

XPowderX™

(XPowder, XPowder12)

A SOFTWARE PACKAGE FOR POWDER X-RAY DIFFRACTION ANALYSIS

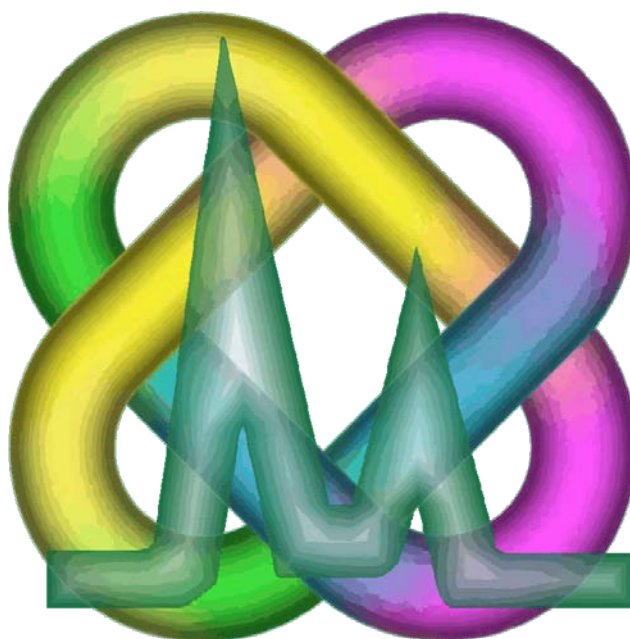
Version 2017.01.xx

Version 2019.06.31 (25/02/2019)

Version 2023.06.01 (25/06/2019)

Qualitative, quantitative and microtexture

[Index](#)



J. D. Martin (2008-2020)

This program uses COD, AMSCD, P2D2, PDF2 or customized databases

[Home](#)

<http://www.xpowder.com/>
email: support@xpowder.com



This User Guide is currently being developed.

XPowderX™

(XPowder, XPowder12)

A SOFTWARE PACKAGE FOR POWDER X-RAY DIFFRACTION ANALYSIS

Qualitative, quantitative and microtexture

This manual is available in www.xpowder.com and can be freely copied and distributed.

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J. Daniel Martin

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This User Guide is currently being developed.

Introduction

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The XPowderX program was developed for the analysis of natural minerals, artificial compounds, biological crystals and other solid materials, using techniques of X-Ray Diffraction (PXRD). Its main applications are the identification and quantification of the crystalline components of solid samples.

The "software" is based on the previous XPowder12 program, which inherits all calculation algorithms and access to databases PXRD (except type "PDF2.DB"). XPowderX can coexist with their predecessors XPowder and XPowder12 on the same computer and share with them databases and sample files.

It has been found XPowderX functionality in Windows XP, 7, 8 and 10 in both configurations 32 and 64 bits. The use in previous systems (like Windows 98, 2000, Millennium, etc.) should be achievable, although not guaranteed,

Because the XPowderX program performs multiple processes of reading and writing to the hard disk, must necessarily have "**System Administrator privileges**." This is especially important when an overly aggressive antivirus is used. In addition, the hard drive must have enough free space to perform these operations read / write (about 1 megabyte).

XPowderX Setup

XPowderX is installed with the "xpowderx_setup.exe" file. Just follow the instructions that are displayed on the screen.

Download setup file from <http://www.xpowder.com>

It is advisable to classify **the XPowderX folder (usually 'C:\XpowderX')** and subfolder as **reliable**.

You should select the "*Create a desktop icon*" option to have the program icon permanently displayed on the desktop.

Once the program is installed, you must provide "**OS administrator privileges**" to meet the requirements outlined in the previous section, by clicking on the icon with the right mouse button and acting according with the requirements of the operating system used.

To perform XPowderX, you must click on the icon



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Size of program window configuration



Figure 1.

The text file "XPowder.ini" is in the program directory (usually C: \ XPowderX \). This file will include, among others, the parameters that configure the size of the program window with respect to the full screen. In the figure the meaning of commands that should be included are shown. The parameters can be changed for each user, according to the characteristics of the screen:

HeightScale = 0.6 (Program height window / height computer screen window).
WidthScale = 0.7 (width of the program window / width computer screen window).
PatternPlotHeightRatio = 0.4 (height of the diffractogram plot / height program window).

- The values of the first two parameters must be less or equal to 1 (1 is used for full screen).
- The third parameter must be between 0.3 and 0.5.

It is possible that these parameters must be modified when small screens are used. In any case, you can work with full screen size by selecting from the menu: "Tools / View / Full screen "

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Databases

They are necessary to carry out the processes of identification and quantification of crystalline phases of the samples analyzed with PXR, which is achieved by analyzing existing d-spacing and intensities matches. The databases are not included in the setup program, so it must be obtained directly by users XPowderX. Several types:

- Databases AMSCD, who are free.
- The basis of PDF2.DAT data to be obtained in the "The International Centre for Diffraction Data (ICDD)"
- P2D2 (Predicted Powder Diffraction Database) is built up by calculating the powder patterns corresponding to the predicted crystal structures from the latest PCOD update. The job is done partly by ZEFSA II (898707 entries) and for the GRINSP data (163520 entries) by the CIF2POW software. The P2D2 database currently includes twelve text files, each with approximately 100000 compounds, which can be automatically indexed by XPowder12, individual or jointly.
- Custom databases directly created by users themselves or imported from other databases ("My database") data.
- **NEW ! Ver. 2019.06.26 Free and** highest quality large custom database (See [appendix 10](#))

Installing databases explained below (See "Advanced Tools", tab "Database")

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Startup screen

When the program first started, you go in as 'Manager' program, while a welcome screen appears: Pressing 'Start', you go in directly to the main screen (next page). [Index](#)



Figure 2

OPTIONAL. Restricted user access and "Passwords" assignment". **Discontinued**

By pressing "Set Password" on the initial screen, the "Manager" program can generate up to four different keys to as many users.

Possible users are "Manager" (without limitations of use of the program), "User 0", "User 1" and "User 2". "Limitations" and "privileges" of the last three can only be set by the "Manager" on the main screen (Menu / Privileges) program. In order for different keys are effective, "Manager" must also change their own password with respect to the preset by the program, which initially is 3692581470.

Originally "Manager" and "User 0" have the same privileges with the exception that only the first can set the privileges of other users. (See also appendix 9)

User	Factory Passwords
User 0	User 0
User 1	User 1
User 2	User 2
Manager	3692581470

After pressing "Set Password", the program shows:



Home screen

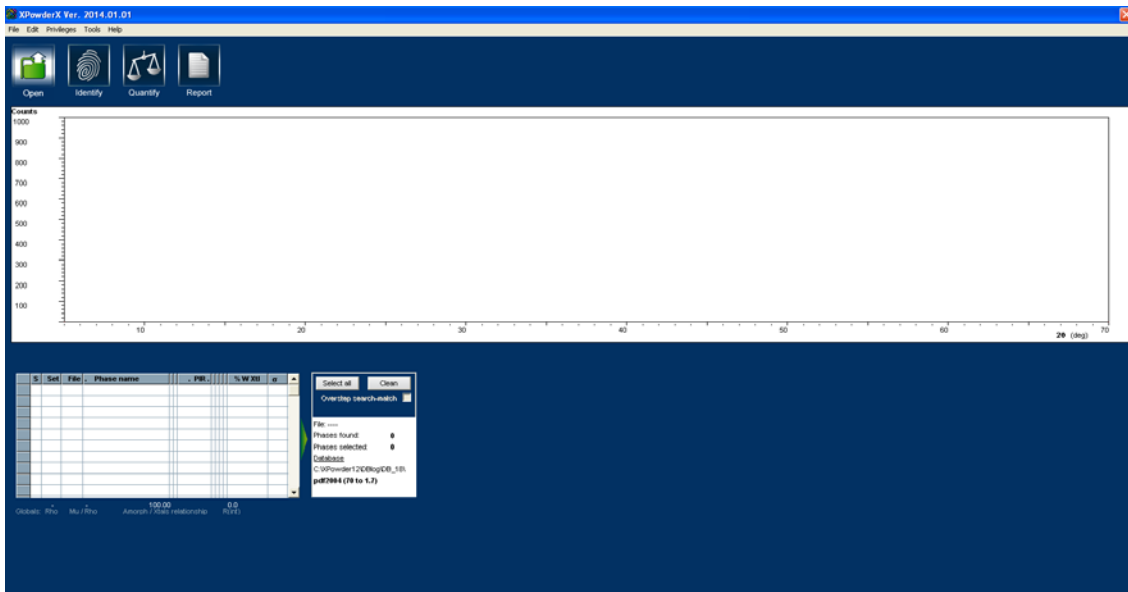


Figure 4

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Procedure for Performing a Routine Analysis

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Step 1. Open diffractogram file Press "Open"  and select the appropriate sample file to be analyzed.

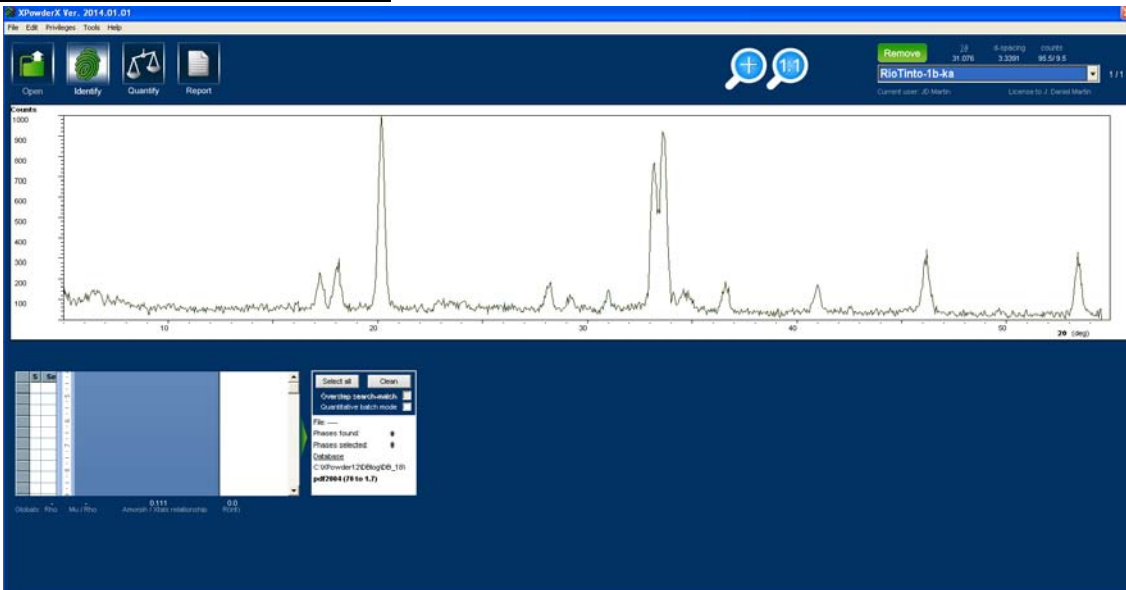




Figure 5.

When the diffractogram is displayed, the "Open" button changes its appearance  while a new button "Identify"  is enabled.

Once opened the diffractogram file, we zoom in on the screen by selecting the area to be expanded with the shift key and dragging with the right mouse button. We may also use the magnifiers buttons on the top of the screen or the tools on the "View" menu -> "Plot limits".

To learn more about step 1


It may be opened up to fifty diffraction patterns simultaneously.

The diffractograms also be opened from the "File" menu:

- "Open new project" performs a similar action to the "Open" button
- "Open old projects", in addition to opening a diffractogram, load the results obtained for the same sample in previous sessions.
- "Resume session from ..." reload any of last four sessions.

To carry out this task you must have already installed at least one database, as explained above.



Pressing the button  the program looks for the best phases in the active database and places them on the composition table according to a goodness of fit, which is independent of the amount of the compound present in the sample.

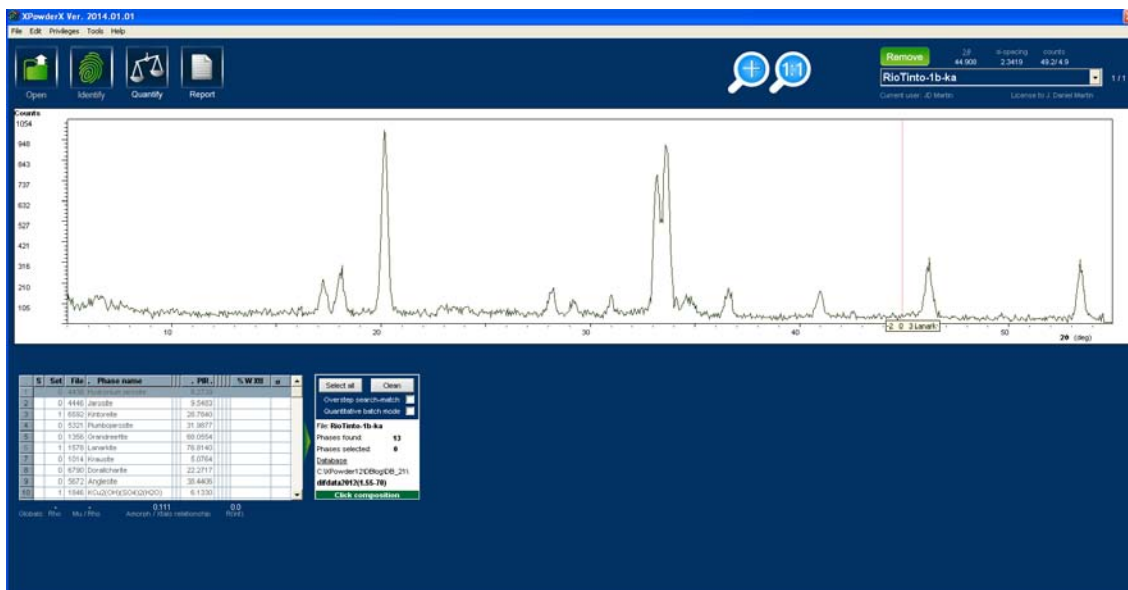


Figure 6.

Now a message on green background ("Click composition") invites you to select the suitable initial components from list, by clicking on the "S" column in the table of results.

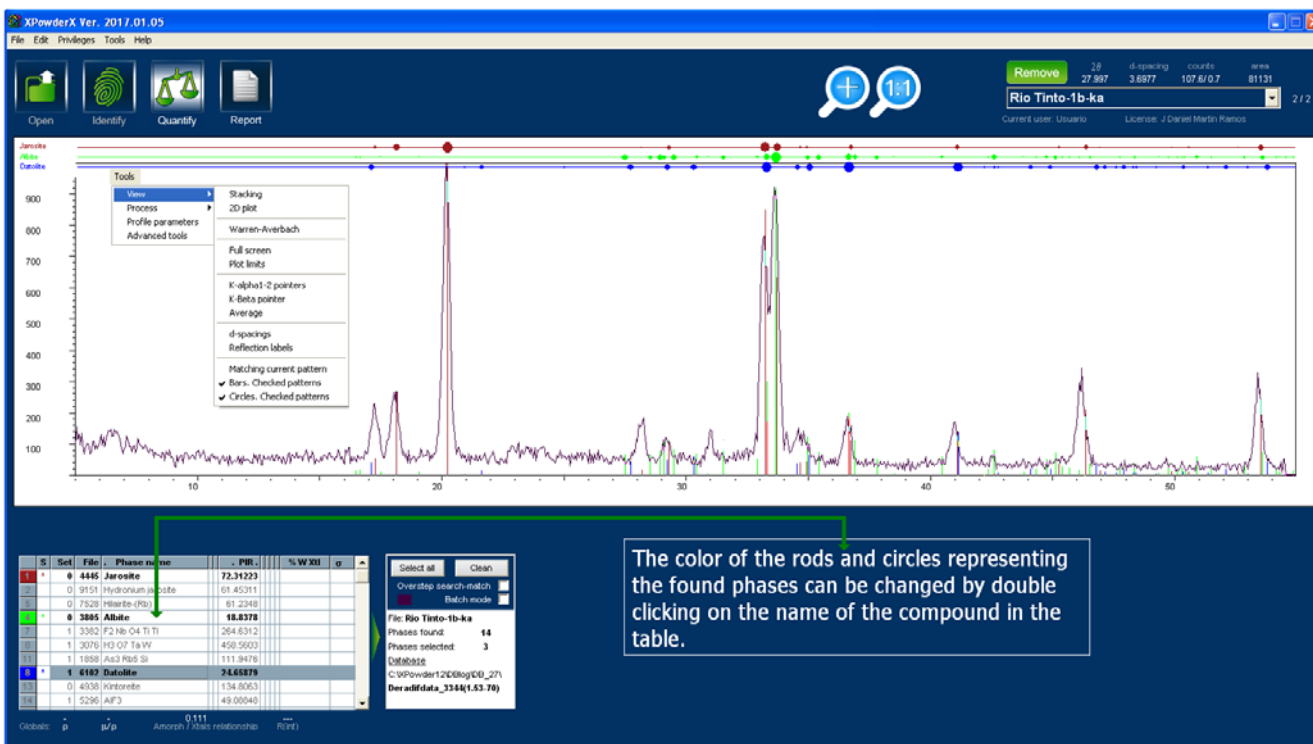


Figure 7.

The appearance of the previous image depends on selected display options (*Main menu / Tools / View*) and may be different from that shown in Figure. The color of the rods and circles representing the phases found can be changed by double-clicking on the name of the compound in the table.


After the components have been selected, changes the appearance of "*Identify*" button and lights the quantization ("*Quantify*"). You can optionally click the "*Clean*" button to remove the remaining phases in the results table.

To learn more about step 2

• Bragg d-Spacing:

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- Phase identification uses d-Spacing of Bragg reflections for searching the best solutions in the database in use. To calculate these d-spacing the program performs a virtual background subtraction and the classic method of "second derivative" to find the maximum. Because the diffractogram is a discontinuous function, the program uses parameters that allow discriminate those that are true reflections from noise intensities (oscillations). Of these parameters, the most important are the "minimum intensity (Minimum %)" and the "sharpening of the peak". These parameters vary for each diffractogram, and can be modified with advanced tools ("*Advanced tools*" tab "*General*"), where the d-spacing values can be further calculated, or updated ("*Compute*"), or deleted ("*Clear all*" completely erases diffractogram reflections, "*Clear zone*" deletes only the reflections included in the currently selected zone). Double-clicking on the graph of the diffractogram clear all nearest d-spacing previously calculated..

• **Identification.** The "Search" tab from the "Advanced Tools" allows to define the number of solutions found during the search. The main options refer to the criterion of fit (FOM, Magic, Classic, 3 reflections, 2 reflections, one reflection), range in that reflection is considered observed ("*2-theta gap*"), minimum intensity ("*Intensity cutoff*"), "subfiles", chemical composition database constraints , etc. (see below).

Identification is made in several stages. First it is considered that a reflection is observed if it is within a 2θ range ("*2-theta gap*" Advanced tools tab "Search") and a minimum intensity required ("*Intensity Cutoff*"). After calculating the Euclidean distance between the phase parameters of the sample and of the database is performed. This distance, being smaller as the identification is correct, allows ordering the phases found in descending order of probability. After an adjustment is performed by least squares and simulated annealing which takes into account all the reflections of the diffractogram, both spaced as intensities ("*Discard except to... N*" and, or "*Fix DB-2-theta zero shift*" in the "*Match*" of advanced tools tab). This latter process can be performed on the major components ("*Largest*"), Minority, ("*Minors*") or all ("*Both*"), manually ("*Next fit*" button) or automatic ("*Automatic*").

• Component selection. We can use auxiliary methods such as:

- Direct visual matching with the database, which allows us to use graphical menu options "*Tools -> View*" ("*Matching current patterns*", "*Bars*" and "*Circles*" Checked patterns).

- Using data sheet for each phase appears in the folder "*Card*" in *Advanced Tools*".

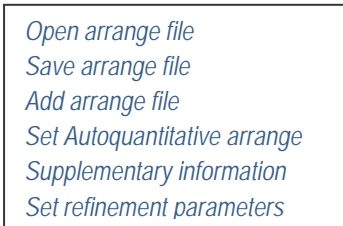
- Advanced tools in "*Match*" tab can restrict the initial search results using least squares methods. The most important tools are "*Discard except top...*", "*Minor / Largest / Both compounds*", "*Fix DB 2-theta zero shift*", etc. See also Appendix 2. Match Tab

- By checking box "*Fix DB-2.theta zero shift*" the program corrects linear and automatically the d-spacing aberrations of the database an experimental pattern, using statistical methods.

- By checking '*Automatic*', the program search the next better fit f of list table of figure 7, when current DB card record is *selected* or *erased*.

- Finally, it is important to make use of any prior knowledge of the analyzed sample to make the best choice (origin, physicochemical properties, references, etc.).

• **Popup menu.** If you place the cursor on the result table and click the right mouse button, the following popup menu is displayed:



Open arrange file
Save arrange file
Add arrange file
Set Autoquantitative arrange
Supplementary information
Set refinement parameters

- "*Open arrange file*" allows opening a table of existing results, which was saved with "*Save arrange file*" and/or "*Add arrange file*".
- "*Set autoquantitative arrange*". Enables the current result table to use the program in "*Autoquantitative*" mode (see below in *Advanced Tools*, "*general*" tab). This command requires 'Auto quantitative full profile' permission' (See Appendix 8, Figure A8.1)
- "*Supplementary information*". Se usa después de realizar el análisis cuantitativo (siguiente apartado)
- "*Set refinement parameters*". Modifies or sets the guidelines to be followed by quantitative calculation.

Step 3. Quantification

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Background: The program can use two alternative methods for quantitative analysis. The first uses diffractogram reference database sheets, while the second uses full XRD profiles (which can be obtained by individual registration of each component or may be calculated). Explained in this **Step 3 (Quantification)** refers to the first method. The manner of carrying out the second method explained below.

In both methods, the weighted combination of the diffractograms of the identified components in the sample that best fits the diffractogram analyzed is calculated. Some experimental factors such as 2θ zero misalignment of patterns and, or, the diffractogram analyzed absorption corrections, background, statistical weight, etc, can optionally be taken into account during the general process of least squares. The fractions of each component thus obtained must be corrected by a scaling factor which includes the sample dependent parameters - such as the structure factor (F_{hkl}), crystallinity and the preferential orientation - and the geometry of the diffractometer. This scaling factor is often simplified due to the difficulty of the calculation. Usually are used the ratio of the intensities of the maximum reflection of the pattern to maximum reflection of mixed corundum 50% weight (I/I_{cor} PDF), or any other pattern (RIR , Reference Intensity Ratio) or so-called "Reflecting Power". Some databases provide these values, which in any case refer to values F_{hkl} , orientation and individual factors crystallinity and in many cases can be very different from the samples that we being analyzed. We recommend using this as the value for the scale factor PIR (Pattern Reference Ratio) parameter for each component is defined by the formula:

$$PIR = (F_p / F_r) \cdot (W_r / W_p)$$

Where:

F_p = Fraction of component p of the mixture calculated for $PIR = 1$

F_r = Fraction of any component used as standard calculated for $PIR = 1$ (can be a common component of the analyzed samples or artificially added, for example quartz or corundum). W_r = known weight of standard.

W_p = known weight of component p

To obtain these preliminary data must be recorded diffractogram of a mixture of known composition, wherein each of the components of the sample, or all of them together and appear alongside the main standard. Each diffraction pattern obtained is used to perform a preliminary quantitative analysis with baseline $PIR = 1$. These preliminary calculations provide the F_p and F_r values used in the formula. The obtained PIR values have universal uses in subsequent analyzes performed on similar samples analyzed with the same diffractometer as initials.

Quality by quantitative analysis is established with according factor R , defined as

$$R = \{ n \sum [w (I_o - I_c)^2] / n \sum w [I_o^2] \}$$

Where I_o and I_c are observed intensities computed in n experimental points. w is a statistical factor weighing. In the example $R = 0.0188$.

The quantitative analysis is performed clicking on the button "Quantify"



The program executes a least squares fit of the experimental diffractogram with the best combination of database sheets. Fractions diffractograms mixtures are used to determine the composition of the sample after performing the following refinements and or corrections::

1. Theoretical Mass Absorption Coefficient (" Mu/Rho ") of the sample in function of the chemical composition and density of each component provided by the database. Some databases do not contain information about composition or density and the program assigns " Mu/Rho " = 1.
2. PIR factor ("Pattern Intensity Ratio"). The program initially uses the RIR ("Reference Intensity Ratio") instead of PIR factor, because that is usually contained in some databases. The PIR factor can be

calculated later when you want to get more accurate quantitative results. When databases do not contain this information, the program assigns $RIR=PIR=1$.

In all cases the correction factors can be modified by the user. The results and the standard deviation of the analysis are written in the results table.

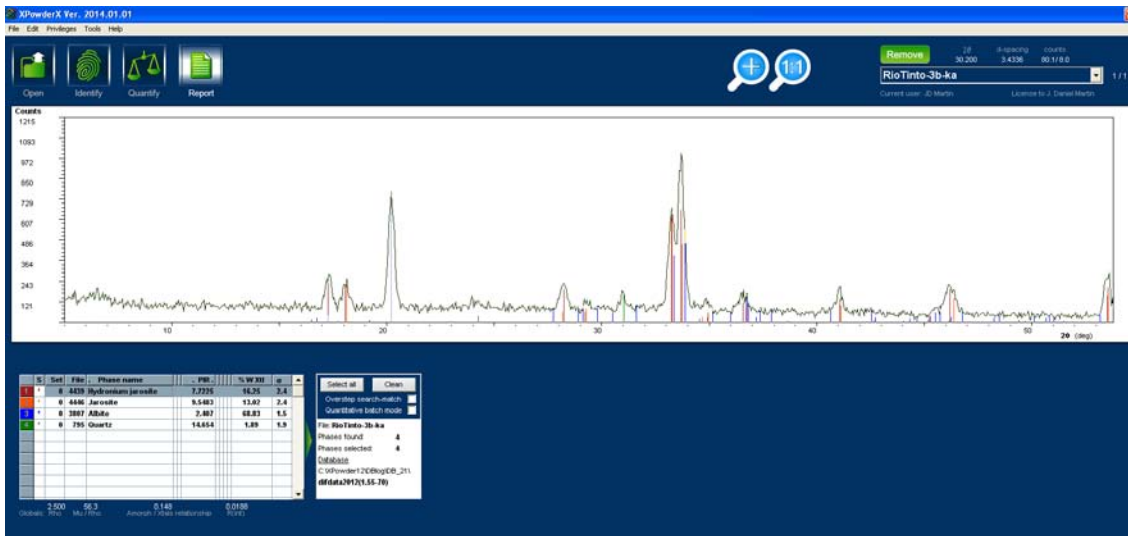


Figure 8.

Pressing the green arrow on the right of the compositional table, can be obtained additional information:

	S	Set	File	Phase name	Euclid	Offset	. PIR.	Fract	μ/ρ	% W Unc	σ	% W Xtl	σ
1	*	0	4439	Hydronium jarosite	0.0834	0.0031	7.7225	0.7700	51.5	16.38	2.4	16.25	2.4
2	*	0	4446	Jarosite	0.1226	-0.0048	9.5483	0.7700	46.9	13.25	2.4	13.02	2.4
3		1	4774	F5 Fe2 H4 O2	0.1571	0.0752	9.6055	0.2527	0.0				
4		0	5334	Beudantite	0.1682	0.0732	34.0411	1.0000	0.0				
5	*	0	3807	Albite	0.2073	0.1091	2.407	1.0000	60.5	68.25	1.5	68.83	1.5
6		0	6044	Zeravshanite	0.6787	-0.0654	7.0332	0.5150	0.0				
7		1	6676	Ammoniojarosite	0.7205	-0.0647	7.7285	0.6588	0.0				
8	*	0	795	Quartz	0.0000	0.0000	14.654	0.1895	19.1	2.12	2.1	1.89	1.9
9													
10													

Globals: Rho 2.500 Mu / Rho 56.3 Amorph / Xtals relationship 0.148 R(int) 0.0188

Select all

Overstep search-match

Quantitative batch mode

File: **RioTinto-3b-ka**

Phases found: **8**

Phases selected: **4**

Database

C:\XPowder12\Blog\DB_21\
difdata2012(1.55-70)

Figure 9.

In the example of figure 9, were maintained some phases identified but have not been included in the quantitative analysis. The columns show:

1. Order number and reflection colors of the database sheets.
2. S Phase is selected (*) / unselected by clicking on this column.
3. Set of database sheet.
4. File of database sheet. Set and File are unique for each record in the database. Originally belonging to the structure of PDF databases, but remain virtually everywhere, just for compatibility..
5. Phase Name. Phase name of compound in database. "Double click" on the box to change the color of sheet
6. Euclid. Euclidean distance between the phase parameters of the sample and of the database. This distance is smaller as the identification is correct.
7. Offset. Average divergence between 2 θ zero shift of the database sheet with of experimental pattern.
8. PIR "Pattern Intensity Ratio" or initial RIR value ("Reference Intensity Ratio").
9. Fract. Value in per unit height at which the phase of the database is best fit to experimental diffractogram before performing any correction adjusts.
10. μ/ρ . Coeficiente lineal de absorción de la fase de la base de datos, calculado a partir de la composición química y densidad.
- 11 % W Unc. Linear absorption coefficient, calculated of phase calculated from the chemical composition and density of the database sheet.
12. σ Standard deviation of column11.
13. %W Xtal. Weight percentage of crystalline phases, after making PIR/RIR and absorption corrections.
14. σ Standard deviation of column 13.

The "Amorph / Xtals relationship" index provides an indicative value of the ratio of amorphous (sl) a crystalline substances, based on the mean value of the intensities, standard deviation and area of the crystal reflections. It should be used only to establish relationships between substances of similar natures and recorded all with the same experimental.

When all opened diffractograms show identical qualitative composition, quantitative analysis can be performed in batches. To do this, press "Quantitative batch mode" from the popup menu in the composition table. In this menu other parameters quantification can also be modified by pressing "Set refinement parameters":

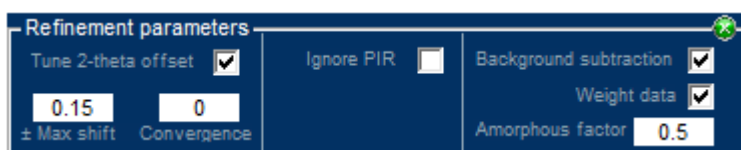


Figure 10.

The content of composition table can be saved in various formats for use in subsequent qualitative or quantitative analysis (in the same menu: "Open arrange file"). You can also retrieve and import composition tables HST, RFR, RUF and AMSCD code type (click on "Save arrange file").

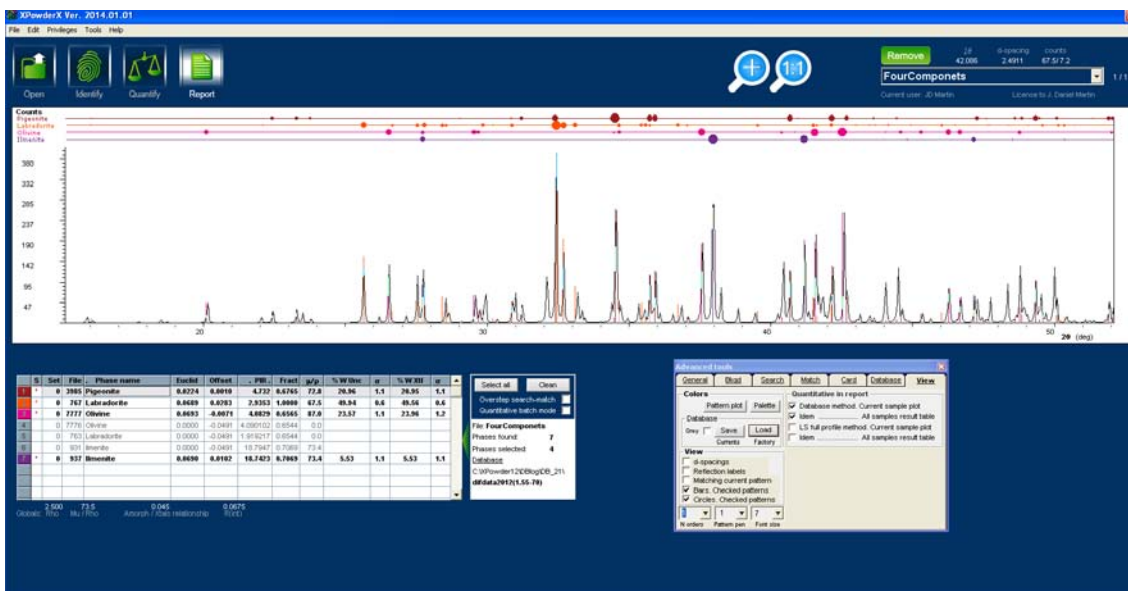


Figure 11. Image shows the results of a good quality qualitative and quantitative analysis. Database reflections are superimposed in the form of circles whose areas are proportional to the intensities.

Automatic quantitative analysis using database records

(Requires 'Auto quantitative database' permission (See Appendix 8. Figure A8.1))

The program allows you to use the list (HST) of components of a group of samples with similar composition, so that quantitative analysis is done automatically when you load the files of each diffractogram.

To do this, select the checking box in the folder **General** Tab of the *Advanced Tools* (arrow in figure). The program will use the composition of the HST file default ('F1a.hst' in the figure) the next time you upload one or more pattern file.

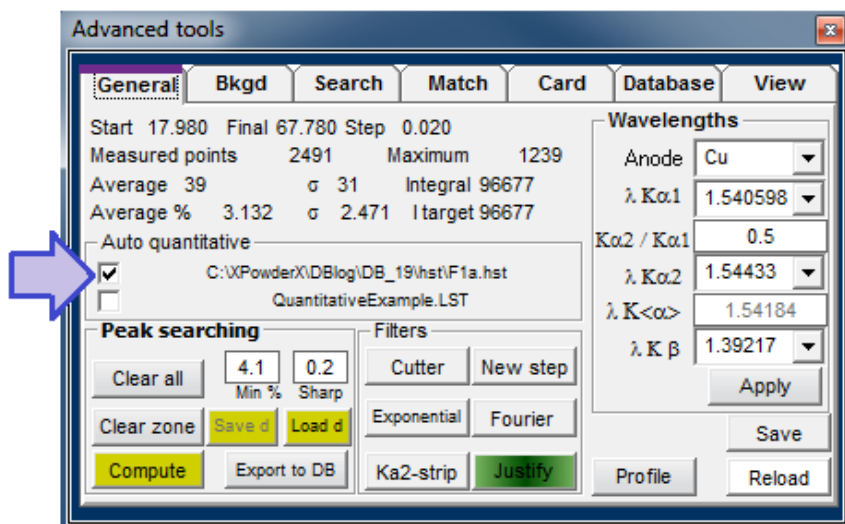


Figure 12.

The X PowderX program has an alternative possibility for performing quantitative analyzes based on experimental diffractogram adjustment to a mixture of the diffractograms of each of the components, obtained experimentally or by adjusting theoretical profiles (See APPENDIX 3 “Least-Square Full-Profile Quantitative Analysis” and APPENDIX 4).

Step 4. Report generation

The "Report" button is used: The size of the printing sheet can be selected in the popup menu.

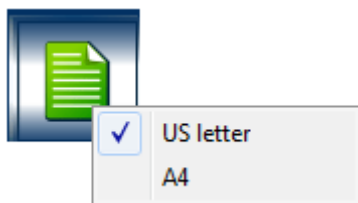


Figure 13

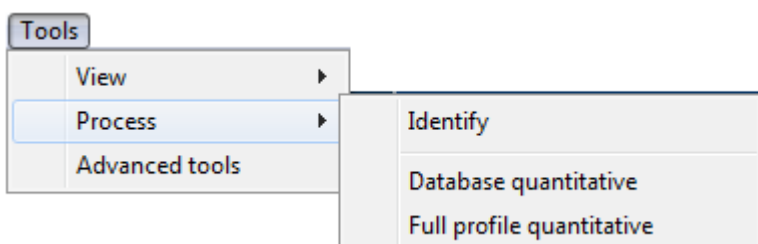
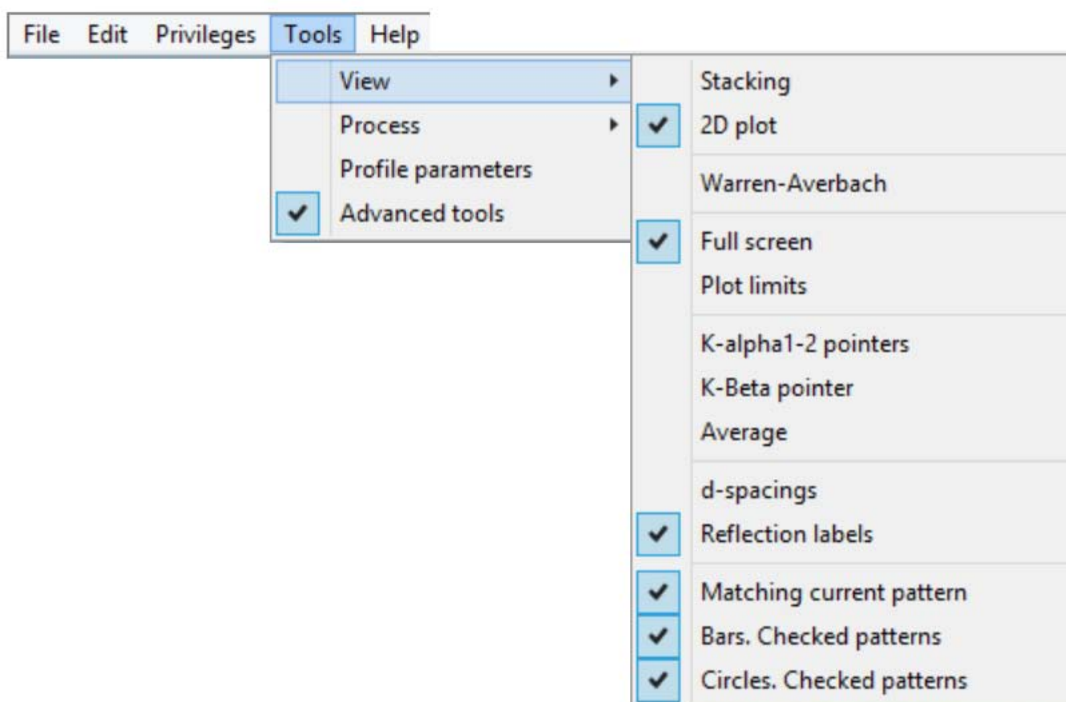
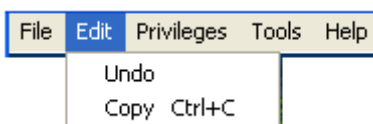
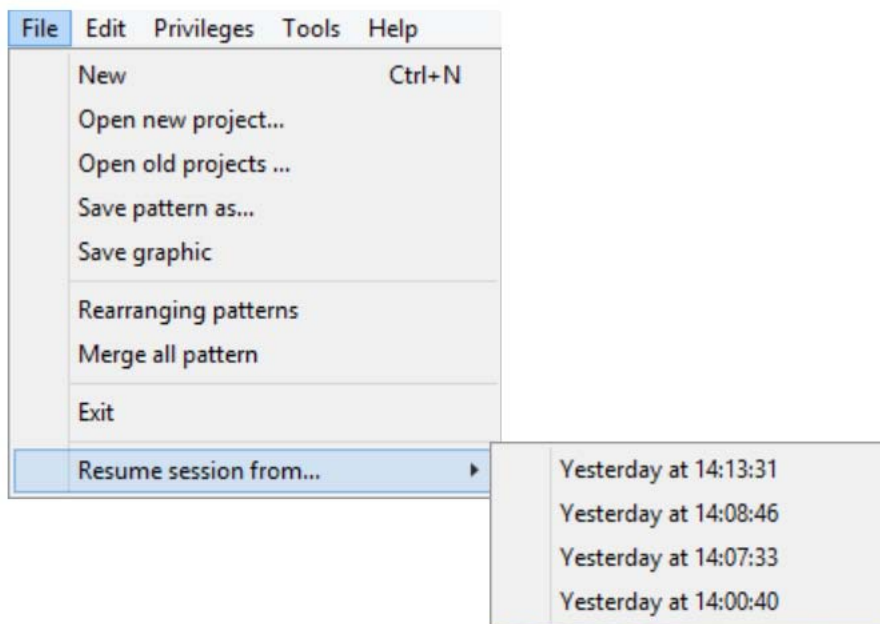
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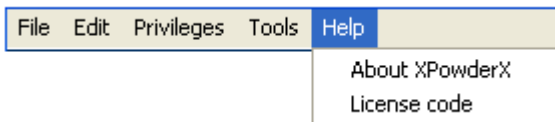
APPENDIX 1. Program menus

APPENDIX 1. Program menus

Home menu On the main screen following popup menus and submenus are available:

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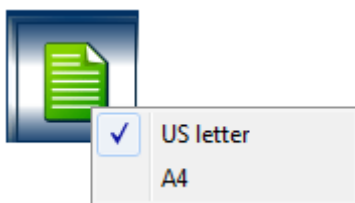




Popup menus

Existen varios:

1. By clicking right mouse button on the "Report" icon you can select the size of the sheet to generate the PDF file:



2. By clicking right mouse button on the composition table shows:

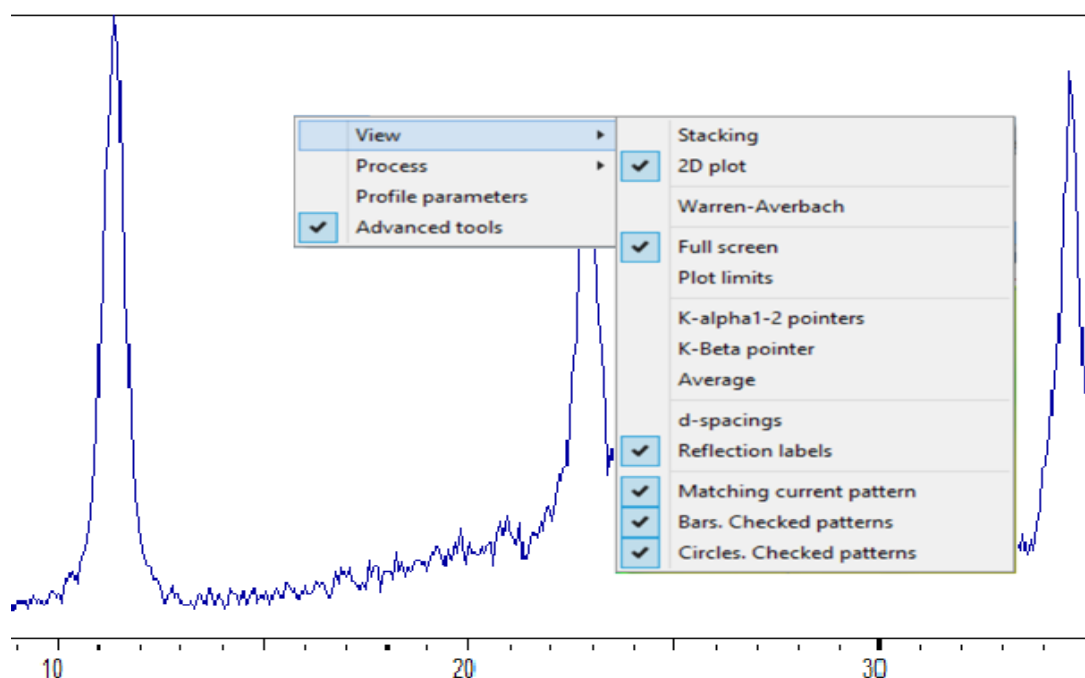
S	Set	File	Phase name	PIR	% W Xtl	σ
1	*	0 2821	Orpiment	0.349	5.31	5.3
2	*	0 3791	Cerussite	0.005	26.89	3.9
3	*	0 3289	Lazurite	0.911	12	7.8
4	*				5.99	6.0
5	*				9.17	9.2
6	*				8.44	8.4
7					6.09	6.1
8	*				10.97	9.9
9					6.68	6.7

Matching
 Globals:
 Set refinement parameters

Checked. Bars
 —
 R(int)

Figure A1.1

3. By clicking right mouse button on any point of the program window the same menu appear when you press "Tools" on the main menu:



APPENDIX 2. TOOLS

APPENDIX 2. TOOLS

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ZOOM

You can select a portion of the diffractogram combining the "Shift" key on the computer keyboard with the left mouse button while dragging the area you want to select. Loupes (1 in image) for the same purpose may also be used.

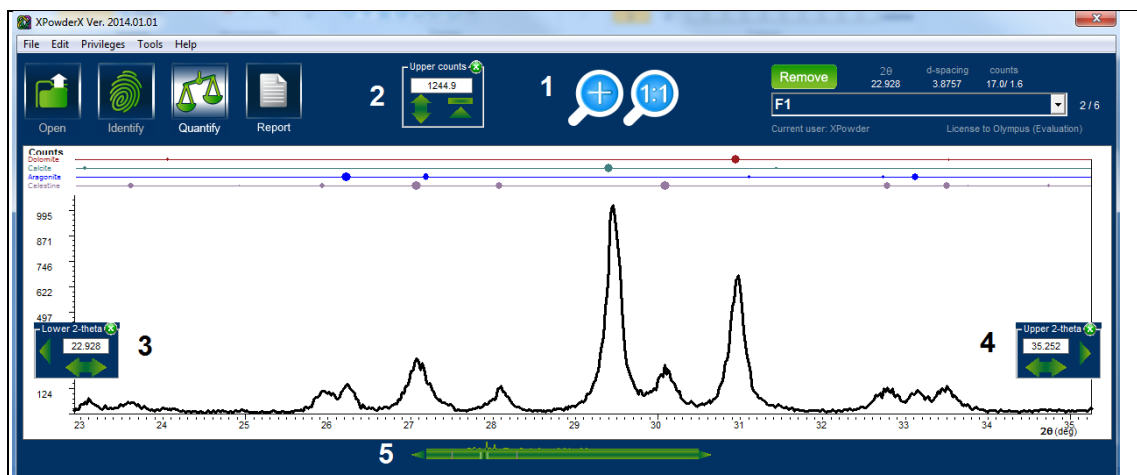


Figure A2.1.

Moreover, by selecting the "View / Plot Limits" menu, the following tools are displayed (the numbers refer to the picture):

2. Intensity scale. The green rectangle scale intensities to the maximum value of the current window. The green up arrow makes the maximum value represented will be the largest intensity of full diffractogram.
3. Control of the lower 2θ angle. The left arrow makes initial $2\theta = 2\theta$ minimum.
4. Control of upper 2θ angle. The right arrow makes upper $2\theta = 2\theta$ maximum.
5. Scroll bar below a thumbnail of the diffractogram, both green cursor arrows on both sides of this bar, vertical traces showing the assets 2θ limits on the main image is. Moving the cursor to this bar, or by pressing the left or right green arrows, the main image moves along the 2θ -axis.

The "Zoom" can be used to observe details in qualitative and quantitative analysis, or to select a **limited angular range** in which to carry out the identification of the reflections included.

REARRANGING PATTERNS

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This tool allows you to change the order of the diffraction patterns in the multiple graphs and reports: Access from the main menu: "*File / Rearranging Patterns*"

To use it, simply drag a row to the new desired position. The "*Invert*" button inverts the order of the diffraction patterns.

Drag the sample name with the left mouse button to the new position.

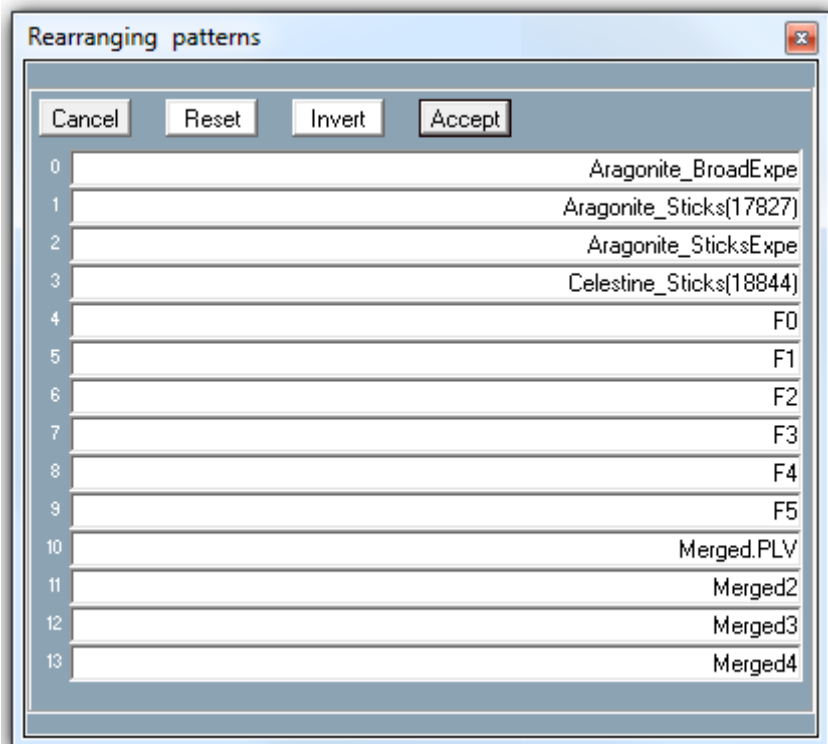


Figure A2.2.

ADVANCED TOOLS

They are displayed in the way explained in the previous section by clicking on **Menu/Advanced tools**). All tools appear together in the folder image, but are grouped into different tabs: **General**, **Bkgd** (Background), **Search**, **Match**, **Card**, **Database** y **View**. [Index](#)

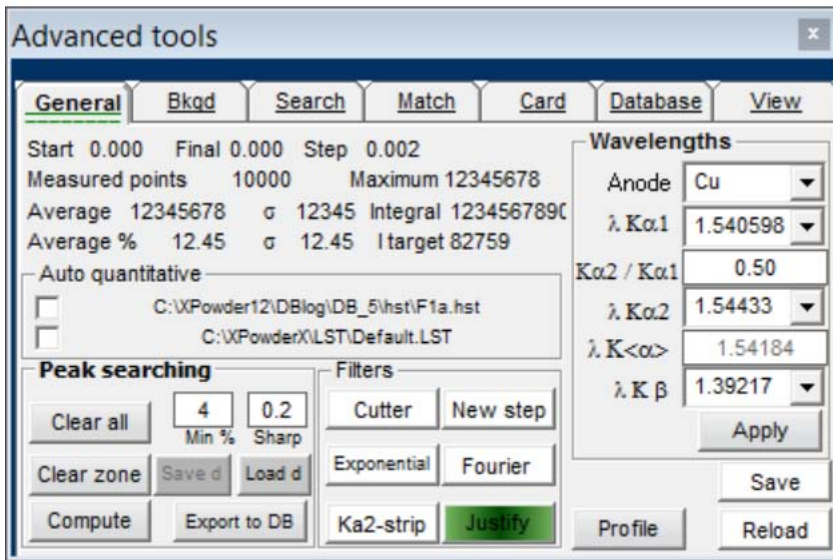


Figure A2.3.

In case that box "Batch mode" is checked some buttons change color to light green. This indicates to the user that all the calculations will be made on all the loaded diffractograms and not only over the current.

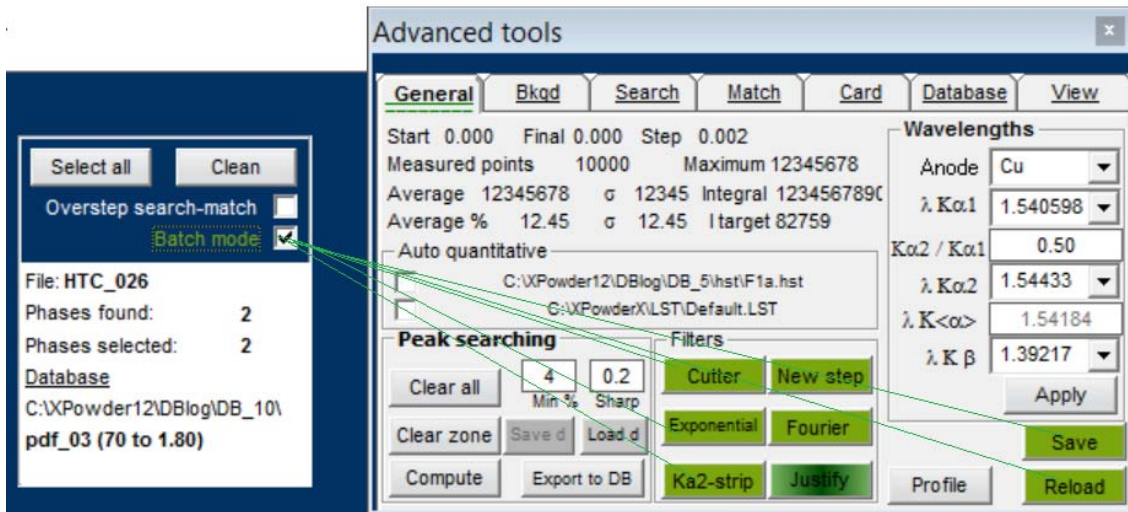


Figure A2.4.

Moreover, when arrows (or double arrows) are used to modify some parameters, these vary in both faster when pressed closer to the tip. For instance:

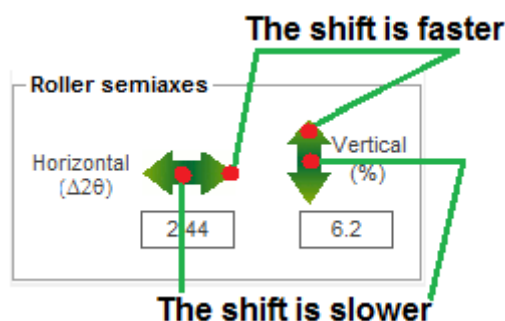


Figure A2.4.

“General” Tab Allows control overall data on the diffractogram

Reload /Save: Reopens/save changes for diffractogram/s.

Profile: Displays analysis tool profiles.

Autoquantitative: When a diffractogram is opened, automatic quantitative analysis according to the contents of the file specified in "XPowderX.ini" and the selected method is performed. (*Database* or "Full Profile")

Peak searching frame: It sets the values to calculate or discard spaced reflections obtained by Bragg's formula, which can be saved or reloaded by "Save d" and "Load d" respectively (these data are stored and linked to the original data file and they can be recovered in later sessions). It also allows generating a file of a personal database, using the calculated d-spacing (*Export to DB*).

Wavelengths frame: Controls the value of the wavelength. "Apply" changes the preset to "XPowderX.ini".

Auto quantitative frame: Contains information for automatic quantitative analysis. When a diffractogram is opened, automatic quantitative analysis according to the contents of the file specified in "XPowderX.ini" and the selected method is performed. (*Database* or "Full Profile").

Filters frame: It contains various mathematical filters that can be applied to the diffractograms. In any case, the changes are saved (for this we must then execute the command "Save")

Cutter: Limits the scanning interval to the current start and end 2θ angles.

New step: Allows modifying the "jump" (2θ step) between successive measurements

Exponential: Smoothing trace of the diffractogram using an exponential filter.

Fourier: Smoothing trace of the diffractogram by using Fourier Transform.

Ka₂-strip. Eliminates the $K\alpha_2$ component by an improved Rachinger Method.

Justify: Standardizes 2θ angles (initial, final and steps) for all those XRD patterns loaded. This action is performed even if the initial data formats are quite different. The order is also available in **2D** and **3D** stacking windows. The range is homogenized using higher initial 2θ values, the smaller final 2θ values and the minor 2θ interval. When some diffractogram has a variable step scan, data are converted into constant step (histograms). Occasionally, when the initial data are too heterogeneous, this command may need to be run twice. All patterns must use the same wavelength.

Wavelengths frame: Select wavelength values. "Apply" modifies the presets in "XPowderX.INI" file.

“Bkgd” Tab Provides tools for controlling background subtraction

Do: Eliminates the background of the current diffractogram.

Minors: Subtract the lower intensity of each of the measured points of diffractogram.

Negative: Removes negative intensities.

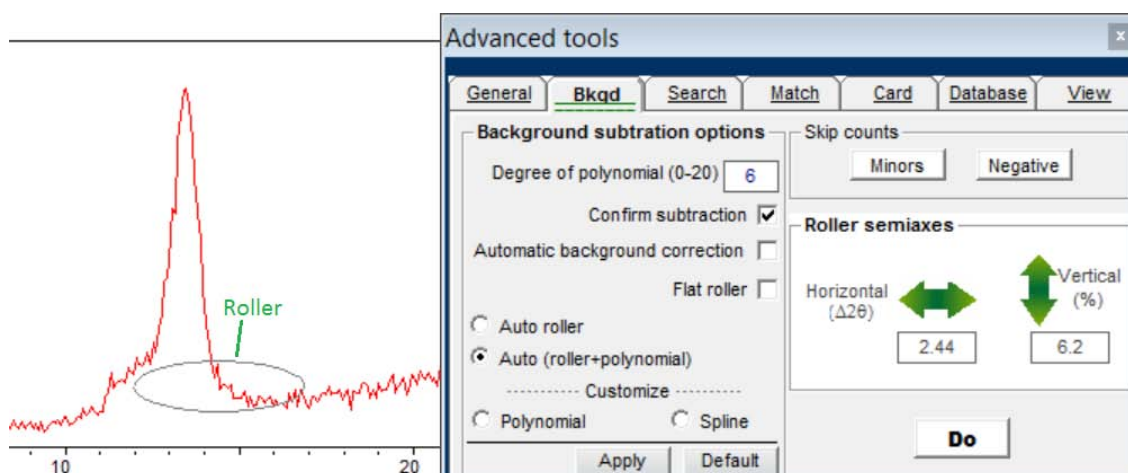


Figure A2.5.

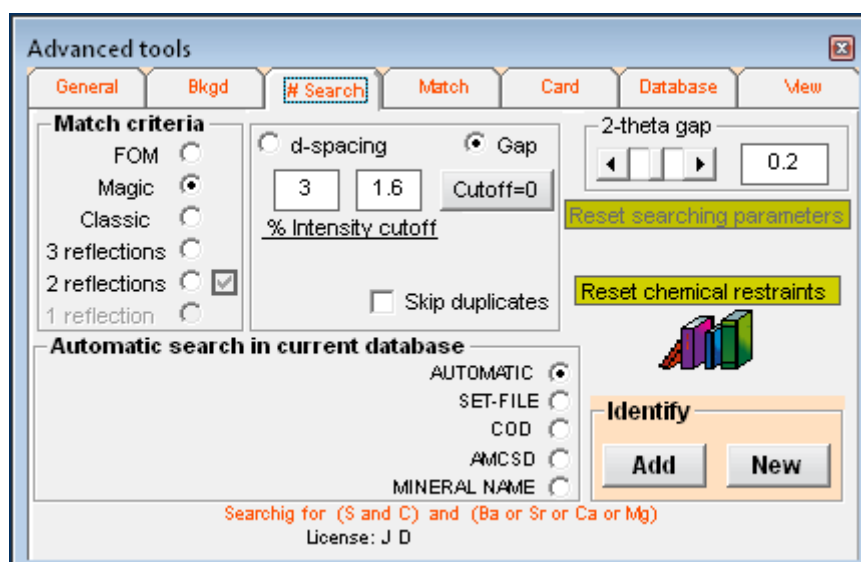


Figure A2.6.

“Search” Tab

The conditions of phase identification contained in the current 2θ intervals established in this tab according to one of the six criteria used by the program. The “2 reflections” and “1 reflection” criteria will be automatically selected by the program are marked respectively when only two or reflection. Intensity cutoff is the minimum intensity that the program will use during the first cycle of identification.

2-theta gap is the maximum 2θ interval at which reflections will be "observed". It is preferable to use excess values.

New: Clears the table composition.

Add: Add new phases on composition table.



Set database subfiles and chemical searching restraints.

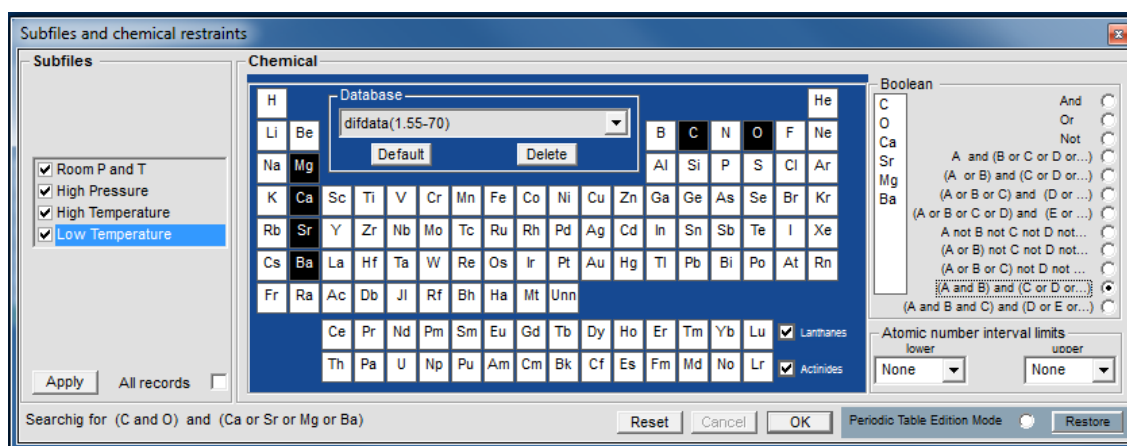


Figure A2.6.

The example shows how narrow the search to Ca, Sr, Mg and Ba carbonates. To this was selected in order C, O, Ca, Sr, Ba and Mg and the last but frame option "Boolean" was checked: *Searchig for (C and O) and (Ca or Sr or Mg or Ba)*.

También pueden eliminarse los elementos de la tabla periódica de uso infrecuente (*Periodic Table edition mode / Restore*):

Excluding elements from the periodic table in the search-match.

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Besides using Boolean constraints, frequent elements can be neglected in the periodic table (*Periodic table edition mode / Restore*):

Very often happen incorrect determinations of crystalline phases, because with those with frequent chemical compositions appear a large number of phases with unusual compositions, but whose number is very large within the content of the databases. The problem is aggravated when the structures allow solid solutions, or when the number of phases is large.

A partial solution to this problem is to remove those elements which are not expected in the sample composition from the periodic table. This possibility has been introduced in the program, using a **tool** which is accessible using the button '**Periodic Table Edition Mode**'.

By clicking the '**Periodic Table Edition Mode**' button, you access the tool of Fig E2.

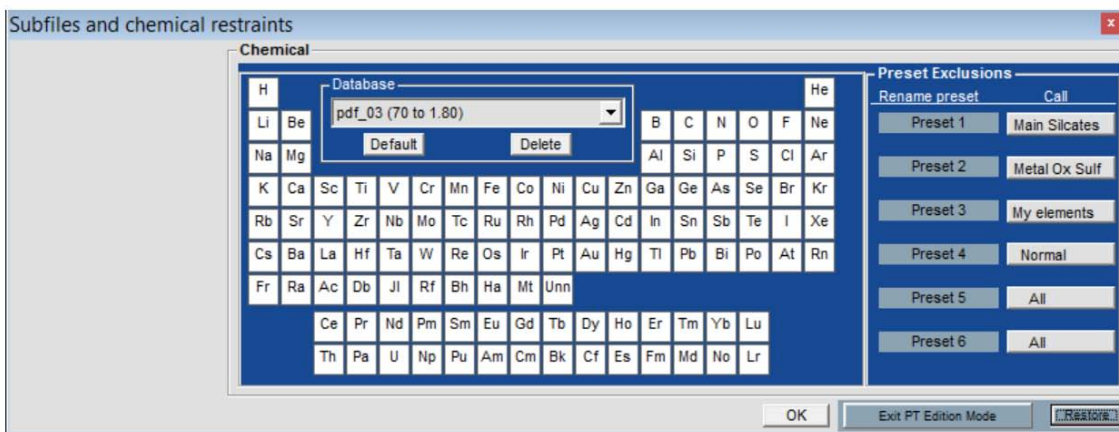


Figure A2.7. Individual elements can be ruled out (by clicking on the box the item as in Figure E3) or sequentially clustered (Figure A2.9).

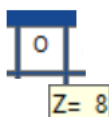


Figure A2.8. When it is Click on in the box of an item, it is discarded and then its symbol is written in white as Tc (Z=43) in picture.



Figure A2.9. Pressing the shift key, clicking the first ('Np', Z= 59 in the picture) and last ('No', Z= 73 in picture), and finally releasing the shift key, the intermediate elements (59 ≤ Z ≤ 73) are discarded .

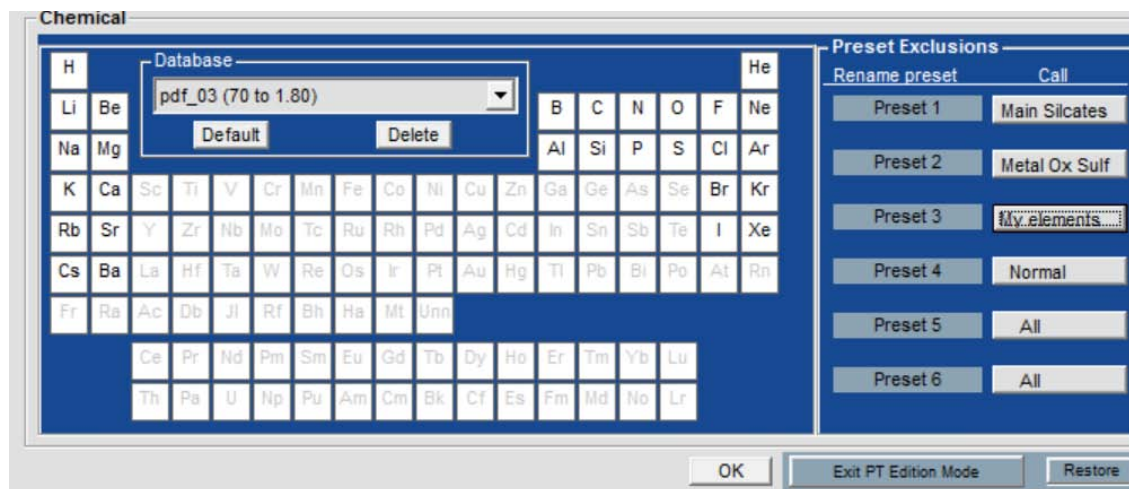


Figure A2.10. Enable the use of custom groupings presets. To do this just click on any of the buttons beneath the header 'Call'. After exclusion of undesired elements, you can save your settings by clicking on any text box beneath the header 'Rename preset'.

'Restore' buttons reset all elements of the periodic table.

A double click on the text box, or simply click on the button ('My elements' in the example), save the preset.

A click on the 'Exit PT Edition Mode' button in Fig, leaves the 'edit mode' of the periodic system. Boolean operations can now be used on the remaining elements only. Discarded *Elements* are recorded in the "Elements.Log" file and *Presets* in the "Preset.Log" file. Both files are charged by the program every time it reboots and does not change unless you delete them manually, or are edited again with the tools shown above.

Match Tab This tool helps you to select the phases encountered during the identification process.

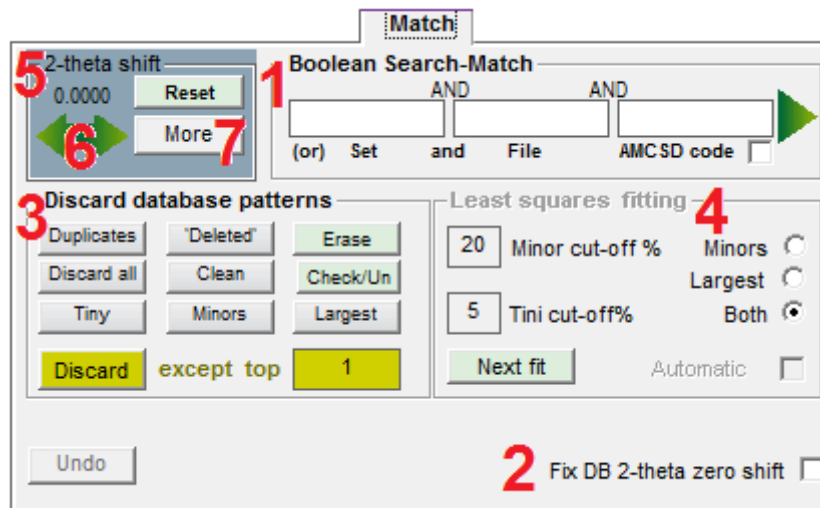
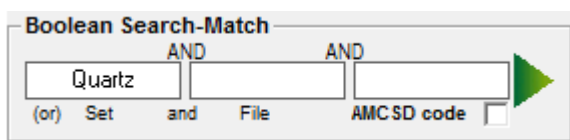


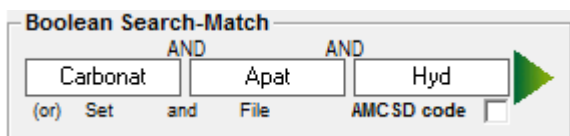
Figure A2.11.

1 Boolean Search-Match: Enables you to manually add compounds to the compositional table.

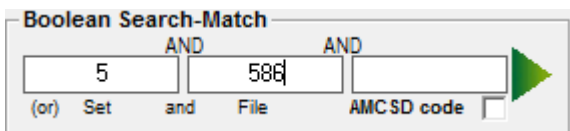
Examples (click on the green arrow  after entering the searching arguments):



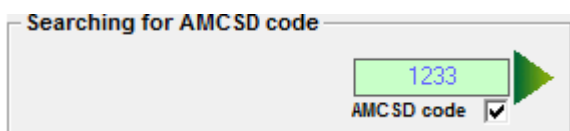
Quartz is added in compositional table (figure 9)



Carbonate-Hydroxylapatite is in compositional table.



Calcite is added in compositional table.




Pyroxene of AMCSD(2014) database is in compositional table.

2 Fix DB 2-theta zero shift. Automatically corrects in the graphic the 2θ divergence between d-spacing of components found in the database and those measured experimentally.

3 Discard database patterns. Removes compounds from the preselected mineral compositional table.

4 Least square fitting. Look for the row of the composition table that best fits to diffractogram by least squares methods using full profile diffractogram according to the chosen option (*Minors / Largest / Both components*). The search ignores the rows that are already selected.

5 2-theta zero shift frame. Enables you to manually compensate in graphic the 2θ zero displacement of experimental diffractogram.

The simplest way to do this correction is to use the double green arrow  to move linearly experimental patterns along 2θ , as in **6** in figure A2.11.

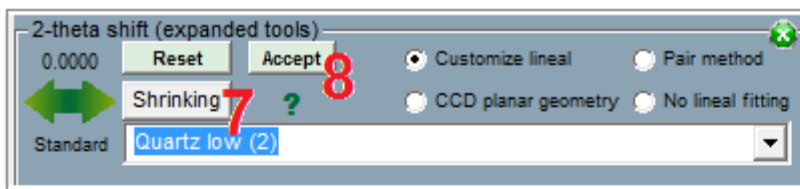


Figure A2.12

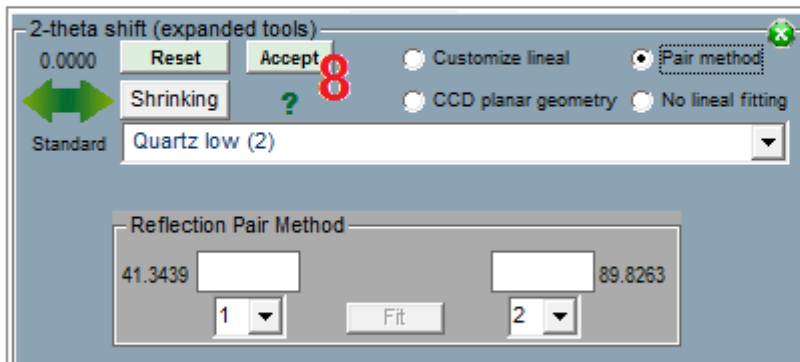


Figure A2.13

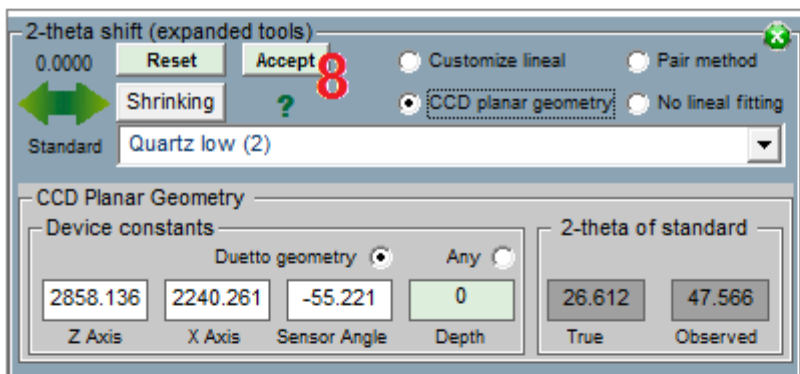


Figure A2.14

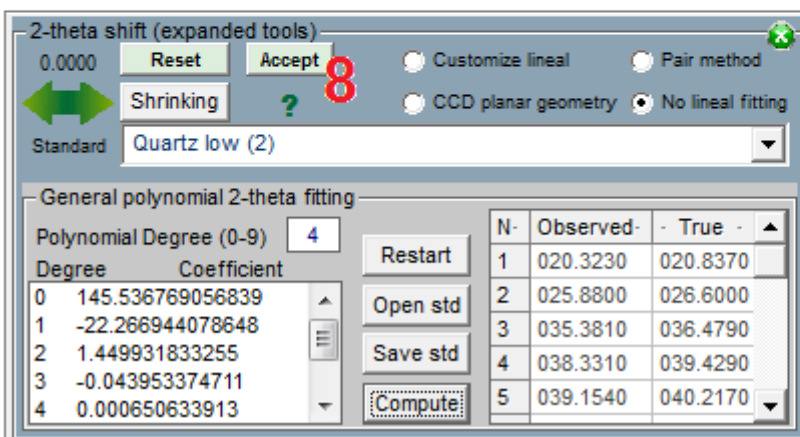


Figure A2.15

There are other more powerful methods, which is accessed by pressing the "More" / "Shrinking" (7) button. In all a help it is shown when the green question mark (?) is pressed (figures A212- A215). The methods are:

- "Customize lineal" (Figure A2.12). A standard mineral can be superimposed on the pattern. Then move the diffractogram horizontally to get the best fit by using green arrows. You can include any mineral editing the text "std.txt" and add it manually, always respecting the format shown. It should be noted that the contents of these files includes the keyword 'Begin standard ', anticathode (according to the definitions file "XPowderX.ini ") values list "2 θ "+ comma (,) + intensities at 1000. Each pattern scale ends with the line "000.0000, 0000". By example :

```
Begin standard
Lambda= Cu
None
000.0000, 0000
```

Begin standard
 Lambda= Cu
 Sodium Chloride (Halite syn)
 027.3024, 0130
 031.6547, 1000
 045.3954, 0550
 053.7887, 0020
 056.4108, 0150
 066.1488, 0060
 072.9777, 0010
 075.2129, 0110
 083.8708, 0070
 090.2991, 0010
 101.0693, 0020
 107.6764, 0010
 109.9103, 0030
 119.3563, 0040
 127.0104, 0010
 129.7306, 0030
 142.0569, 0020
 000.0000, 0000

Begin standard
 Lambda= Cu
 Calcium carbonate (Calcite Syn)
 022.9948, 0120
 029.3704, 1000
 Etc.

- **“Pair method” (Figure A2.13).** To apply this method will require two different orders of a reflection, that appear on the angles θ_1 and θ_2 respectively.

When there is a shift of the origin Δ_θ of the scale of the θ angle, the equation of Bragg requires:

$$n_1 \cdot \lambda = 2 d \sin(\theta_1 - \Delta_\theta)$$

$$n_2 \cdot \lambda = 2 d \sin(\theta_2 - \Delta_\theta)$$

$$N = n_1/n_2 = \sin(\theta_1 - \Delta_\theta) / \sin(\theta_2 - \Delta_\theta)$$

$$N = (\sin\theta_1 \cdot \cos\Delta_\theta - \cos\theta_1 \cdot \sin\Delta_\theta) / (\sin\theta_2 \cdot \cos\Delta_\theta - \cos\theta_2 \cdot \sin\Delta_\theta)$$

If numerator and denominator are divided by $\cos(\Delta_\theta)$

$$N = (\sin\theta_1 - \cos\theta_1 \cdot \tan\Delta_\theta) / (\sin\theta_2 - \cos\theta_2 \cdot \tan\Delta_\theta)$$

$$\tan\Delta_\theta = (\sin\theta_1 - N \sin\theta_2) / (\cos\theta_1 - N \cos\theta_2)$$

it appears the zero shift (deviation, error) of 2θ angle.

$$\Delta_{2\theta} = 2 \cdot \Delta_\theta$$

To carry out the correction, you should select two orders of a reflection of Bragg (could be any, even non-consecutive reflections). By placing the cursor $n = 1$ on the first reflection (ie, approximately 18.6 degrees) shows that the position of second order is not correct (ie, the second cursor, approximately 17.7 degrees). Pressing “Alt+ left mouse button” the correction is automatically carries out.

- **“CCD planar geometry” (Figure A2.14).** This nonlinear correction is used with flat detector diffractometer where the sample position is not be fitted accurately. Requires knowing the approximate distance between the sensor and the sample, and the angle between sensor and X-ray beam. Can be used either one reflection standard (True and Observed boxes and Compute) or the Customize cursor to move the diffractogram to the correct position The method requires using a

sample component with known diffraction pattern (standard "std.txt" list) and the correction is performed automatically when you drag with the left button of the standard diffractogram any reflection from the situation observed in their true position. If that does not use a standard, successive tests can be performed ("trial and error") to achieve acceptable results.

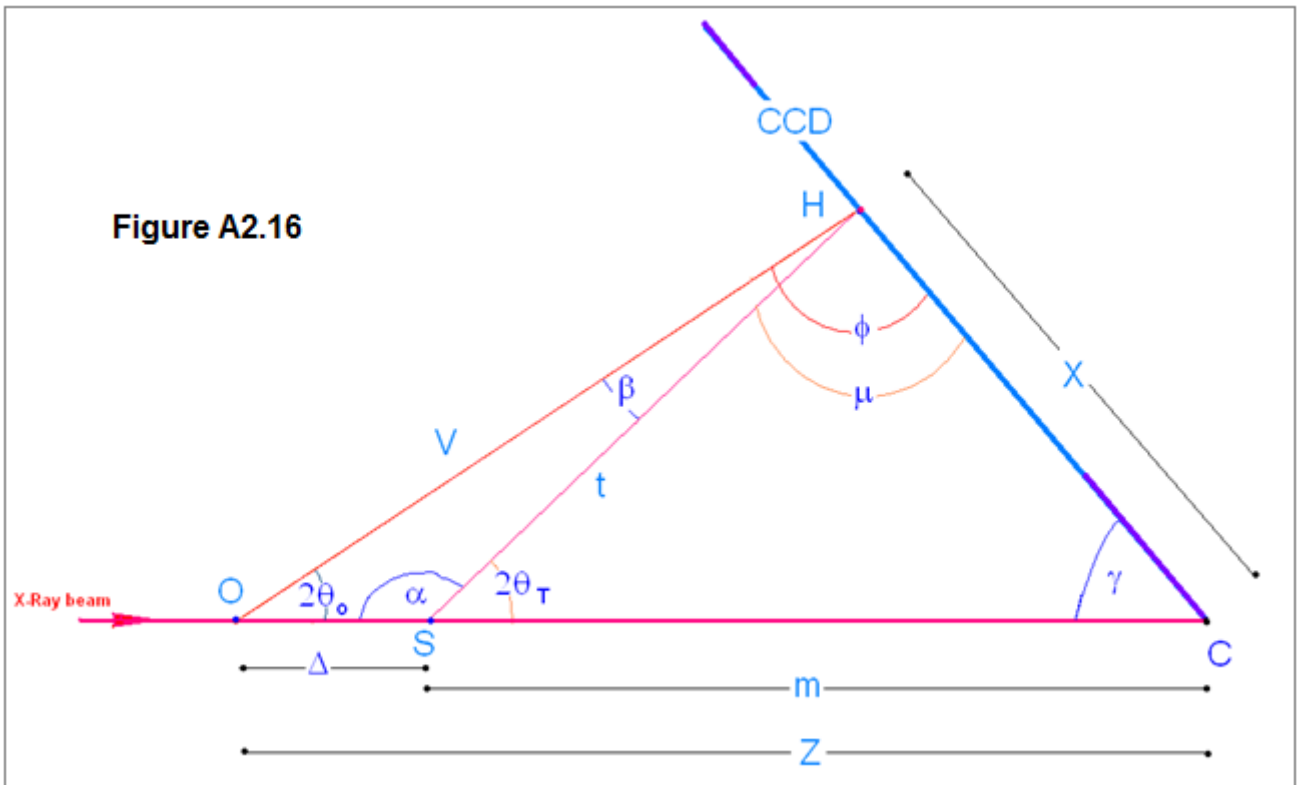


Figure A2.16

O = Diffractometer centre (ideal sample position)

S= real sample position

$\gamma = 90^\circ$ - Sensor angle

Z= Axis Z length. Distance between O and CCD along primary X-Ray beam

X = Coordinate along Axis X

Δ = Displacement of diffractometer center ("Depth")

$2\theta_o$ = Observed (measured) 2θ

$2\theta_T$ = True 2θ .

2θ correction in function of 'depth' X-Ray penetration (= sample offset along primary X-Ray direction)

Δ is a know or estimated data

In **OHC** triangle, by using sine theorem:

$$\sin 2\theta_o / X = \sin \gamma / V = \sin \phi / Z \quad \gamma = 90^\circ \text{ - Sensor angle}$$

$$V = X \cdot \sin \gamma / \sin 2\theta_o \quad [1]$$

$$X = Z \cdot \sin 2\theta_o / \sin \phi \quad \phi = \pi - \gamma - 2\theta_o$$

$$X = Z \cdot \sin 2\theta_o / \sin (\pi - \gamma - 2\theta_o) \quad [2]$$

In **OHS** triangle, by cosine theorem:

$$t^2 = \Delta^2 + V^2 - 2 \Delta V \cdot \cos 2\theta_o \quad [3]$$

And by sine theorem :

$$\sin \alpha / V = \sin 2\theta_o / t \quad \sin \alpha = \sin(\pi - 2\theta_T) = \sin 2\theta_T$$

$$\sin 2\theta_T = V/t \cdot \sin 2\theta_o \quad [4]$$

By replacing V [1] and t [3] in [4]

$$\sin 2\theta_T = (X \cdot \sin \gamma) / (\Delta^2 + V^2 - 2 \Delta V \cdot \cos 2\theta_o)^{1/2}$$

Where V and X are calculated by [1] and [2]

This formula let to correct the deformation of 2θ scale of any diffractogram obtained from CCD. Δ can be estimated from a reflection standard (see next page) or by a cursor changing Δ value while the new diffraction pattern is matched.

Calculation of 'depth' X-Ray penetration (= sample offset along primary X-Ray direction) from a standard reflection

$2\theta_T - 2\theta_o$ are know data

n OHS triangle, by sine theorem:

$$\sin \alpha / V = \sin 2\theta_o / t = \sin \beta / \Delta \quad [6]$$

$$\beta = \pi - \alpha - 2\theta_o = \pi - (\pi - 2\theta_T) - 2\theta_o = 2\theta_T - 2\theta_o$$

On the other hand:

$$\sin \alpha = \sin 2\theta_T$$

[6] can be rewrited:

$$\sin 2\theta_T / V = \sin 2\theta_o / t = \sin (2\theta_T - 2\theta_o) / \Delta$$

Turn out Δ :

$$\Delta = [V \cdot \sin (2\theta_T - 2\theta_o)] / \sin 2\theta_T \quad [7]$$

Where:

$$V = X \cdot \sin \gamma / \sin 2\theta_o \quad [1]$$

$$X = Z \cdot \sin 2\theta_o / \sin(\pi - \gamma - 2\theta_o) \quad [2]$$

$$\gamma = (90^\circ - \text{SensorAngle}^\circ)$$

Z = axisZ (distance from ideal simple position to CCD along X-Ray beam direction). **Z is an independent variable.**

Then

$$\Delta = [Z \cdot \sin \gamma \cdot \sin (2\theta_T - 2\theta_o)] / [\sin (\pi - 2\theta_o - \gamma) \cdot \sin 2\theta_T] \quad [8]$$

Figures A2-16 and A2.17 show a very fast procedure that corrects 2-theta errors caused by the misalignment of the experimental device, caused either by geometric conflicts due to the nature of the object analyzed (three-dimensional objects or with curved surface , size and position...), or simply by errors induced by the diffractometer operator itself. This process allows to recover experimental data that could not be used in another case to perform qualitative routine analysis by X-ray diffraction.

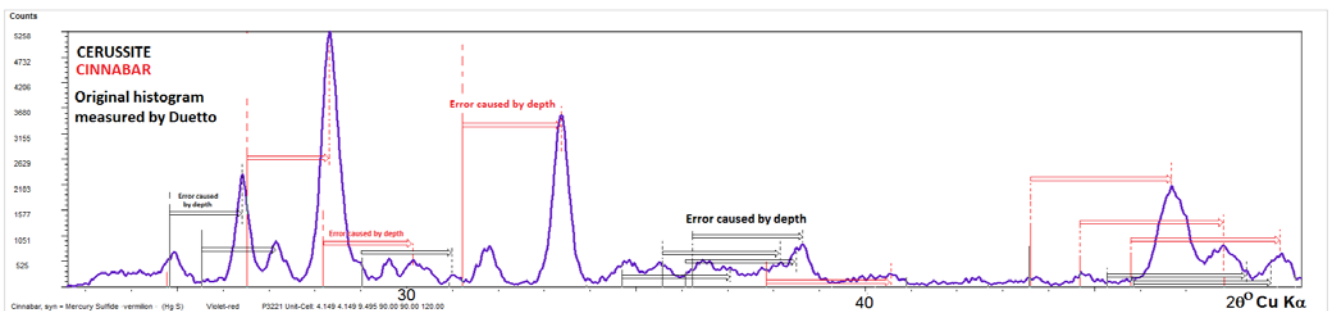


Figure A2.17. The XRD of sample containing both Cerussite and Cinnabar pigments was measured with Duetto, having an unknown and arbitrary strong depth error Δ (figure A2.16) , which is an independent variable in formula [8]. The displacement errors of measured peaks are not homogeneous, because they depend on the γ and θ values, which are the arguments of several sine functions in formula [8].

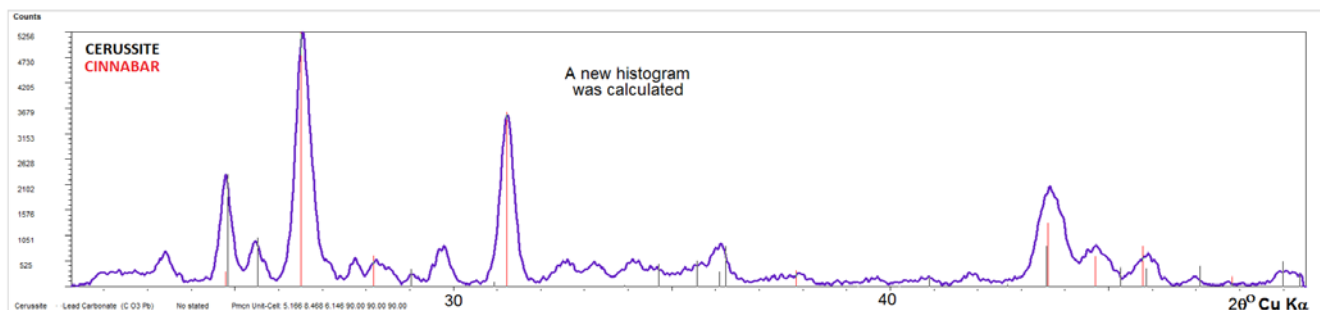


Figure A2.18. It is sufficient to drag any peak of the diffractogram from the current position to the correct one, which is shown by the vertical lines of the corresponding to database values (just in the opposite direction of any arrow in Figure A2.17). When raising the mouse button, the non-linear correction formula [8] of the angular displacement is performed on all points of the entire diffractogram and a new histogram is computed. Now, all Cinnabar reflections and all Cerussite reflections simultaneously are corrected and displayed in the true 2θ angular positions. The vertical straight lines are from the database. Finally press 'Accept' (8) as in figures A1.12-A2.15

- **“No linear fitting” (Figure A2.15).** This is a general purposes algorithm that allows any non-linear adjustment of 2θ by using a standard sample and an up to 9 maximum polynomial degree. This method can be used instead of previous **“CCD planar geometry”**, but requires examination of reflections of the full 2θ angular interval. After performing the angular correction, by pressing **‘Accept’ (8)** in figure A2.15, an similar image to of figure A2.18 is achieved.

In addition, the last two non-linear adjustment procedures (**“CCD planar geometry”** and **“No linear fitting”**), can be used to study the depth of different compounds, when they are layered structure. This happens, for example, with the pigments used in the paints, where various layers are located at different depths, with differences of up to several microns. However, a good fitting to true 2-theta angles requires that there is at least one standard having a known constant stoichiometry and good crystallinity, among the all analyzed compounds. In general, pigments obtained from minerals, with their inevitable isomorphous substitutions in the form of solid solutions, different degrees of hydration or any other crystalline defects, cannot be considered good standard. In this case, it will be daring to attribute the deviations of theta to certain depths of each layer. For example, these criteria could not be used in the example of Figures A216 and A217, because both Cerussite and Cinnabar are minerals that contain many crystalline defects and therefore their d-spacing, FWHM and HKL intensities are variable.

It is convenient to keep in mind that after making this **powerful correction**, experimental data (X, Y) lose their original structure histogram, since the angular interval between successive points is no longer constant. This is not a problem for the X Powder program, since it can analyze indistinctly histogram structure data like others in which the angular interval is not constant. However, this capability is not contemplated in most XRD-based search-match programs, so X Powder finally calculates a new diffractogram that maintains all the experimental values but with a new histogram structure. The final process uses virtual data computed by fitting additional points to a moveable parabolic function. In this way, the profiles of the reflections maintain exactly the original forms and, of course, the parameter values of their mathematical distribution functions. In addition, this last action allows users of Duetto and other similar devices to export the data so that they can be interpreted by other programs.

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Card Tab Shows the original sheet of the database and color assigned to graphics, which can be changed by double clicking on the colored box. It also lets you export the current database sheet to a personal database (*Export to DB*)

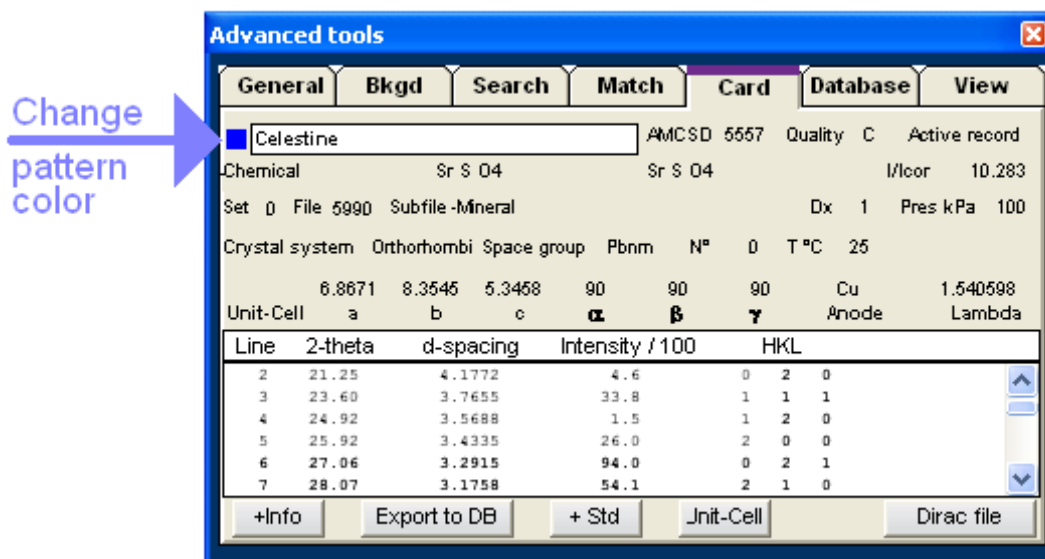


Figure A2.21.

The "Dirac file" button allows you to create a file in text format PLV with the reflections contained in the database and values FWHM = 0. These files are useful as pre-theoretical diffraction patterns generation with distribution functions, asymmetries and step values Caglioti convolution which can be adjusted (see APPENDIX 4).

Database Tab Allows manage databases.

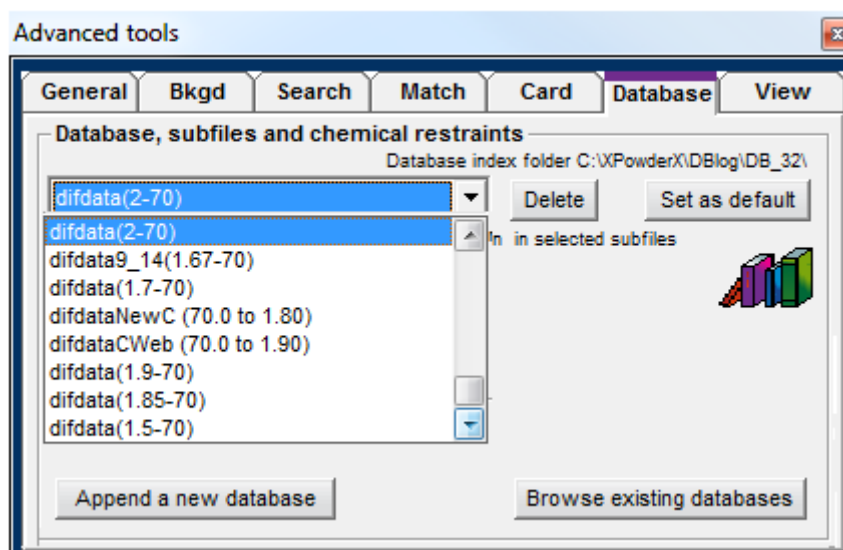


Figure A2.22

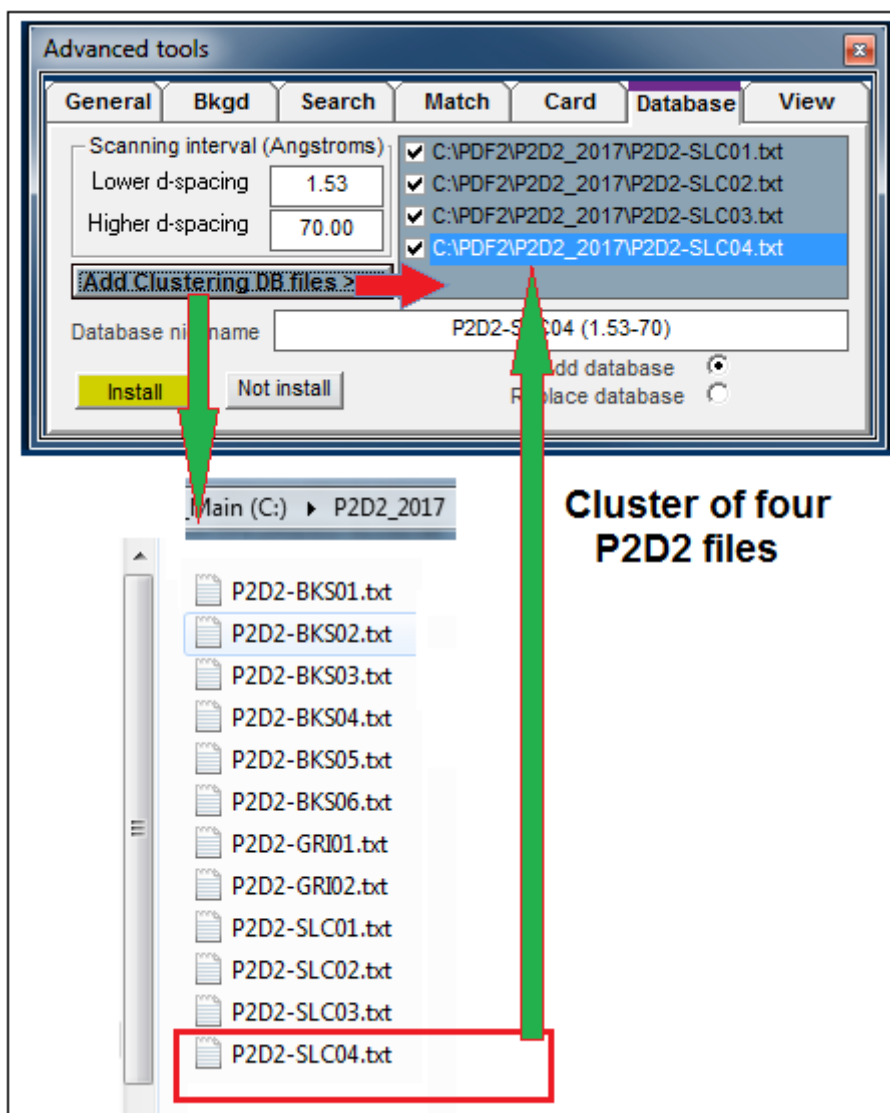



Figure A2.22B

Also, the icon  sets restrictions on chemical composition and allows you to select database subfiles, like **Match tab**.

Database installation

The databases are not attached to the program and must be purchased separately. The databases recognized by X Powder X are 'PDF2.DAT' (between 500MB and 550MB or so, depending on the version) and 'DifData.txt' (approximately 65 MB).

In order to begin the installation of a new base, press '**Append a new database**' (figure A2.22.), read the 'advertisement' and click 'Accept'.

Now look for the archive of database. It is desirable that the databases are on your hard drive rather than on a CD-ROM or DVD in order to optimize the searching speed.

Database files could be:

- ICDD: 'PDF2.dat'
- AMCSO: 'cifdata.txt' (optional) + 'difdata.txt' (required). In any case, 'cifdata.txt' must be installed before the 'DifData.txt'. 'cifdata.txt' (approximately 31 MB) is an auxiliary file of 'difdata.txt', its use is optional and it can be deleted once the setup has been completed.
- P2D2 'zeolites' text format database (*.txt)

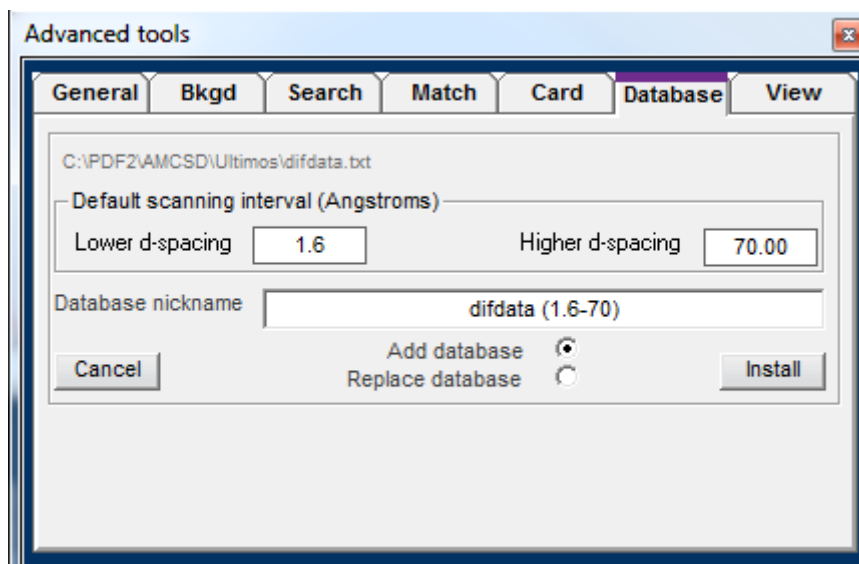


Figure A2.23

You must also assign a 'nickname' to current database installation and *d-spacing* scanning interval in order to optimize the searching algorithms (figure A2.23). This allows an unlimited number of installations of the same database with different 'nickname's for each.

You can also choose (figure A2.23) to replace the currently used database (Replace database) or add it (Add database) to the list of figure A2.22

* * *

PDF2.DAT. It is the most popular database and is sold by the ICDD. For installation in XPowderX only need the file 'PDF2.DAT', because XPowderX creates its own index. PDF2 contains several sub-files that include all branches of solid materials used in science and technology:

- Inorganics
- Organics
- Minerals
- Metal and alloys
- Common phases
- NBS (National Bureau Standards)
- Forensic
- Educational
- Zeolites
- Explosives
- Super conducting materials
- Cements
- Corrosive materials
- Polymers
- Detergents
- Pigments
- Pharmaceutical
- ICSD
- Ceramics

PDF2 can be purchased at:

ICDD Internet site: www.icdd.com E-mail: info@icdd.com
Postal Address: International Centre for Diffraction Data
12 Campus Boulevard
Newtown Square, PA 19073-3273 U.S.A.
Telephone (610) 325 9814
(610) 325 9814 (General information)
(610) 325 9810 (Sales)

The quality of the PDF2 records is very heterogeneous, since there are diffractograms obtained with different radiation, different geometries or instrumental conditions. There are even not indexed or wrongly indexed phases. They also contain theoretical diagrams calculated from their crystal structures. In general the quality of the records is good and the file is completed and improved year after year.

In order to install the ICDD database, only 'PDF2.DAT' file from PDF-CDROM is necessary without any other file index.

Highest quality large custom databases from CIF files (i.e. Crystallography Open Database -COD). See [APPENDIX 10](#). *Creating a custom massive database powder diffractogram.*

AMCSD databases (American Mineralogist Crystal Structure Database. Diffraction pattern have been calculated from the crystal structures published in the scientific literature. In general the quality is high and the database includes many entries of isomorphic series at high temperatures and high and very high pressures.

The records have a homogeneous quality and, although these are calculated, fit well with experimental diffractograms. The biggest errors occur in minerals whose structure and unit-cell were published long ago, as they were based on values of inadequate wavelength or inaccurate tools. This results in systematic errors on calculated d-spacing and hinders the identification. By contrast, diffractograms based structures published in the last few decades are very accurate. The *Difdata.txt* and others AMCSD files, does not includes chemical formulas in itself (it only indicate the name of a mineral). However, the composition is found in the '*CifData.txt*' file provided in parallel and can be loaded prior to *difdata.txt* installation. Even without this operation, XPowderX assigns a chemical formula to correct 96% of the records.

CifData.txt. is a complementary AMSCD database (American Mineralogist Crystal Structure Database) . It contains the structural and compositional data that have helped generate sheets of diffractograms database 'DifData.txt'. The installation under the program XPowder is not necessary (but desirable). In any case must be installed before the 'DifData.txt'.

P2D2 (Predicted Powder Diffraction Database. Download: [Predicted Powder Diffraction Database](#)) is built up by calculating the powder patterns corresponding to the predicted crystal structures from the latest PCOD update. The job is done partly by ZEFSA II (898707 entries) and for the GRINSP data (163520 entries) by the CIF2POW software. The P2D2 database currently includes twelve text files, each with approximately 100000 compounds, which can be automatically indexed by XPowderX, individual or jointly (*cluster* figure A2.22B).

MyDatabase.MyD. It is a database that can easily be created and customized by the user. The generated files have the extension MYD and they can be installed at any time on various computers, just like any other database.

- ***Advanced Tools / Tab General /'Export do DB'***. It allows generates the database record card for the current experimental diffraction pattern and add to actual '*My database*' .
- ***Advanced Tools / Tab Card /'Export do DB'***. It allows to export a s record card from a existing database to actual '*My database*' .

'**Import crystal data**' is disposable only from '**Advanced Tools / Tab General /'Export do DB'** and allows import crystallographic data from a pre-existing data base record card. The '*My database*' tools is shows in figure A2.24

After the edition of the new record card, it is included in the '*My database*' by pressing 'Add' .

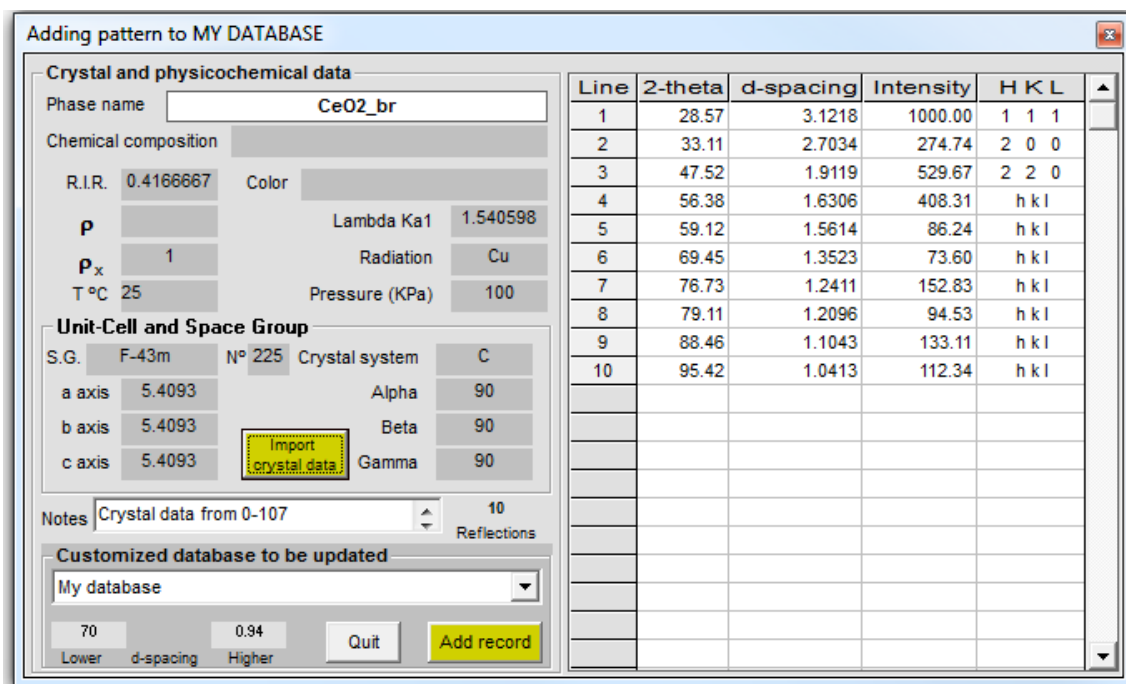


FIGURE A2.24. 'Import crystal data' is disposable only from 'Advanced Tools / Tab General /Export do DB' and allows import crystallographic data from a pre-existing data base record card. The content of most boxes are editable, like for example the Phase name, unit-cell parameters, intensities or HKL values.

* * *

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View Tab Allows select what is shown on the main screen: Color active diffractogram ("Pattern"), the color palette of the all loaded diffractograms (Palette). The palette used in the database can be saved and reloaded. Furthermore you can select that graphic on the screen different number of orders Bragg, cursors and $K\alpha_2$ $K\beta$, font sizes, line width or different display. Moreover they can be selected different methods of visual comparison with data from databases (lines, circles with intensity proportional to area, record database (Active, All uploading patterns) ...

You can select a display type mode (single pattern, stacked in mode Pile or in '2D maps' where the intensities are displayed as false color.

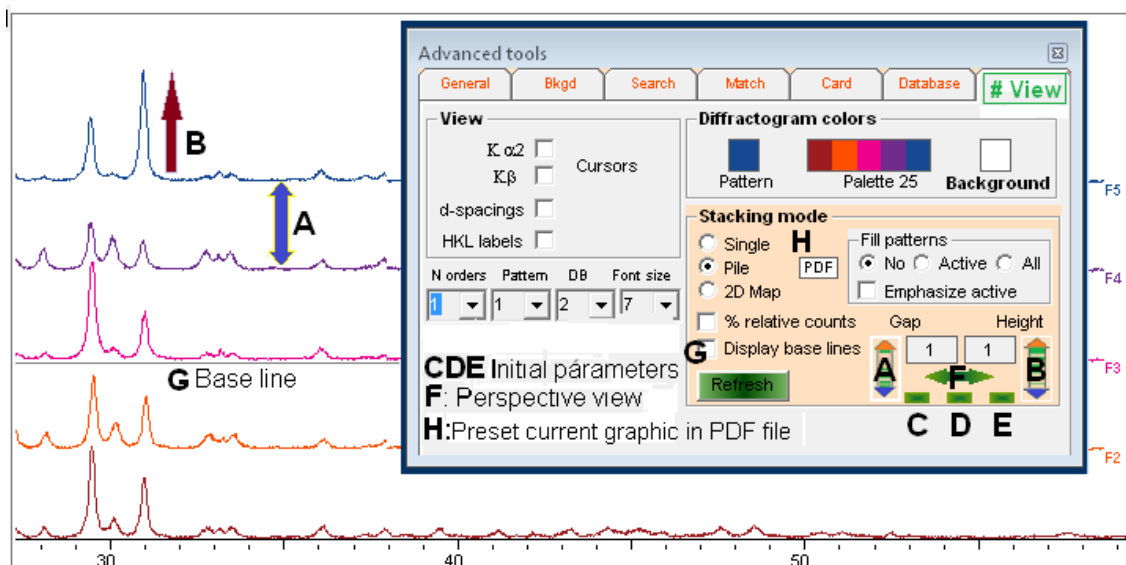


Figure A2.25.

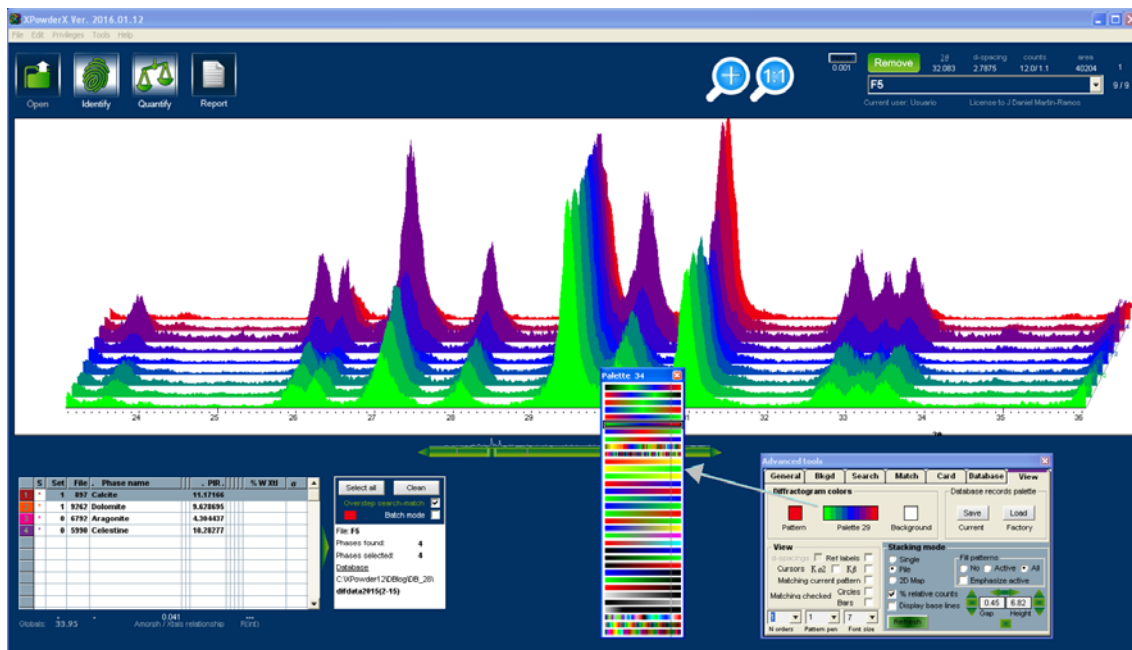


Figure A2.26.

The active diffractogram can be selected in the text box top right of the screen (HTC_014 in the example). When selecting the "Fill patterns / All" option, a "double click" on any diffractogram allows selected as the current pattern. At the same time the diffractogram current color becomes virtually in its complementary, until a new diagram is selected. You can turn this virtual color and definitive color, if the "double click" is supplemented by "Alt" key on the keyboard. This allows to mark at the same time several diffraction patterns within the sequence to show some important fact. The example used initially palette "Green / Black" and shows a phase transformation (dehydration "hydrotalcite" during heating) where the start and end of the transformation have been marked. The "double click" can be performed on small rectangles to the right of the chart, even when the "Fill patterns / All" option is not selected. When the color changes created the "double click" a new palette is selected shall be canceled.

The green arrows allow to control the maximum height and separation of diffractograms. The green rectangles allow calculating the appropriate values. The color palette and color of the current diagram can be selected ('Palette' and 'Pattern plot'). You can also select the filling (options 'Fill pile')

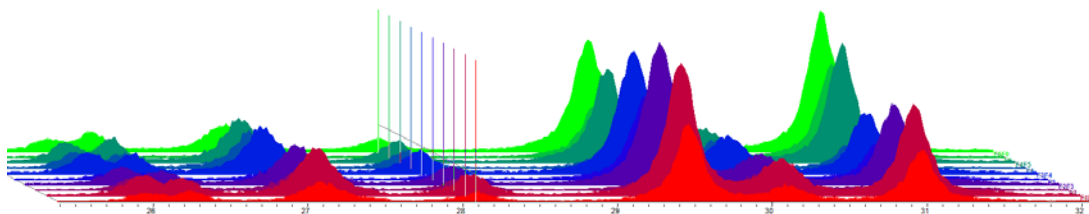


Figure A2.27

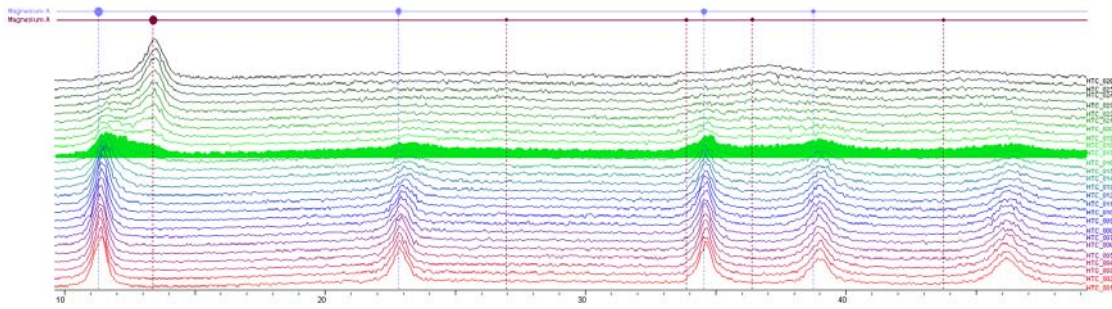


Figure A2.28.

The figure shows an example where the boxes "Circles" and "Bars" have been selected in addition to "Fill patterns / Active" option.

Mode "2D Map". All the uploaded diffractograms are shown consecutively. 2θ shown abscissa, ordinate each interpolated diffraction patterns and intensities are displayed as contours, false color scale or both. If the data format is "PLV" and temperature record is indicated in one (other than the first) header line of each file ("*Temperature = 120*", for example) the temperature is displayed on ordinate axis when diffractograms are correlatively uploaded.

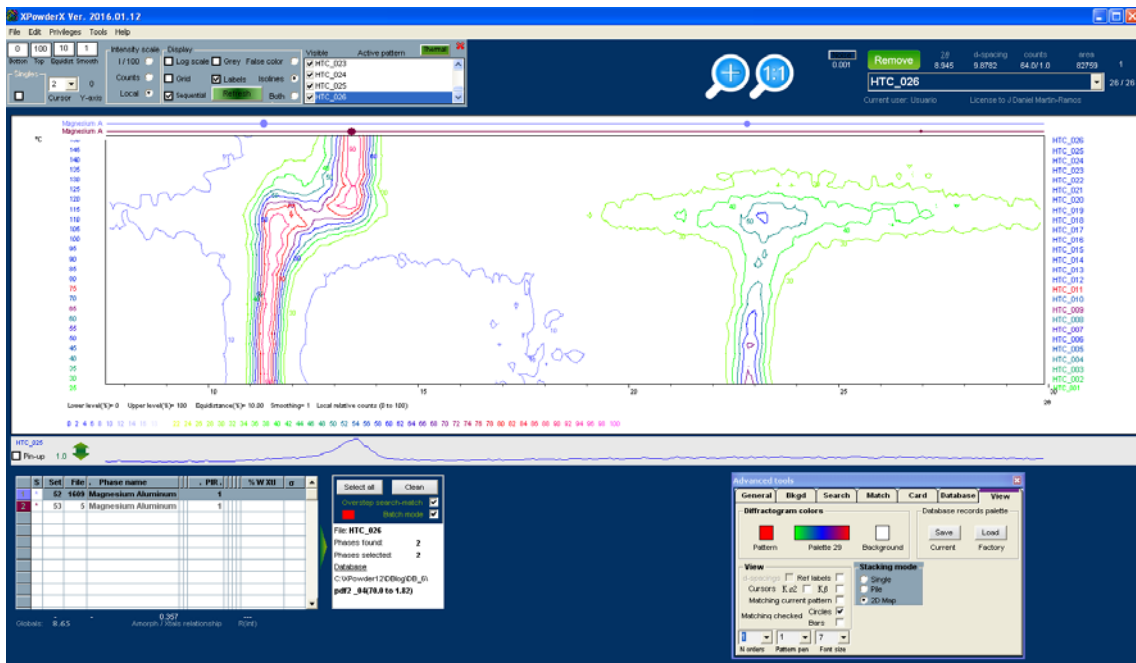


Figure A2.29.

The options in this presentation of data are automatically displayed when the cursor is positioned at the upper right of the screen. It is possible that some of the options shown require additional press the command "Actualize" so that the results are displayed on the screen. We also have included a small "spreadsheet" that can be used to calculate the expansion coefficients for different crystallographic directions.

You can zoom in horizontally, drag with the left mouse cursor. The active diffractogram is shown in the small window below the 2D image and switches to move the cursor vertically above the main figure.

A click on the main image calculated the Bragg spacing in the current plot. If "Pin-Up" box is checked, the lower current diffractogram not changed (is anchored) and spaced calculations are referred exclusively to him.

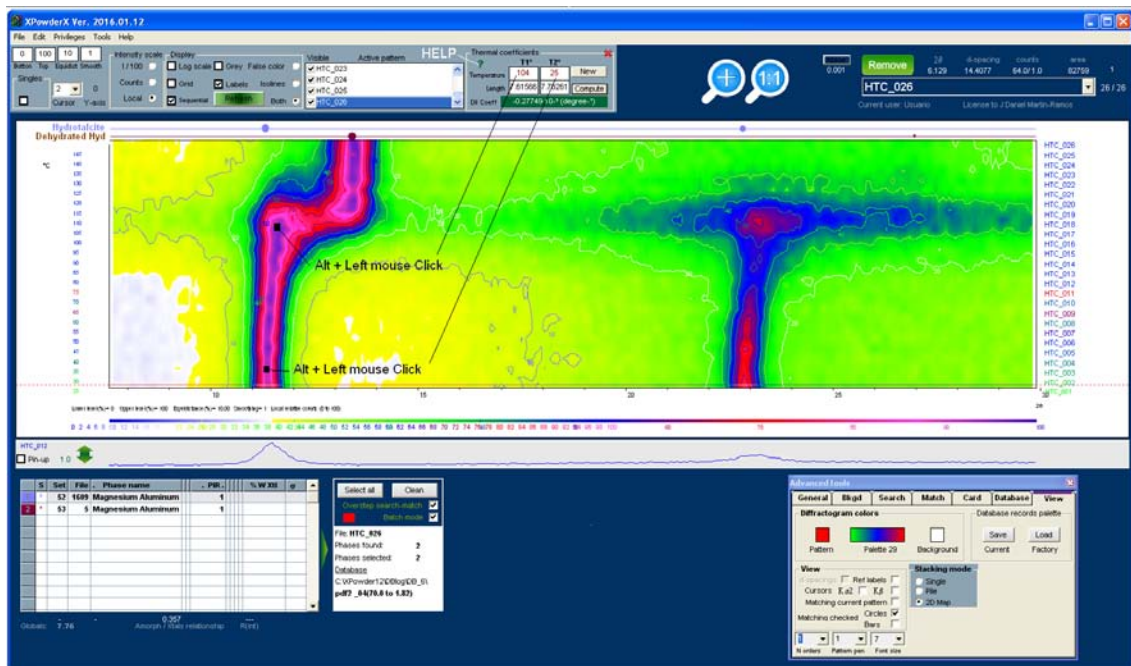


Figure A2.30.

These graphs are useful to observe reflections of very low intensity, whose occurrences are detected by the constancy of the lines along the vertical axis (See Figure A2.30, 52 and 57.5 2θ green bands)

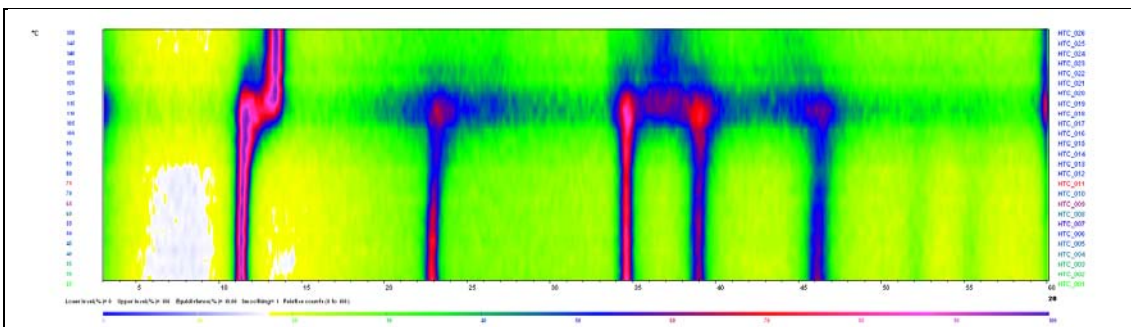


Figure A2.31.

APPENDIX 3

Least-Square full profile quantitative analysis

Access: "Tools / Process / Full profile quantitative"

(It requires 'Auto quantitative full profile' permission' See Appendix 8. Figure A8.1)

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APPENDIX 3. Least-Square full profile quantitative analysis

(It requires 'Auto quantitative full profile' permission'. See Appendix 8. Figure A8.1) [Index](#)

This is the most accurate way to quantify phases through X-Ray diffraction by the powder method. However requires a careful handling of samples, both of which are used as standard as those that are analyzed.

The method requires the record of diffraction patterns of pure crystalline compounds with the same composition and similar crystallinity to those present in the specimen. When the pure crystalline phases are not available, their diffraction patterns can be calculated using the suggested method in Appendix 4.

The quantitative analysis is performed, by non-linear full-profile full-matrix least-square methods to find the better mix of diffractogram of components to the experimental pattern.

If the crystallinity among the specimens and standard patterns are very different, it is desirable to make records with different crystallinity patterns. The program will make the weighting of each of them, as if they were separate phases. May also be included diffractograms of amorphous substances for global quantification in blends of other crystalline phases. The use of internal standards of known weight (eg 10% of corundum Al_2O_3) allows absolute quantitative analysis.

During the analysis the 2θ zero displacement and the *mass absorption coefficient* are refined. Data must be statistically weighted.

Once obtained the diffractograms standard patterns, it is easy for serialized quantitative analysis with a precision that is generally higher than those obtained by Rietveld methods or RIR-database based correction.

The quantitative analysis is more accurate when made with care the following:

- The volume of standard sample and specimen used in all registrations should be the same. A minimum % of inner standard compound can be artificially added to the specimen.
- The pressure of compaction of crystalline powder should also be similar.
- It is necessary to use a stable sample pattern to control derives of the X-Ray meter. The best thing is to use is a pressed tablet having similar absorption coefficient which samples to be analyzed, wherever possible.
- The same radiation, monochromatization system, set of slits, detector and values of discrimination of the detector should be used forever.
- The diffractograms of the analyzed pattern and the components patterns should preferably be in the same session.
- Where then is necessary to create new standard patterns, must be measured also shows stable tablet pattern, in order to correct derive or decay.
- The historic change of intensity is corrected by a factor, which is the ratio between the two measures ($I_{\text{old}}/I_{\text{new}}$). To this value, you can use a single reflection, or rather the cumulative intensity of several reflections and even entire diffractogram.
- Exceptionally, they can be used calculated diffractograms from the crystal structure, through programs such as Cerius, Mercury, etc., whenever possible to normalize the intensity by a appropriate factor. Suggested in Appendix 4 method can also be used.

The Methods is accessed from the "Tools / Process / Full profile quantitative" menu. The tool looks like figures A3.1 and A3.2.

The left part contains the list of substances patterns that are included in the analysis by checking.

- 'Scale normalization factor'. Weighing scheme for statistical normalizing of components. It is defined as the ratio between the percentage of a particular component versus another used as a standard (for example corundum, quartz or any common component), calculated for initial 'scale' values=1, or by checking the box 'Ignore Scale Factors' in figure A3.2. These values ('Pattern Intensity Ratio'= PIR factor) are experimentally calculated on a mixture of known composition and depend not only on the number of electrons and volume of the unit cell of each component, but the angular range explored an experience data and normalization method (*Height, Area, None*). When these values are unknown, they can be replaced with caution by RIR factors (*Reference Intensity Ratio*), provided that the criterion of normalizing '*Height*' is used.
- 'New / Open / Save scheme'. Begin, open or save and LST file.
- 'Set scheme default'. The list of current patterns is automatically loaded the next time that the tool is used for quantitative analysis.
- 'Pattern color' change component color.
- 'Factory colors' reload default components palette.
- 'Save palette'. Save current colors collection.

The right part includes two tabs ('Scheme Setup' and 'Do full Profile Quantitative').

The '**Scheme Setup**' tab (figure A3.1. lets you create or edit the list of addresses of the files containing the diffractograms of partial components ("c:\xpowderx\lst\example.lst" in the picture).

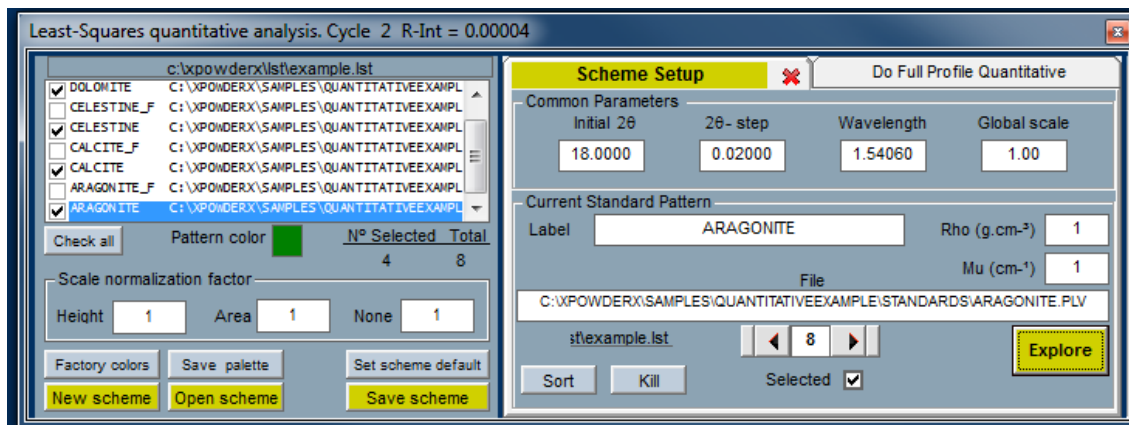
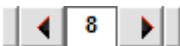


Figure A3.1.

- 'Explore'. Browse the component file location
- 'Common Parameters'. Parameters to be common to all components diffractograms.
- 'Label'. Nickname assigned to the component.
- 'Rho(g.cm⁻³)'. Density of component. Optional, Used only for absorption correction.
- 'Mu(cm⁻¹)'. Linear absorption correction coefficient of component. Optional, Used only for absorption correction.
- 'Selected'. The component will appear checked in the list on the left.
-  Allows view and edit the list of components of the current list.

The '**Do Full Profile Quantitative**' tab (figure A3.2) lets you set the parameters that configure the analysis and carry out it ('Quantify').

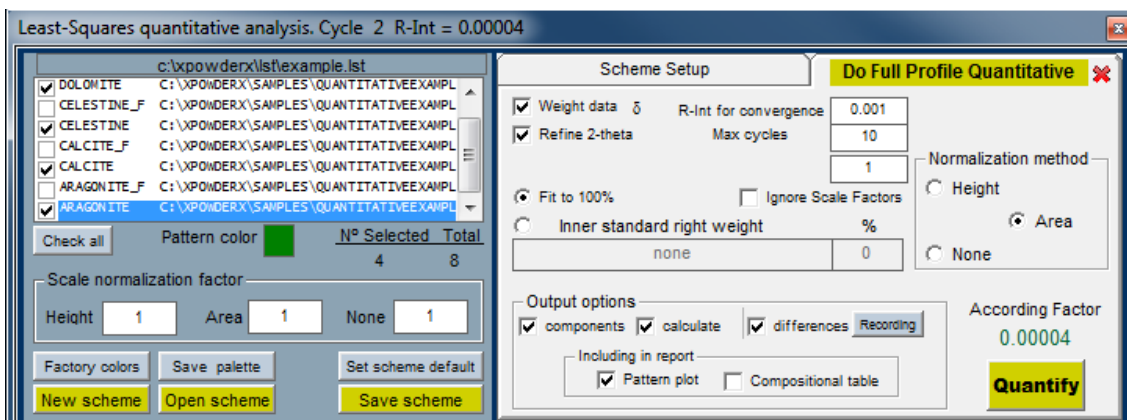


Figure A3.2.

- '*According Factor*'. The agreement factor is defined

$$\left\{ \frac{\sum [w(I_o - I_c)^2]}{\sum w [I_o^2]} \right\}$$

where I_o are observed intensities and I_c calculated intensities. n = number of experimental points

- '*Weight data*'. Intensities are weighted (w) with statistical purposes for '*According Factor*' computation.
- '*Refine 2-theta*'. 2θ of components will be fitted.
- ' *δ R-Int for convergence*'. When computation reaches the selected value, the analysis stops even have not been completed cycles. Smaller values provide more accurate results.
- '*Max cycles*'. Limits the number of least squares cycles.
- '*Normalization method (Height/ Area/ None)*'. Select statistical normalization method and appropriate *PIR* value from *LST* list.
- '*Ignore Scale Factors*'. All '*Scale factors*' values are set to 1).
- '*Fit to 100 %*' option. The sum of the components is forced to add up to 100.
- '*Inner standard right weight*'.

In turn provides two options:

- Without internal standard (Free weighting): If not selected any internal standard (*none*), diagram calculated will be fitted in accordance with the experimental, but the results have a relative nature, generally do not total 100.
 - With internal standard. You can select from a list of components whose weight is known as internal standard. You can use a component of the mixture itself or added artificially. To select the internal standard, you double-click on the appropriate line of the list, or on the box '*none*'. In the latter case the active compound is selected from the list. A new double-click on this box, discarding the internal standard. The quantitative composition must be entered manually in the text box '%'. The result of the analysis will be absolute in this case
- '*Output options*' (See figure A3.3.) Display respectively '*components*' traces, '*calculated*' patterns, and '*differences*' diffractogram. The latter can be saved in text *PLV* format.'

'Pattern plot'. This option allows to display the picture (including *Output options*) in the final PDF report.

'Compositional table' allows include a quantitative compositional table in the final PDF report, when analysis is done in batch mode.

- 'Quantify' do quantitative analysis. See figure A3.3.

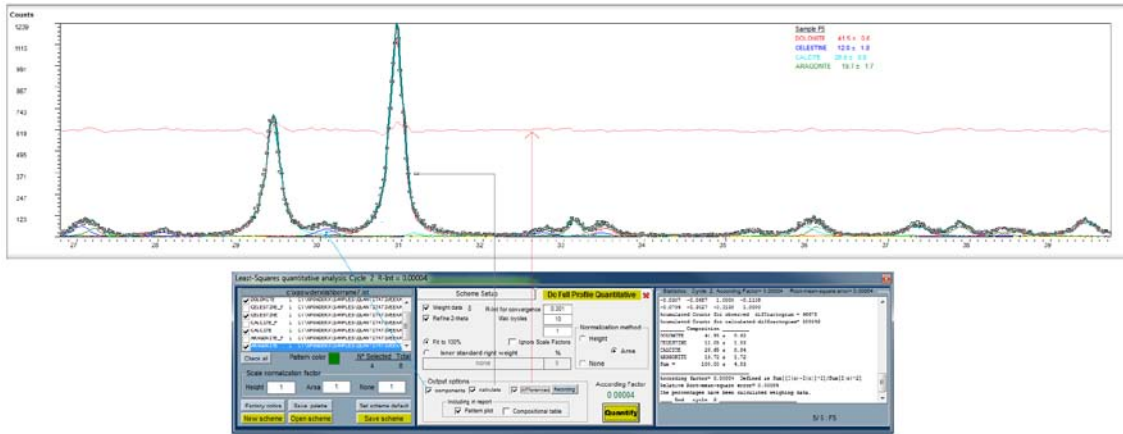


Figure A3.3

LST file example

Sc_None= 1.25651

Initial 2-theta= 18.0000
 2-theta Step= 0.02000
 Wavelength= 1.54060
 Global Scale = 1.00
 Fitting 100 = True
 Weight data = True
 2-theta Correction = True
 Normalization = Area
 Begin Standard
 Label= ARAGONITE
 Enabled = True
 Rho(g.cm⁻³)= 2.933
 Mu(cm⁻¹)= .9592246
 Sc_Height= .48294
 Sc_Area= .44277
 Sc_None= .91907
 File= C:\XPOWDER\SAMPLES\ARAGONITE.PLV
 Begin Standard
 Label= CALCITE
 Enabled = True
 Rho(g.cm⁻³)= 2.712
 Mu(cm⁻¹)= 1.314874
 Sc_Height= 2.03993
 Sc_Area= .42532

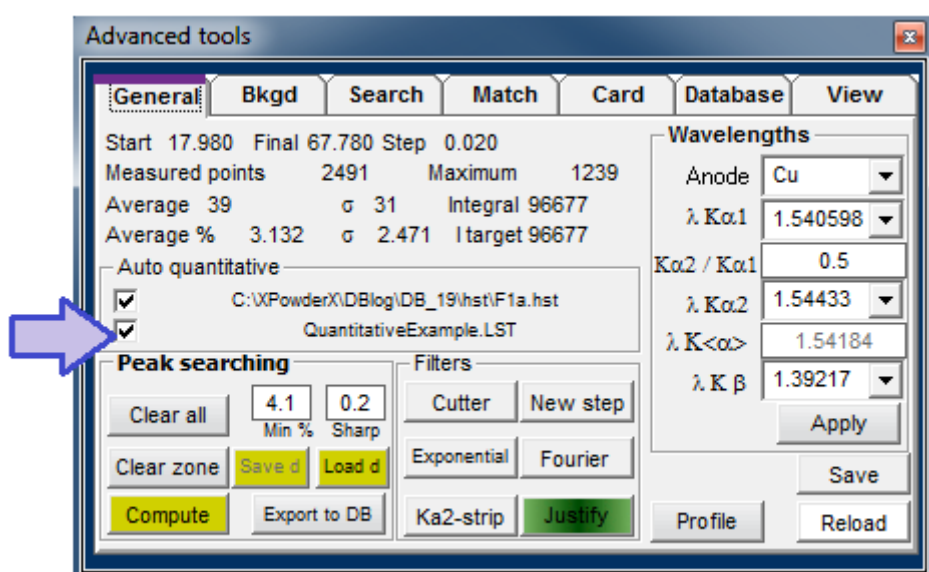
File= C:\XPOWDER\SAMPLES\ CALCITE.PLV
 Begin Standard
 Label= CELESTINE
 Enabled = True
 Rho(g.cm⁻³)= 3.978
 Mu(cm⁻¹)= .3163185
 Sc_Height= 1
 Sc_Area= 1
 Sc_None= 1
 File= C:\XPOWDER\SAMPLES\ CELESTINE.PLV
 Begin Standard
 Label= DOLOMITE
 Enabled = True
 Rho(g.cm⁻³)= 2.876
 Mu(cm⁻¹)= 16.30926
 Sc_Height= 2.64522
 Sc_Area= .51043
 Sc_None= 1.17029
 File= C:\XPOWDER\SAMPLES\DOLOMITE.PLV
 END

Automatic Least-Square full profile quantitative analysis

(Requires 'Auto quantitative full profile' permission' See Appendix 8. Figure A8.1)

The program allows you to use the list (LST) of components of a group of samples with similar composition, so that quantitative analysis is done automatically when you load the files of each diffractogram.

To do this, select the checking box in the folder **General** Tab of the *Advanced Tools* (arrow in figure A3.4). The program will use the composition of the LST file default (QuantitativeExample.LST in the figure) the next time you upload one or more pattern file.



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APPENDIX 4

**A new fast method for full-profile quantitative analysis of
components using 'Dirac' and convolution**

APPENDIX 4. A new fast method for full-profile quantitative analysis of components using 'Dirac' patterns and convolution

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The program can generate theoretical XRD where the FWHM width, the function type, asymmetry, function Caglioti, $K\alpha_2$ component etc are adjusted to a previous stick mode and intensities, which can also be generated by the program or extracted from bibliography. Thus, these generated theoretical diffraction patterns can be used latter to easily perform accurate quantitative analysis by adjustment to the full profile of the experimental diffraction. To access the tools that perform these calculations select a reflection of the main plot (with "Shift key + left-click" mouse) and use '*Tools / Profile Parameters*' in the main menu. The tool shows in the following figure A4.1.

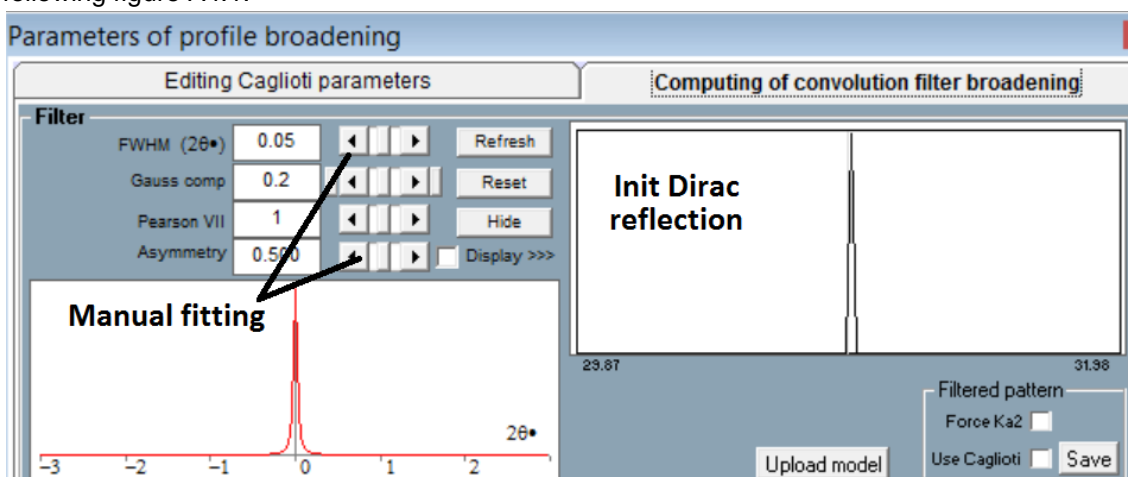


Figure A4.1. Profile broadening tool.

As starting pattern, it is useful to use a diffractogram with profile width 0 ('Dirac' diffractograms), that can be created from databases (using '*Advanced Tools*' / *Card Tab* / *Dirac file* 'button' or Bragg reflections from an experimental diffractogram in *File* / *Save as ... Pattern Dirac* / *Stick*). Starting profiles should not contain $K\alpha_2$ reflections, but optionally these will be included latter in the generated diffractogram.

XPowderX allows you to use the reflections of experimental samples as model in order to generate other full profile diffractograms from initial stick pattern, but with profile geometry similar to experimental model.

The diagram of the actual substances used as models must be free of $K\alpha_2$ component. Otherwise the command '*K-Alpha-2 stripping*' in '*Advanced tools*' must be used.

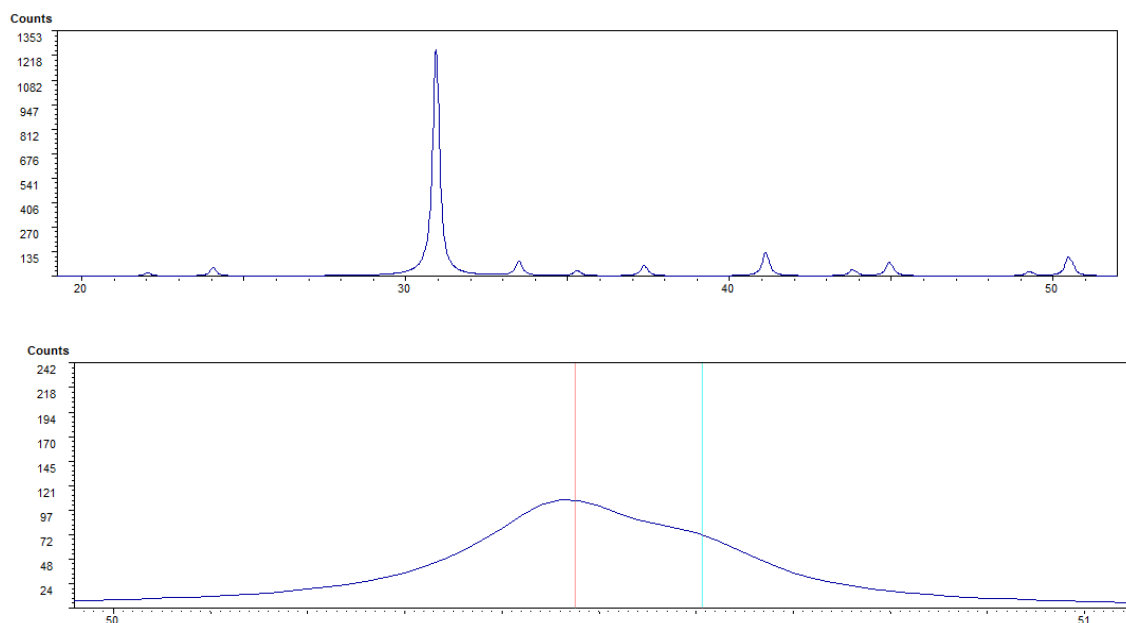


Figure A4.2. Final dolomite diffractogram generated from a model of low crystallinity. In the detail, the lower image shows the $K\alpha_1$ (red cursor) and $K\alpha_2$ component (turquoise cursor).

The method consists on fitting full profile diffractogram to their components, either experimental or calculated by least square statistical methods, or simulated annealing. Additionally, PIR scale factors are used.

Where the components are calculated, they can be obtained from an experimental diffractogram of a highly crystalline pure compound, or one theoretical type 'Dirac' (see below). These diffractograms are referred to as 'starting pattern' or 'stick pattern'.

A '*model diffraction pattern*' deconvolution with the 'starting pattern' is used to obtain the appropriate 'function filter' in order to obtain the final 'broadening pattern' of individual compounds. The '*model diffraction pattern*' may be, for example, the diffractogram of any sample recorded in our laboratory.

The final 'broadening patter' of each component is then obtained by the convolution product of the 'stick pattern' with the 'function filter'. Optionally, you can add the Caglioti broadening equation and/or correction for $K\alpha_2$ inclusion.

This 'broadening pattern' allows obtaining high quality quantitative analysis very quickly, as explained in detail in the attached example.

4.1. Stick patterns generation in

These PLV data format files contain all data from a diffractogram, including the beginning angle, step, lambda, etc. All the intensity values are zero except for those corresponding to 2θ angles of the d-spacing of any phase (figure A4.3).

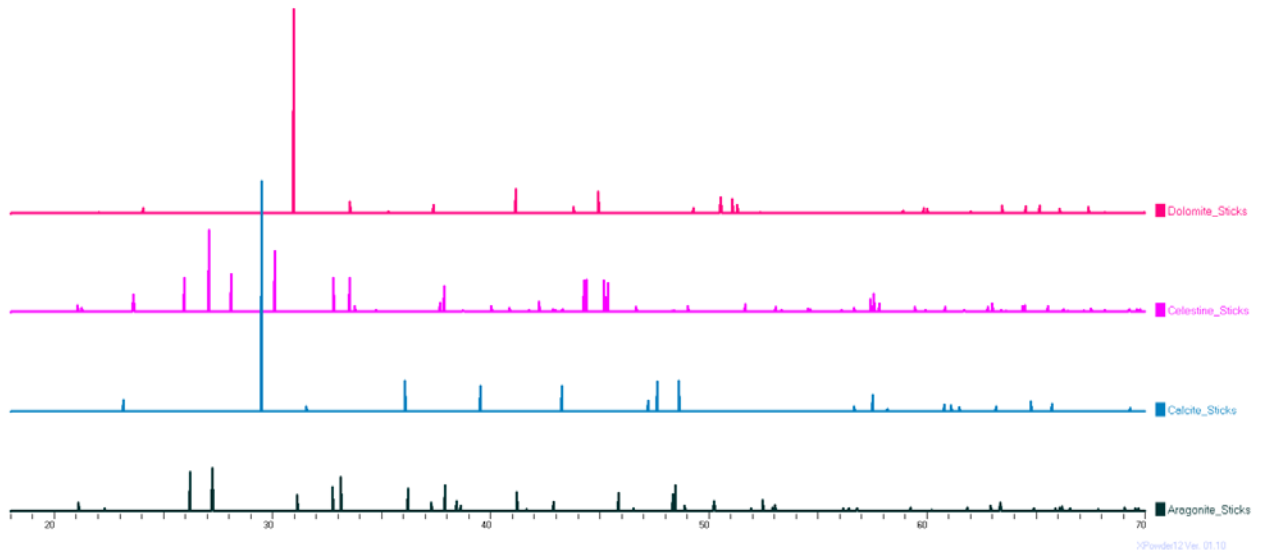


Figure A4.3. Initial stick model before adding profile by convolution, $K\alpha_2$ and Caglioti function.

The 'Dirac' button lead to generate these diffractograms from any card of a database (figure A4.4) or from the main menu (Save Pattern As..., Figure A4.5. These stick starting files should not contain $K\alpha_2$ reflections, but optionally these will be included latter in the final full-profile diffractogram.

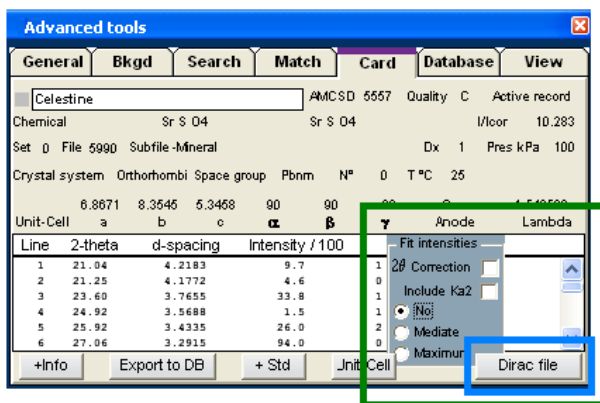


Figure A4.3. Saving experimental Bragg peaks.

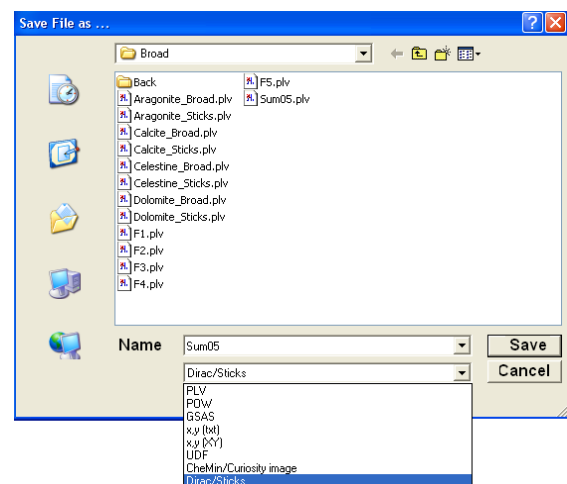


Figure A4.4. Saving DB record as 'Dirac' file.

These kinds of files could be used to simulate realistic experimental diffractograms of pure phases by convolution with distribution functions (Gauss, Cauchy, Pseudo Voigt, Pearson VII), asymmetry and FWHM computed by Caglioti equation.

4.2. Broadening profile

Broadening profile generation from external diffraction pattern model [Index](#)

This tool, located in the principal menu 'Tools' (Figure A4.5), allows creating any pragmatic theoretical profile by the modification of FWHM values, the Gaussian/Lorentzian components, the Pearson VII exponent and the asymmetry. If the 'Display' box is checked, the convolution product of this filter with the current experimental diffractogram will be displayed. The small screen on the right shows (in purple) the original diffractogram, Dirac in this case, on the selected 2θ interval.

When the cursor is positioned on the upper-right corner of the graphic, 'magnifying glass' and shift arrows are (figure A4.6). They allow us to focus and to shift the 2θ interval of the chosen reflection respectively.

The adjustment of the function filter can be done both manually, using the cursor (FWHM, Gauss, etc), and (or) automatically through an experimental or theoretical diffraction pattern model. This model can be any sample belonging to a batch that becomes capable of being quantified, and whose diffractogram has been recorded on our diffractometer.

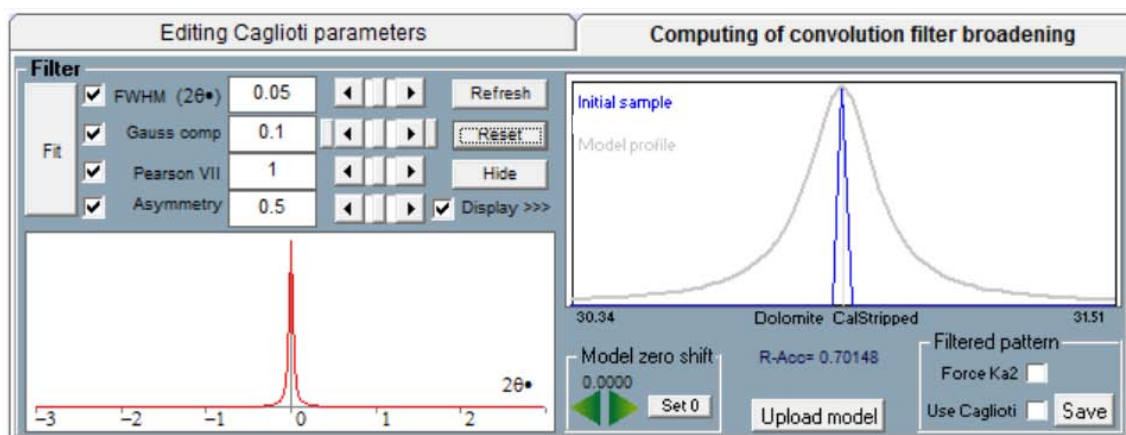


Figure A4.5. Clicking on 'Fit', the final broadened profile is computed (see figure A4.6).

The tool 'Upload model' lead to load this model (in grey at figure A4.6) and adjust the 2θ position by 'Model zero shift' arrows.

The 'Fit' button is now available and allows obtaining automatically the correct filter function (red on the left of figure A4.6). Equation [4.2] lets achieve the final pattern **C** (green in figure A4.6) by convolution with the principal 'Dirac' diffractogram (purple in figure A4.6). It would simulate the experimental conditions (including even the instrumental function as the sample parameters). The program uses '*simulated annealing*' methods, by the minimization of the **R-Acc** value, defined in the classic way.

$$\mathbf{R-Acc} = \frac{\sum_i w_i (I_i - C_i)}{\sum_i w_i I_i} \quad [4.1]$$

Where,

I = Counts of each pattern point (i), o = Measured counts, c = Calculated counts,

w = Statistical weight

The figure A4.6 shows the fitted final convolution product **C** in green.

$$\mathbf{C} = \mathbf{A} * \mathbf{B} \quad [4.2]$$

Where

A= filter function

B= Theoretical diffractogram (Dirac) or experimental high crystallinity X-Ray pattern.

C= Final diffractogram fitted to the experimental lab conditions (grey).

The grey profile corresponds to any sample of our routine at the lab. It could be observed the concordance of this profile with the **C** calculated and the final **R-Acc** value (= 0.07705) enough small.

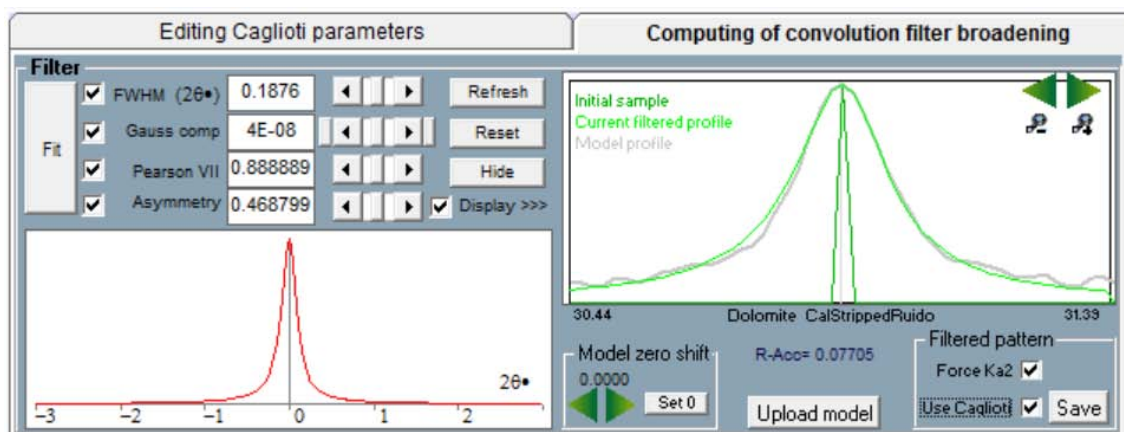


Figure A4.6. Initial filter (left, red), Dirac (purple), experimental model (grey) and preliminary convolution plot (green). Notes R-Acc value = 0.03073.

The button 'View' show the result of the convolution product in the principal screen as well.

The calculated diffractograms (**C**) could be saved (Save) including Caglioti FWHM adjustment and $K\alpha_2$ inclusion if case. Caglioti equation [4.3] parameters can be modified and edited in the tab 'Editing Caglioti parameters' (figure A4.7). For setting the initial U, V, W, P parameters, the 'pattern model' can be used as in **APPENDIX 7** of this user guide.

Now, the full calculated diffractograms (C) could be saved (Save) including Caglioti FWHM adjustment and $K\alpha_2$ inclusion, if case.

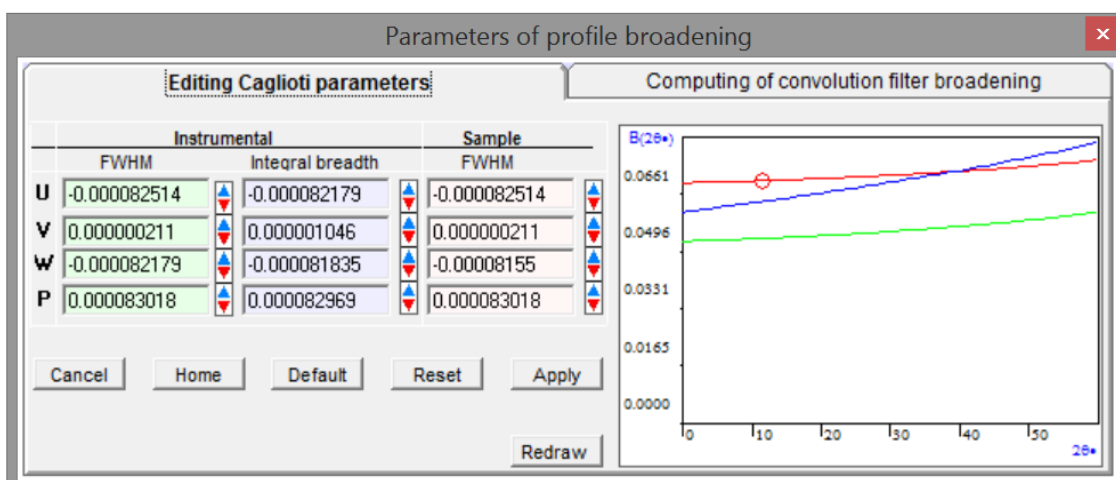



Figure A4.7. Caglioti functions for sample and instrumental profiles. Small circle shows the position of the current profile.

The function to be applied on the calculation of the broadened profile is drawn in red. The small circle shows the position of the current profile used as a model for obtaining the convolution

filter. The parameters U, V, W and P can be changed manually using the arrows ( in 'Sample/FWHM' column). This action continually redraws the function. It should be noted that the change on the parameter **W** lets move the curve vertically, along the ordinate axis.

$$\text{Caglioti equation: } \mathbf{B}^2 = \mathbf{U} \cdot \text{Tan}^2\theta + \mathbf{V} \cdot \text{Tan}\theta + \mathbf{W} + \mathbf{P}/\text{Cos}^2\theta \quad [4.3]$$

(The values of **U**, **V**, **W** and **P** are calculated to express **B** value in 2θ radians. However this value is shown in the graph as 2θ degrees).

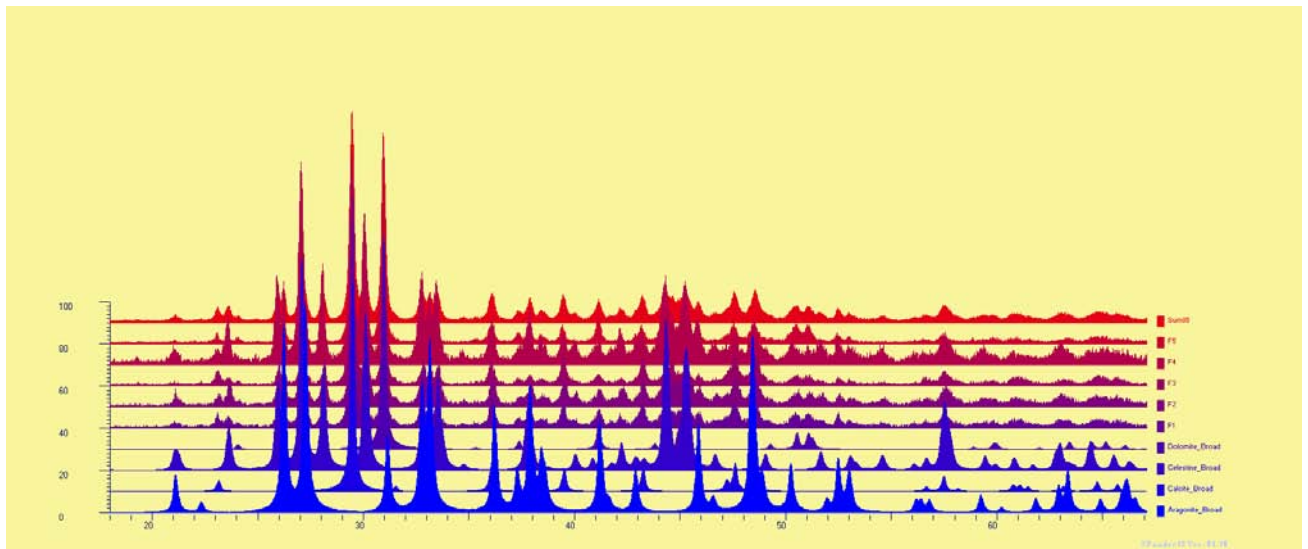


Figure A4.8

By this way, the theoretical diffractograms of *Aragonite_Broad*, *Calcite_Broad*, *Celestine_Broad* & *Dolomite_Broad* have been obtained and appear together with the diffractograms of experimental samples (F1, F2, F3, F4 y F5) and another one corresponding to the average (Figure A4.8). Now, the experimental samples may be quantified in terms of its theoretical component patterns.

4.3. Extended practical example of uses of 'Dirac-Convolution' broadened diffractograms for accurate full-profile quantitative analysis of components.

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The examples to be used here are located in the 'Samples\QuantitativeExample' directory of the program. PIR scale factors are also calculated. It is recommendable for the user to check the following steps:

4.3.1. Upload diffractograms: F1, F2, F3, F4 & F5.

4.3.2. Identify the phases of any sample (F5 in the example)

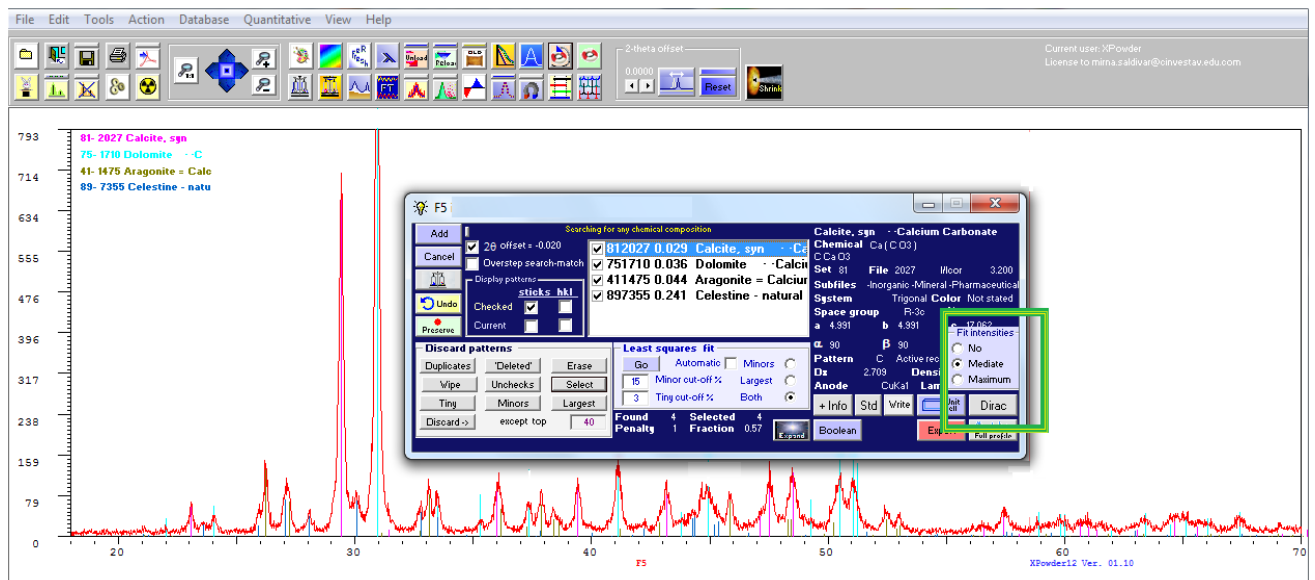


Figure A4.9

4.3.3. In Figure A4.9, Expand the tool and calculate 'Dirac' diffractograms for the components ('Calcite_Sticks.plv', 'Dolomite_Sticks.plv', 'Aragonite_Sticks.plv' and 'Celestine_Sticks.plv'). The options 'No', 'Mediate' & 'Maximum' refer to the fitting between intensities of the experimental diffractogram (0, balanced, maximum respectively) and the database contained. In the example, the 'Mediate' option was used.

4.3.4. Upload on turn the four components diffractograms ('Calcite_Sticks.plv', 'Dolomite_Sticks.plv', 'Aragonite_Sticks.plv' y 'Celestine_Sticks.plv'), to apply in each of them the convolution filter and save the respective filtered diffractograms as in 4.2 section. Thereby create the new patterns with suitable profile broadenings ('Calcite_Broad.plv', 'Dolomite_Broad.plv', 'Aragonite_Broad.plv' y 'Celestine_Broad.plv').

- Ideally, this is explained by only using the 'Dolomite_stick.plv' pattern.

4.3.4.1. Select one isolated reflection of dolomite_stick (30.48 $2\theta$$31.43$) in blue in the example

4.3.4.2. Upload model (e.g. sample F5, grey in Figure A4.10). It is advisable to use a model in which the background has been subtracted before. In the example the original sample without any modification is used. In some case, it might be necessary to modified by hand the zero of the model using 'Model zero shift' tool.

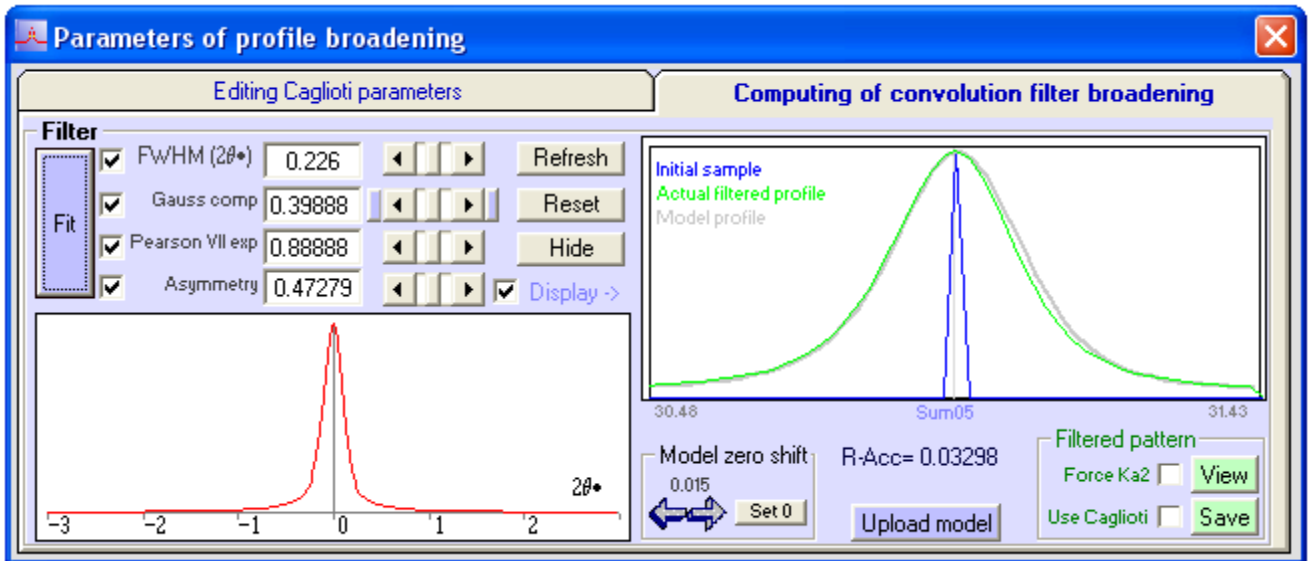


Figure A4.10

4.3.4.3. Click 'Fit' in order to calculation of broadened pattern. The result appears in green on figure A4.10 with **R-Acc** = 0.03298.

4.3.4.4. 'Save' -> ('Dolomite_Broad.plv'). The full final pattern is on figure A4.11. Figures A4.12 and A4.13 show other patterns involved in the example.

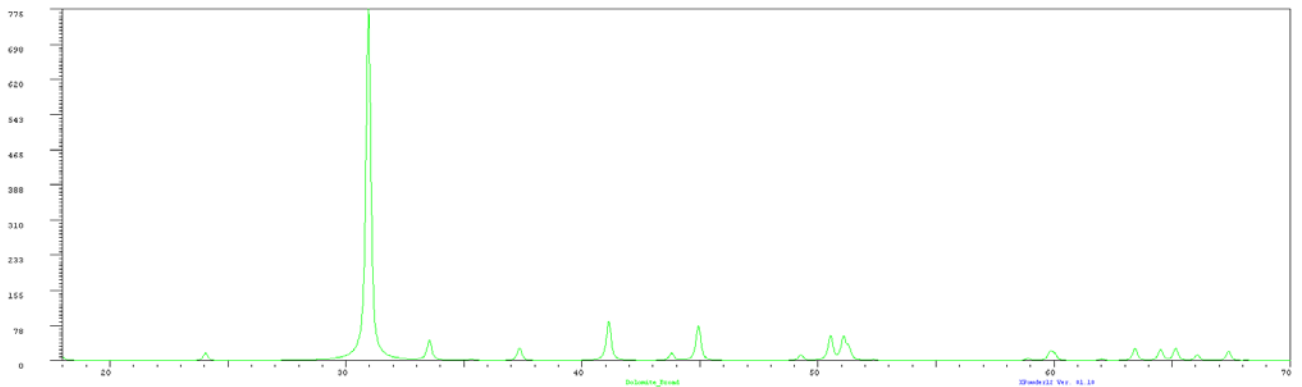


Figure A4.11.

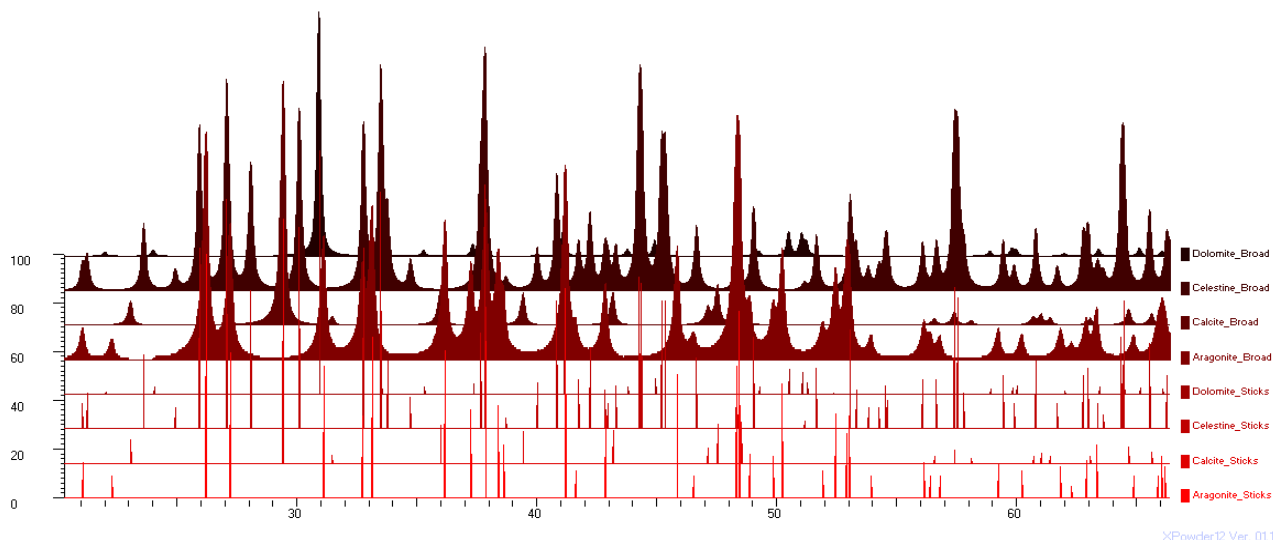


Figure A4.12. The figure shows the individual XRD patterns of the components, both initial (Sticks) and final (Broad).

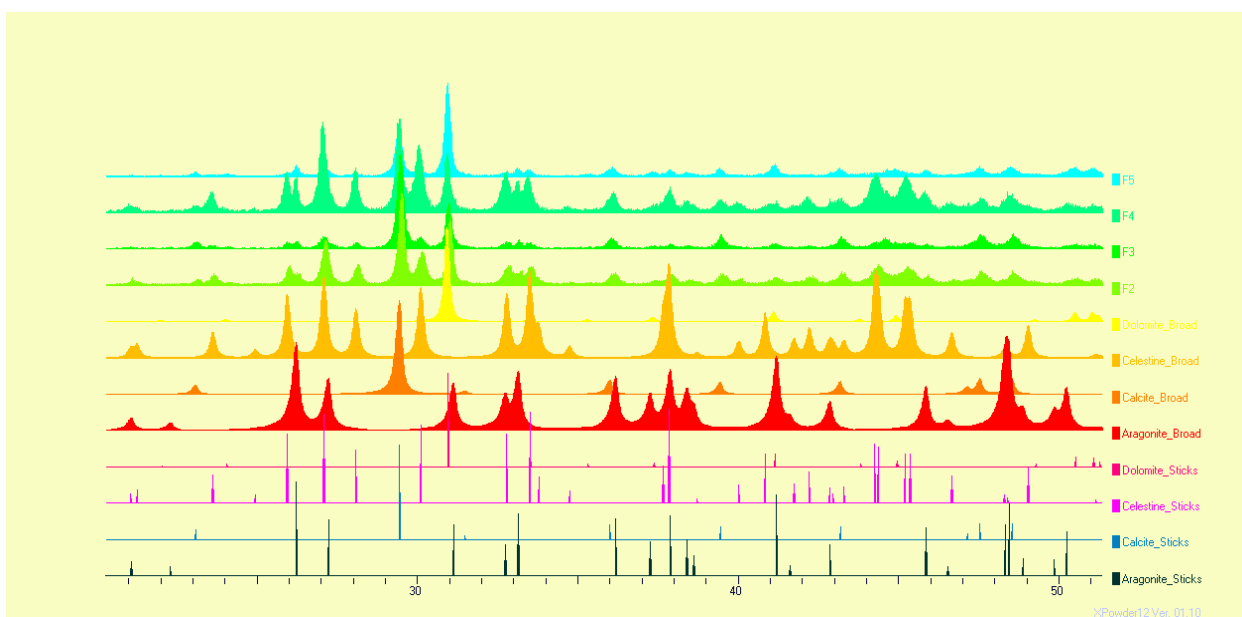


Figure A4.13. The figure shows all the patterns involved in the procedure. F1, F2, F3, F4, F5 are the samples to be quantified. 'Xxxx_Broad' are the broadened patterns of components. 'Xxxx_Sticks' are the 'Dirac/d-spacing' pattern components.

4.3.4.5. Now, you must create a list within the standard patterns in the quantitative tool, using 'Examine' for each phase, as in Appendix 3, using an initial scale factor= 1. At the end, it is necessary to save this list with any name (eg 'ListOfPhases.LST').

4.3.4.6. Now, we carry out a previous quantitative analysis of **a known composition sample** (it could be created artificially), marking the 'Ignore Scale factor' cell. It could be done for any normalization criteria. In the example is used the statistical criteria '*Height*'. Optionally any other criteria could be used (*Area* or *None*).

4.3.4.7. Results of preliminary quantification are showed in the figure A4.14. Optionally, the experimental sample could be showed together with the partial components (with different colors), differences (no in the figure A4.14) and calculate diffractograms (grey circles). The determination error is expressed by parentheses, just after each percentage, and it affects to the last significance numbers.

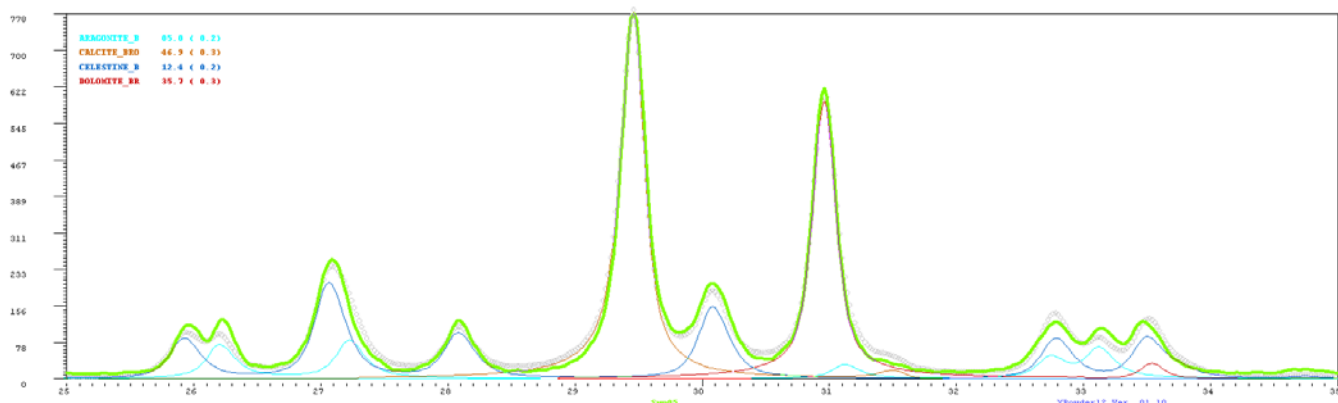


Figure A4.14. Quantitative decomposition of phase components in experimental sample *Sum5*. Circles are the calculated pattern.

4.3.4.8. Now is necessary to calculate the scale factors (PIR= Pattern Intensity Reference) by an easy calculation:

$$\text{PIR} = (X_{1P}/X_{1S}) \cdot (E_S/E_P)$$

$$\text{Or similarly } \text{PIR} = (E_S/X_{1S}) \cdot (X_{1P}/E_P) = S \cdot (X_{1P}/E_P) \quad [4.4]$$

Where $S = E_S/X_{1S}$ is a scale constant for each compositional model, measured, which is calculated only with the data of the component taken as a standard in the reference sample.

Where,

- * E_S is the true and known % the standard compound weight content in reference phase. This compound must also be present in all analyzed samples, although it can show variable values.
- * X_{1S} is the % calculated for standard compound in reference sample for init PIR=1
- * X_{1P} is the calculated % of every one of the other compounds in reference sample for init PIR=1
- * E_P is the % true and known weight of every one of other components in reference sample.

Obviously, the PIR value for the reference phase ('*Celestine*' in the example) is '1' in all normalization criteria cases. However, it can be seen that an external weighed standard (like 10% *Corundum*, 15% *Quartz*...) that allows application of these factors to extend to samples with different compositions can be added to this sample of known composition.

Take into account that the reference component could be added artificially to all samples (for example a 5% in weight). This allows the final quantitative analysis without the necessity of fitting the total to 100%.

In last three columns on the chart of the following calculation, the PIR factors calculated by the three normalization criteria are reflected. The inclusion of the complementary data *Rho* and *Mu* (in figure A3.1) allows the absorption corrections and the media theoretical density calculation of the sample (no here).

Finally, the **PIR normalized scale factors** in the model (figure A4.14) must be introduced and then the list has to be saved again as in section 4.3.4.6. This list would be used at any time for analyze any number of samples in 50 samples groups. To indicate that the model generation could seem complicated at the beginning. At some point the user will realize that it is not.

This list can be used in AUTOMATIC MODE (AUTOQUANTITATIVE). To do this you need to edit the file and enter the lines:

[Standard quantitative]

StAutoQuantitative= c:\xpowder12\ListOfPhases.LST

StQuantitative_StEnabled= True (or False case NOT AUTOQUANTITATIVE)

(See Appendix 3 for more details)

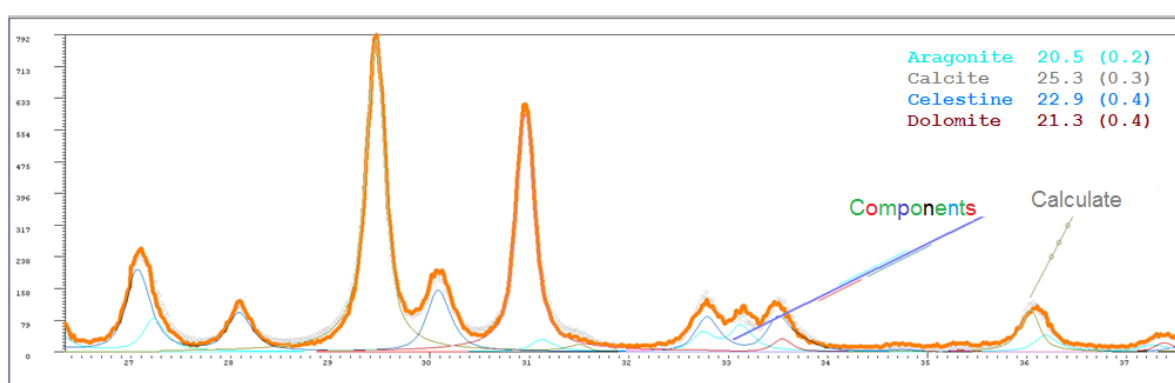


Figure A4.15. Final model is completed. Now, all samples can be routinely analyzed one by one way in batch mode up to fifty.

The created model in the example have been done in half an hour nearly and now it could be used afterwards, at any time, in a routine way in industrial control process, mining and quarrying, basic investigation, etc.

The output of results can be saved using 'File/ Save Log File as TXT' on home screen or as PDF .

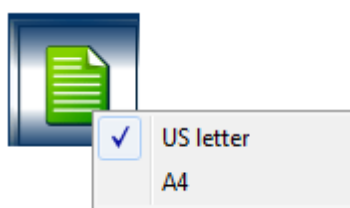


Table A4.1. S = Standard, P = other phases

PIR= (X_{1P}/X_{1S}) · (E_S/E_P)	X(with 'Ignore Scale factor')			Real % weight E (% , mg, etc)	Complementary data			PIR		
	Height ₁	Area ₁	None ₁		μ/ρ (cm ² ·g ⁻¹)	ρ (g·cm ⁻³)	μ (cm ⁻¹)	Height	Area	None
Aragonite	10.50	39.70	49.80	20.50	53.4	2.927	156.30	0.45	0.56	0.85
Calcite	98.60	45.80	89.00	35.30	63.9	2.711	173.23	2.46	0.37	0.88
Celestine (Standard)	26.00	79.90	65.70	22.90	79.2	3.978	315.06	1.00	1.00	1.00
Dolomite	75.00	33.50	76.60	21.30	46.9	2.863	134.27	3.10	0.45	1.25

Table A4.2 shows a part of the report generated for the samples analyzed here. All these examples are incorporated diffractograms during program setup.

(\XPowderXProgramDi\Samples\QuantitativeExample).

Table A4.2.

Smpl	ARAGONITE	CALCITE	CELESTINE	DOLOMITE	Rint	Cycles	sigma.
F1	19.7(0.2)	39.7(0.3)	20.0(0.3)	20.7(0.4)	0.01257	2	0.00097
F2	17.2(0.3)	33.2(0.4)	31.8(0.3)	17.8(0.5)	0.01497	3	0.00104
F3	15.7(0.2)	52.3(0.3)	13.7(0.2)	18.3(0.3)	0.00940	2	0.00092
F4	25.5(0.5)	22.4(0.8)	41.8(0.5)	10.4(1.0)	0.02629	3	0.00136
F5	22.6(0.2)	30.4(0.3)	06.5(0.2)	40.5(0.2)	0.00915	3	0.00089
Sum	20.5(0.2)	35.3(0.3)	22.9(0.2)	21.3(0.4)	0.00930	3	0.00090

Sum fitted 100%. The percentages have been calculated weighing data. 2-theta angles have been refined
Normalization criteria: Max. counts = 1

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APPENDIX 5. Unit-Cell refinement

This option requires activate the "*Unit-cell refinement*" privilege (*Home Menu / Privilege*).
Access: "*Advanced tools / Tab Chart / Unit-Cell*" (*Figure A2.21, Appendix 2*).

This option requires activate the "*Unit-cell refinement*" privilege (*Home Menu / Privilege*).
Access: "*Advanced tools / Tab Chart / Unit-Cell*" (*Figure A2.21, Appendix 2*).

XPowder has an advanced procedure that allows comfortably the refinement of the unit-cell even if the sample has several components. The input unit-cell initial parameters should be close to **a**, **b**, **c**, α , β and γ actual values. The output results include the optimized new lattice parameters with corresponding statistics and the possibility to systematic study of extinctions of space-group and come to existence of partial or total superstructures.

As is well known, these data from initial cell unit are very difficult to calculate from the powder patterns, so that, wherever possible, it should be results obtained by methods of single crystal, such as those that often of database records. If the substance has been previously identified and the lattice parameters are included among the information in the database, such values can be used as initial values, XPowderX read them directly from database.

It can also use the data of cell isomorphous substances, even though the chemical composition is very different. In other cases, it is sometimes possible to calculate '*ab initio*' the unit-cell from powder patterns, through the use of specific programs, which often use methods of 'trial and error' to propose possible solutions ('TREOR', etc).

XPowder uses a non linear least squares routine that allows the simultaneous refinement of the lattice parameters **a**, **b**, **c**, α , β and γ , and the instrumentals (horizontal and vertical) displacement of the sample.

As a general way it is always preferable to devote some time to make the necessary alignments in the diffractometer, rather than trusting the quality of results to the purely mathematical refinement of instrumental parameters. This is because the number of parameters to refine (6 from unit-cell and 2 instrumentals) may be too high compared to the available number of reflections. On the other hand, if the patterns are poor quality, it is possible that during the successive refinement cycles, the parameters really interesting, ranging from too bad correct values and there is no convergence in the overall refinement process.

Some parameters to be refined, can be linked or fixed, so as to facilitate the calculation by using smaller matrices. For example, if a tetragonal unit-cell is refined, the parameters **a** and **b** can be linked (**a = b**) and the values of α , β and γ can be fixed ($\alpha = \beta = \gamma = 90^\circ$). If, moreover, the diffractometer is correctly aligned, you can skip the instrumental correction, so that only the cell parameters **a** and **b** are refined.

On other cases, particularly when there are isomorphism or order-disorder case, it may be interesting to refine a unit-cell of high symmetry in a system of lower symmetry (for example, a crystal with initial orthorhombic cell can refined in monoclinic system or even in the triclinic system). This strategy is often used in structures *spinel* type, *perovskite*, *garnet*, etc.

Before making the refinement of a unit-cell, the displacement of 2θ angle should correct using a standard pattern (better internal standard), remove the component $K\alpha_2$ (*'K α_2 stripping'*) and 'read' the d-spacing of experimental pattern (better manually through the left mouse button on the main chart which automatically). The elimination of the component $K\alpha$ is not indispensable, but in many cases can improve the precision of refined parameters up an order of magnitude. It is not desirable to do background subtraction in any case.

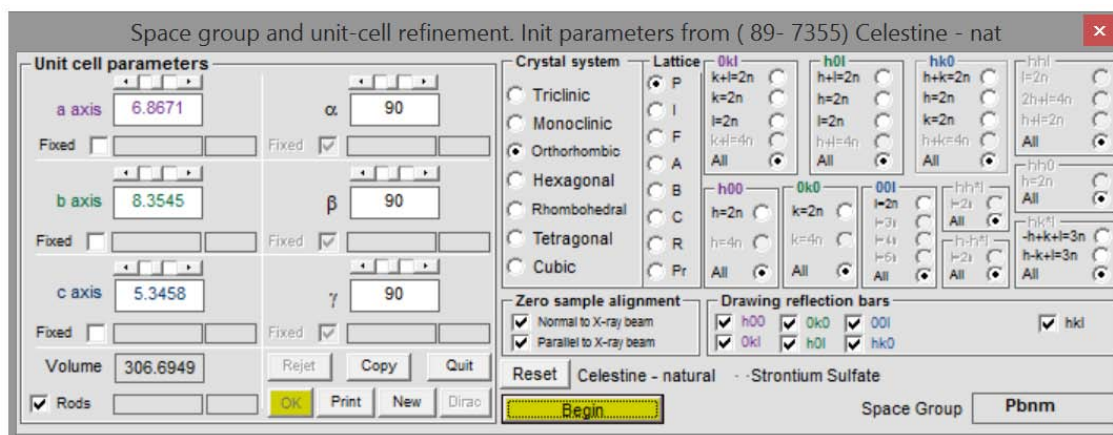


Figure A5.1 shows that the program has selected automatically constraints due to the space group of crystalline phase (orthorhombic **P** lattice, $\alpha = \beta = \gamma = 90$) and restraints for the instrumental alignment parameters. By clicking **Begin** comes the unit-cell refinement process

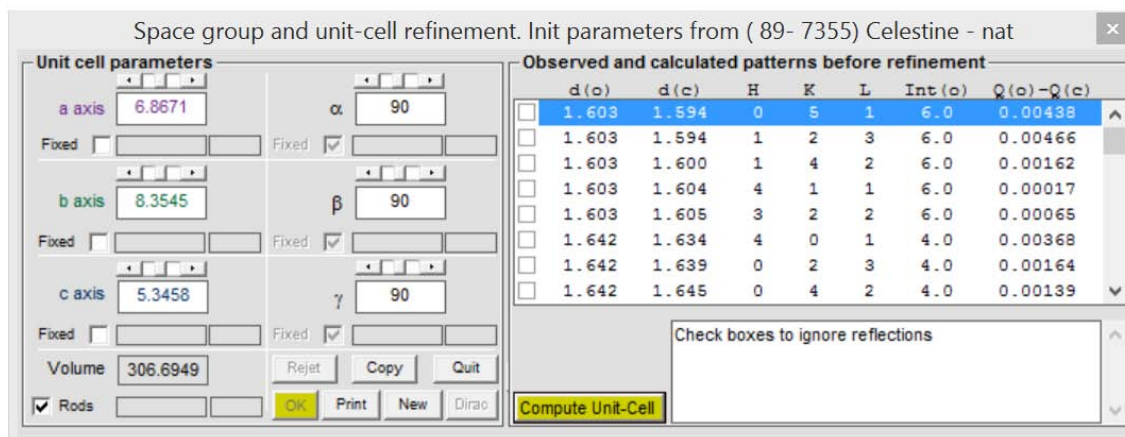


Figure A5.2.

The list on the right of Fig A5.2, shows the previous observed **d(o)** and calculated **d(c)** d-spacing, **HKL** reflection index, referring to 1000 observed intensities (**Int**) and the difference between the observed and calculated squares of reciprocal vectors **Q(o)-Q(c)**. The list can be scrolled to exclude of next refinement (tick) those reflections whose value '**Q(o)-Q(c)**' is too high ($Q_{hkl} = 1/d_{hkl}^2$). At this point, the program is paused until you press the button **Compute Unit-Cell**, which will provide new results (Figs. A5.3. and A5.4). The new Unit-Cell is close to previous, just because we have slightly modified the terms of refinement.

Under the list of figure A5.4 there is a summary which contains the number of data used in the latest refinement (45), the number of refined variables (lattice axes **a**, **b** and **c**), and the overall According factor for **Q(o, c)** that, being very close to zero, indicates that the refinement has been done correctly. In addition to this, the calculated errors for each of the results are obvious signs of quality refinement (0.0084 Å for **a-axis**, 0.0104 for **b-axis**, 0.0069 for **c-axis** and 0.52 cubic Å³ for **Unit-Cell volume**).

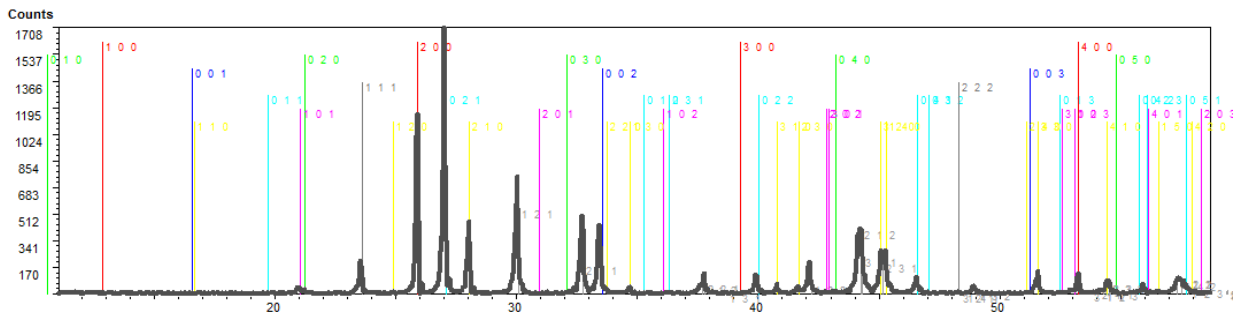


Figure A5.3.

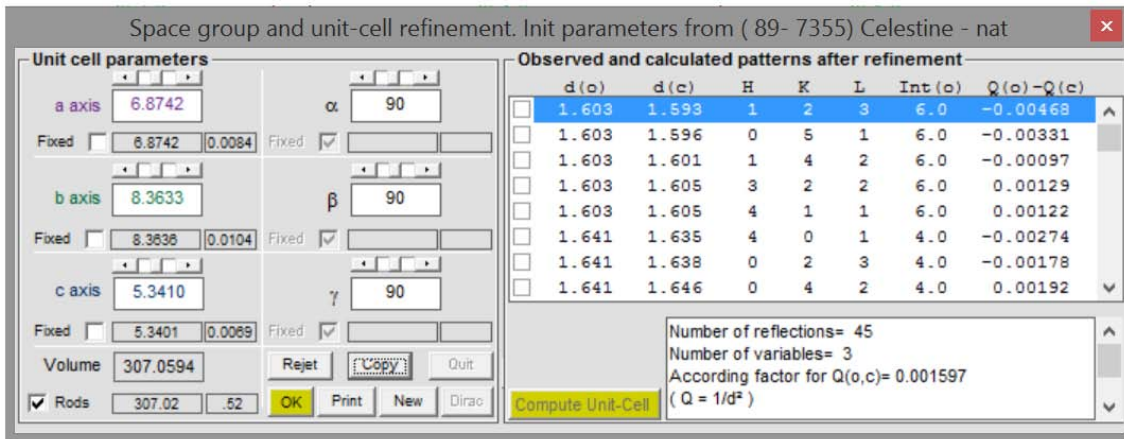


Figure A5.4.

With the **New** order (Fig. A5.4), the unit-cell refinement of another component of the sample can be done. In the example, by choosing 'Gypsum' and clicking **Unit cell**, the results for the new phase are obtained directly (Fig. 9.6).

By pressing **OK** will get the final figure A5.5. It can observe that in the main graphic (figure A5.3.) have been drawn calculated HKL lines for the refined Unit-Cell, but in a primitive and lacking space symmetry elements (screw axes or glide planes). HKL types are grouped by colours at different heights. The colours are those of the axes of the **Unit cell parameters** framework. The reflections h00, 0k0, 00l, 0kl, h0l, hk0 and hkl show from top to bottom. This distribution is done to facilitate the fast identification of isolated reflections. These can be studied in detail by 'zoom' on the upper main graphic (*Shift + left mouse button*).

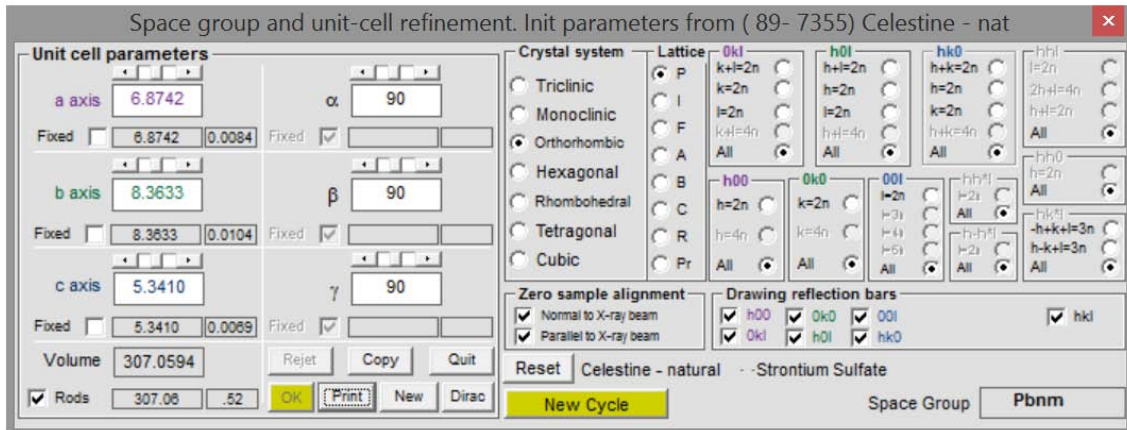


Figure A5.5.

According to Figure A5.5. now you can do:

- Show / Hide reflections of the refined unit-cell. (Box **Rods**).
- Restrict the drawing of hkl reflection groups attached to specific symmetry space elements (*Bravais* lattices, screw axes or glide planes, '0kl, h0l,..., hh*l' frames). Initially there are no restrictions except those due to the lattice type. It can see that by stopping the cursor on the respective option buttons, a message appears overlapped, which contains information on the space symmetry associated with the systematic extinctions, linked to each HKL group, which facilitates the study of space group.
- Draw the reflections by groups (**Drawing reflection rods** frame).
- Modify 'manually' calculated axes and angles values using cursors.
- Fix/Refine parameters in the next cycle (**Fixed** check-box of each crystalline parameter or instrumental parameters of the framework **Zero sample alignment**).
- Changing the crystalline system and Bravais lattice for the next cycle of refinement.
- Ignore the results in order to initiate a new unit-cell refinement with different conditions (**Reset**).
- Quick printing of current data (**Print**).
- Copy the graphic to the clipboard (**Copy**) like on "Main Menu-> Edit / Copy"
- Back to the main menu (**Quit**).
- Make the refinement of another crystalline phase of the specimen pattern and listed in the tool '*Matching*' (**New**).
- Perform a new cycle of refinement using the refined parameters such as new initial parameters (**New Cycle**).

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Example: The determination of the ratio Ca / Mg in magnesium carbonates by PXRD is usually performed through Unit-Cell refinement. The most likely result is obtained then by linear interpolation between the parameters of cell in terms of ending pure phases which have well established Unit-Cell parameters and chemical composition. This is the general procedure used to obtain the exact term of any mineral having solid solution composition. What makes X PowderX interesting for this analysis is that this program calculates Unit-Cell parameters with a single mouse click.

By using the program X PowderX, this **realistic** example has been developed in approximately two minutes.

1. Load an example of *Calcite* diffraction pattern.
2. K_{α2} stripping (it is an optional but advisable action). On the other hand, the internal standard and the 'spline' interpolation function, can improve the quality of the unit cell refinement.
3. In database, search-match and select an correct crystalline phase.
4. Click Unit-cell refinement in 'Advance tools / tab 4)
5. The unit cell is now refined (figure A5.5) :

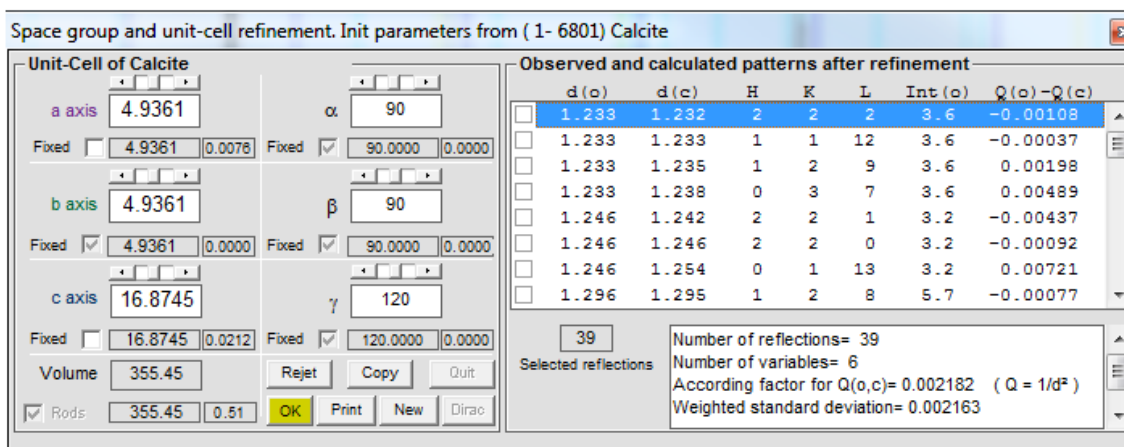


Fig A5.6. *a-axis* = 4.9361 ± 0.0076 Å , *c-axis* = 16.8475 ± 0.0212 Å , *Volume* = 355.49 ± 0.51 Å³

6. Results: Now, magnesium content of the specimen can be calculated using varied linear regression lines (Fig 4.7 to 4.15). Error assessment: $\Delta[\text{Mg}] = m \cdot \Delta(\mathbf{p})$; where $\Delta(\mathbf{p})$ = error of the crystallographic parameters or unit-cell volume and *m* slope of the adjustment line.

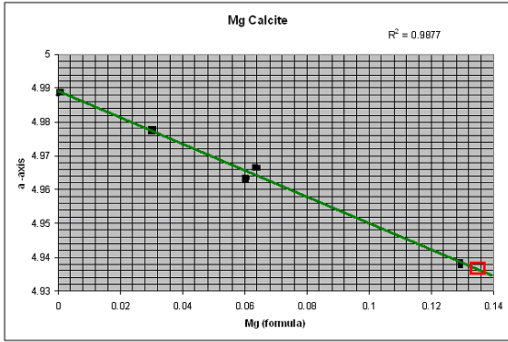


Fig A5.7 $Mg = -2.5548 \cdot a + 12.7953 = 0.13 \pm 0.01$

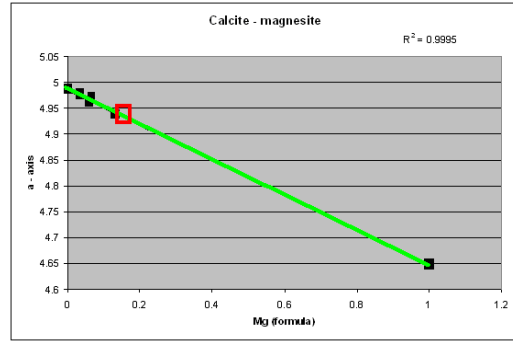


Fig A5.8 $Mg = -2.935 \cdot a + 14.6252 = 0.13 \pm 0.01$

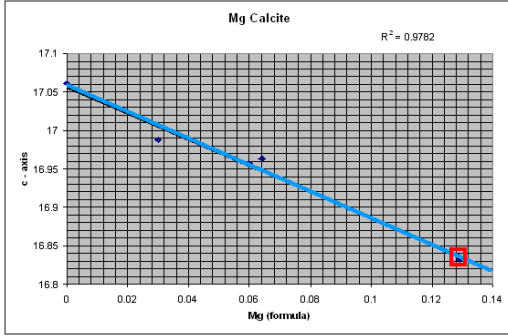


Fig A5.9 $Mg = -0.587 \cdot c + 10.00645 = 0.12 \pm 0.01$

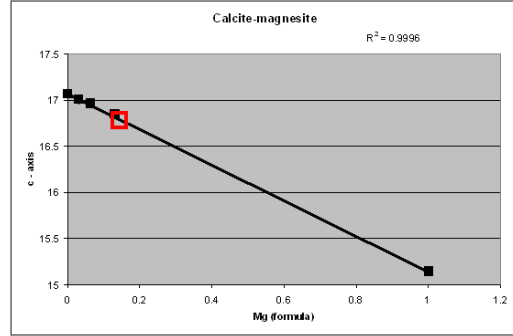


Fig A5.10 $Mg = -0.5188 \cdot c + 8.855 = 0.12 \pm 0.01$

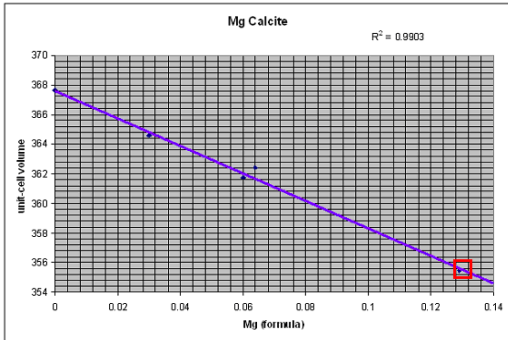


Fig A5.11 $Mg = -0.0119 \cdot Vol + 4.35 = 0.13 \pm 0.04$

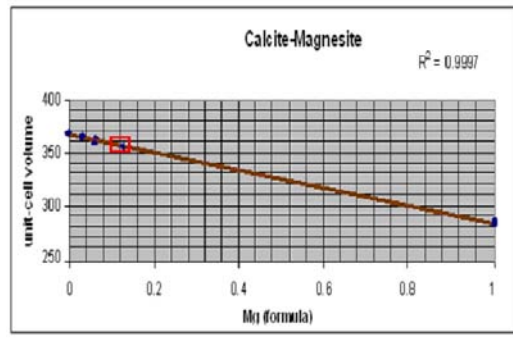


Fig A5.12 $Mg = -0.0107 \cdot Vol + 3.94 = 0.12 \pm 0.04$

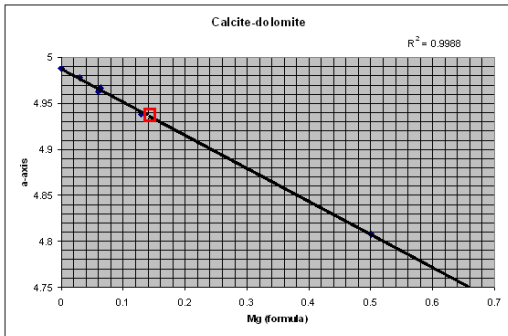


Fig A5.13 $Mg = -2.77932 \cdot a + 13.86 = 0.14 \pm 0.01$

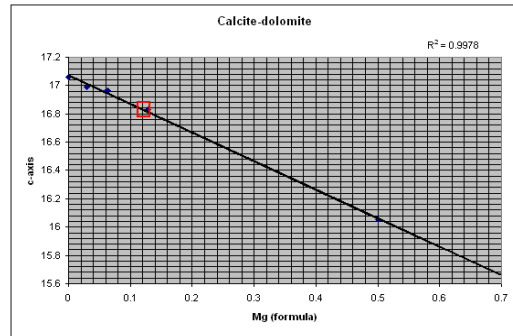


Fig A5.14 $Mg = -0.49417 \cdot c + 8.437 = 0.11 \pm 0.01$

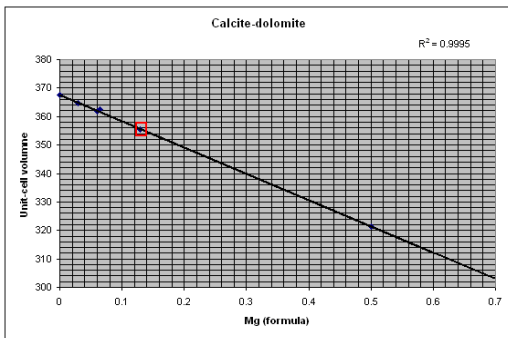


Fig A5.15 $Mg = -0.0108 \cdot Vol + 3.98 = 0.13 \pm 0.04$

Isomorphous Substitution Tool. X PowderX Program can do this automatically using a tool that calculates the terms interpolated from the values of ending cells. This tool is derived from the 'Unit-Cell' tool, by double clicking on the text box of any refined lattice parameter. In the example, a carbonate type "rich-Ca dolomite" has been identified. Then, the Unit-Cell was refined. The exact compositional term of the partial solid solution series was obtained by double clicking on the box of the refined parameter *b*. The extreme terms and vicarious elements can be changed into text boxes of figure 4.16. The editable file 'SolSol.txt' in the program directory/auxiliary subfolder is a collection of unit-cell of exact composition phases as in the example:

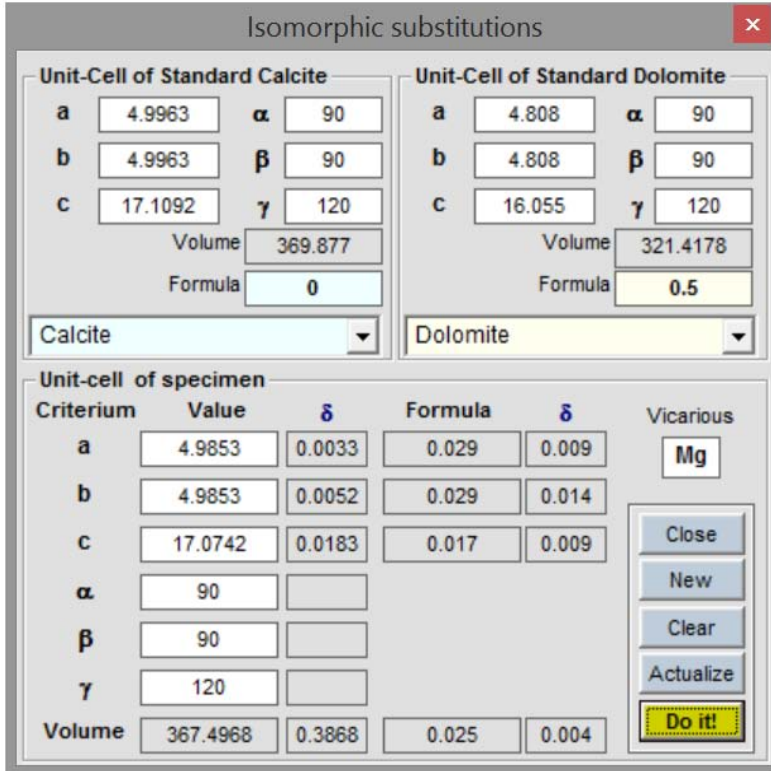


Figure A5.16.

['SolSol.txt' example file](#)

Calcite
 4.9963
 4.9963
 17.1092
 90
 90
 120
 Dolomite
 4.808
 4.808
 16.055
 90
 90
 120
 Magnesite
 4.646
 4.646
 15.139
 90
 90
 120

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APPENDIX 6. Profile analysis

'Profile analysis' requires activate the "*Profile parameters fitting*", '*Scherrer, Willianson-Hall, Caglioti*' '*Warren-Averbach analysis*' and all '*Filtering options*' privileges (*Home Menu / Privilege*).

Access: *Advanced Tools / Tab 1 General / Click 'Profile'*

APPENDIX 6. Profile analysis

'Profile analysis' requires activate the "Profile parameters fitting", 'Scherrer, Williamson-Hall, Caglioti' 'Warren-Averbach analysis' and all 'Filtering options' privileges (Home Menu / Privilege).

Access: Advanced Tools / Tab 1 General / Click 'Profile'

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6.1. Background

The reflection profiles provide information on the crystallinity. This concept not can be defined uniquely as it covers many aspects of the real crystal, as are the average crystal size, the size and distribution of crystal mosaic (it is often called in diffraction as 'coherent domain'), its form and habit, uniformity in both, dimensions (including here the inhomogeneous deformation due to active or residual tension) and composition of the lattice, etc.

This leads to significant changes to four elements of the observable profile:

- Absolute and relative values of the integrated intensity of the profile.
- Profile broadening.
- Distribution function.
- Asymmetry.

6.1.1. Absolute and relative values of integrated intensity. This value increases with the square of the average diameter of the crystal sections, perpendicular to each reciprocal vector, which produces the HKL reflection. In the same way, the average of absolute intensity of the total diffracted by a powder sample is a good measure of its overall crystallinity. By contrast, the 'relative average' value, the most general expressed as a percentage (and also its standard deviation), is inverse function of the overall crystallinity (the latter two figures are virtually independent of the experimental conditions). All this are applied both to individual reflections and full pattern. Here, the concept of crystallinity refers primarily to the size of grain. These values are displayed directly by the program when the sample is loaded. These figures appear on the 'Advanced tools', tab 'General' screen in numerical format (Figure A6.1).

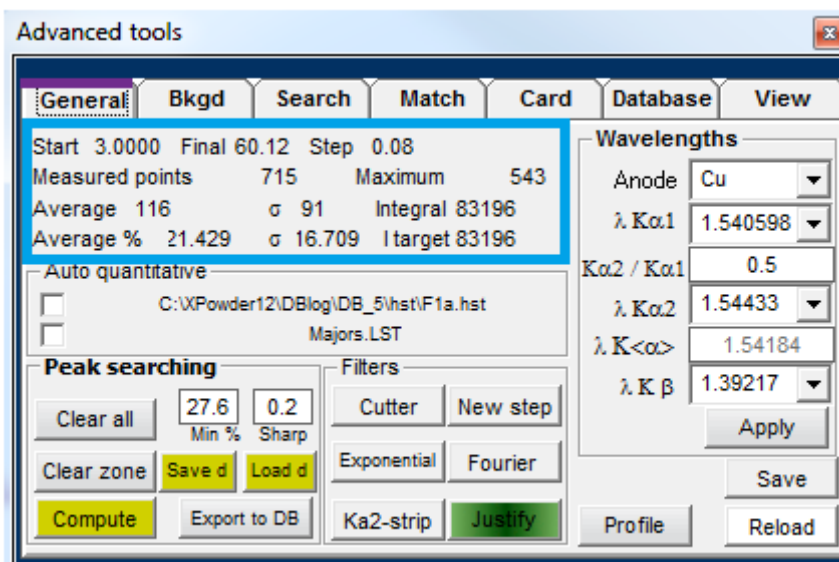


Figure A6.1

6.1.2. Line broadening. The simplest measurement of dispersion (line breadth) is the full width of the intensity distribution at half of the maximum intensity (*FWHM*). If the distribution is not symmetrical **XPowder** calculates the half of the maximum intensity on the left (w_1) and right (w_2) hand side of the peak ordinate. The *asymmetry* is defined as w_2/w_1 . **XPowder** also includes the *integral breadth* β , defined as the width of a rectangle having the same area and height as the observed line profile. *Area asymmetry* (A_2/A_1) has similar sense with *asymmetry*, by using of the left (A_1) and right (A_2) hand side areas of the peak ordinate.

The shape of the profiles is measured by the *shape factor* ϕ , defined as the ratio of the *FWHM* to the *integral breadth*. Thus, the calculated parameters for a profile are:

FWHM = Full width at half maximum.

Asymmetry = w_2/w_1

Integral breadth β

Area asymmetry = A_2/A_1

Shape factor ϕ = $FWHM / \beta$

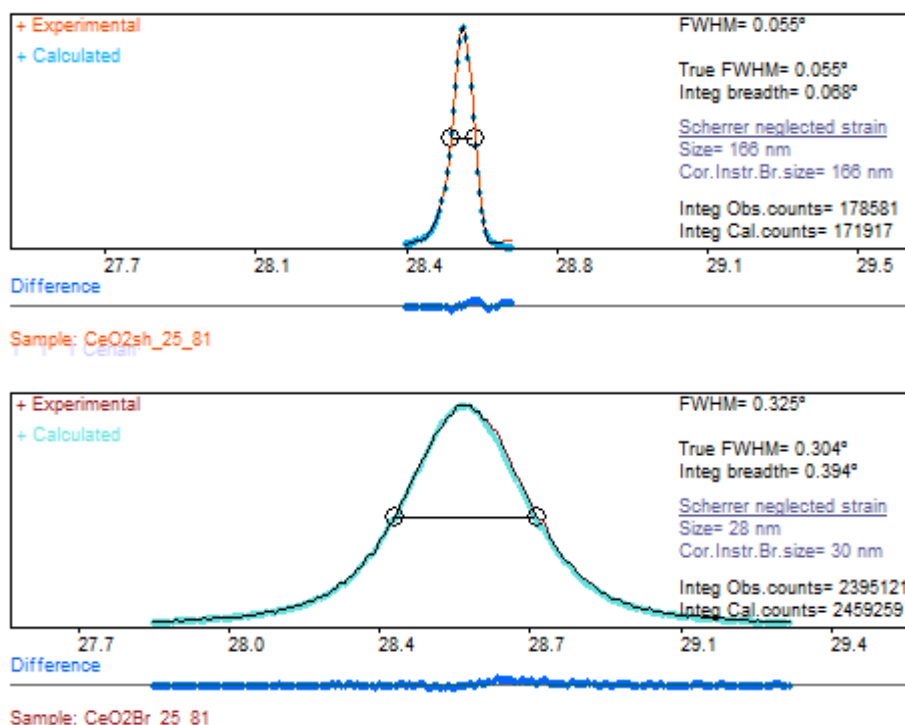


Figure A6.2. Powder individual profiles of CeO_2 111 reflection of low powder size (above) and large size (below) grains. As will be seen below, there increase in the size of the mosaic is related to sample larger crystals (as evidenced by the decrease in the width of the profile). The $K\alpha_2$ component of radiation has been eliminated, to adjust the profile to a *pseudovoigt* function.

The causes of the widening and shape of the profiles are:

- Instrumentals
 - 1. The radiation is not strictly monochromatic.
 - 2. Geometry and diffractometer optical. Instrumental function.
- Related to the specimen.
 - 3. High percentage of amorphous materials (high background).

- 4. Mosaic size (*coherent domain size* in diffraction terms).
- 5. Heterogeneities and distortions of the unit cell
- 6. *Non Uniform Strain* (or simply '*Strain*')

'*Non Uniform Strain*' (or simply '*Strain*') and '*Uniform Strain*' are two different concepts. The first cause a heterogeneous dispersion of the d-spacing values, resulting in a widening of different profiles in each θ . In the second type, the sizes of all the unit cells modifying alike, as for thermal expansion or Pascal pressure, which causes a non-linear displacement of the 2θ angles of the reflections patterns, but not the widening of the profiles.

Of all these possible causes of widening the profiles, only the latter two are related to the nature of the analyzed crystals and are often referred as 'microtexture'. It is therefore necessary to find a suitable procedure to subtract the effects of the first three, which are alien to their own crystals, so that the shape of the 'pure profile', to say the profile due exclusively to that microtexture, will be isolate.

1. Monochromatism. Of course, acquire the patterns with monochromatic radiation through the use of serialized monochromators or synchrotron radiation is convenient. But this is not always possible, so in some methods of microtexture analysis (Scherrer analysis or Williamson-Hall) is needed, as a preliminary step, the complicated process of elimination of the $K_{\alpha 2}$ component (stripping). X Powder X is done with sufficient quality through the push of the 'Advanced tools / Tab General' 'Ka2-stripping' button. If the Williamson-Hall methods are used, the elimination of $K_{\alpha 2}$ also must be performed on the experimental *instrumental function* (see next item).
2. Instrumental function. The calculation of the so-called '*instrumental function*' is more complicated. This function describes the profile shape induced solely by the diffractometer that finally determines the resolution of this technique. The *instrumental function* in theory can be calculated as the product of convolution of the curves generated by each of the components of diffractometer (X-ray source, the sample surface, divergence of the rotation axis, transparency of the specimen, set of divergence and reception slits, monochromator, etc). The details of this calculation can be seen in the book of HF Klug and L.E. Alexander, '*X Ray Diffraction Procedures*', whose 2nd edition has been printed by Wiley & Sons in 1974. In general this theoretical calculations are very complicated, because it is very difficult the parameterization of the functions of each element of convolution. Instead, experimental patterns of very high crystallinity compounds (B_6La , CeO_2 , etc.) are often used in order to uses as an *instrumental function*. Then, the *instrumental profile broadening* can be calculated by the Caglioti equation (see also Appendix 7):

$$B^2 = U \cdot \tan^2\theta + V \cdot \tan\theta + W + P/\cos^2\theta$$

Where B is the width of the profile for each pure angle θ . U, V, W and P have to be adjusted from the *very high crystallinity standard pattern* (Ce_2O , B_6La , *Corundum*,...). Other times and whenever possible, the *instrumental function* can be obtained from a sample that possesses not only a high crystallinity, but a similar composition to the studied specimen. In this case, the Caglioti function is not used. The calculation of the Caglioti function is performed automatically by X Powder, as explained further down.

3. Background. Some methods of microtexture analysis, using only the reflection widths (Scherrer and Williamson-Hall), require to remove the background before making adjustments in the distribution functions of the crystal reflections. However, except in

cases where it is really excessive, the background should never be removed. The background should never be eliminated when using the Warren-Averbach methods, of course

6.1.3. Distribution function. It describes the shape of the bell of the distribution accounts around the maximum of diffraction.

The distribution function used by X PowderX to model the *pure profiles* (profiles cleaned of instrumental interference) is:

$$P(x) = \Phi_{(0)} \left\{ \gamma \cdot e^{-\pi x^2 [4 \cdot \text{Ln}2/\pi] / (B)^2} + [(1-\gamma) \cdot B^2 / 2(B^2 + x^2)]^p \right\}$$

Where:

x = Free variable (in 2θ or in $\sin\theta/\lambda$ units)

B = Reflection broadening (refinable parameter or experimental data)

γ and p are refinable parameters

If $\gamma = 1$, $p=0$ the function is *Gaussian*

If $\gamma = 0$, $p=1$ the function is *Lorentzian* (or *Cauchy*)

If $\gamma=0$, $p>1$ *Pearson VII*

If $\gamma=0$, $p<1$ *Super Lorentzian*

If $\gamma=0$ to 1, $p=0$ *Pseudo Voigt* (*Gaussian + Lorentzian*)

If $\gamma = 0$ to 1, $p \neq 1$ *Mixed function*

$\Phi_{(0)}$ = Function value for $x = 0$ (maximum)

6.1.4. Asymmetry. X PowderX adjusts, independently the right and left sides of the diffraction profiles, so it is possible to quantify the asymmetry of both, areas as B parameters.

With a strictly monochromatic radiation, sometimes, the slope of the profiles is softer towards lower 2θ angles. This can be attributed to a lack of uniformity in the size of the unit cell, due to partial hydration process that causes increased volume crystalline, by way of example.

If the slope is softer towards larger 2θ , the cause is more difficult to explain. Sometimes this can occur in the process of crystallization from a solid solution, in which the more modern cells are formed from isomorphic elements of smallest radii. On the contrary, can be caused in the process of dissolution where the more soluble terms are largest radio elements. In any case, systematic measures from the parameters of asymmetry and form factor described above can be established.

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6.2. Profile analysis methods based on width and shape of the diffraction profiles.

The use of strictly monochromatic radiation allows very simple treatments of profiles in terms of variance, so that when the profiles are adjusted to *Cauchy* functions, you can write:

$$B_{\text{total}} = B_{\text{Instr}} + B_{\text{sample}} = B_{\text{Instr}} + B_{\text{size}} + B_{\text{strain}}$$

If the profile function is *Gaussian* the relationship is as follows:

$$B_{\text{total}}^2 = B_{\text{Instr}}^2 + B_{\text{sample}}^2 = B_{\text{Instr}}^2 + B_{\text{size}}^2 + B_{\text{strain}}^2$$

From the analysis of the *distribution function* used by X Powder, a more general relationship can be inferred for the *pseudo voigt*:

$$B_{\text{total}}^{(1+\gamma)} = B_{\text{Instr}}^{(1+\gamma)} + B_{\text{sample}}^{(1+\gamma)} = B_{\text{Instr}}^{(1+\gamma)} + B_{\text{size}}^{(1+\gamma)} + B_{\text{strain}}^{(1+\gamma)}$$

This equation allows easily deduce the value of the width of the reflections when this type of profile function is adequate. The γ parameter is calculated automatically by X PowderX, and correspond to the Gaussian component of the *Pseudo Voigt* function.

6.2.1. The Scherrer Method.

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It is used to calculate the coherent domain size (uncorrected strain) from a single reflection profile (λ supposed monochromatic):

$$\text{Size}(\mu\text{m}) = K \cdot \lambda(\text{\AA}) / (10 \cdot B_{\text{size}} \cdot \cos\theta)$$

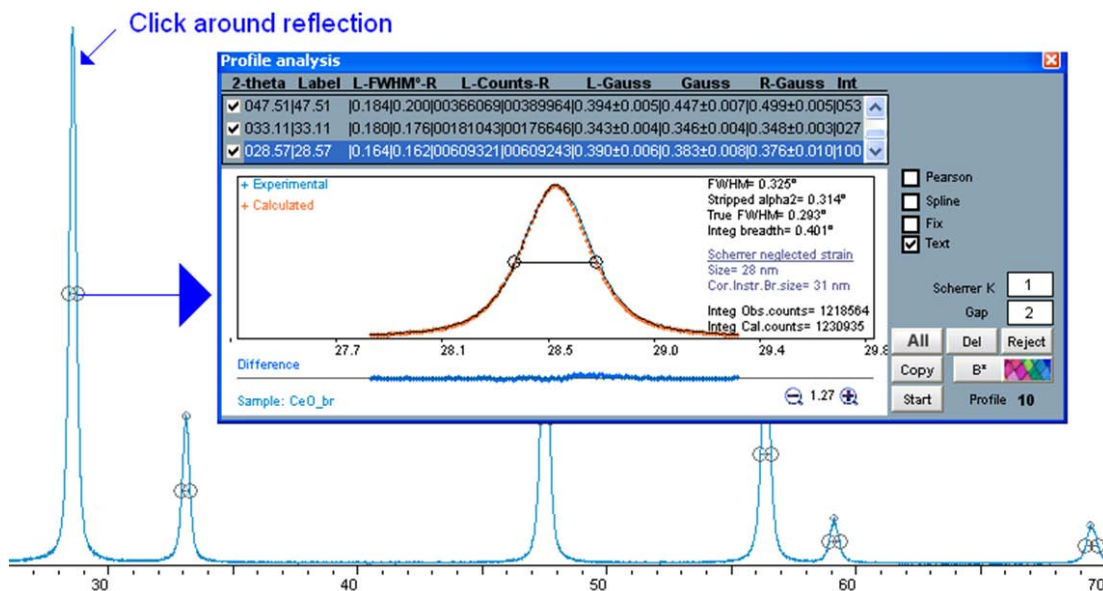


Figure A6.3.

The coherent domain size '**Size(μm)**' is often expressed in nanometres (hence the 10 that appears in the denominator). λ (Å) is the wavelength of monochromatic radiation and θ_0 is the central angle of reflection.

The width of the reflection B_{size} can be *FWHM*, or the β *integrated width*, expressed both in **radians**. When the instrumental role is known, $B_{\text{sample}}^{(1+\gamma)}$ can be obtained by the suitable relationship $B_{\text{sample}} = B_{\text{total}} - B_{\text{Instr}} \approx B_{\text{size}}$. Otherwise, it can make a gross oversimplification assuming that $B_{\text{size}} \approx B_{\text{total}}$. **Strictly, $B_{\text{sample}} = B_{\text{size}}$ only for $\theta = 0$** (where $B_{\text{strain}} = 0$, see below). **K** is a experimental constant ($0.8 < K < 1.1$), with different value when β instead *FWHM* is used. Optionally X Powder calculates this value but generally uses $K = 1$

To measure the size of the coherent domain with Scherrer method, click just about any reflection profile on diffraction plot, and the automatic adjustment to a 'pseudo Voigt' function is obtained (γ is also fitted), as shown in Figure A6.3. It is desirable to make a proper $K\alpha_2$ stripping, and even a '*Spline*' interpolation, before starting the calculations. If you wish to obtain results expressed in absolute values, which can be compared with those of other laboratories, the *instrumental function* should also be set in advance. The background subtraction is not desirable to make, unless cases of very poor quality patterns. In any case, the background subtraction should not be too 'aggressive'.

The computed data are:

- 2θ of the maximum ('2-theta' column).
- If the object 'Matching' is present, *hkl* index are shown, on the contrary 2θ is printed. (Column 'Label').
- Values' FWHM 'expressed in degrees of 2θ , both to the right side (R) as to the left (L). Columns '(L)', 'FWHM^o', '(R)'
- Gaussians components (γ) of the adjusted functions by the *Right* and *Left*, as well as the error of those values (Columns' Gauss-left ', ' Gauss-full 'and' Gauss-Right '). The statistical values for left, full and right profiles are also shown to the right of the chart with red, white and blue respectively.
- Drawings of the adjusted and difference functions (blue).
- Drawing and value of experimental FWHM.
- Corrected FWHM Value for the instrumental function (True FWHM) that should be calculated for each diffractometer. In any case, the program uses latest available function.
- Integral Breadth in $2\theta^o$. Coherent domain size in nm without correction instrumental ('Scherrer'). $K = 1$ is used and the widening of the profile caused by 'Strain' is not taken into account.
- Idem with instrumental correction ('Corr Scherrer'). $K = 1$ is used and the widening of the profile caused by 'Strain' is not taken into account.
- Experimental profile integral counts (Integral Obs. Counts).
- Calculated profile integral counts (Integral Cal. Counts).

When the box **Fix** is checked, the position of the highest profile is set at the exact angle 2θ , which has made the 'click' with the mouse. In another case, the program finds the position of the maximum.

When the box **Pearson VII** is checked, the exponent **p** of the general distribution function is refined.

When the box **Spline** is checked the experimental data are interpolated virtually, through an a cubic spline, and the position of the maximum with more precision is obtained.


The box **Gap** contains the interval which will be used in adjusting the distribution functions, on both sides of the maximum.


If the box **Text** is unchecked, any comments appear on the image.


The button allows you to start a new list of measures. It is used when switching experimental options, or at star the fitting of special functions such as those of Caglioti, or Williamson-Hall microtexture analysis.


The button lets you select all the profiles of the header list for subsequent calculations (Caglioti, Williamson-Hall, for example).

The button lets you remove the current profile of the list (blue stripe).

The button  moves the graphic to clipboard.

The button  lets you remove the last fitted profile.

The button  lets calculate the Caglioti equation. If the sample is a very high crystallinity specimen, enables you to adjust the instrumental function.

The button  performs the calculation of the size of mosaic and '*Strain*', according to the method of **Williamson-Hall** (See 6.2.2.1. section. **Warren-Averbach** method is also available from 'Main menu / Tools/ View/Warren-Averbach (See 6.2.2.2. section).


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6.2.2. SIZE AND STRAIN ANALYSIS

'Size and Strain analysis' requires activate the "*Profile parameters fitting*", '*Scherrer, Williamson-Hall, Caglioti*' '*Warren-Averbach analysis*' and all '*Filtering options*' privileges (*Home Menu / Privilege*).

6.2.2.1. THE WILLIAMSON-HALL METHOD

'Williamson-Hall Method' requires activate the "Profile parameters fitting", 'Scherrer, Williamson-Hall, Caglioti' and all 'Filtering options' privileges (Home Menu / Privilege).

Access: The button  performs the calculation of the size of mosaic and 'Strain', according to the method of **Williamson-Hall**. See figure A6.3.

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Background

The method of *Scherrer* explained above, uses a single X-Ray reflection for the calculations of mosaic size, but provides no information on the 'strain' (ε), since this affects the profile differently in each 2θ value:

$$\varepsilon = B_{\text{strain}} / (4 \cdot \tan\theta)$$

$$B_{\text{strain}} = \varepsilon \cdot 4 \cdot \tan\theta$$

Where, B_{strain} is the variance of the distribution due to 'strain', expressed in radians, and ε is the 'strain' defined as $\varepsilon = \Delta d/d$. We note that the B_{strain} value is zero at the origin ($\theta=0$).

The effect of 'strain' on the broadening of the profile is generally very small compared to due to the magnitude of the mosaic. To correct the effect of 'strain', the method of *Williamson-Hall* can be used.

The variance of a pseudo voigt distribution having γ Gaussian component can be expressed:

$$B_{\text{size}}^{(1+\gamma)} + B_{\text{strain}}^{(1+\gamma)} = B_{\text{sample}}^{(1+\gamma)} = B_{\text{total}}^{(1+\gamma)} - B_{\text{Instr}}^{(1+\gamma)}$$

The method of *Williamson-Hall* calculates separately, the size and the 'strain' by two or more orders of a reflection HKL, but gave no information on the size distribution, provided by the method of *Warren-Averbach*, which will be explained later. Thus,

$$B_{\text{sample}}^{(1+\gamma)} = B_{\text{size}}^{(1+\gamma)} + B_{\text{strain}}^{(1+\gamma)}$$

$$\text{Size}(\mu\text{m}) = K \cdot \lambda / (10 \cdot B_{\text{size}} \cdot \cos\theta) \quad (\lambda \text{ in } \text{\AA}, B \text{ in radians})$$

By removing and replace the values of B_{size} and B_{strain} , we get:

$$B_{\text{sample}}^{(1+\gamma)} = \{K \cdot \lambda / [10 \cdot \text{Size}(\mu\text{m}) \cdot \cos\theta]\}^{(1+\gamma)} + \{\varepsilon \cdot 4 \tan\theta \cdot \}^{(1+\gamma)}$$

By rearranging, we get

$$\{B_{\text{sample}} \cdot \cos\theta\}^{(1+\gamma)} = \{K \cdot \lambda / [10 \cdot \text{Size}(\mu\text{m})]\}^{(1+\gamma)} + \varepsilon^{(1+\gamma)} \cdot \{4 \cdot \sin\theta\}^{(1+\gamma)}$$

This is the expression of the equation of a *straight line* $y = b + a \cdot x$, whose function values are

$y = \{B_{\text{sample}} \cdot \cos\theta\}^{(1+\gamma)}$ and independent variables are $x = \{4 \cdot \sin\theta\}^{(1+\gamma)}$. If the experimental values x are plotted versus y , the absolute values of $\text{Size}(\mu\text{m})$ and ε can be obtained from the *straight regression line*.

In this way, for $x=0$ we can obtain the value of $b = \{K \cdot \lambda / [10 \cdot \text{Size}(\mu\text{m})]\}^{(1+\gamma)}$ and the slope is $a = \varepsilon^{(1+\gamma)}$. From b and a we obtain **Size(μm)** and **ε** respectively.

As can be seen easily, the size obtained depends on the *hkl* direction and at least two observations are needed (eg 111 and 222). In isometric crystals can be used occasionally reflections from different directions, although the detailed analysis tends to give a much richer information.

This analysis is done via the button **Williamson-Hall** of the figure A6.3.

The figure A6.4 shows an automatic *Williamson-Hall* analysis for all reflections of a diffractogram of CeO₂. The three models correspond to Gaussians, Lorentzian and Pseudo Voigt models respectively. FWHM has been used as broadening criterion. The constant K value from *Scherrer* equation was optimized (K = 0.824) (box **Guessing Scherrer K** marked). The values of 'Strain' are expressed in% and are very low, according to the values of the slope of the straight lines in all cases.

Other disposable options such as **Integral Bread**), **Weight data**, instrumental correction (**Inst.Corr**), right side, full side or left side profiles (selecting in the **Profile zone** framework), etc can be used.

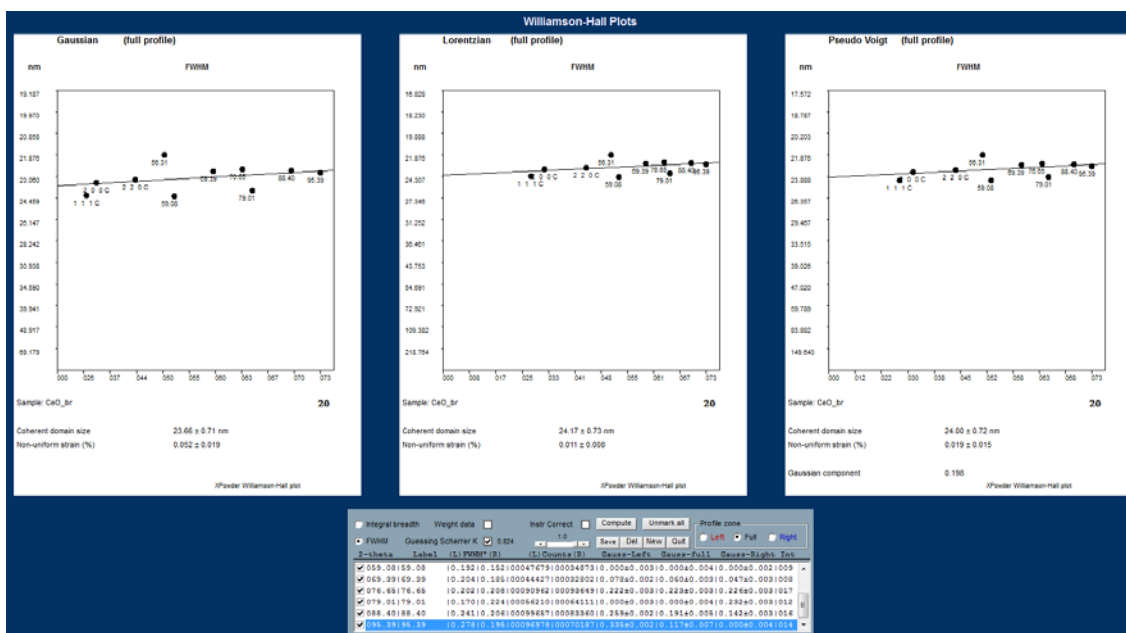


Figure A6.4

Figures A6.5 and A6.6 show the *Williamson-Hall* analysis performed on the h00 reciprocal direction, with and without instrumental correction respectively.

Both the method of *Scherrer* (6.2.1. section) as the *Williamson-Hall* (6.2.2.1. section) provide size values, as measured on directions HKL, whose calculations involved in the entire volume of crystalline domains. That is the criterion used for statistical weight is the volume. The term '*volume weighted*' is used to refer to the sizes obtained, as opposed to the '*area weighted*' provided by other methods such as the *Warren-Averbach* (6.2.2.2. section) which is explained below. In general the weight methods based on '*volume*' provide values greater than those achieved with '*areas*'.

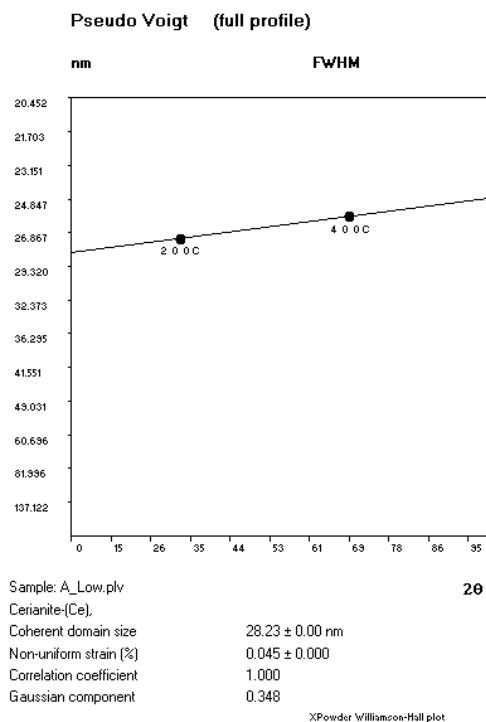


Figure A6.5. Williamson-Hall plot for h00 direction. Instrumental correction was done.

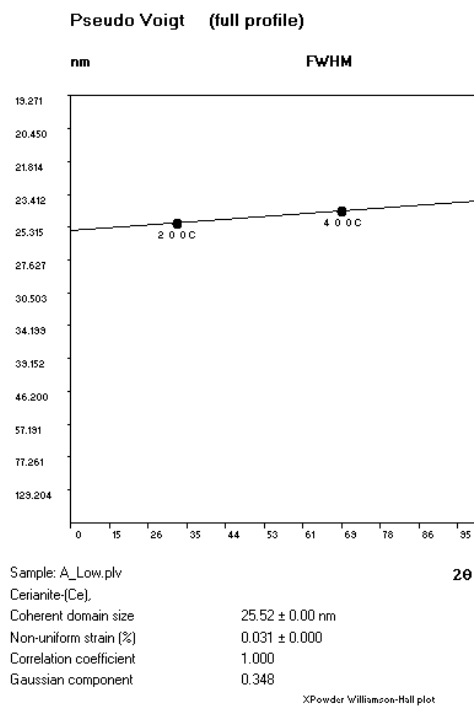


Figure A6.6. Williamson-Hall plot for h00 direction. Instrumental correction was not done

6.2.2.2. THE WARREN-AVERBACH METHOD

'Warren-Averbach Methods' requires activate the "Profile parameters fitting", 'Scherrer, Willianson-Hall, Caglioti' 'Warren-Averbach analysis' and all 'Filtering options' privileges (Home Menu / Privilege).

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This approach It is accessed by pressing the "Main menu/ Tools / View / Warren-Averbach" (Figure A6.7).

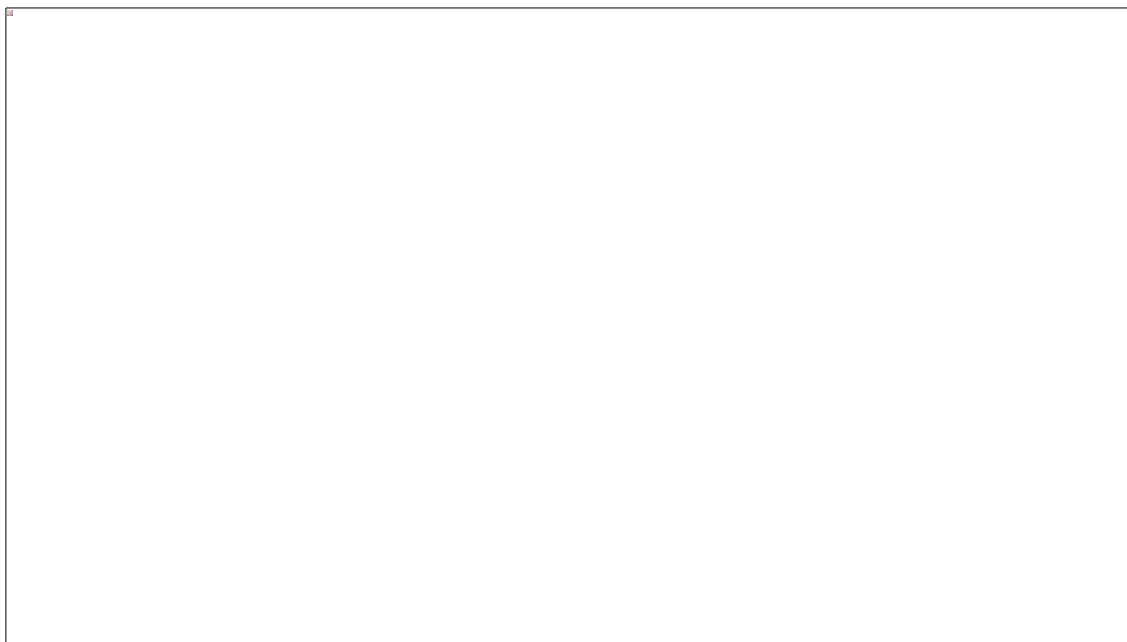


Figure A6.7. The Warren-Averbach tools.

Background

A more comprehensive and accurate study of the diffraction profiles based on Fourier analysis, attends the role of total profile (R_{total}) as a result of the convolution of the instrumental profile (R_{Instr}) with the function generated by the sample (R_{sample}), being the latter the product of convolution of the size function (R_{size}) and due to strain function (R_{strain}).

$$R_{total} = R_{Instr} * R_{sample} = R_{Instr} * R_{size} * R_{strain}$$

The method requires the representation of diffractograms in reciprocal space, instead of doing it in classic 2θ function. Obtaining histograms diffraction in this space has very experimental difficult, as it requires appropriate programming of diffractometer very different than usual. X PowderX uses an alternative path based on the theoretical calculation of histograms (ie diffractograms with $\Delta 2\theta$ constant) based on typical 2θ plots, (which is the usual way of presenting the data) through interpolation methods for cubic spline. It has been proven the effectiveness of this method that allows you to create reciprocal graphs with the same quality and form of profiles than those obtained experimentally. The method is used both for the *instrumental function* as to the *sample function*.

The *Warren-Averbach* method is a highly elaborated approach of size and strain analysis by powder X-Ray method which uses the deconvolution of the structural line profile (true profile) and the Fourier transform for evaluation of size of the coherent domain and strain (to say: space dispersion $\Delta d/d$ %). This method states that the absolute values of Fourier cosine

coefficients are then product of the size and the strain coefficients (Bertaut 1949). The coefficients can be numerically calculated and then related to the distribution of the column length (L), defined as the distance in the crystallite, perpendicular to the diffracting planes hkl (parallel to diffracting \mathbf{q}_{hkl} vector). The convolution of the size broadened and strain broadened profiles in reciprocal space is the product of their Fourier transforms in real space. The absolute cosine Fourier coefficients ($A_{L,q}$) of the true profile are:

$$A_{L,q} = {}^sA_L \cdot {}^\varepsilon A_{L,q} \quad [6.1]$$

Being

sA_L absolute cosine Fourier coefficients size dependents,

${}^\varepsilon A_{L,q}$ absolute cosine Fourier coefficients strain (ε) L and q dependents and

$$q = 2 \cdot \sin\theta / \lambda$$

If two or more order of the reflection for hkl planes are available in the diffractogram, separate information for size and strain can be extracted assuming small strain values and Gaussian strain distribution for all values of L. Applying logarithms to [6.1]:

$$\begin{aligned} \ln(A_{L,q}) &= \ln({}^sA_L) + \ln({}^\varepsilon A_{L,q}) \\ &\approx \ln({}^sA_L) - 2\pi^2 L^2 q^2 \langle \varepsilon^2 \rangle \end{aligned} \quad [6.2]$$

where ${}^\varepsilon A_{L,q} = e^{-2\pi^2 L^2 q^2 \langle \varepsilon^2 \rangle} L$ (theoretical expression value for ${}^\varepsilon A_{L,q}$) and $\langle \varepsilon^2 \rangle$ is the mean-square strain for the correlation distance L.

In successive plots of (${}^\varepsilon A_{L,q}$) versus q^2 at fixed L values, sA_L are obtained from the intercept of the strain lines (at abscissa = 0) and ${}^\varepsilon A_{L,q}$ from the slope of the strain equations. Note that they are a strains coefficients curve for each q profile.

General procedure in W-A analysis.

1. The sample and instrumental profiles are normalized to maximum value=1 (figure A6.8.down) and plotted in the reciprocal space with constant step (abscissa = $2 \cdot \sin\theta / \lambda$, ordinates = counts/1, figure A6,8, up).
2. Deconvolution is carried out in order to obtain the 'structure profile' ('pure profile', 'physical diffraction line') of the sample pattern (figure A6.8, up).
3. Absolute values of cosine Fourier coefficients (A_L) from the structure profile are calculated and normalized to $A_0=1$, and plotted versus column length L, perpendicular to the reflecting plane hkl (parallel to reciprocal q diffraction vector. Figure A6.9).

The average L_{AREA} size (uncorrected strain) is calculated from the tangent of the coefficients curve in $(A_0, 0)$ point for $A_L=0$ in inflection point (2^{nd} derivate=0, grey line in figure A6.9).

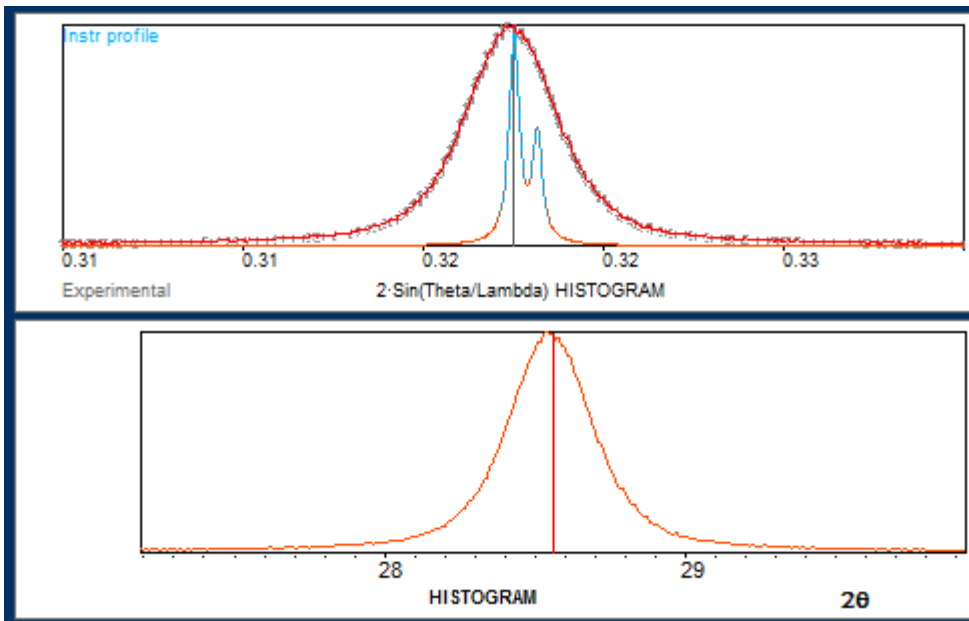


Figure A6.8. Reciprocal (up, after instrumental profile deconvolution) and initial 2θ (down) histograms.

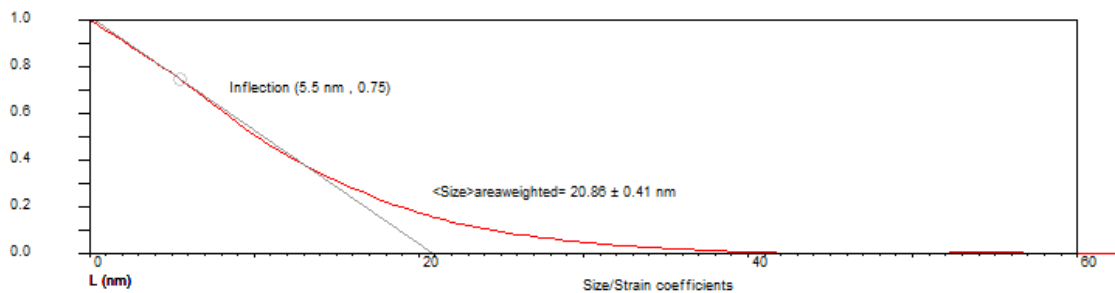


Figure A6.9. L_{AREA} size perpendicular to 111 is 20.86 ± 0.41 nm for uncorrected strain.

4. By selecting an upper Bragg's order line of hkl, size and strain coefficients values can be separate, according to [2]

$$\ln(A_{L,q}) = \ln({}^s A_L) - 2\pi L^2 \langle \varepsilon^2 \rangle q^2 \quad [6.3.]$$

that is the straight line equation

$$y = b + a \cdot x$$

where

$$b = \ln({}^s A_L)$$

$$a = -2\pi L^2 \langle \varepsilon^2 \rangle$$

$$x = q^2$$

$$y = \ln(A_{L,q})$$

$${}^s A_L = e^b [3]$$

$${}^e A_{L,q} = \exp(aq^2) \quad [6.4]$$

$$\langle \varepsilon^2 \rangle = -a/2\pi L^2 \text{ (average value)} \quad [6.5]$$

Then, it can be obtain the **pure Size** Fourier-Cosine coefficients plot (column length probability to be greater or equal to L) and the average area weighted size value ($\langle L_{AREA} \rangle = 50.60 \pm 1.02$ nm in example of figure A6.10) perpendicular to the (111) selected crystalline face (parallel to selected \mathbf{q} reciprocal vector, the $\epsilon_{L,q}$ **Strain** Fourier-Cosine coefficients plots for each analyzed profiles (figure A6.11) and the **Strain** ($\delta d/d = \langle \epsilon^2 \rangle^{1/2}$) versus column lengths plot (figure A6.12).

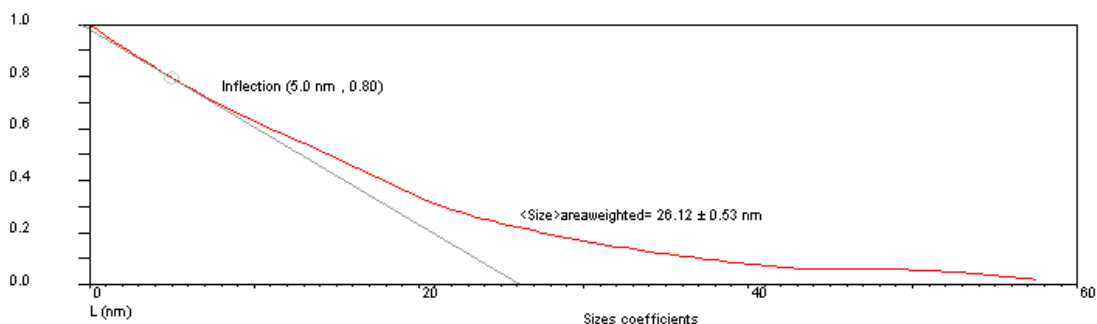


Figure A6.10. Corrected Strain L_{AREA} Size perpendicular to 111 is 26.12 ± 0.53 nm.

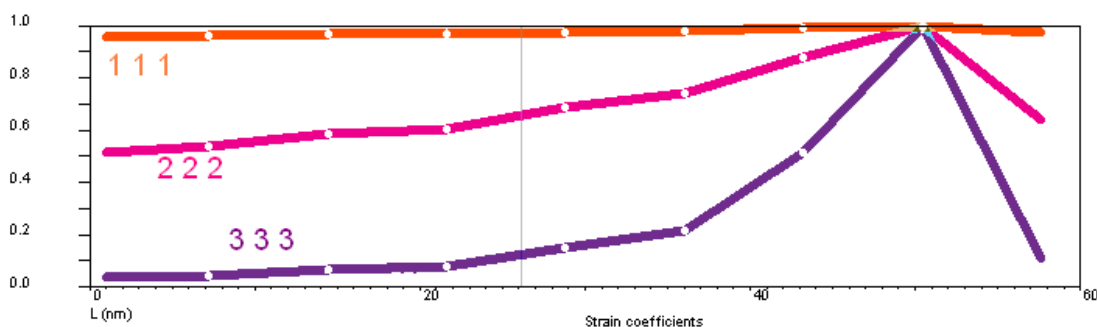


Figure A6.11. Strain Fourier coefficients for 111, 222 and 333 reflections

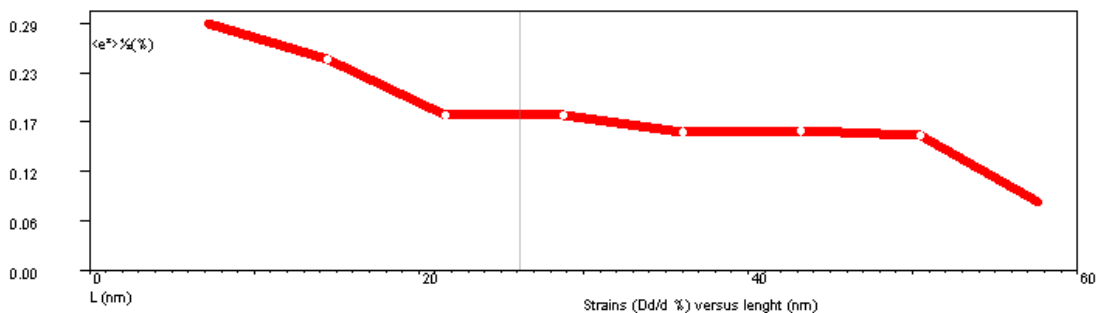


Figure A6.12. Strain versus L_{AREA} size for hhh.

Log-normal distribution.

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Additionally in most cases of small particles or nanocrystalline powder, the column length size can be calculated by fitting to the log-normal distribution function [6.6.]. See also figure A6.13.

$$f(x) = \frac{1}{\sqrt{2\pi}\sigma} \frac{1}{x} \exp\left\{-\frac{[\ln(x/m)]^2}{2\sigma^2}\right\} \quad [6.6]$$

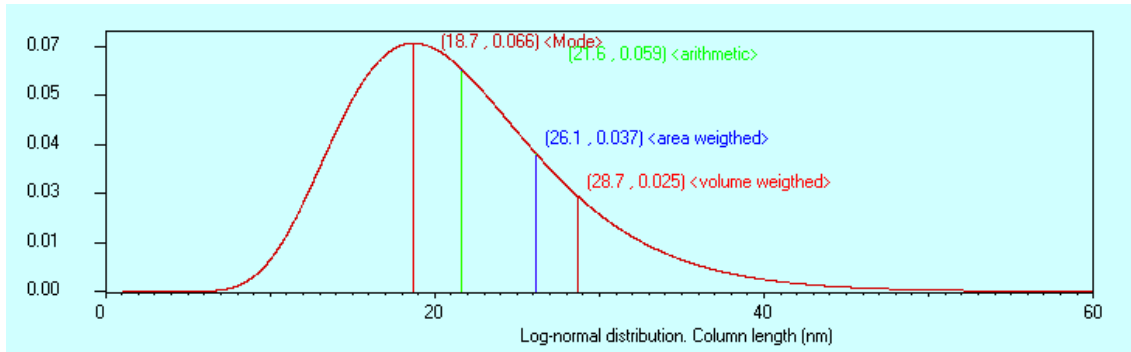


Figure A6.13. Log-normal distribution

How does X PowderX do this?

Selecting profiles of isolated reflections

Select the profiles by draping around the reflection with the left mouse button in any histogram. The selected profile will be enlarged in lower-left graphics in Figure A6.7. Upper plot is the reciprocal histogram and lower is the 2-theta histogram of selected interval. Alternatively input 2θ lower and upper limit values and pulse **Actualize**. Optionally, use **Centre** in order to improve the symmetry of the profile in the θ interval.

Main tools and options

Figure A6.14. General tool display for Warren-Averbach method using a Cerianite (CeO₂) sample.

Example: Warren-Averbach analysis of milled low crystallinity CeO₂_br pattern file
(Figures A6. to A6.14)

Current Profile figure A6.14 frame

2-theta limits: Lower and upper 2-theta of the selected reflection. The values can be input directly, by using of the displacement bar or by draping in the histograms.

Centre : The reflection is placed in the centre of the selected interval according to the **Average** or the **Maximum** of the profile. It will be automatically executed when **Fourier Coeff** are clicked and the **Automatic** option was checked above.

Maximum or **Average**: Criteria used to centralize the profile.

N polynomial: Select de order of the polynomial for fitting the column length L_{AREA} . Default value is 3. No used

Points: Number of cosine coefficients to be included in polynomial regression (A_0 to A_{points}). Default value is 10. No used

Equal interval: Restriction to force all width profiles are the same. This box is checked automatically when the first profile has been analyzed by **Fourier Coeff**.

<Area weighed Size> : Value of the computed area-weighted column length (L_{AREA} nm) for current analysis (both WA corrected or uncorrected strain)

Scherrer Size : Value of Scherrer size in nm for the current profile.

PROFILE n: Ordinal number of the actual profile

h k l: Editable label for actual profile (3 3 3 in the example of figure A6.14)

Fourier Coeff: Compute in turn **Centre** (if the centre box is checked), **Actualize** and the average area weighed L_{AREA} size (uncorrected strain) is calculated from the tangent of the coefficients curve in ($A_0,0$) point for $A_L=0$ (figure A6.9). Uses [7], **N polynomial** and **Points** parameters. Results are display as table of figure A6.15.

<input checked="" type="checkbox"/>	Q = 0.3204 .Size(uncor. strain)=20.4±0.40 nm (1 1 1)
<input checked="" type="checkbox"/>	Q = 0.6405 .Size(uncor. strain)=15.8±0.33 nm (2 2 2)
<input checked="" type="checkbox"/>	Q = 0.9603 .Size(uncor. strain)=18.5±0.37 nm (3 3 3)

Figure A6.15

When two or more reflections have been analyzed, the Warren-Averbach analysis is enabled (Button 'Compute Warren-Averbach').

WH Vol weighed size Estimated volume weighed size (nm). This value can be improved from X PowderX **Williamson-Hall** plot module and can be changed manually by the user. It is used by program for computing σ .

2-sin(θ)/ λ step Editable value of the used step in reciprocal histogram.

Max L : Upper limits in nm for column length in graphics. Default value is 45 nm.

N orders Allow to show the first N Braggs reflection orders from the actual position of cursor.

Inflection point figure A6.14 frame

X value: Centre for $\langle \text{Size} \rangle_{\text{AREA}}$ calculation

Gap (nm): Interval of X value for lineal regression in order to obtain then $\langle \text{Size} \rangle_{\text{AREA WEIGHTED}}$ value

Restraint X value: Bind inflection point to actual **X value** amount.

Wipe Reset profile counter and analytical results.

Actualize Compute and redraw graphics according to actual parameters. It will be automatically executed when **Compute Coeff** is clicked.

Exit Close Warren-Averbach tools and enter XPowderX home screen.

Compute Warren-Averbach This button is enabled only when they have been selected two or more profiles as in the table of figure A6.15.

This order automatically computes full [6.1] to [6.5] Warren-Averbach analysis using the profiles selected and draws figures A6.10 to A6.12. The tabulated results also are shown as in figure A6.16.

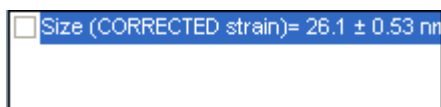


Figure A6.16

Note: Use right mouse button for others pop-up contextual menus. *Help* menu shows a quickly W-A user guide.

Instrumental Profile Tab

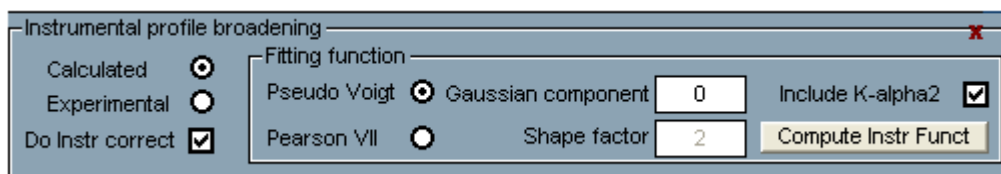


Figure A6.17. Options for computation of Fourier Coefficients and Log-Normal distribution.

Calculated: Allow calculate the instrumental profile by using the Caglioti approximation and selected distribution function (**Pseudo Voigt** or **Pearson VII**) by using an instrumental-standard sample (The National Institute for Standard and Technology- NIST, LaB₆ by example).

Experimental Enable the use of a sample of equal composition and 'infinite' crystallinity for instrumental broadening effects correction.

Compute Instr Funct Computes and shows the current instrumental profile.

Include K-alpha2 The effects of the doublet $K\alpha_{1-2}$ will be corrected if checked.

Do Instr correct The instrumental correction will be applied if checked. Default option is 'Checked'.

Pseudo Voigt. The Pseudo Voigt distribution function will be used in the least squares fit using then current 'Gaussian component' value.

Pearson VII The Pearson VII distribution function will be used in the least squares fit using then current 'Shape factor' value.

Log normal size distribution Tab

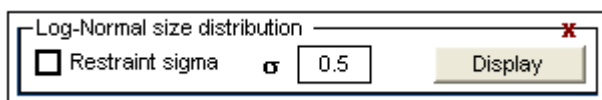


Figure A6.15.Options for computation of Fourier Coefficients and Log-Normal distribution.

Restraint sigma: Bind σ to actual value

σ : Dispersion for log normal distribution. If **Restraint sigma** is checked the σ value is not calculated.

Display Computes log-normal size analysis [6.6] and draw graphic of probabilistic distribution of L values (figure A6.13). The used parameters in [6.6] are $x = L_{\text{area}}$ and σ .

Others parameters and commands

Home. XPowderX main screen.

Wipe. Restart selection of profiles for Warren-Averbach analysis

Generated WA output files

They are generated in the subfolder "Sample directory\WA\File name*.**".

Ss1.COF (example)

1 1 1_2 2 2_3 3 3_	Analyzed reflections separated by '_'
Init Q = .307504424086868	Initial $\text{Sin}\theta/\lambda$ of interval profile.
Central Q = .32040931040811	Central $\text{Sin}\theta/\lambda$ of profiles.
Final Q = .333314196729353	Final $\text{Sin}\lambda/\theta$ of interval profile.
Histogram Q interval = 3.874501	$\text{Sin}\lambda/\theta$ / step of profile histograms.
1 , 1 , 0.9507649 , 0.4466602 , 1.701842E-02 , 0	N lines for each computed point(*)
7.207186 , 0.698083738861815 , 0.9534699 , 0.4673826 , 2.140244E-02 , 0.287385	
14.41437 , 0.377447228334247 , 0.9581903 , 0.5057251 , 3.188081E-02 , 0.2377922	
21.62156 , 0.235138647639452 , 0.9610426 , 0.5302919 , 4.051796E-02 , 0.1863586	
28.82874 , 0.160431082603869 , 0.9704628 , 0.6196454 , 0.089013 , 0.193028	
36.03593 , 0.120059847865352 , 0.9769666 , 0.6893597 , 0.1525723 , 0.1778001	
43.24311 , 4.29827386966812E-02 , 0.9864784 , 0.8046686 , 0.3334045 , 0.1725621	
50.4503 , 9.12871557815724E-02 , 1 , 0.9999998 , 0.9999999 , 0.1730742	
57.65749 , 2.86568378778336E-02 , 0.973839 , 0.6549615 , 0.1177933 , 0.1043658	

(*) Content of each L point in all W-A plots (9 points in example).

1st column: L = column length (nm) value for X axis.

2nd column. Fourier Size Coefficient

3, 4 and 5th columns. A column for Strain Fourier Coefficient of each reflection (3 in example)

6th column. Strain versus L in %.

File name N br.RUN. Sample full pattern histogram in reciprocal space (odd rows= $\sin\theta/\lambda$, even rows= counts)

File name N sh.RUN. Instrumental broadening full pattern histogram in reciprocal space (odd rows= $\sin\theta/\lambda$, even rows= counts)

File name N br.RNL. Current selected profile histogram in reciprocal space ($\sin\theta/\lambda$, counts)

File name N sh.RUN. Current selected instrumental broadening profile histogram in reciprocal space ($\sin\theta/\lambda$, counts)

(In all cases name= sample label, N= historical integer, br= broadened for sample, sh=sharpened for instrumental)

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1. Select first order profile by draping with left mouse button in any histogram (example: 1 1 1 reflection).
2. Centre profile and zoom (click . Figure A614. Optional).
3. Change instrumental profile parameters (Figure A6.17. Optional).
4. Compute Fourier coefficients (Figure A614. Click).
5. Repeat 1 to 4 in order to analyze another order profiles (Example: Select in turn 2 2 2, 3 3 3, etc. reflections)
6. Click . Figure A6.14
7. Compute Size Distribution for log-normal model (Click . Figures A6.14 and A6.15. Optional)

Lectures.

Balzar, D., Audebrand, N., Daymond, M.R., Fith, A., Hewat, A. Langford, J.I., Le Bail, A., Louër, D., Masson, O., McCowan, C.N., Popa, N.C., Stephens, P.W. and Toby, B.H. (2004) *J. Appl. Cryst.* **37**, 911-924

Bertaut, E.F. (1949). *C. R. Acad. Sci. Paris*, **228**, 187-189, 492-494.

Warren, B.E. *X-ray Diffraction*. (1969). Reading, Mass. Addison-Wesley. 1990 Edit. 381 p.

Lucks, I., P. Lamparter, E.J. Mittemeijer, *An evaluation of Methods of Diffraction-Line Broadening Analysis. Applied to Ball-Milled Molybdenum*, *J. Appl. Cryst.* **37**(2004) 300.

APPENDIX 7. THE CAGLIOTI FUNCTION

APPENDIX 7. THE CAGLIOTI FUNCTION

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It can be calculated automatically when the ' B^2 ' button in Figure A6.3. is pressed. The adjustment is made from all profiles analyzed, clicking near the reflections in the diffraction pattern plot, as in figures A62 and A6.3. Using a sample of high crystallinity (B_6Al for example) allows for the instrumental function of the diffractometer. Caglioti function is calculated for both FWHM values for integrated profiles widths from values of U, V, W, P initial and approximate.

The Caglioti equation calculates the width of the diffraction peaks (B), through the adjustment of the three parameters (U,W,W,P) of the formula:

$$B^2 = U \cdot \tan^2\theta + V \cdot \tan\theta + W + P/\cos^2\theta \quad [7.1].$$

In principle, this function was used to synchrotron diffraction, but also can be used with any other of X-ray monochromatic radiation. There must have an efficient monochromator or eliminate analytically $K\alpha_2$ component, so that the function of Caglioti can be used correctly. $K\alpha_2$ stripping can be done by XPowderX with enough precision, where values of wavelengths and reason $|K\alpha_2| / |K\alpha_1|$ are sufficiently accurate.

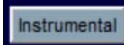
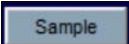
To adjust these parameters (U,V,W,P), we have to calculate individual profiles, as stated above and then press the button ' B^2 '. The program shows:



In the plot of figure , the values of experimental widths and initial Caglioti functions are shown (Red circles= FWHM, Green circles= Integral broadening), both in algebraic and graphic form (the last one previously saved on the hard drive of your computer). You can adjust both the 'instrumental function' (when using a standard sample of a very high crystallinity), as the 'sample function' which can be used latter in theoretical profile calculations, or initial profile data in Rietveld analysis programs. Before making the Caglioti adjustments, XPowderX automatically calculated the 'pseudo-voigt' average profile of the sample, whose Gaussian component appears in the top frame.

In this example, the "*Instrumental*" option must be chosen, because we want to adjust the instrumental function of the diffractometer. By pressing "Compute" the functions are calculated and adjusted for FWHM (red) and 'Integrated broadening' (green).

The least-square adjusted functions are drawn with thick points in the analyzed 2θ interval and with thin points in the extrapolated zones. The numerical values are printed on the bottom right. If it is then pressed "Close", the calculations will be discarded.

- If  is pressed, the calculated values will be applied to all instrumental corrections which are required in the future. Also, the file 'Xpowder.ini' (or 'XPowder12.ini') is updated:
- Touching , the UVWP calculated values will be applied for theoretical real profile calculations.

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APPENDIX 8

User Privileges

Discontinued

APPENDIX 8. User Privileges

Discontinued

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The use of constraints on certain choices of this program is optional and depends only on the main user (Manager).

Restricted access users and "Password" assignment.

By pressing "Set Password" on the initial screen, the "Manager" program can generate up to four different keys to as many users (See figure 2). Possible users are "Manager" (without limitations of use of the program), "User 0", "User 1" and "User 2". "Limitations" and "privileges" of the last three can only be set by the "Manager" on the main screen (Menu / Privileges) program. In order for different keys are effective, "Manager" must also change their own password with respect to the preset by the program, which initially is 3692581470.

User	Factory Passwords
User 0	User 0
User 1	User 1
User 2	User 2
Manager	3692581470

Originally "Manager" and "User 0" have the same privileges with the exception that only the first can set the privileges of other users (See also figure 3). All preset factory options are checked for both 'Manager' and 'User 0' except 'Auto quantitative database' and 'Auto quantitative full profile' because an initial inappropriate use of these options can make the program into undesirable loops. These options can subsequently be changed by the manager.

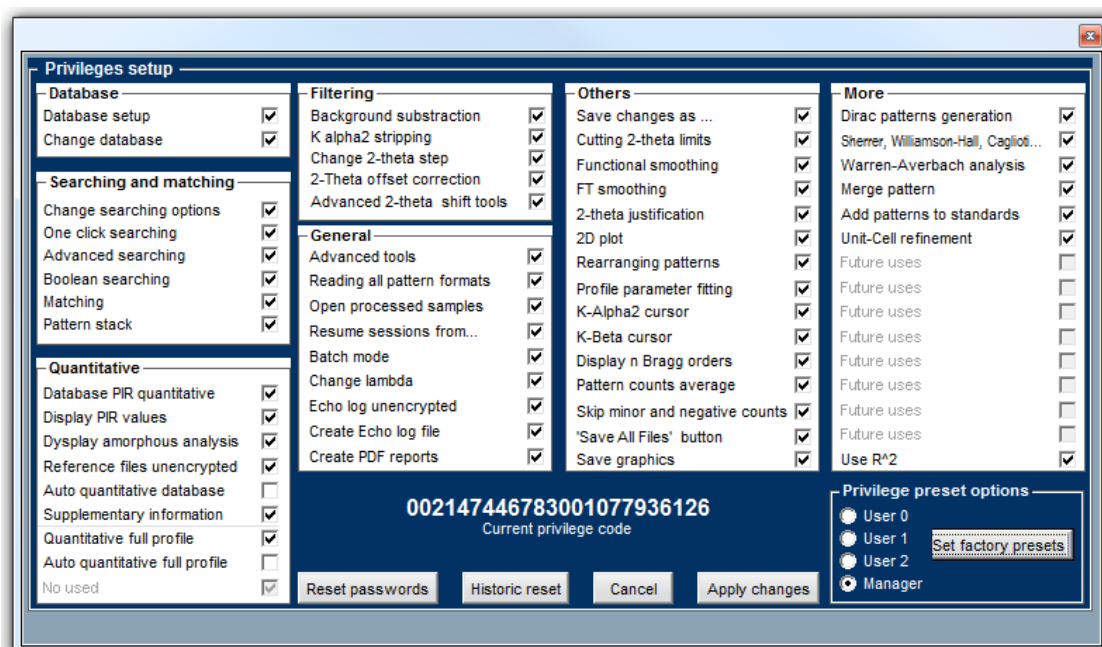


Figure A8.1. Discontinued

APPENDIX 9

Program folders structure and auxiliary files

Usual Folder Structure of XPowderX

```
C:\XPowderX  \Auxiliary
              \DBLog\DB_0\HST
              \DB_1\HST
              \DB2\HST
              \...
              \DB_n\HST
              \LST
              \PDF_Reports
              \Samples      \Examples
                          \QuantitativeExample
                          \Thermo
              \User_Guide
              \Default.cnf  (optional)
```

Files in folders

C:\XPowderX Main program folder

XPowderX.exe (program file)

C:\XPowderX \Auxiliary

Chem_Cell.idx General Unit-cell and Formula for Minerals. Binary
Default.O_T Observed and computed 2θ for non linear 2θ -zero shift for a misaligned diffractometer. Text.
Elements.log. Selected elements for current Periodic Table. Binary.
Mu_Rho.txt. Linear absorption coefficients and A_w of main elements. Text.
Preset-Log. 5 Preselected configurations of elements of Periodic Table. Binary
PresetPatternColors.txt. RGB of 50 patterns. Editable text file.
Readme.txt
SolSol.txt. Standard unit-cell parameters for common isomorphic minerals. Text.
Std.txt. Observed 2θ for Standard patterns
XPowderX.ini. General XPowder configuration parameters. Editable text file.
Default.cnf Optional. Diffractometer control parameters (Device, communications, etc).

C:\XPowderX\DBLog\DB 0\...\DB n. Database file logs

Alfa.idx Alphabetic file index
DB.log Installation of database including nickname, kind and origin of data patterns hardware location.
Magic.idx Magic numbers of record cards file index.
 \HST
 Historic output / re-input old work sessions.

C:\XPowderX\LST. Configuration files for Full-Profile Full-Matrix Quantitative Analysis.

C:\XPowderX\PDF Reports. Output graphics and pdf files generated by XPowderX

C:\XPowderX\Samples. Default folder for sample files.

C:\XPowderX\User Guide. Current document.

XPowderX.ini (example)

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It is a text file, which contains basic information about the initial configuration of the program and it can be modified through a text editor. Some data is updated from the XPowderX program itself. The following example in green, it commented line by line (right in red).

Lines begin with # or REM are not read by the program. Do not include in 'XPowderX.ini' file notes in blue.

```
[XPowderX] Head
SampleDir= C:\XPowderX\samples      Sample subdirectory in the directory program.
Logo= logo.jpg
PatternFormatDefault = PLV          Initial sample file format (All, PLV, Raw, RD, , etc.)
GeneralScaleFactorCounts = 1.0      The experimental intensities will be multiplied by this
                                     factor before being read by the program

# PLV TXT
DataBaseIndexFolder= Default
# C:\XPowder\DBlog\
# C:\XPowder12\DBlog\
# Default
# C:\XPowderX\DBlog\
currentLd= Cu , 1.540598 , 1.54433 , 1.39217 , 0.5 Default anode: Anode,  $\lambda K\alpha_1$ ,  $\lambda K\alpha_2$ ,  $\lambda K\beta$ ,
                                      $I K\alpha_2 / I k\alpha_1$ 

lambda= Cr , 2.28970 , 2.29351 , 2.08480 Normalized  $\lambda$  values: Anode, ,  $\lambda K\alpha_1$ ,  $\lambda K\alpha_2$ ,  $\lambda K\beta$ 
lambda= Fe , 1.93604 , 1.93991 , 1.75653
lambda= Co , 1.78897 , 1.79278 , 1.62075
lambda= Ni , 1.65784 , 1.66169 , 1.50010
lambda= Cu , 1.5405981 , 1.54433 , 1.39217
lambda= Mo , 0.70930 , 0.713543 , 0.63225
lambda= Ag , 0.559363, 0.563775 , 0.49701
lambda= W , 0.208992, 0.213813 , 0.184363
lambda= Dummy , 1.5405981 , 1.54433 , 1.39217
lambda= Synchrotron, 1.5406, 1.5406, 1.5406 Idem for Synchrotron radiation (Alike three  $\lambda$ 
                                               values).

HeightScale= 0.6
WidthScale= .65
# 0.6 < (Height/Width)Scale <=1
PatternPlotHeightRatio = 0.4
# 0.3 < PatternPlotHeightRatio <=0.5

hRoller= 2.44      Horizontal initial value of 'roller' in  $2\theta^\circ$ , for background subtraction.
vRoller= 6.2      Idem vertical in % counts
FlatRoller= 0
BackgroundCriteria= 1
BackGroundPolynomia= 6
InitBackgroundSubtraction= False
Interpolate= 2      Initial number of points to be interpolated by spline.

[Full profile Standard quantitative]
StAutoQuantitative= QuantitativeExample.LST
StQuantitative_StEnabled= False

[Database quantitative]
DbAutoDbQuantitative= C:\XPowderX\DBlog\DB_19\hst\F1a.hst
DbQuantitative_DbEnabled= False
zeroShiftRefine = True
Db2ThetaPatternRefine = True maximum  $\Delta 2\theta^\circ$  for L.S. adjustment in searching ( $0 < \Delta 2\theta^\circ < 0.4$ )
DbWeigtData = True
```

Amorphous_Whole_RIR= 0.5
Amorphous_Polynomial_Coef = 0 1
QGlass -25.84834635 3.75921668 0.62036523 -0.05354303 0.00156098 -0.00001570
[Searching/Matching]
DefaultDatabase= 28
InitMatchingCriteria= 1
InitMatchingCriteria= 0=FOM 1=Magic 3=Classic 4= 3 reflections 5= 2 reflections 6= 1
reflection (not selectable by user)
AutomaticSearching= False
peakSearchMinInt = 4 Minimum initial intensities (%) in 'Searching'
SkipDuplicateS = True [If True: 'Searching' shows the better solutions from equal
phases](#)

[Profile, Caglioti coefficients]
[FWHM]
InstrumentalU-Width= -0.000082476
InstrumentalV-Width= 0.000000211
InstrumentalW-Width= -0.000082184
InstrumentalP-Width= 0.000083019

[Integral broadening]
InstrumentalU_WidthIB= -0.000082264
InstrumentalV_WidthIB= 0.000001243
InstrumentalW_WidthIB= -0.000081794
InstrumentalP_WidthIB= 0.000082973

[Initial PdfSubfiles]
Deleted pattern= True [If True, Deleted PDF patterns are included in 'Searching'](#)
Inorganic= False [If True 'Inorganic' PDF patterns are included in searching.](#)
Organics= False [Idem 'Organic'](#)
Mineral= True [Idem for 'Minerals'](#)
MetAl= False [Etc. Can be modified from running XPowder](#)
CP= False [Idem](#)
NBS= False [Idem](#)
FORensic= False [Idem](#)
EDUcational= False [Idem](#)
ZEOlite= False [Idem](#)
EXPlusive= False [Idem](#)
SCMaterial= False [Idem](#)
CEMent= False [Idem](#)
CORrosive= False [Idem](#)
POLymer= False [Idem](#)
DETergerent= False [Idem](#)
PIGment= True [Idem](#)
PHARmaceutical= False [Idem](#)
ICSD= False [Idem](#)
Ceramics= False [Idem](#)

[amcds]
AMCSDroom= True
AMCSDpressure= True
AMCSDhighTemperature= True
AMCSDlowTemperature= True

[Devices]
#Include = PW1710
#Include PW3710

[Duetto]
AxisX = 2240.261

AxisZ= 2858.136
SensorAngle= 0
Depth = 0

DbQuantitative_DbEnabled= False
DbQuantitative_DbEnabled= False
DbAutoDbQuantitative= C:\XPowderX\DBlog\DB_19\hst\F1a.hst
StQuantitative_StEnabled= False
DbQuantitative_DbEnabled= False
DbAutoDbQuantitative= C:\XPowderX\DBlog\DB_19\hst\F1a.hst
DbAutoDbQuantitative= C:\XPowderX\DBlog\DB_19\hst\F1a.hst
DbQuantitative_DbEnabled= False
DbQuantitative_DbEnabled= False
DbQuantitative_DbEnabled= False
DbAutoDbQuantitative= C:\XPowderX\DBlog\DB_19\hst\F1a.hst
DbQuantitative_DbEnabled= False
DbAutoDbQuantitative= C:\XPowderX\DBlog\DB_19\hst\F1a.hst

[www]

QuantiXSite= <http://www.QuantiX.com> e_mail = support@quantix.com

Std.txt example

This file contains standard patterns and is used to correcting instrumental no lineal 2θ misalignment. Each standard begins with the key '*Begin standard*', after the chemical symbol for the element of used anode, the name of the compound and a list of 2θ and intensities in scale thousand (separated by commas). The end of each pattern is a row with the key 000.0000,000. The first of the patterns whose name is 'None', lack of data and its presence is necessary, as in the following example:

Begin standard	060.6048, 0050	104.2542, 0030	000.0000, 0000	088.9972, 0080	077.5737, 0010
Lambda= Cu	060.9139, 0040	118.8626, 0100		090.7050, 0021	079.7871, 0020
None	061.2713, 0030	124.2775, 0100	Begin standard	091.1794, 0100	079.9552, 0010
000.0000, 0000	062.9841, 0020	150.8580, 0070	Lambda= Cu	094.8164, 0010	081.0554, 0030
	064.6004, 0050	000.0000, 0000	Aluminum (Syn)	095.2357, 0190	081.3796, 0030
Begin standard	065.5200, 0030		038.4720, 1000	098.3804, 0020	083.7256, 0010
Lambda= Cu	069.1476, 0010		044.7380, 0471	101.0638, 0140	084.8748, 0010
Sodium Chloride (Halite syn)	070.1536, 0020	Begin standard	065.1333, 0219	102.8171, 0010	087.3647, 0010
027.3024, 0130	072.7817, 0020	Lambda= Cu	078.2271, 0239	103.3008, 0031	090.7551, 0020
031.6547, 1000	073.6395, 0010	Silicon(2)	082.4352, 0071	104.6351, 0010	092.7170, 0010
045.3954, 0550	076.2077, 0010	028.4106, 1000	099.0783, 0021	109.5222, 0010	094.5576, 0010
053.7887, 0020	077.0839, 0020	047.2499, 0550	112.0410, 0082	109.8503, 0010	095.0107, 0010
056.4108, 0150	080.8346, 0010	056.0584, 0300	116.5600, 0080	110.8154, 0010	096.1174, 0010
066.1488, 0060	081.4486, 0030	069.0537, 0060	137.4500, 0081	110.9755, 0040	098.6254, 0010
072.9777, 0010	082.0136, 0010	076.2928, 0110	000.0000, 0000	114.0680, 0030	102.0830, 0010
075.2129, 0110	083.6656, 0030	087.9290, 0120		116.0804, 0130	102.4429, 0010
083.8708, 0070	084.6848, 0010	094.8431, 0060	Begin standard	116.6098, 0100	103.7659, 0010
090.2991, 0010	086.3782, 0010	106.5978, 0030	Lambda= Cu	117.8378, 0080	104.0809, 0010
101.0693, 0020	092.9588, 0010	113.9622, 0070	Corundum	000.0000, 0000	106.0248, 0010
107.6764, 0010	094.5853, 0030	127.4020, 0080	025.5760, 0720		000.0000, 0000
109.9103, 0030	094.8949, 0040	136.7419, 0030	035.1498, 0980	Begin standard	
119.3563, 0040	096.0477, 0020	000.0000, 0000	037.7672, 0440	Lambda= Cu	
127.0104, 0010	097.5282, 0010		041.6834, 0010	Quartz low (1)	Begin standard
129.7306, 0030	099.0396, 0020	Begin standard	043.3402, 1000	020.8264, 0220	Lambda= Co
142.0569, 0020	102.1170, 0010	Lambda= Cu	046.1754, 0020	026.6217, 1000	Quartz ·· (79-1906)
000.0000, 0000	102.8261, 0010	Calcium Fluoride (Fluorite	052.5480, 0480	036.5006, 0080	024.2697, 0148
	103.7715, 0010	Syn)	057.4981, 0960	039.4111, 0080	031.0354, 1000
Begin standard	103.9963, 0030	028.2350, 0920	059.7375, 0030	040.2379, 0040	042.7044, 0129
Lambda= Cu	105.7159, 0020	032.7239, 0010	061.1238, 0040	042.4168, 0060	046.1689, 0067
Calcium carbonate (Calcite	106.0151, 0040	046.9516, 1000	061.3031, 0090	045.7572, 0040	047.1493, 0009
Syn)	107.2017, 0010	055.7016, 0330	066.5144, 0380	050.0838, 0140	049.7232, 0037
022.9948, 0120	109.4260, 0020	058.4099, 0010	068.2018, 0570	050.5537, 0010	053.7215, 0062
029.3704, 1000	110.3477, 0020	068.5964, 0100	070.4114, 0011	054.8066, 0040	000.0000, 0000
031.3808, 0030	000.0000, 0000	075.7643, 0090	074.3001, 0010	055.2655, 0020	
035.9231, 0140		078.0951, 0010	076.8727, 0017	057.1730, 0010	Begin standard
039.3546, 0180	Begin standard	087.2734, 0170	077.2342, 0010	059.8804, 0090	Lambda= Co
043.0940, 0180	Lambda= Cu	094.1097, 0070	080.4151, 0012	063.9282, 0010	Silicon ·· (77-2108)
047.0672, 0050	Silicon(1)	105.6840, 0040	080.6922, 0070	065.6859, 0010	033.2200, 1000
047.4328, 0170	039.8796, 1000	112.9358, 0060	083.2078, 0010	067.6728, 0060	000.0000, 0000
048.4552, 0170	046.3690, 0250	115.4390, 0010	084.3481, 0050	068.0531, 0070	
056.4865, 0040	067.7484, 0200	126.0590, 0080	085.1346, 0010	068.2451, 0080	
057.3326, 0080	081.6145, 0200	135.0546, 0030	086.3465, 0040	073.3786, 0020	
058.0049, 0020	086.1906, 0100	138.3980, 0020	086.4996, 0040	075.5847, 0020	

Note: The last two standard patterns have been created in the example from the X PowderX program itself from database records, for tubes with anode of cobalt. This involves first obtaining the different 2θ angles of the reflections, using the formula with the value of Bragg wavelength described in the database information. Subsequently, these values are normalized

to the exact wavelength, for the same anode defined in the X PowderX.ini file (eg *currentLd = Cu, 1.540598, 1.54433, 1.39217, 0.5*).

There are commercial programs that do not perform this normalization of λ and can cause during the operation of correcting, 2θ zero shift higher than the value that is tried to correct. In any case, what is more correct to directly enter the values of 2θ angles and intensities, observed directly on experimental patterns obtained in well aligned diffractometers.

SolSol.txt example

It is a text file containing the final stages of isomorphic series that can be used to interpolate chemical compositions. Data from each phase are written on successive lines:

Phase name, axis a, axis b axis c, α , β , γ

Calcite
4.9963
4.9963
17.1092
90
90
120
Dolomite
4.808
4.808
16.055
90
90
120
Magnesite
4.646
4.646
15.139
90
90
120
Forsterite
4.752
10.192
5.978
90
90
90
Fayalite
4.815
10.4597
6.0818
90
90
90

This file allows to control and collect data from Philips PW1710 and 3710 (00/12) diffractometers.

```
[PW1712]
[Diffraction communication port]
CommPort = 1
BaudRate = 9600
DataBits = 8
StopBits = 1
Parity = N
[Scan parameters]
ScanMode = CONTINUOUS
StartAngle = 3
EndAngle = 80
StepScan(2 - theta°) = .040
IntegrationTime(sec) = 0.4
ScanRate(2 - theta° / sec) = 0.1
Batch_mode= 0
[Pulse height analyzer]
LowerLevel = 35
UpperLevel = 70
[Diffraction setting]
Monochromator= Graphite 2°
Filter= None
Slit_1 = AUTOMATIC
ReceivingSlit = 1/0.1/1
AutomaticSamplerChanger = PW 1775
Rem PW 1775,No, ...
Spinner= PW 1774
Rem PW 1774, No
ThermoController = Comm3:9600,N,8,1
Rem False / Comm3:9600,N,8,1
MaxTemperatureCentigrade= 250
GraphicRecorder = PW 8203A
Rem PW 8203A, PW 8203, NO
SingleGobelMirror = NO
GeneratorVoltage(Kv) = 40.00
TubeCurrent(mA) = 40.00
Stand_by_2theta = 5.00
DiffractionSite= <<To be personalized>>
[Profiles]
01 Profile 026.00 003.00
02 Profile 035.00 003.00
03 Profile 044.00 003.00
04 Profile 000.00 000.00
05 Profile 000.00 000.00
06 Profile 000.00 000.00
07 Profile 000.00 000.00
08 Profile 000.00 000.00
09 Profile 000.00 000.00
10 Profile 000.00 000.00
11 Profile 000.00 000.00
12 Profile 000.00 000.00
```

Other specific '*.cnf' files can be created for particular applications, through editing 'default.cnf', or using the 'File-> Save Setup file', in the acquisition diffractogram module. Also it can be used 'Load Setup file' in same module.

APPENDIX 10. Highest quality large custom databases from CIF files

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Recently, we have added to XPowderX (Ver 2019.06.10 and later) a procedure that allows us to simultaneously convert collections of to approximately 20000 crystal structure files to an single database file containing the *ascii* diffractogram data of compounds selected according to your own research topics. The original files must be placed in a single folder and must include the description of the crystalline structures of the selected compounds (as examples, cif files of Crystallography Open Database -COD- , AMCSD or those generated by the programs that calculate such structures, such as the .RES of the XSHel program of Sheldric, 1963, etc).

The number of records of the databases that can be created is unlimited. For example, if you include the CIF files between '9000000.cif' and '9014008.cif' of the folder number 9 of COD that contains the mineral structures, you can generate in a single session, a database of 16731 records containing exclusively mineral diffractograms (See figure 10.3A). It can also include mineral diffractograms that are scattered by other COD folders different from 9. In this case, the number of mineral diffractograms generated is close to 25,000.

The diffractograms thus generated may come from different sources (CIF, RES, etc.). You can also create one or unlimited databases where diffractograms of different substances (organic, inorganic, complex, organometallic, minerals, proteins, pigments, medicines, explosives, cements, etc.) can coexist. It is also possible to create custom databases. For example, a database can be created containing only Silicates or compounds containing Fe and Cu, large molecules, and, or, small molecules, etc.

Also, and as examples, you can obtain databases that only contain compounds where Fe and Mg appear simultaneously (Fe <AND> Mg) or optionally simultaneously (Fe <OR> Mg) by using appropriate Boolean operators.

The diffractograms are generated with the Lorentz-Polarization, multiplicity of hkl, effects of the monochromator crystal (optional) and automatic slit (optional) corrections. Also, corrections for 'Anomalouss scattering' and 'Absorption' can also be optionally made.

The program recognizes non-standard orientations of the space groups, as well as the different axial crossings of the trigonal and hexagonal lattices.

The time to generate a database depends on the size of the unit-cells and the number of calculated patterns. As an example, the mineral database shows in figure 10.1A takes about two hours to be generated.

In summary, each researcher can generate with a single click of the left mouse button, a personal database of diffractograms according to their research needs.

REMARKS

A) It is preferable not to use either the desktop or long names for the data entry and exit folders, as conflicts may arise when the input files of various operating systems are processed.

B) Remember to mention the authors of the COD files. The most frequent references include:

COD reference database 2012

Gražulis, S.; Chateigner, D.; Downs, R. T.; Yokochi, A. F. T.; Quirós, M.; Lutterotti, L.; Manakova, E.; Butkus, J.; Moeck, P. & Le Bail, A.; Crystallography Open Database - an open-access collection of crystal structures, J. Appl. Cryst., 2009, 42, 726-729.

When your research relies on the subset of COD containing mineral data from AMCSD (the range 9* datasets), then please mention this source database:

Downs, R. T. & Hall-Wallace, M. (2003). "The American Mineralogist Crystal Structure Database". American Mineralogist 88, 247-250."

INSTRUCTIONS.

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1. Download the databases of crystalline structures in the usual directions (see below, COD) and unzip the files in any folder on your computer.

2. Click on 'menu/PXRD database CIF Gener' as figure 10.1A shows

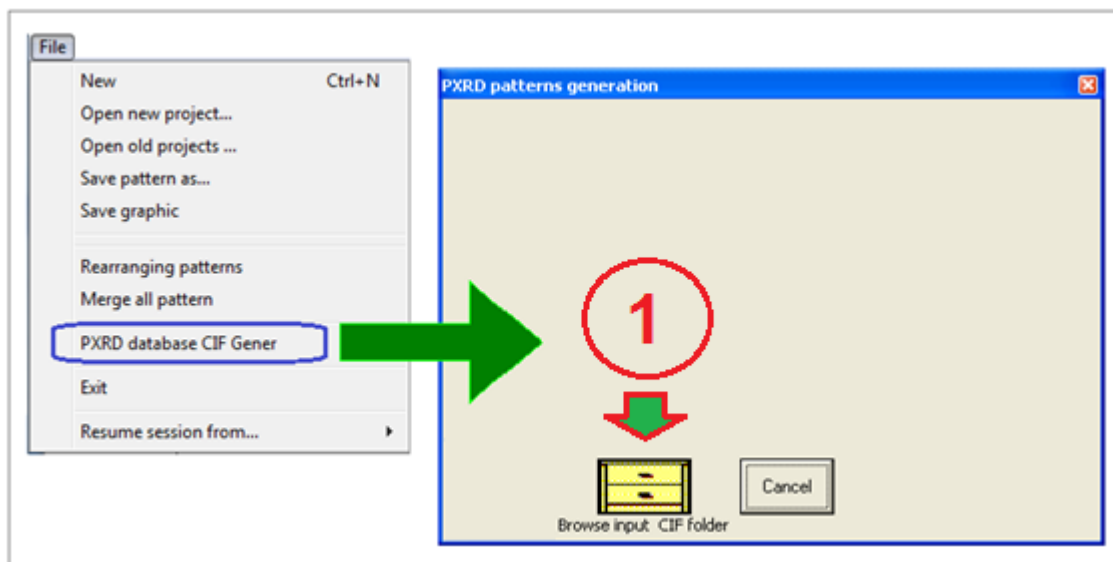



Figure 10.1A. Access tools for 'PXRD database patterns generation'. Files with the selected structures must be placed in a single folder, which must be located through the browser (1).

3. Browse the folder that contains the files with the crystalline structures  as figure 10.2A shows.

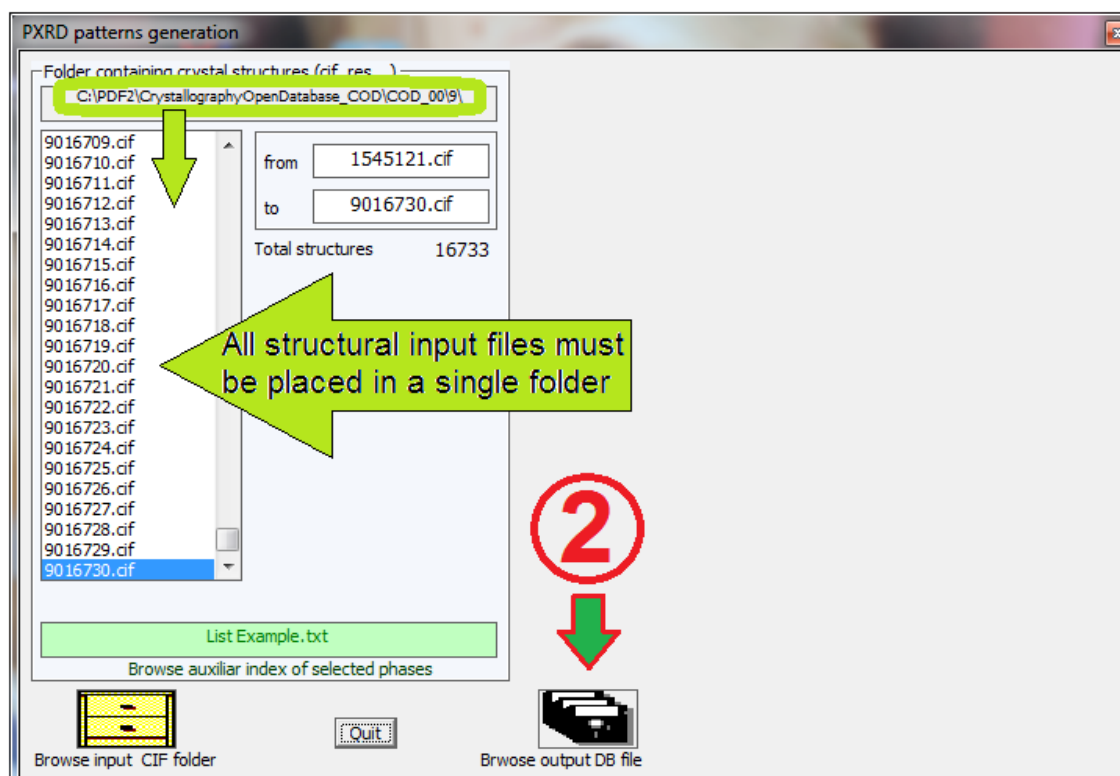



Figure 10.2A. The database that will be generated using the 'structure input files of the single input folder' must be selected using the browser (2).

4. Select the folder where the database will be generated.  as figure 10.3A shows

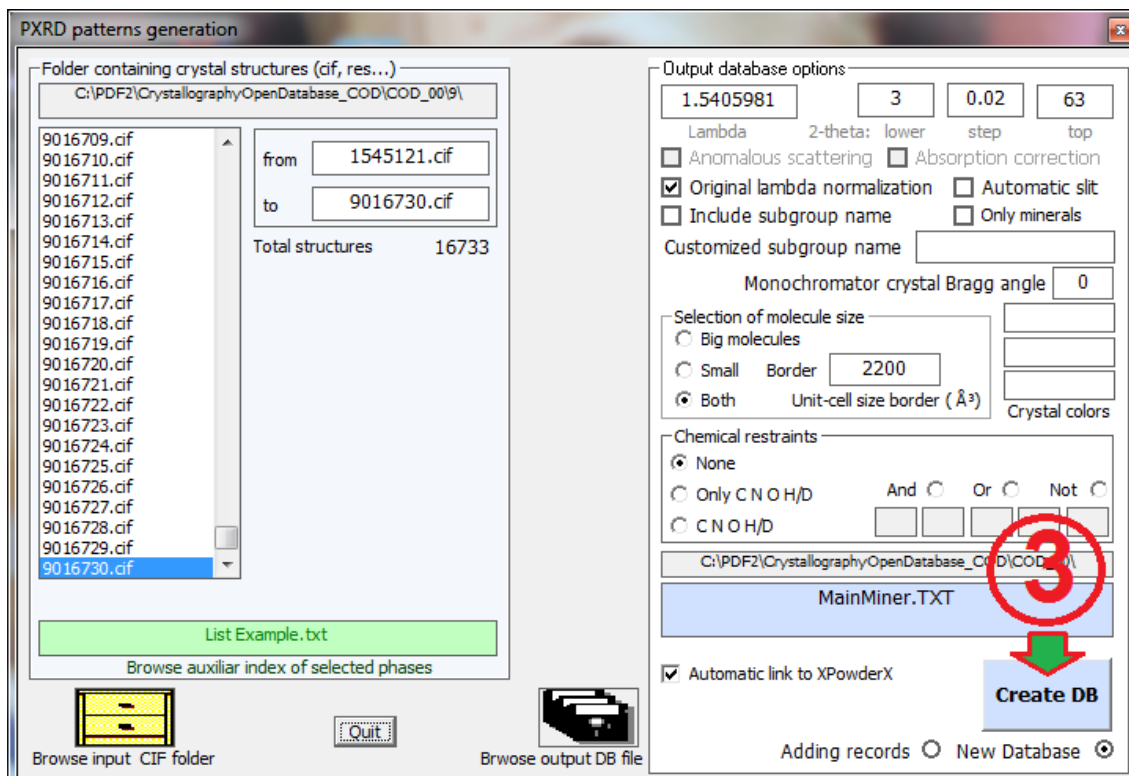
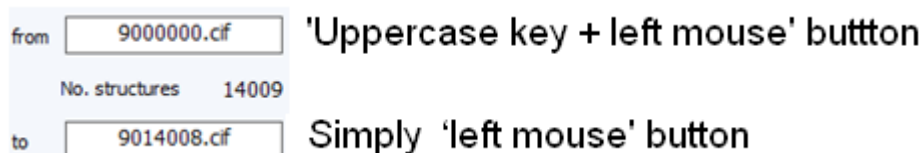


Figure 10.3A. Clicking (3), the diffractogram database of all the structures contained in the incoming folder will be generated. The entire process can take several hours.

The diffractograms will be generated sequentially between the limits indicated in the 'from' and 'to' boxes. **The entire process can take several hours although it can be done in several sessions, using properly the option (8) instead of (9) (figure 10.4A) in successive sessions.**

The number of input files can be reduced by modifying the upper and lower limits of the contents of the input folder. To do this, just click the item on the left list ('uppercase key +left mouse button' and simply 'left mouse button' to modify the lower and upper indexes respectively.



It is possible to use some options (Name of database file output, create or complete a previous one, correction for monochromator crystal or automatic slit, 2-theta limits and step, output lambda fixed value, normalization of input lambda values, etc), or filters to reduce the number of generated diffractograms (Unit-Cell volume, Chemical composition when available, etc).

5. Auxiliary lists containing structures.

5.1. Name phase list: A good option to create good quality databases is to do a list of structures with the names of the phases that should be included in the database, as shown in the example (4) in Figure 10.4A. These lists must be saved in a text file with any of the extensions 'txt', 'tab' or 'cho'. The example (4) contains a list of names of minerals in alphabetical order, whose structures must exist in the input folder, as 'cif' files and it can be found in the subfolder 'Auxiliary' within the X PowderX folder (Mineral_List_Example.txt). When the 'Create DB' command is executed, the program will only select the structural files of the input folder, but will only create the diffractograms included in the list. The procedure is slow and may take several hours, but the results are excellent.

5.2. CIF file names list: Faster than the previous option is to create a list with the files containing the selected crystalline phases, as shown in (5) (Figure 10.4A). You can also include the name of the phase separated by a

comma as in (6), but you cannot mix both formats in the same file. Both lists type must be saved in a text file with any of the extensions 'STC'.

Using both (5.2) options requires knowing the names of the CIF files that contain each crystalline phase, but this task is easy by creating a small auxiliary input / output program that provides this information. You can also use the tools that COD provides in this regard. As an example, in the subfolder 'Auxiliary' you can find a file called "MainMinerals.STC" that includes the names of 3818 CIF files of COF of the most frequent minerals

6. Clicking (3) **Create DB** in figure 10.3A, the diffractogram database of all the structures contained in the incoming folder will be generated. The entire process can take several hours.

7. If box (7) (figure 10.4A) was checked, after the creation of the new database, in addition to it being registered in a text file with the extension 'TXT', the program will automatically create the necessary index files to automatically link it to XPowder and add at the end of those that were previously installed on your computer. From this point, you can use this database without further delay.

Of course, the database file 'TXT' can be deleted at any time or, on the contrary, installed again with specific formats on it or other computers you own, without having to re-carry out the actions explained in this appendix 10 (See also Appendix 2, p 42).

Notice: It is preferable not to use either the desktop or long names for the data entry and exit folders, as conflicts may arise when the input files of various operating systems are processed.

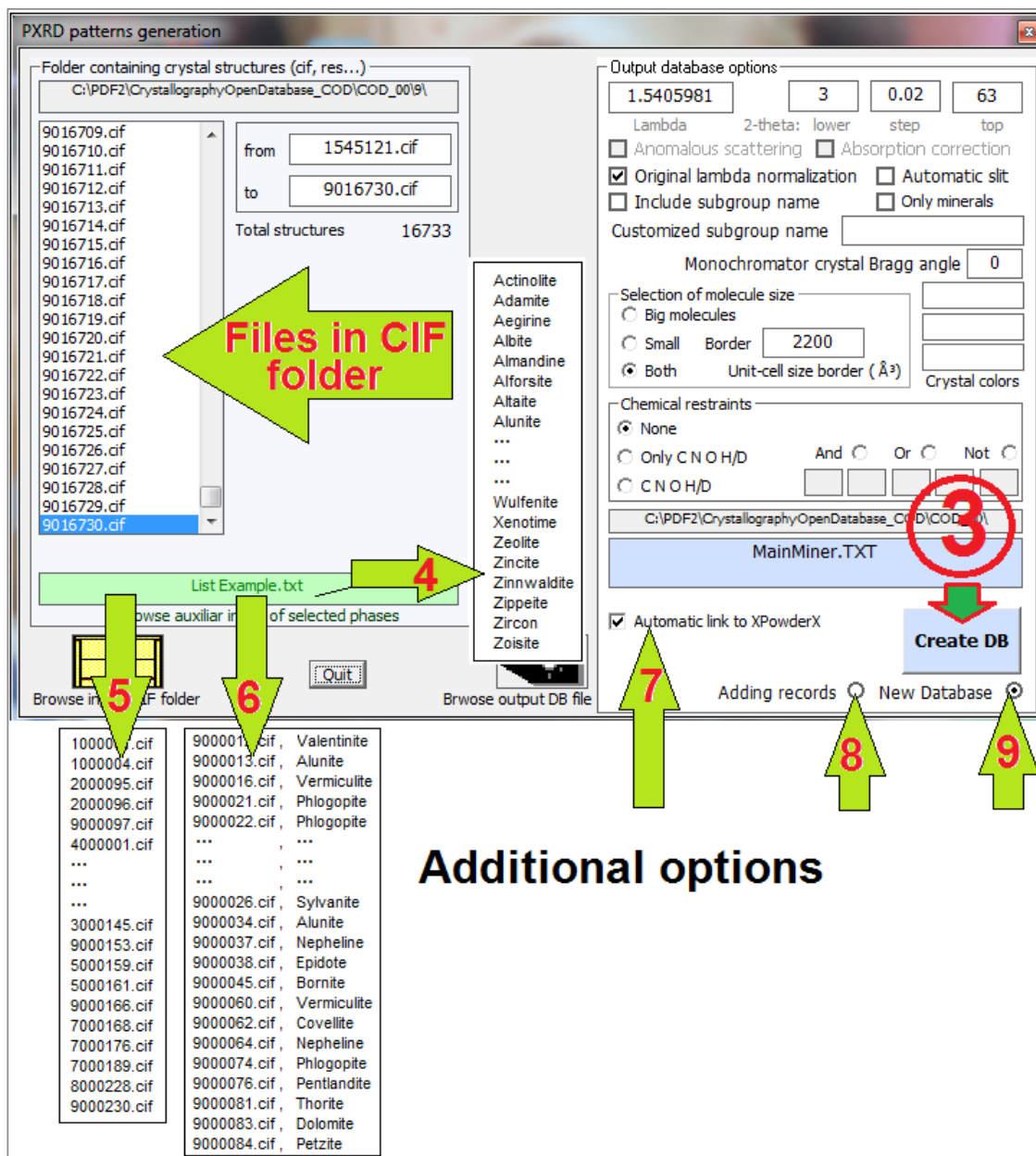


Figure 10.4A.

Additional options.

Warnings: The creation of diffractogram files is based on the interpretation of text CIF files, which have a very varied format that includes tables with number of columns and variable contents. It also requires the interpretation of numerous symmetry operations associated with matrices that include very different rotations and translations. The symmetry operations of the CIF files do not have standard formats and may include strange characters such as tabs and other non-printable characters whose interpretation is not simple. Also unit cells and space groups have no standard orientations. For example, all possible orientations of crystallographic axes are used in trigonal, orthorhombic or tetragonal space groups.

Although all symmetry operations have been scrupulously reviewed, there may be errors not detected so far. As an example, an error in the assignment of multiplicities of hkl reflections in the R-3 space group has been detected and corrected during the last week (December 1/2019).

The author of the program would be very grateful for the communication of any mistake that may be observed.

Main links for the free database COD (Crystallography Open Database)

1 Home page

<http://www.crystallography.net/cod/>

2, Searching

(Selects 'restriction / Search/'. Then <http://www.crystallography.net/cod/result.php> 'list of COD numbers')

3. Finally, using the **Web browser**, the whole CIF tree [1/ to 9/ CIF COD files (9= minerals)] can be fetched at:

Partial database output example

```
=====
_END_
Galena
'Pb S'
Ramsdell, L. S.. (1925) ' The crystal structures of some metallic sulfides Locality: Colorado, USA'.
American Mineralogist 281 - 304 Vol 10
# CIF file is available in the Crystallography Open Database (COD),
  _database_code_amcsd 0000002
  _database_code_COD 9000001
CELL PARAMETERS: 5.9300 5.9300 5.9300 90.000 90.000 90.000
SPACE GROUP: F m -3 m
# X-Ray wavelength in cif: 1.540598
# Anode in cif:
X-RAY WAVELENGTH: 1.540598
# Space Group Number = 225
# Standard Sp Group N = 225
# Laue Group Number = 11
# HM Laue Group = m3m
# Crystal system number = 7
# Crystal system = cubic
# Cell formula units = 4
# F000 = 392
_chemical_formula_sum 'Pb S'
_exptl_crystal_density_meas 7.621
_exptl_crystal_density_diffn 7.621
# Unit-Cell volume = 208.5280
# Top Intensity = 4327866
MAX. ABS. INTENSITY / VOLUME**2: 99.528
  2-THETA INTENSITY D-SPACING H K L
  26.00 591440 3.4243 1 1 1(8)
  30.12 4327866 2.9646 2 0 0(6)
  43.12 3252299 2.0962 2 2 0(12)
  51.04 433949 1.7880 3 1 1(24)
  53.48 1166073 1.7120 2 2 2(8)
  62.62 560991 1.4823 4 0 0(6)
=====
_END_
Cinnabar
'Hg S'
Ramsdell, L. S.. (1925) ' The crystal structures of some metallic sulfides Locality: unknown'.
American Mineralogist 281 - 304 Vol 10
# CIF file is available in the Crystallography Open Database (COD),
  _database_code_amcsd 0000006
  _database_code_COD 9000004
CELL PARAMETERS: 4.1500 4.1500 9.5100 90.000 90.000 120.000
SPACE GROUP: P 32 2 1
# X-Ray wavelength in cif: 1.540598
# Anode in cif:
X-RAY WAVELENGTH: 1.540598
# Space Group Number = 154
# Standard Sp Group N = 154
# Laue Group Number = 7
# HM Laue Group = -32m
# Crystal system number = 5
# Crystal system = trigonal
# Crystal axis = Hexagonal Lattice
# Cell formula units = 3
# F000 = 288
_chemical_formula_sum 'Hg S'
_exptl_crystal_density_meas 8.171
_exptl_crystal_density_diffn 8.171
# Unit-Cell volume = 141.8430
# Top Intensity = 2680871
MAX. ABS. INTENSITY / VOLUME**2: 133.248
  2-THETA INTENSITY D-SPACING H K L
  24.76 5722 3.5929 1 0 0(6)
  26.50 1504649 3.3608 1 0 1(12) /0 1 1(12)
  31.16 2680871 2.8680 1 0 2(12) /0 1 2(12)
  37.82 6852 2.3769 1 0 3(12) /0 1 3(12)
  43.58 545091 2.0751 1 1 0(6)
  45.72 955495 1.9829 1 0 4(12) /0 1 4(12)
. . .
. . .
. . .
```


APPENDIX 11. Use of 'Filter Color' tool in Search-Match processes in minerals and pigments.

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Some X-ray powder diffractogram databases include the color of the crystalline phases between their properties, but this is not usual. Even in the mineral databases, they are not widely included. The consequence is that the use of color is not usually omitted in Search-Match processes. However, the use of this property can be decisive when investigating minerals and pigments of works of art, since in both cases color is a determining argument when making an accurate diagnosis. Since version 2019.06.31, the XPowder program includes a new tool that facilitates this work.

For this, the minerals and pigments have been distributed in eleven files in text format, which correspond to the colors BLACK, BLUE, BROWN, COLORLESS, GRAY, GREEN, ORANGE, PINK, RED, WHITE and YELLOW. In addition, an additional group that includes OPAQUE phases. These files are very complete, but program users can add new compounds to the respective lists using a simple *ascii* text editor. It is clear that this tool can only be applied to the phases that are included in at least one of these lists. Any mineral or pigment can be in as many groups as possible colors can show under visible light. On the other hand, no order is required for the names of the minerals within the color file.

The files that contain each color are automatically installed in the "*Program_Directory\Auxiliary\ColorOfMinerals*" folder, from the version 2019.06.31 an later. It is likely that new colors will be incorporated in subsequent versions of the program.

Example of Color file: Blue.txt

Yushkinite
Abelsonite
Adamite
Adamsite
Afghanite
Agardite
Alarsite
Allophane
Alpersite
Alumohydrocalcite
...
...
...
Zincowoodwardite
Zoisite
Zugshunstite
Aerinite

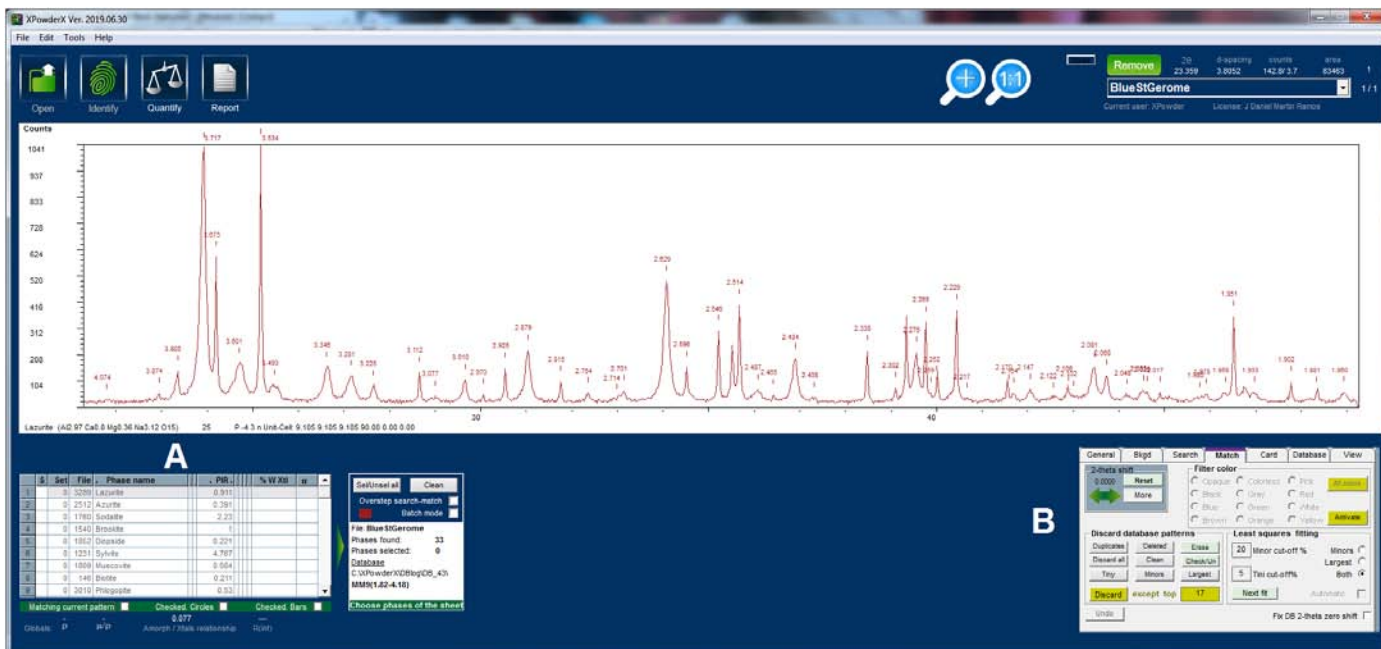



Figure A11.1. The usual initial result of a *Search-Match* process  is shown by XPowderX in a list like that on the left side of the figure (A). The new '*Filter Color*' search tool is shown on the right side (B). The '*Filter Color*' tool is started by pressing the '*Activate / Update*' button. From here, when selecting a specific color, only the pigments in this *base-list* of the selected color will be displayed in A. The *base-list* can be updated at any time by pressing '*Update*'. '*All colors*' allows to place in the list A To the *base-list* at any time

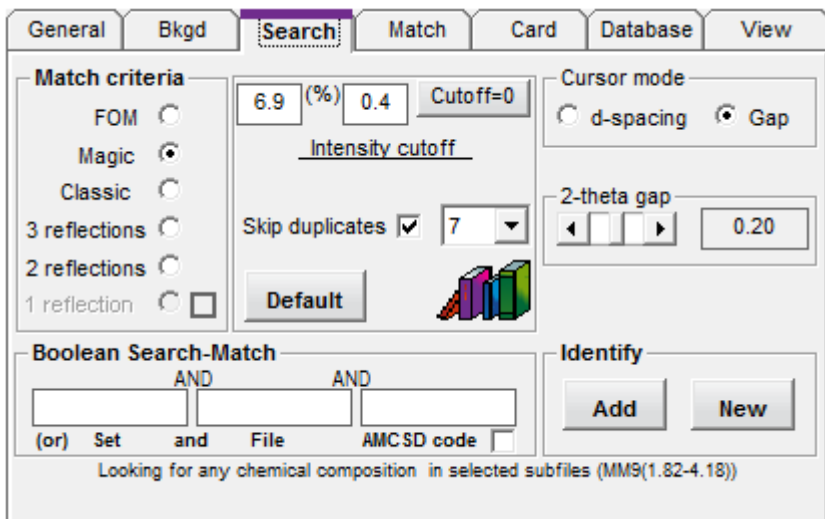


Figure A11.2 Note: For reasons of space, the '*Search*' tab has been slightly modified and it has now included Boolean search options, which in previous versions of XPowderX were in the '*Match*' tab (Figure A11.1.B).

A Normal output of a searching-match process showing 121 possible solutions

S	Set	File	Phase name	. PIR .	% W Xtl	σ
1	0	3289	Lazurite	0.911		
2	0	2512	Azurite	0.391		
3	0	3598	Scapolite	0.838		
4	0	3819	Hydrocerussite	2.542		
5	0	3907	Graphite	0.468		
6	0	2772	Corundum	0.313		
7	0	11	Vermiculite	3.507		
8	0	1760	Sodalite	2.23		
9	0	1540	Brookite	1		

B The color tool is started by pressing the 'Activate / Update' button

C By checking the 'Blue' option, only the 26 blue compounds of base-list appear in the list D.

S	Set	File	Phase name	. PIR .	% W Xtl	σ
1	*	0	3289	Lazurite	0.911	
2	*	0	2512	Azurite	0.391	
3	0	2772	Corundum	0.313		
4	*	0	1760	Sodalite	2.23	
5	0	2853	Covellite	6.271		
6	0	1852	Diopside	0.221		
7	0	2006	Cordierite	0.328		
8	0	3039	Zoisite	0.172		
9	0	302	Quartz	1.466		

D From the list we select the most likely blue pigments: * Lazurite, * Azurite and * Sodalite. Computer display 'Phase selected 3'.

E By checking the 'Black' option, only the 27 black compounds of base-list appear in the list F.

S	Set	File	Phase name	. PIR .	% W Xtl	σ
1	*	0	3289	Lazurite	0.911	
2	*	0	2512	Azurite	0.391	
3	*	0	3907	Graphite	0.468	
4	*	0	1760	Sodalite	2.23	
5	0	2853	Covellite	6.271		
6	0	3318	Fayalite	0.233		
7	0	2809	Ferberite	2.183		
8	0	1626	Staurolite	0.379		
9	0	2845	Chalcoite	0.005		

F From the list we select the most likely black pigment: * Graphite. Computer display 'Phase selected 4'.

G By checking the 'Colorless' option, only the 30 compounds of base-list appear in the list H.

S	Set	File	Phase name	. PIR .	% W Xtl	σ
1	*	0	3289	Lazurite	0.911	
2	*	0	2512	Azurite	0.391	
3	*	0	3819	Hydrocerussite	2.542	
4	*	0	3907	Graphite	0.468	
5	0	11	Vermiculite	3.507		
6	*	0	1760	Sodalite	2.23	
7	0	3787	Aragonite	1		
15	0	302	Quartz	1.466		
16	*	0	3791	Cerussite	0.005	

H Finally, from the list we select the most likely colorless pigments: * Cerussite and *Hydrocerussite. Computer display 'Phase selected 6'. All or part of the process can be repeated or restarted at any time.

Figure A11.3. As an example: How to use this 'Filter Color' tool in a step-by-step process. The example has been recorded on the blue clothes of a scene from an old painting. It is important to keep in mind that the compounds selected for a given color are maintained in successive match stages, because selections for each color are only made between the non-checked compounds. It should also be considered that the 'Undo' button and others of the 'Match' tab as 'Minors' etc, can be used at the same time as the 'Filter Color' tool

- A) Normal output of a searching-match process showing 121 possible solutions
- B) The color tool is started by pressing the 'Activate / Update' button
- C) By checking the 'Blue' option, only the 26 blue compounds of base-list appear in the list D.
- D) From the list we select the most likely blue pigments: * Lazurite, * Azurite and * Sodalite. Computer display 'Phase selected 3'.
- E) By checking the 'Black' option, only the 27 black compounds of base-list appear in the list F.
- F) From the list we select the most likely black pigment: * Graphite. Computer display 'Phase selected 4'.
- G) By checking the 'Colorless' option, only the 30 compounds of base-list appear in the list H.
- H) Finally, from the list we select the most likely colorless pigments: * Cerussite and *Hydrocerussite. Computer display 'Phase selected 6'. All or part of the process can be repeated or restarted at any time.

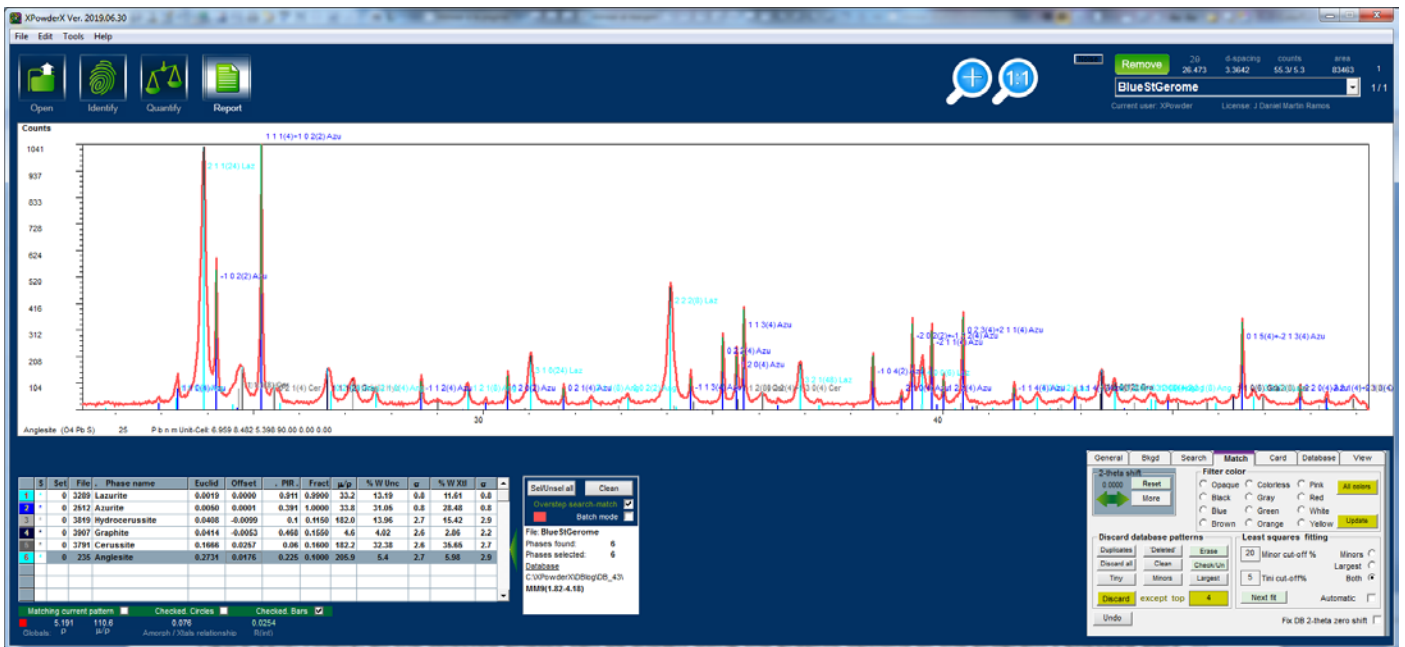



Figure A11.4. Finally, all the selected phases can be shown using the graphic options of the program (**'Checked Bars'** in the example). In the example, **'Sodalite'** was unselected because of its similarity with **'Lazurite'** while **'Anglesite'** was include from figure A12.3(H) list. Semi-quantitative analysis based on **'database patterns'** and PIR model was also carried out 

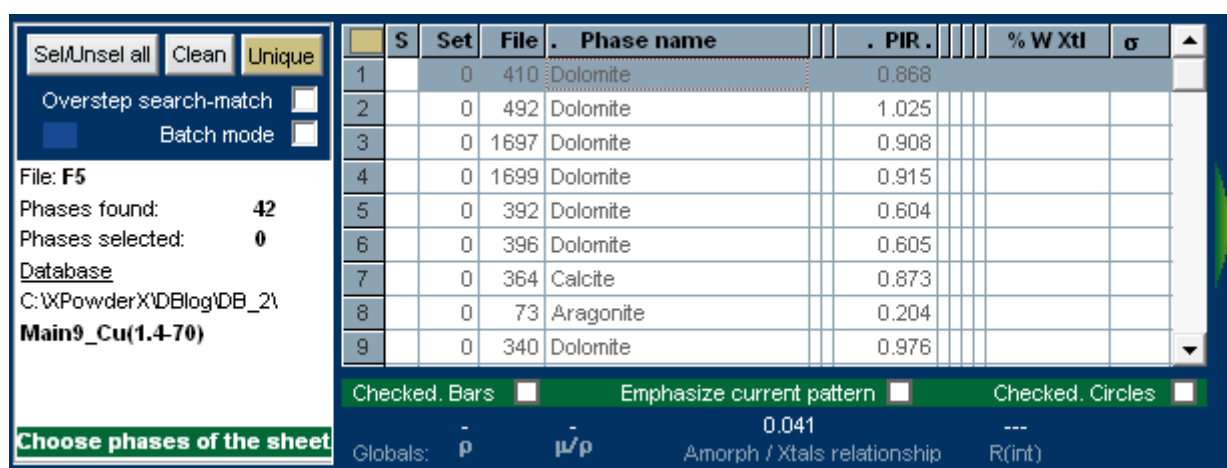
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APPENDIX 12. Use the 'Unique' button to select the best solutions within of the similar phases found

Many chemical species sometimes generate diffractograms with small differences between them, which are due to the presence of solid solutions and other crystalline or compositional defects. Or they may simply correspond to differences between the crystallinities of each sample analyzed. This should not be understood in the sense that they could hinder the process of identifying the crystallographic phases present but, on the contrary, allow the analytical capacity of the crystalline powder diffraction method to be expanded.

Other variations observed with respect to the usual records may be due to the experimental method itself or to sporadic uncontrolled imbalances in the geometry of the diffractometer, both those that were used to create the database and to record the experiences in our own laboratory.

The consequence is that sometimes the list of repeated phases found is too large and the choice of the best solutions is subjectively decided by the researcher. In this way, although they may be correct, they are often not the most appropriate. The list of phases found is automatically sorted in decreasing order of this value, as shown in the table in Figure A12.1.



S	Set	File	Phase name	PIR	% W Xtl	σ
1	0	410	Dolomite	0.868		
2	0	492	Dolomite	1.025		
3	0	1697	Dolomite	0.908		
4	0	1699	Dolomite	0.915		
5	0	392	Dolomite	0.604		
6	0	396	Dolomite	0.605		
7	0	364	Calcite	0.873		
8	0	73	Aragonite	0.204		
9	0	340	Dolomite	0.976		

Figure A12.1. Click the green arrow on the right to enlarge the sheet

The figure shows a table of results where, the similarity between the values of the Euclidean hyperdistances of the diffractograms (which is the first and most important criterion to explore the database), results repetition of phases have been identified. The button **Unique** allows a calculation by general criteria of non-linear least squares over the full range of 2θ . This action allows to automatically obtain a single list with the best possible solutions, in decreasing order of Euclidean distance this value, as shown in the expanded table in Figure A12.2 (green arrow on the right of the table). However, this single value is usually not enough to try to select the best possible solutions.

Throughout the process, some experimental parameters are normalized, both those corresponding to those used to obtain the patterns from the database and those used in personal records (for example, wavelength values).

Occasionally, some result may remain duplicated in those cases where numerical adjustments cannot resolve 'overly' correct solutions. Zero offset errors, local changes in the linearity of the abscissa axis, and orientation factors are also corrected.

Now it is possible to do, for example, quantitative analyzes based on the data sheets of the databases, but it will be necessary to previously do an experimental adjustment of the RIR correction factors (RIR Reference Intensity Ratio,

PIR Pattern Intensity Ratio in this program). In the example (Figures A12.2 and A12.3) shown, PIR factors calculated automatically by default by the program have been used, but not other factors such as those that can be deduced from experimental data, which would have been more accurate (see Appendix 3).

S	Set	File	Phase name	Euclid	Offset	PIR	Fract	μ/ρ	% W Unc	σ	% W Xtl	σ
1	*	0	392 Dolomite	0.0556	-0.0149	0.604	1.0000	46.9	53.33	0.5	52.39	0.5
2	*	0	364 Calcite	0.0563	-0.0150	0.873	0.5842	63.9	21.55	1.0	21.72	1.0
3	*	0	73 Aragonite	0.0578	0.0099	0.204	0.1105	63.9	17.45	1.6	17.72	1.6
4		0	1153 Magnesite	0.2337	-0.0756	0.508	0.0549	0.0				
5	*	0	1520 Celestine	0.3016	-0.0301	0.398	0.0947	79.2	7.67	1.6	8.18	1.7

Checked. Bars	<input checked="" type="checkbox"/>	Emphasize current pattern	<input type="checkbox"/>	Checked. Circles	<input type="checkbox"/>
2.929	56.0	0.041	0.0660		
Globals: ρ	μ/ρ	Amorph / Xtals relationship	R(int)		

Figure A12.2. Click the green arrow on the right to shrink the content of the sheet

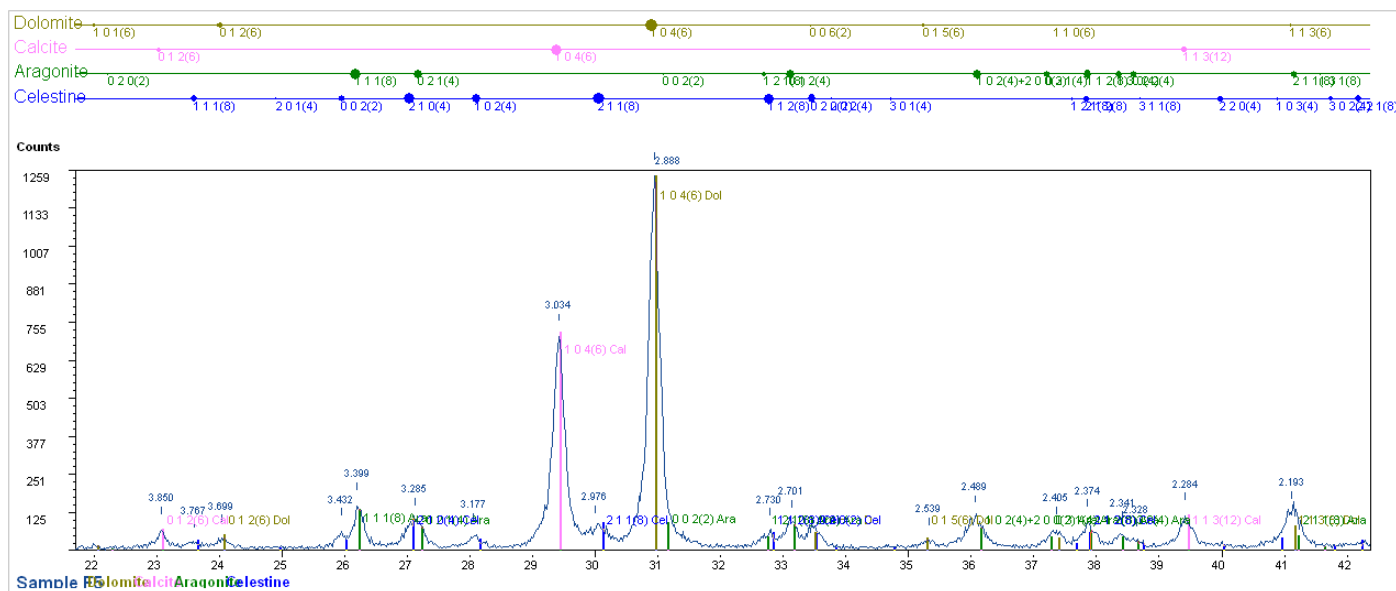


Figure A12.3. Quantitative analysis using database and PIR factors.

The quantitative analysis procedure can also be improved by up to an order of magnitude by using full diffraction profiles for the individual phases as explained in Appendix 3 and 4.