α is the angle between b and c, etc.), then the unit cell volume is given by the formula:

$$\text{Volume} = abc(1-\cos^2\alpha-\cos^2\beta-\cos^2\gamma+2.\cos\alpha\cos\beta\cos\gamma)^{1/2}$$

This is tedious to calculate on a hand calculator for triclinic crystals, where a, b, c, α , β , γ are all different. It is very easy to calculate this using spreadsheet trigonometry functions. For quartz, the volume of the unit cell parallelepiped is from the above formula

$$a*b*c*\sin120 = a^2*c*\sin 120^\circ = 4.913^2*5.404*.866025 = 112.96 \text{ \AA}^3$$

The unit cell dimensions in Angstroms are also typed in the Line Type 4 (see below).

Number 3: The crystal density. This is readily calculated from the formula:

$$\text{Density} = \text{cell mass}*1.6604/\text{cell volume}.$$

Here, the density = $180.26*1.6604/112.96 = 2.650 \text{ g./cc.}$

Numbers 1 to 3 are used to quantify the Weight % of a mineral with the SMV formula:

$$\text{Wt\% mineral} = \text{SMV}_{\text{mineral}} / \sum \text{SMV}_{\text{all minerals}}$$

where S is the Rietveld scale of a mineral and M and V are the unit cell mass and volume of a mineral.

Numbers 4-9. The next 6 numbers are the mass absorption coefficients for Mo, Cu, Fe, Co, Ni and Cr radiations. Mass absorption coefficients for the elements are given in the Table in

Section 1.5 of the Siroquant Technical Manual. The mass absorption coefficient M_{tot} of a compound is simply the weighted average of the elemental coefficients M_{element} .

The Table gives for Mo radiation $M_{\text{Si}}=6.70$ and $M_{\text{O}}=1.50$. The weight fraction of Si in quartz is $28.086/(2*16+28.086) = 0.4674$, while the weight fraction of oxygen is $1.0 - 0.4674 = 0.5326$.

Hence the mass absorption coefficient of quartz mineral for Mo radiation is

$$0.4674*6.70 + 0.5326*1.50 = 3.9$$

The other 5 coefficients are found in a similar way. The calculation is easily done with a hand calculator.

Line Type 3:

This line is a title, enclosed in quotes. The line should contain the mineral name, a space group symbol from the International Tables, Vol.1 and the space group number, the latter preceded by an '#' symbol for easy searching for the space group in the Structure Databank with an editor. A chemical formula here is desirable. These data must be added and stored in a Microsoft Access database using the same name as the user's Custom *.dat file, used for mineral identification when creating a 'hkl' file (see Section 4.4).

Line Type 4:

Line, Type 4 contains the six unit cell dimensions a, b, c, α , β , γ , which are given in the structure analysis paper for the mineral (in angstroms and degrees).

Line Type 5:

This line contains 6 integers describing certain features of the crystallography.

- *Integer 1:* In the example for quartz the first integer is 6. This means there are 6 symmetry cards of Type 6 to follow. If you look in the International Tables at Space Group number 152, as given in the Line, Type 3, you will see various equivalent positions (x, y, z) typed for atomic sites of multiplicity 6,3 and 2 in the unit cell. Always use the *general* position (x, y, z) and not any special position, for the symmetry positions.
- *Integer 2:* This defines whether the crystal atomic arrangement has a centre of symmetry or not. The number is 1 for a centric structure (which has atoms at (x, y, z) and (-x,-y,-z)) or 0 for a non-centric structure (atoms at (x, y, z) only). This can be easily seen by inspecting the equivalent positions for the Space Group. For proper quantification it is important to get this number correct. For quartz, the six equivalent positions do not contain a position (-x,-y,-z) so this integer is 0 in this case.
- *Integer 3:* The third integer is the number of atoms in the "asymmetric unit" of the crystal structure (i.e. the number of atoms in the basic list of atoms without repetition by the symmetry positions). For Si, only one atom is needed in the quant.dat atom list; the other two Si atoms in the unit cell are obtained by the equivalent positions. Although the general position (x, y, z) is six-fold, it is found that only 3 Si coordinates are unique when the transformations are made, so the Si special position (x, 0, 0) is three-fold and not six-fold. For oxygen, also, only one atom is needed in the atom list, at its general position (x, y, z); the other 5 oxygen positions in the unit cell are different one from the other when generated by the equivalent positions of the Lines, Type 6. All atoms in the unit cell are generated by the symmetry operations of the program when these unique atom sites for Si and O are entered. Thus Integer 3, the number of atoms in the atom list below in Lines Type 7, is two for quartz.
- *Integer 4.* This integer is the number of different types of atoms in the atom list. For quartz, we have two different types of atoms, namely silicon and oxygen.
- *Integer 5.* This number gives the Bravais lattice centering of the crystal structure. We

have the following integers:

I-centering	1
F-centering	2
A-centering	3
B-centering	4
C-centering	5
Triple rhombohedral cell on hexagonal axes	6
Rhombohedral cell on rhombohedral axes	7
Primitive unit cell (no centering)	7

These symbols (I, F, A, B, C, P) can be read on the space group symbol in the International Tables (top right-hand corner in the 1965 Edition). The rhombohedral space groups are listed under R but give rhombohedral and triple hexagonal equivalent positions (x, y, z), etc. There are two ways of entering rhombohedral structures. Use the triple hexagonal cell (6) in preference to the primitive rhombohedral cell (7) as unit cell refinement is more stable with the former. With the latter, some information is lost on the a-axis as not all (hkl) permutations are used in the unit cell calculation, being lost in the formation of multiplicity groupings.

For quartz, we have a space group symbol starting with a 'P', so this lattice is primitive and Integer 5 is typed as 7.

- *Integer 6*: This is the total number of temperature factor types in the atom list. For quartz, we have two different temperature factors (Line, type 9), which are 0.012 and 0.019. This number is thus 2. The temperature factors are isotropic and are the quantities 'u', which is the usual Debye-Waller isotropic temperature factor divided by $8\pi^2$.

Lines, type 6.

These are the atomic position symmetry cards, given in the Space Group Tables, Vol.1 of the International Tables for X-ray Crystallography. Always use the set of general positions (x, y, z). Type the basic position (x, y, z) as well as the others. If there is a position (-x, -y, -z) given in this set, only type half of these positions, namely those which cannot be related to any other by a centre of symmetry. This is the case for Integer 2 =1 (centric crystal structure). Lattice centering positions are not typed.

Each symmetry line has the format:

$$X_1, Y_1, Z_1, T_1 \quad X_2, Y_2, Z_2, T_2 \quad X_3, Y_3, Z_3, T_3$$

where the subscript 1 refers to the 'x' field of the symmetry card, 2 refers to the 'y' field and 3 refers to the 'z' field. T is the translational component. Thus the first symmetry line of quartz in the present example reads (x, y, z) and the second reads (-y, x-y, 2/3+z). Note that the symmetry positions for quartz are different to those given in the International Tables; this is the notation given in Wyckoff's book 'Crystal Structures', 2nd Ed., 1963, with a different origin. This is perhaps the only case in the Structure Databank where the International Tables convention has been changed.

Lines type 7:

These are the atom lines, one line for every atom in the basic unique atom list. In the quartz example we see two lines, one for the silicon atom and one for the oxygen. For each atom line we have:

- The atom name enclosed in quotes (up to 6 characters allowed in an atom name).

- After the atom name we have the scattering factor serial number of the atom. Silicon has a 1, as it is the first scattering factor type in the list of scattering factors to follow in the Lines, Type 8. Oxygen has a 2, as it is the second scattering factor type.
- Next in the atom line are the three positional coordinates (x, y, z) of the atom in fractions of the unit cell edge as given in the structure paper for the mineral.
- The next number for the atom is an occupancy factor of the atom site in the unit cell. If an atom is in a general position (x, y, z), it has an occupancy of 1.0. Oxygen is in a general position in quartz, so its occupancy factor is 1.0. If an atom is in a special position, i.e. there are fewer atoms in the unit cell than given by the number of general positions, then it will have an occupancy factor of less than 1.0. In the quartz example, the general position is 6-fold, whereas the silicon atom has special y- and z- coordinates of 0.0, giving only 3 unique Si atoms in the unit cell instead of the six generated by the symmetry operations. The Si atom thus is given an occupancy factor of 0.5 to get the correct number of Si per cell.
- If you have mixed site occupancies, do not use an “average” X-ray scattering factor, as then you will not be able to apply precise anomalous dispersion corrections to the ‘average’ atom. Instead, apportion up the site with the various atoms occupying the site correctly weighted; the total of all the individual occupancies is then the normal site occupancy.
- Check the structure paper carefully to make sure the site is not partially occupied; if this happens, use the partial occupancy factor in the paper for the site on top of the crystallographic occupancy. Thus, if a general (x, y, z) site occupancy 1, is said in a paper to be only 50% occupied by an atom on average, then the actual occupancy factor used for the atom is 0.5 and not 1.
- Finally, the last number in an atom line is the temperature factor type. Si has a ‘u’ value of 0.012, so it is temperature factor type 1 (see last line, Type 9, of the mineral entry). O has a temperature factor ‘u’ of 0.019, so it is given temperature factor type 2. The actual temperature factors are typed in the Line Type 9.

Lines Type 8:

These are the X-ray or neutron scattering factor types, for each type of atom in the unit cell. There are two lines for each type of scattering factor:

- The first line contains the X-ray polynomial coefficients a_1 , b_1 , a_2 , b_2 for the scattering factors of atoms as given in the International Tables for X-ray Crystallography, Volume 4, p99-101.
- The second line contains the X-ray polynomial coefficients a_3 , b_3 , a_4 , b_4 and the neutron scattering length in units of 10^{-12} cm. If you never use neutron data a dummy value of the neutron factor can be typed for your entry. A table of neutron scattering lengths for the elements and some isotopes is attached to this Note for those who will use neutron data.

Line type 9:

The final entry for the mineral is a line containing the different thermal vibration parameter types. Different atoms can have the same thermal parameter type, e.g. more than one atom in a crystal can be assigned a thermal vibration parameter ‘u’ of 0.012 and so on. There are generally two or three types in a mineral entry, a lower parameter for metallic elements and higher for non-metals. A look through the Structure Databank will give a general idea of the magnitudes of these parameters for certain atom types or groups.

In the quartz example Si has a thermal vibration type 1, so it is given a ‘u’ value of 0.012 and similarly O, type 2, is given a ‘u’ of 0.019.

5.3 Short-Cuts In Typing Structure Database Entries

- Save a backup copy of your Databanks first, in case of mishaps. Notepad or WordPad can be used to save the Databank file in text format.
- Refer to your structure paper. It will give a certain space group, with or without a space group number (1 to 230). Look up the number in the International Tables if it is not in the paper. Search quant.dat with the editor for a '#nnn', where nnn is the space group number, to find an existing entry with the same space group number. It is very likely you will find one with the same number as most minerals tend to fall in groups of common space groups.
- If you find one with the same group, highlight and copy this entry to the end of (just before the last line, the terminator line '9999'). You then have a template entry for your new mineral which is easy to type over. The equivalent positions are now they're already correctly typed for you and proof-checked for errors. This copying method leaves only a small chance for errors in a typed equivalent position.
- There is a small chance that you will not find an entry with your space group number. In this case look up your International Tables, Vol. 1, for a space group with similar equivalent positions to your case, preferably with the same number of equivalent positions. Search for this space group in quant.dat. You will soon find a reasonably good template, with not too much editing of the equivalent positions. *If you need to overwrite equivalent positions, proofread these carefully from the International Tables afterwards, as errors here will give serious errors in computed XRD profiles.*
- The next job once you have the template with correct equivalent positions (Lines Type 6) is to type up the atom lines, type 7. If you have 10 oxygen atoms in the list, then take an oxygen line from the old entry, give it the new serial number for the new mineral entry and make the coordinates blank '. . .'. Copy this line 10 times. This saves deletions of old coordinates when typing the new coordinates. When all atoms of all types have been typed up, proof-check the coordinates carefully. Then count up the number of atoms and atom types and enter these control integers in Line Type 5.
- The scattering factors can then be entered in the correct order on the template (Lines Type 8). Edit out scattering types not in your mineral, and copy further needed scattering types from other entries in quant.dat that you need into your template. You will rarely need to fully type up a new type, as the 303 mineral entries in the quant.dat database in Version 2.0 of Siroquant cover practically all elements of interest.
- Now go through your entry and change all old line serial numbers to the desired serial number of the new phase.
- The other numbers in the template can then be calculated as described above and overtyped into the new mineral entry.
- Any copied data from other parts of quant.dat has a very high probability of being error free. Statistics being what it is, it cannot be guaranteed that all of quant.dat is error-free within a confidence level of 100%. However, any errors found should be reported to Sietronics.
- Finally, check over your complete new entry for errors. *Remember, any remaining errors here will cause errors, possibly severe, in your results with tasks including the new mineral, so this final check is vitally important.*

5.4 Typing Up An Access Database Entry For Your New Mineral

The Structure Database, called quant.mdb comes with your copy of Siroquant Version 3.0.

The mdb files are edited with Microsoft Access. Note that later versions of Access use a different format for *.mdb files. The mdb files can be edited in later versions of Access but

the format and the structure of the database must not be changed.

Open the Access program and click 'File'. Then click 'Open Database' and you will see the name quant.mdb (or custom.mdb). Double click on quant.mdb (or custom.mdb) and you will see the names 'Groups' and 'Mineral'. 'Groups' is for starting a new Group of minerals, such as Hydrates. If your mineral is already in an established Group ignore this heading, otherwise start another Group. Then double click on Mineral and you will open the full QUANT.mdb Database. Scroll to the bottom of the Database and enter the data for the new mineral under the various headings. The name is to identify the mineral on the screen when you create a (hkl) file for the new phase. When you finish entering the data for the new mineral, exit the screens and then Access. The data you typed is automatically saved. As mentioned we recommend that you make up your own "CUSTOM." quant.dat type and QUANT.mdb type files for your mineral entries. As you make *.hkl files and analytical task *.tsk files the new directory paths will be included automatically.

5.5 Checking the results with the new mineral against an ICDD database card.

First, enter Siroquant and create a *.hkl file for the new mineral, for example, the file 'qz.hkl' for quartz. Then create a new task and add 'qz.hkl' to the task. Load any XRD pattern that covers the 2θ range normally used. Then enter the name of the task, say 'datachk.tsk'. Unclick the automatic prescale, select 1 cycle and the zero damping factor and click the refinement start button. The task will run for a second or two and the screen will naturally show a poor profile fit. Under the Results – Long Results menu items, the PlotGR tab is used to display the reflections. This file will show the calculated XRD pattern for quartz, also 2θ and the plane Miller indices h, k, l.

5.6 Phase Entries – General Notes

1. Read description of quant.dat above. Users must put their own phases into their own databank, with a different name than quant.dat. Note there must be a corresponding Access database file (MDB) using the same table structure as quant.mdb.
2. All entries are in free format (reals or integers separated by blanks).
3. All phase entries start with quant.dat serial number, except last record (9999). The serial number must be less than 8000.
4. Structural Data can be found in Wyckoff, R.W.G., "Crystal Structures", Second Edition, Wiley and Sons, N.Y., 1963, or in the BIDICS Series: "Bond Index to the Determination of Inorganic Crystal Structures", compiled by I.D. Brown, M.C. Brown and F.C. Hawthorne, Institute for Materials Research, McMaster University, Hamilton, Ontario, Canada, L8S 4M1. The latter covers structural papers from 1969 to 1982, and is identified by the code ISSN 0318-126X. Further information can be obtained from I.D. Brown. Also for many years, Structure Reports, Ed. International Union for Crystallography, Utrecht, Osthoek, was a crystal structure reference. Now earlier book databases are superseded by the personal computer database ICSD, or Inorganic Crystal Structure Database, containing about 90,000 structures.
5. Symmetry positions can be obtained from the International Tables for X-Ray Crystallography, Volume 1, Kynoch Press, Birmingham (U.K.) (1952).
6. X-Ray scattering factor data is obtained from the International Tables for X-Ray Crystallography, Volume 4, p.99-101, Birmingham (U.K.), International Union of Crystallography (1974).
7. Neutron scattering lengths "b", may be obtained from G.E. Bacon, "Neutron Diffraction", 3rd Edition, Oxford, Clarendon Press (1965), or more recently from L. Koester and W.B. Yelon "Summary of Low Energy Neutron Scattering Lengths and Cross Sections", obtainable from Sietronics Pty Ltd. If neutron data is not used, type a dummy value of "b" in your table.

8. $\frac{\mu}{\rho}$ values are readily calculated with the formula

$$\left(\frac{\mu}{\rho}\right) = X_1 \left(\frac{\mu}{\rho}\right)_1 + X_2 \left(\frac{\mu}{\rho}\right)_2 + \dots$$

where X_i is the weight fraction of atom "i" in the compound.

9. You will need to be reasonably familiar with basic simple crystallographic theory and be able to read and understand papers written about mineral crystal structures. Guesswork in filling in the numbers in will inevitably result in incorrect quantifications. For example, calling a mineral crystal structure centric instead of non-centric will double the apparent number of atoms in the unit cell and cause the quantification to be too low by a factor of two, even though Siroquant will still fit the data (with a Rietveld scale of half the real value). If you are not really a crystallographer, then you will probably need to find one to help you, or, failing that, Sietronics Pty Ltd will arrange to construct the mineral entry for you, for a fee.
10. The mineral programmer will need a paper describing the crystal structure, which contains atomic coordinates and isotropic temperature factors. You will need to do a literature survey and choose the best available structure analysis, as the quality of published data is variable in quality. The original paper should be used rather than an abstracted tabulation as transcription errors are found regularly in structure data compilations. Even some original papers can occasionally contain an incorrectly typed coordinate. Depending on the significance of mistyped numbers, the effect of these errors can be minimal or severe on Siroquant analysis results.
11. A crystallographer should be able to pick up errors in original papers. One way of finding coordinate errors is to calculate a few inter-atomic distances and then compare with the published distances. Checking another analysis of the same compound should also help to locate gross typographical errors. An error in the paper should be suspected if the new entry does not give good agreement between an ICDD card and the powder pattern calculated with Siroquant (see below, in the Section 'Checking your results with the new mineral against an ICDD database card'). On the other hand, your entry may be quite correct, while the ICDD card may be of low quality. A quality index is given on every card and explained in the ICDD Alphabetical Index. Also, a check on your own observed XRD powder pattern should be made wherever possible.
12. A copy of the International Tables for X-Ray Crystallography, Volume 1, Symmetry Groups, 1965 or later Editions, is needed to check the crystal Space Group data for your entry.

6. Siroquant Error Messages

Error messages in Version 3 have been replaced with direct links to the help files. These should supply the user with information they may need.

In previous versions sometimes TRACSCAL would 'blow-up' usually because some parameters have refined to bad values. This still may occur but we encourage users to report these problems. With Version 3 we have far superior facilities to track these faults down.

Please reports all problems promptly and supply all the files associated with the task, usually the pattern file, any hkl files and all files with the task's filename (*taskname.**).