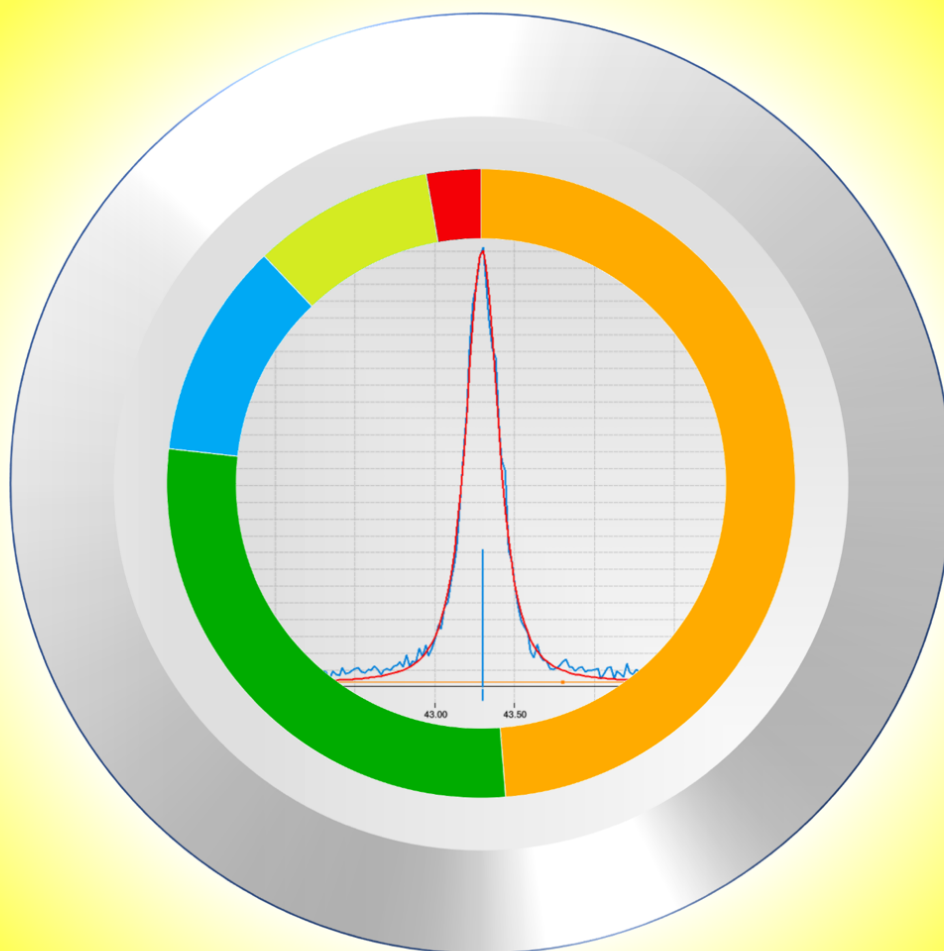


# MATCH!

Phase Analysis using Powder Diffraction



Manual





Dr. Holger Putz



Phase Analysis using Powder Diffraction

Manual

Version 4.2

(second revised version)

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## Welcome!

Welcome to Match!, our software for phase analysis using powder diffraction data! You are certainly eager to start working with it, so just go ahead and try!

After program startup in the default "Beginner" mode, Match! will automatically run a quick qualitative and (semi-) quantitative analysis, starting with the import of the diffraction data file, and lead you step-by-step through the whole process.

Here are some additional hints that may help to get you started:

If you have not installed Match! on your computer yet, please follow the guidelines in the software maintenance chapter starting on p. 139. If you intend to run Rietveld refinement calculations with Match!, you also must install FullProf (see p. 140).

Throughout most chapters in this manual, the COD-Inorganics reference database that is installed along with Match! is used. If you would like to apply a different reference database (like the ICDD PDF or your own data (user database)), please read the chapter "Reference pattern database" starting on p. 92 to learn how to setup Match! accordingly.

Once you have setup the software on your machine, please follow the chapter "Quick start" on p. 10 in which the basic usage of the program is demonstrated. Afterwards, we recommend to take a look at the chapter "Common operations" on p. 15 where you will learn about the most frequently used tasks in Match!, as well as "General usage instructions" (p. 18) where topics like mouse operations etc. are covered.

Afterwards, you are ready to tackle your own phase analysis projects. Typically, they will be more complex than the simple quick start example, so we strongly recommend to read the chapter "Qualitative phase analysis" starting on p. 30 to get instructions how to perform tasks beyond the simple, automatic operation demonstrated in the "Quick start". This is also recommended for more advanced users, because in this chapter many operations that you will use very frequently in phase analysis are explained, in addition to a lot of background information that will provide you with a deeper understanding of the whole process.

If you are an experienced user and would like to get a quick overview on how to operate the software, please take a look at the chapter "Table of mouse button and key combinations" on p. 146 in the Appendix.

If you need help or are in doubt how to perform a certain operation, the first place to look at is the online help. There are two basic keyboard shortcuts you should always keep in mind in this context:

- F1 (<Cmd+> on the Mac) will open the online help at the index page, so that you can easily search for information about a given keyword/issue.
- <Ctrl+J> (<Cmd+J> on the Mac) will display a table of all mouse operations and keyboard shortcuts that can be used.

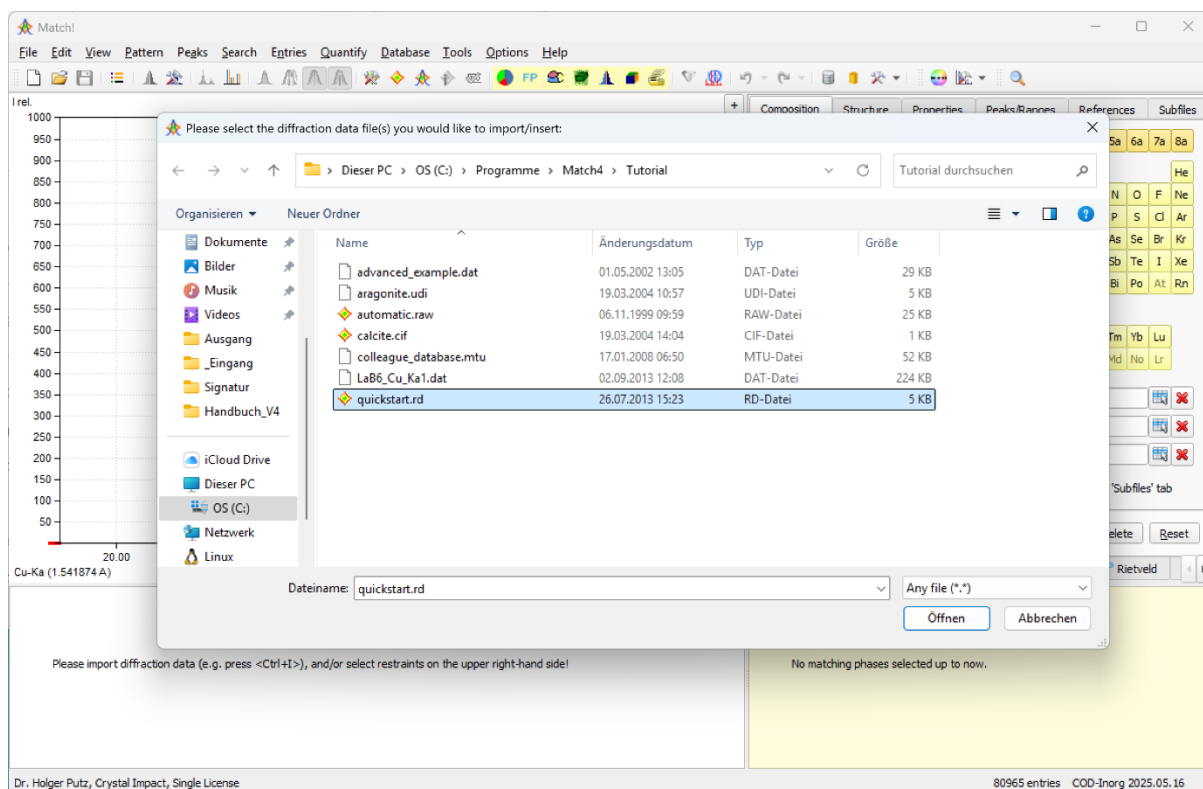
This manual can also be a valuable source of information. Finally, tutorial videos are available on our web page

<https://www.crystalimpact.de/match/videos.htm>

where common operations are demonstrated in practice.

This tutorial will give you an introduction to the Match! software. You will perform a rather simple phase analysis exercise and will be guided through the most important features of the software, so that you can start using it in your own projects right away. The basic aim of this chapter is to give you a first impression of the basic handling of the software: Pattern import, search-match, phase selection (qualitative analysis), quantitative analysis, report printing.

If you have not already done so, please start the Match! software now<sup>1</sup>. In this chapter, we assume that you are using the default (factory) settings of Match!<sup>2,3</sup>, so the software will open and display a “File/Open” window right away (Fig. 1).



**Fig. 1:** Match! has just been started. In its default “Beginner” setting, it opens a window in which you can select the diffraction data file you would like to analyze.

You now must select the diffraction data file you would like to import. For this example, please mark the file “quickstart.rd” in the “Tutorial” subfolder of Match!’s program directory, then press “Open”.

In the default user level<sup>4</sup> “Beginner”, Match! will now run a qualitative and (semi-)quantitative analysis. As a start, it will ask if you already know about the chemical class your sample belongs to (e.g. “mineral”), as well as if you know that certain elements or phases are present. Match! can use this additional information in the qualitative phase

<sup>1</sup> If you do not know how to install or run the software, please have a look at the chapter “Installing and running Match!” starting on p. 83.

<sup>2</sup> If you or a colleague have adjusted some Match! settings earlier, please reset Match! to the factory settings before you follow the tutorial session. To do so, please start Match! now (if it is not already running), cancel the “File / Open” window (if required), then select the “Restore factory settings” command from the “Options” menu, to reset all options to the original ones selected by Crystal Impact. Please confirm (by clicking “Yes”) that you would like to do so, and confirm to keep your reference databases when you are asked for this. Match! will now operate exactly like it has just been installed.

<sup>3</sup> Please note that this tutorial session has been carried out using the COD-Inorganics as reference database. If you use another reference database like the ICDD PDF or your own diffraction data, the results may be different! Besides this, all screenshots in this manual have been captured on a Windows 11 system. On other operating systems, their basic contents will be the same, although there may be slightly different window frames.

<sup>4</sup> The user level can be adjusted at the top of the “Automatic” page of the “Options” window (e.g. available from the “Options” menu).

analysis, but for this example, we assume that you don't know anything, so please **answer “No” to all three questions**<sup>5</sup>.

Match! will run a search-match calculation and present the result. Your Match! window should now look like Fig. 2.

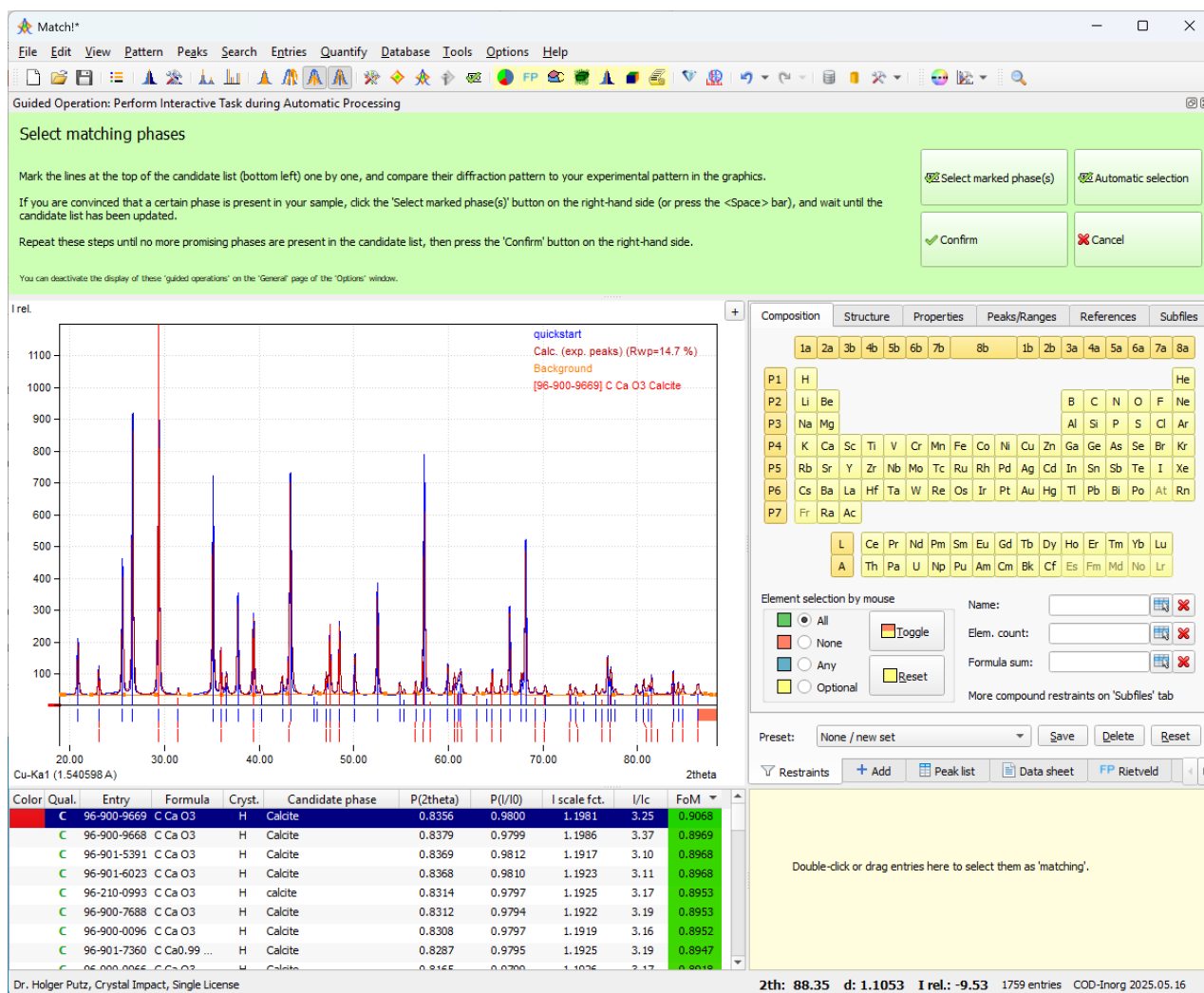


Fig. 2: Match! has run the raw data processing as well as the search-match calculation automatically, and now gives instructions how to select the “matching phases”

At the top, a new area with light-green background has been added which is used for the so-called “Guided Operations”<sup>6</sup>.

If Match! cannot perform a certain task automatically (like the selection of restraints or matching phases), the user is given detailed instructions in a new window called “Guided Operations” and is then asked to manually accomplish the task. The contents of this area may vary depending on the situation, giving you instructions what to do or decide next. The user finally indicates the completion of the task by pressing a corresponding “Confirm” button.

The text in the light-green area asks you to perform the crucial step of qualitative phase analysis: The selection of the matching phases, i.e. the phases that you assume to be present in your sample. This selection is typically guided by the result of the “search-match” calculation (the “figure-of-merit” (FoM) values), as well as a **visual inspection of the agreement** of the entry marked in the candidate list with the experimental pattern.

<sup>5</sup> If you don't want Match! to ask you about this information anymore later on, please click on “No (don't ask again)” instead. You can recall these “don't ask again” settings in the “Options” menu.

<sup>6</sup> You can toggle the display of the “Guided Operations” on the “Automatic” or “General” page of the “Options” window. “Guided Operations” are typically not shown in the “Expert” user level.

The entry with the best (largest) so-called “figure-of-merit” (FoM) has already been marked in the **candidate list** at the bottom left, so that you can now evaluate the agreement of its diffraction pattern in (by default) red color with the blue experimental diffraction pattern in the pattern graphics.

As you see, the entry with the best (highest) figure-of-merit belongs to the phase  $\text{CaCO}_3$  (Calcite), and its coverage of (at least some) experimental diffraction peaks is satisfactory.

To select the marked entry as “matching”, please press the space bar while the first entry  $\text{CaCO}_3$  (Calcite) is still marked in the candidate list. Alternatively, you can also click on the “Select marked phase(s)” button in the green “Guided Operations” area, double-click on the corresponding entry, or drag the corresponding entry from the candidate list to the match list on the right-hand side (using your mouse).

The selected phase will now be displayed in the match list on the lower right-hand side. The composition (phases and elements) calculated from the entries that are currently present in the match list is shown as **pie charts** on the top right.

The remaining entries belonging to the same phase as the selected entry have now vanished, because the corresponding peak intensities are now “occupied” by the selected phase/entry (Fig. 3).

You might note the column “I/Ic” on the right-hand side of the candidate list. Here, you can see if the corresponding entry contains the parameter I/Ic required for (semi-)quantitative phase analysis (p. 49). If you are using the COD as reference database (which is by default installed along with the Match! software), this parameter is available for all entries, since it has been calculated along with the diffraction pattern in the data import process. However, if you are using the ICDD PDF or other reference databases, there may be entries that do not contain the I/Ic parameter, so these entries would not be suitable for semi-quantitative phase analysis.

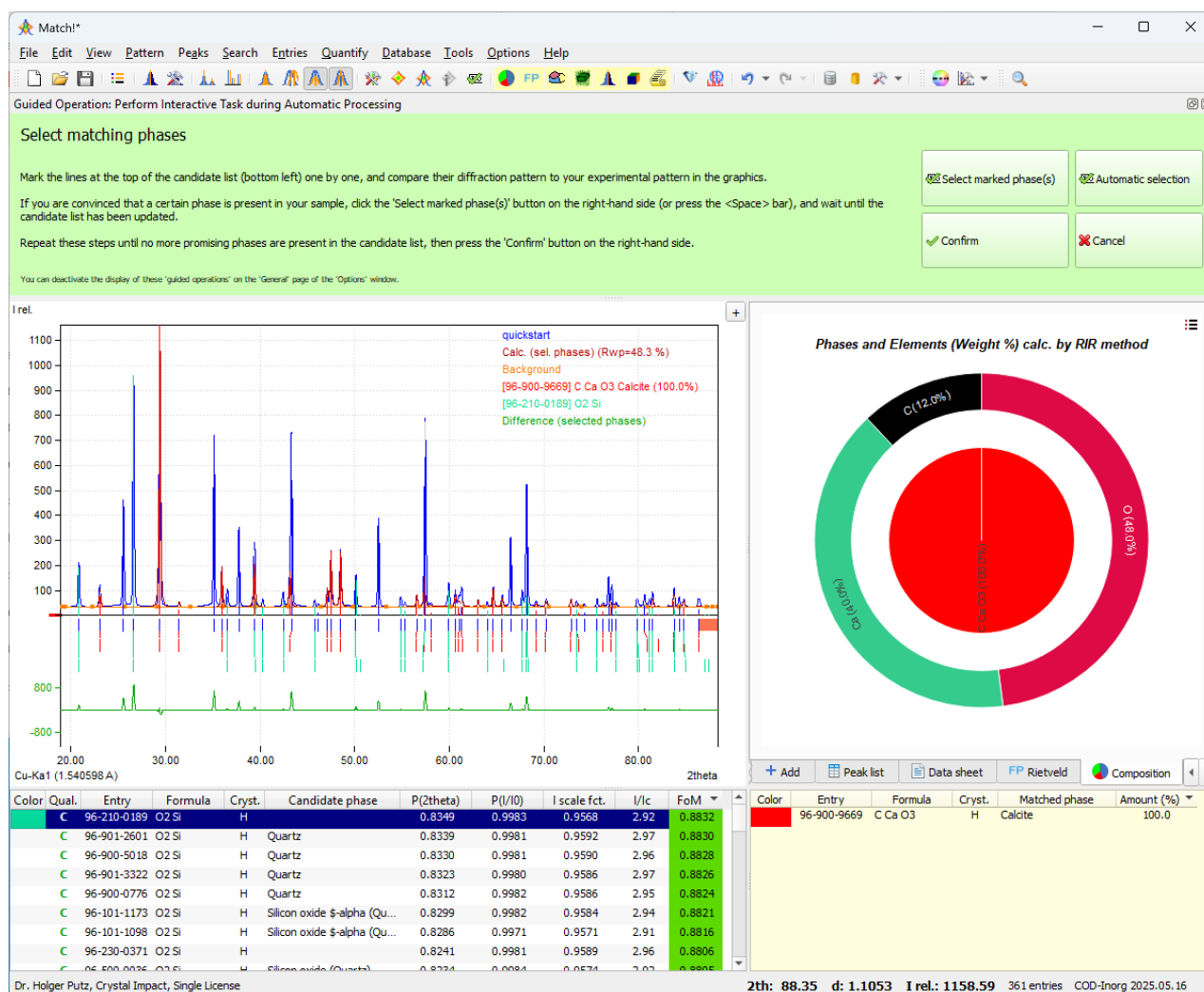


Fig. 3: The first phase ( $\text{CaCO}_3$ , Calcite) has been selected as “matching”. The phase and elemental composition are displayed as a combined pie chart. Currently, there is just a single phase (red inner circle equivalent to 100%).

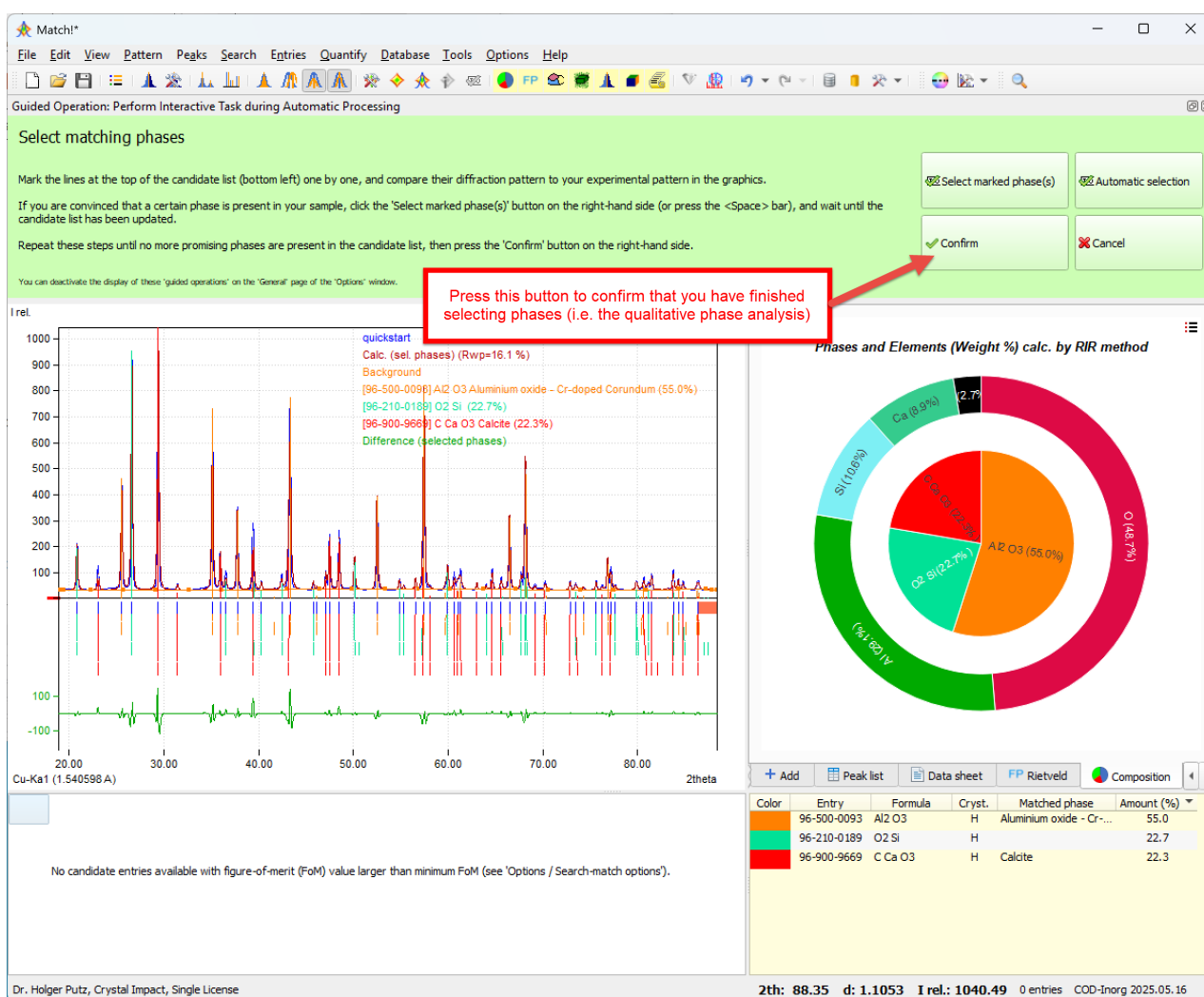


There are still several entries left in the candidate list with good (high) figure-of-merit values with green background color. In addition, there are several experimental peaks in the pattern graphics that are not covered by the red peaks from the phase “Calcite”. Hence, it is rather likely that there are more phases present in the sample.

The next best-matching entry has already been marked in the candidate list automatically, so you can clearly identify the second phase being  $\text{SiO}_2$ . Again, please press the space bar when the corresponding entry is marked (or press “Select marked phase(s)” in the green area), just as you have done before for Calcite. By doing so, you have selected this entry as matching as well.

The next “unmatched” line in the candidate list belongs to an entry describing the phase  $\text{Al}_2\text{O}_3$  (Corundum). Please compare it visually to the experimental pattern, then press the space bar to select it.

As you see (Fig. 4), there are no entries left in the candidate list at the bottom left. Hence, it is highly probable that all (major) phases in the sample have been identified. To confirm this, please press the “Confirm” button in the green area at the top.



**Fig. 4: The identification of phases in the unknown sample is complete. Note the pie chart as well as the column “Amount (%)” in the candidate list in which the weight percentage of the matching phases in the sample are given.**

At this point the semi-quantitative phase analysis is also completed: Please have a look at the inner pie chart circle or the column “Amount (%)” in the match list: Here you can see that your sample contains about 55% (weight-percentage) Corundum, about 23%  $\text{SiO}_2$  (Quartz) and 22% Calcite.

There is nothing left to do but display the report. In the “Beginner” user level, Match! will display a small hint (arrow) close to the “Display Report” button in the toolbar. To display the report, you can either click this button, press the combination  $\langle\text{Ctrl}+\text{R}\rangle$  on your keyboard ( $\langle\text{Cmd}+\text{R}\rangle$  on the Mac), or select the “Report” command from the “View” menu. This will open the dialog window shown in Fig. 5.

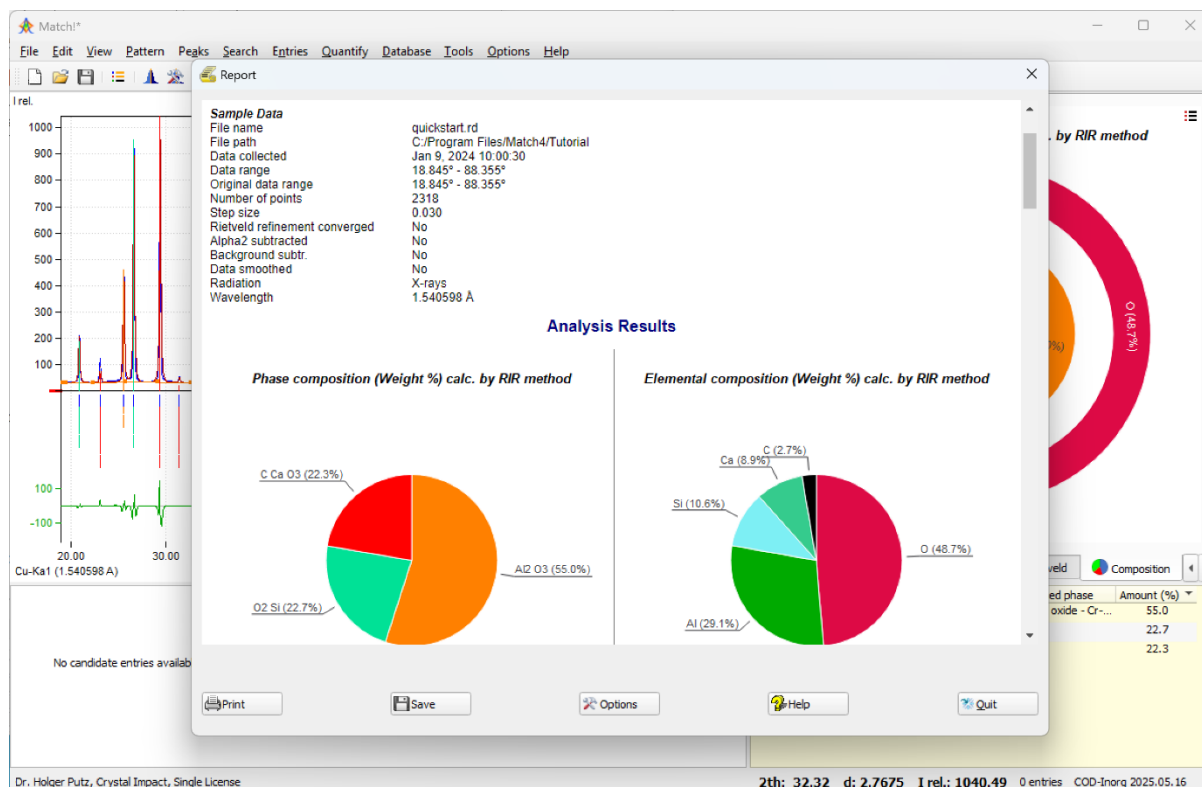


Fig. 5: Once you have finished selecting the “matching phases”, you can display the Report providing the detailed results of the analysis, optionally also as pie charts visualizing the phase as well as the elemental composition.

As you see, the report contains a detailed analysis of your sample. The most important information is given at the top of the “Analysis Results” section: Here, you can see **pie charts** showing the **phase** and **elemental composition**, as well as the list of matching phases, i.e. the phases that are most likely to be present in your sample, along with the corresponding arbitrary amounts (based on a semi-quantitative analysis). In our case, the sample consists of 55% Corundum (Al<sub>2</sub>O<sub>3</sub>), 22.7% Quartz (SiO<sub>2</sub>) and 22.3% Calcite (CaCO<sub>3</sub>).

Well, that’s it already! If you like, you can now print or save the report, simply by pressing the corresponding buttons at the bottom of the Report window.

## Common operations

After this first quick “run-through”, you should now be familiar with the very basic usage of Match!. In this chapter, you will find more information how to perform the most frequently used functions and operations. As you will see, you won't have to dive any “deeper” into the software than is required by your actual task.

### Working area

The Match! program window consists of four major parts (the so-called “working area”):

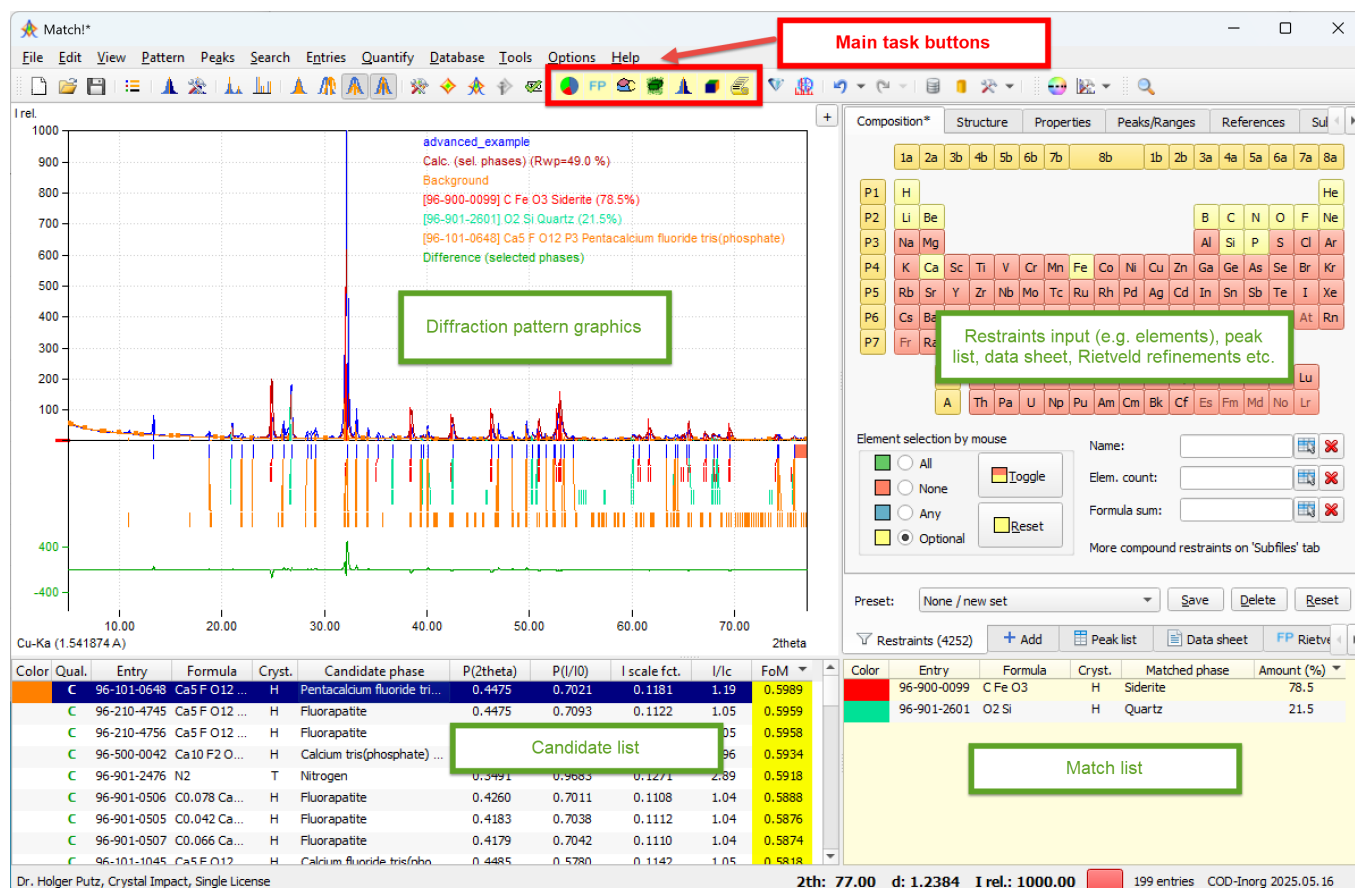


Fig. 6: Screenshot of the Match! program window: The four working areas as well as the main task buttons are marked.

In the **diffraction pattern graphics** (displayed in the panel on the upper left-hand side) you will perform operations like visual comparison of diffraction patterns, zooming, peak editing, background modification etc.

The **candidate list** at the bottom-left of the screen displays a list of the entries of the current answer set, along with numerical parameters indicating the quality of the agreement of the corresponding diffraction patterns with the pattern of the unknown sample.

On the upper right-hand side, several tab sheets are available, with the “**Restraints**” tab (showing the periodic table) being in front normally. Here, you can easily define criteria that must be fulfilled by potential candidate entries/phases, like the presence or absence of certain elements, the color, the density etc.

You can easily switch between the Restraints tab and other controls and information at this place by clicking on the corresponding tabs at its bottom. For example, you can also display the **peak list** that contains the numerical data of the peaks both of the “unknown” diffraction pattern as well as of all entries marked and /or selected in the candidate list and match list. Using this tool, you can also analyze the quality of the peak correlations.

At the same place, the **data sheet** displays (nearly) all information available for a certain entry in the diffraction database.

Finally, this area of the program window is also used for the control of **Rietveld refinements** or a graphical display of the composition as **pie charts**.








The **match list** on the lower right-hand side contains the “matching phases” (phases that have been found/identified in your sample), along with their relative amounts. Entries can be moved from the candidate list to the match list e.g. by double-clicking or dragging with the mouse.

## Main tasks

In the Match! program window, the “**main tasks**” (like phase analysis, degree of crystallinity calculation or crystallite size estimation) are available as **dedicated buttons** in the central area of the toolbar (yellow/orange background):



Pressing one of these buttons runs the corresponding analysis task as automatically as possible:

-  Run a quick **qualitative and (semi-) quantitative phase analysis**. This task is also run automatically at program startup (or “File / New”) when Match! is used in the default “Beginner” user level (see below).
-  Perform a **Rietveld refinement** calculation (in combination with **FullProf**; “FP”) (p. 60).
-  **Crystallite size estimation** based on the peak widths (FWHM values) (p. 73)
-  **Degree of crystallinity analysis** (DOC) using the background line (p. 52)
-  **Raw data processing** of raw / profile powder diffraction data, to get **peak positions, intensities** and **peak widths** (FWHM values) (p. 20)
-  **Indexing** (unit cell determination; in combination with Dicvol or Treor) (p. 81)
-  View or print the analysis **Report**

## Guided operations

Using “Guided Operations”, even inexperienced users can perform the most common phase analysis tasks: With most of the buttons/commands just mentioned, Match! will **take care about any data or information that may be required automatically**:

If Match! cannot perform a certain task automatically (like the selection of restraints or matching phases), and “Guided operations” have been activated on the “General” page of the “Options” window (which is the default setting), **you will be given detailed instructions** in a light-green area at the top, and then asked to manually accomplish the task. When you have finished, you can indicate this by pressing a corresponding “Confirm” button.

“Guided operations” are active when using the default “Beginner” **user level** (see below). If you are using a different user level (maybe “Expert”), you can activate them e.g. on the “General” or “Automatic” page of the “Options” window.

## User level

When you run Match! for the first time (or have reset it to the factory settings (menu “Options / Reset to factory settings”), Match! will use the default “Beginner” level of automation (“user level”).

In the “Beginner” mode Match! performs a qualitative and (semi-) quantitative phase analysis more or less on its own. All you need to do is select the diffraction data file you would like to analyze (you will be prompted automatically for it once the software has been started). Afterwards, Match! will automatically process the raw data,

determine the peaks, ask you for potential additional information about the sample (like elements or phases that may already be known to be present), and then run the search-match calculation.

All that remains to do is to select the “matching” phases (e.g. by double-clicking or dragging the corresponding entries from the candidate list on the left-hand side to the Match list to the right), and finally display the report containing e.g. the list of matching phases as well as their arbitrary amounts (e.g. by selecting “View/Report”).

In the “Expert” mode you must perform nearly all actions manually. This mode is especially recommended for experienced users who would like to analyze more complicated samples.

You can customize the user level (“automatic processing” behavior) on the “Automatic” tab of the “Options” window also later on. In addition to selecting user levels like “Beginner” or “Expert” you can also select individual automatic steps according to your requirements and thus **create own “user levels”**.

To switch over to e.g. the “Expert” more, simply close the report now (press “Quit”), then select the “Automatic options” command from the “Options” menu. Once the “Options”-dialog is displayed, bring the “Automatic” page into front, and select your “user level” in the combo box at the top. In addition (or as an alternative), you can select each single step that shall be carried out automatically using the options below. Finally, please do not forget to mark the “Save as defaults” checkbox at the bottom before closing the dialog, to make your changes permanent.

## Other tasks

With Match! you can also perform a variety of other tasks:

- Search the reference database (apply **restraints**): Page 40
- Pattern decomposition (**Le Bail method**) (in combination with FullProf): Page 70
- **Crystal structure solution** (along with Endeavour: Page 90
- Use other reference databases, e.g. any **ICDD PDF database** product: Page 92
- Create, maintain and apply a **user database**: Page 103
- Repeat similar analyses: Page 132
- Control Match! using **batch script files**: Page 133

## General usage instructions

You should now be familiar with the basic usage of the Match! software. In this chapter, you will find more information about some frequently used functions and operations.

### Context menus

First, please note that many operations can be run (as well as options set) using so-called “context menus”. You can open the corresponding context menus and get access to the commands by **right-clicking** into the corresponding area of the screen. Try to do so in the diffraction pattern graphics, the candidate list, the match list and the peak list!

### Mouse and keyboard shortcuts

A variety of operations like peak editing, zooming and tracking can be controlled using the mouse in combination with certain keyboard buttons. In addition, a lot of common commands cannot only be run from the menu but also by pressing key combinations like <Ctrl+I> (<Cmd+I> on the Mac) for the import of diffraction data.

You should look at the chapter “Table of mouse button and key combinations” on p. 146 in the Appendix. This table can also be displayed within the software by pressing <Ctrl+J><sup>7</sup>. Knowing the keyboard shortcuts and mouse operations by heart will speed up your work and make it much easier!

### Zooming and tracking/panning

To **zoom into a certain area** in the diffraction pattern graphics, press the left mouse button and keep it pressed while moving the mouse across the area you are interested in; Match! will adapt the graphics accordingly.


Alternatively, you can simply **double-click** the left mouse button, to focus into the area around the current mouse position. Double-click again to view the full pattern again.

Another available option is to **use the mouse wheel for zooming**: Move the mouse cursor to the region in the diffraction pattern you would like to focus on and turn the mouse wheel away from you in order to **focus right into this area** (or out again, if you turn the mouse wheel into the opposite direction).

Once you have zoomed into the diffraction pattern, you can **shift the pattern by keeping the “Shift” button on your keyboard (or the center mouse button/wheel) pressed** while moving the mouse around (the so-called “tracking” or “panning”).

Finally, it is also possible to **exactly define the area (intensity and 2theta)** you would like to display. A corresponding dialog is now provided for this purpose (menu “View/Define zoom area...”).

### Axis scaling

The scaling of the x- and y-axis in the diffraction pattern can be changed easily: Simply click on the axis label, and select the scaling you are interested in. As an alternative, you can make these selections on the “Graphics” page of the “Options” dialog; you can directly open this page either by pressing <Ctrl> + <Alt> + G (<Cmd> + <Alt> + G on the Mac), or by clicking on the corresponding button  in the toolbar.

On the **x-axis** of the diffraction pattern graphics you can select 2theta, d-values or 1/d.

For the **y-axis**, you can select relative intensity (I rel.), count (cts), as well their corresponding logarithmic and square-root representations.


In order to make the current scaling permanent (i.e. to be used as default), please open the “Graphics options” dialog from the “Options” menu, mark the “Save as default” checkbox on the bottom left, then press “OK”.


<sup>7</sup> On the Mac, you have to press <Cmd+J> instead.



## Colors, line styles and fonts

You can define individual colors, data point symbols and line styles for experimental diffraction data, calculated patterns, reference patterns etc. It is also possible to define the fonts for text labels in the diffraction pattern as well as the dialog elements (texts on buttons, in dialog windows etc.).

Most of these settings are defined in the “Colors and line styles” dialog that can either be opened from the “Options” menu, as well as by pressing the corresponding button  in the toolbar. Note that you can make your changes permanent by marking the “Save as defaults” checkbox at the bottom of the dialog.

Colors and line styles for **experimental diffraction patterns** are selected in the “Experimental patterns” window that can e.g. be opened by pressing the corresponding button  in the toolbar, or by running the “Experimental patterns...” command from the “Pattern” menu.

## Light or Dark Mode

Match! can either use the “normal” (“light”) mode for its display or use a so-called “dark mode” that can be advantageous in dark surroundings. You can select which mode to use in the “View / Display mode” menu.

The options in this menu depend on the operating system:

### Windows

In the “View / Display mode” menu you can choose between “Light”, “Dark” or “Automatic”. In the latter case, the mode is taken over from the Windows operating system setting<sup>8</sup>.

The latter can be adjusted by pressing the “Windows” button, selecting “Settings”, “Personalization” and then selecting the “Mode” or “Color” (depending on the Windows version you are using).

### macOS<sup>9</sup>

On the Mac, the only display mode available is “automatic”, i.e. it is always taken over from the operating system setting (which can be “Light”, “Dark” or “Automatic”). The selection method for the display mode depends on the macOS version you are using:

In **macOS 10.14 “Mojave”, 10.15 “Catalina”, 11 “Big Sur” or 12 “Monterey”**, please select “System Preferences...” in the “Apple” logo (🍏) menu, select “General”, and finally select the “Appearance” (“Light”, “Dark” or “Automatic”). “Automatic” is not available in macOS 10.14 “Mojave”.

In **macOS 13 “Ventura”** (or more recent), please select “System Preferences...” in the “Apple” logo (🍏) menu, then select the “Appearance” (“Light”, “Dark” or “Automatic”).

### Linux

In the “View / Display mode” menu you can choose between “Light” or “Dark”. The “Automatic” mode is currently not available in Linux, in contrast to Windows or macOS.

## Undo / Redo

Match! provides an undo/redo facility: You can undo nearly any operation until you return to the new empty Match! document where you started. On the other hand, you can also return to the state before you executed the “undo” command(s) using “redo”. You should use these options extensively to try different options!

<sup>8</sup> The “Light” or “Dark” mode settings are only available in Windows 10 (or later).

<sup>9</sup> Note: The Light and Dark Mode options are not available in macOS versions before 10.14 “Mojave”!

## Raw data processing

Most important for a reliable analysis is the quality of the diffraction data on which it is based (e.g. peak positions and intensities for qualitative analysis using peak-based search-match or the exact definition of the background for profile fitting search-match). This chapter provides you with detailed information how to best process your raw diffraction data to achieve this goal.

### Basics



One of the key functionalities in Match!, the qualitative analysis (often abbreviated as “search-match”), is to a large degree based on either the Bragg peak data (peak-based search-match using d-values and intensities) or the definition of the background of your sample’s diffraction pattern (profile fitting search-match). Although the determination of the peak data or the background definition from the raw data can be run automatically before a search-match calculation (as you have seen in the “Quick start” chapter), the computer is still not able to equal the “eye” of an experienced powder diffraction specialist who is normally much better e.g. in distinguishing between background, noise and peaks. Hence, with normal and especially with low quality diffraction data it is worthwhile to invest some time in a critical evaluation of the peak data or background. Match! offers several functions which make this procedure as comfortable as possible.

In the following, we assume that Match! is working in the “Expert” user level (so that it does not perform any operations automatically). You can switch Match! to this user level (e.g. if you have selected “Beginner” when running Match! for the first time) at the top of the “Automatic” tab of the “Options” dialog (which can be opened from the “Options” menu)<sup>10</sup>.

Here are some suggestions for a reasonable workflow<sup>11</sup> for raw data processing:

### Trim diffraction pattern

After importing your raw diffraction data file into Match! (e.g. by pressing the ‘+’ button in the upper right corner of the pattern graphics, or by using the “File/Import/Diffraction data” command in the menu), take a critical look at your data. Sometimes there are areas (typically at low 2theta values) that contain effects which have nothing to do with your sample, e.g. cutoff or primary beam radiation.

If this is true, you should remove these “surplus” area(s) (“trim” your diffraction pattern), to focus on the analysis of your sample’s diffraction pattern. You can do so by moving the mouse cursor to the left (or right) of your diffraction pattern<sup>12</sup> until it changes ( or ) , press the left mouse button, and move the mouse to the right or left until the area you would like to remove has been marked. After releasing the mouse button, your diffraction data will be trimmed (i.e. the unwanted areas will be removed).

### Alpha2 subtraction

If the radiation used in your diffraction experiment does not only contain the alpha1 but also the alpha2 component, you can now subtract the alpha2-contribution (menu “Pattern/Subtract alpha2”). However, please note that this is **not mandatory**: It is perfectly possible (even advisable) to perform a complete phase analysis with the alpha2-contribution still present! Stripping the alpha2-contribution may even be a disadvantage if your data contains a significant amount of noise, because the noise will be increased, and surplus “ghost” peaks may be introduced in peak searching (see below).

### Background definition

The contribution of the background radiation (simply called “the background”) is first determined automatically during the import of the diffraction data. It is displayed as an (by default) orange colored curve with small squares (control points) at the bottom of the raw (profile) diffraction data right after the import (Fig. 7).

<sup>10</sup> Don’t forget to mark the “Save as defaults” checkbox in the corner on the lower left-hand side of the “Options” dialog, if you would like to make this setting /user level permanent!

<sup>11</sup> We recommend to switch over to the “Expert” user level for these tasks, as described in the “User levels” chapter on p. 25.

<sup>12</sup> You must have fully zoomed out for this to work, i.e. your diffraction data limits must be equivalent to the limits of the pattern graphics.



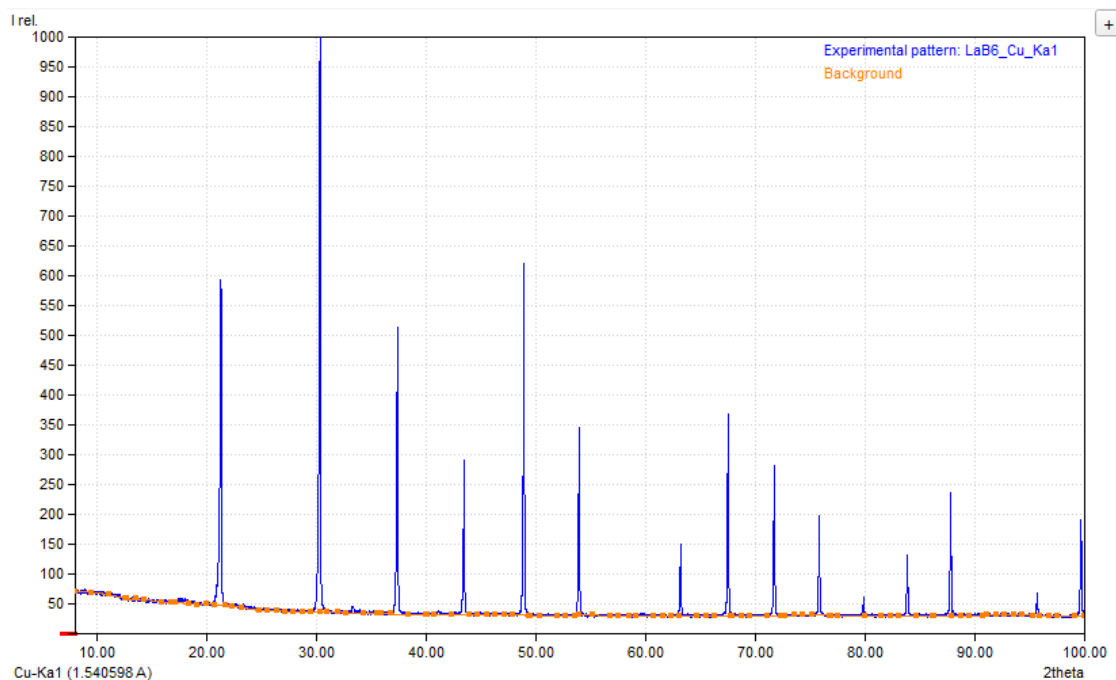


Fig. 7: The orange curve at the bottom of the imported raw (profile) diffraction data is the so-called “background” caused e.g. by the experimental setup.

There may be cases though in which the automatic determination does not give a satisfactory result, so that you would like to correct it. This should be done before running the peak searching or profile fitting search-match command!

Sometimes the automatically determined background does not completely detect all structures, either because the background is too “rigid” (in which case amorphous “humps” are not fully covered, leading to surplus peaks when using the automatic peak searching), or too flexible (in which case profile areas that belong to the peaks may be covered (i.e. hidden) by the background).

You can correct these issues by pressing <Ctrl+F2> (if you would like to increase the background flexibility) or <Ctrl+F3> (if the background shall be more rigid (cover less of the peak sockets), i.e. in order to decrease the flexibility) until the visual agreement between the orange curve and the estimated background is acceptable.

It is also possible to modify the shape of the background curve manually, simply by dragging around the control points of the background curve using the mouse. You can easily add more control points if required if a critical part of the curve cannot be modeled right yet, or delete surplus control points (e.g. on a straight line), by clicking the right or left mouse button if the mouse cursor is at the corresponding position (Fig. 8).

To do so, please make sure that the background curve is currently displayed<sup>13</sup>. Afterwards, please note the small squares on the curve. These are the so-called “background control points” just mentioned. You can shift these points by first moving the mouse on top of them, pressing the left mouse button, and moving the mouse around.

If you would like to add more control points (e.g. to be able to model a certain critical range of the background curve more accurately), you can do so by first moving the mouse to the desired position on the background curve. The mouse cursor will change (a ‘+’ sign will appear on the top left of the cursor); you can now press the left mouse button to add a control point at the corresponding position of the background curve.

To delete a control point, simply move the mouse cursor on top of it, then press the right mouse button.

Please take a look at the chapter “Table of mouse button and key combinations” on p. 146, too, in order to learn how to modify the background control points using the mouse. You can also watch a corresponding tutorial video on our web page:

[https://www.crystalimpact.de/match/video\\_working\\_in\\_graphics.htm](https://www.crystalimpact.de/match/video_working_in_graphics.htm).

<sup>13</sup> You can toggle the displaying of the background curve e.g. by right-clicking in the diffraction pattern and selecting “Background” from the context menu that opens.

**Please note:** If you intend to strip the alpha2 contribution in your profile data using the corresponding command from the “Pattern”-menu, please make sure to do so first before you modify the background manually, because your manually defined background will be overwritten by the alpha2 stripping function.

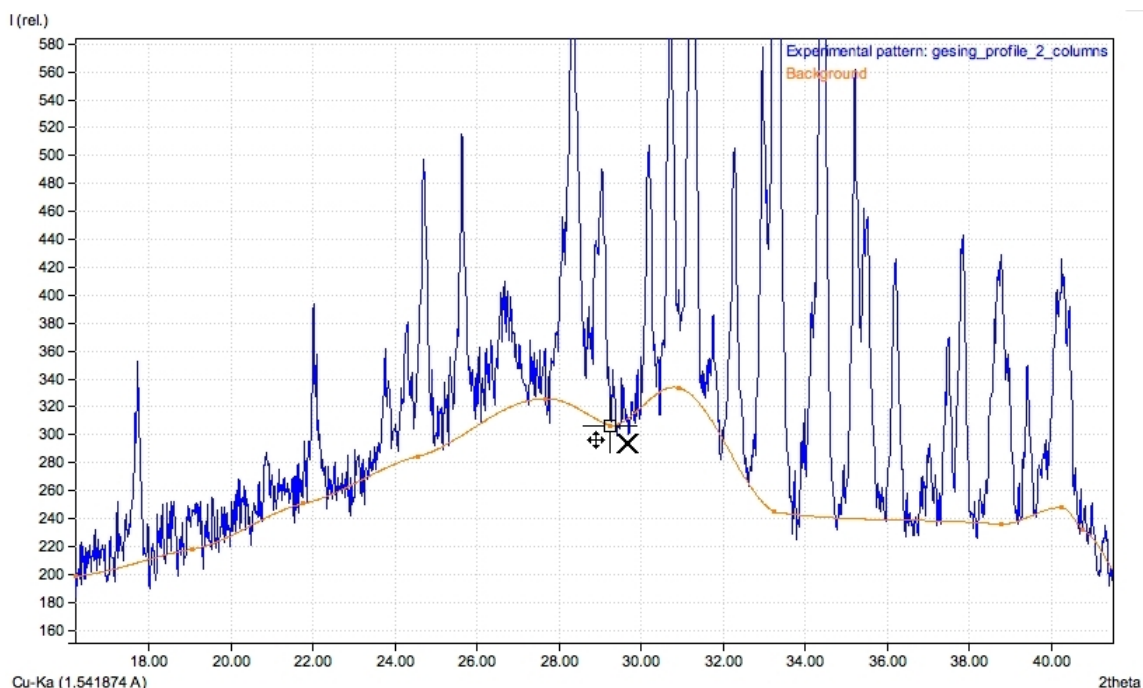



Fig. 8: As the mouse cursor indicates, you can modify the background control point behind the cursor: In order to shift it, press the left mouse button, in order to delete it, press the right button.

## Raw data smoothing

If the pattern looks very rugged, you might try to run one or two steps of “raw data smoothing” (menu “Pattern/Raw data smoothing” or keyboard shortcut <Ctrl+F4>), but keep in mind that small peaks might be extinguished if you overdo it, resulting in a potential loss of minority or even minor phases.

## Peak searching

If you intend to use the normal peak-based search-match function for qualitative analysis, the most important part of the raw data processing is the searching for diffraction peaks, since the peak positions and intensities are the actual input to this. Match! uses the well-known second-derivative method<sup>14</sup> to perform the peak searching.

To get an initial set of peak data (that can be fine-tuned later), run the automatic peak searching by selecting the menu command “Pattern/Peak searching/Peak search”, by pressing the keyboard shortcut <Ctrl+K>, or by clicking on the corresponding toolbar button . Alternatively, a peak search is carried out automatically along with profile fitting by using the menu command “Pattern/Peak searching/Peak search and fit” (or by pressing <Ctrl+Shift+K>), as described on p. 26) is executed without any peak data present. As a result, the profile fitting can be used as an alternative to the normal peak searching, both manually as well as during the automatic raw data processing.

Before running the peak search we strongly recommend checking and maybe **correct the background**. You should always keep in mind that **if the background is too high in certain parts of the diffraction pattern, this may prohibit the detection of peaks in this area!** You could e.g. try to **reduce the background flexibility** by pressing <Ctrl+F3> one or two times (<Cmd+F3> on the Mac).

If the raw diffraction data are very rugged, you could try to smooth your raw data (see above) before running the peak searching.

With very low-quality data, however, it may be better not to use the automatic peak searching and add the peaks manually (see below).

<sup>14</sup> W.N. Schreiner & R. Jenkins, “A second derivative algorithm for identification of peaks in powder diffraction patterns”, Adv. X-Ray Anal. **23**, 287-293 (1980).

**Please note:** It is rather important to check (and maybe correct) the background (p. 20) before running peak searching, to get accurate results and reduce the risk of getting surplus peaks or missing small peaks because they are hidden by the background!

## FWHM

If you use the normal peak searching functionality, Match! will try to determine the FWHM (Full Width at Half Maximum) separately for each peak automatically. If this is not possible, it will use the corresponding default value (which can be adjusted on the “Raw data” tab of the “Options” dialog). If you would like to obtain even more accurate FWHM values, you should apply profile fitting instead of or after the peak searching.

## Integrated intensities

Normally, the intensity values that are calculated during the peak searching procedure are **integrated intensities**, considering both the height as well as the FWHM of each peak. You can view the integrated intensity values in the peak list on the upper right-hand side. An exception to this is the relative intensity scaling of the vertical axis, in which case the integrated intensity values are scaled to a maximum value of 1000.0.

## Peak searching sensitivity

One task associated with peak searching is to decide which “hump” or structure in the raw data corresponds to a Bragg peak, and which is just an artifact or noise. Obviously, there must be a certain parameter “sensitivity” using which the software can make this decision.

When peak searching (in any variant just described) is carried out for the first time, a default sensitivity is used which takes the noise found in the raw diffraction data into account. This default sensitivity has been chosen to obtain good results with a large variety of diffraction patterns. However, it may nevertheless be necessary to adjust the sensitivity for your special data. Note that you can also modify the default peak search sensitivity values for peak searching and profile fitting separately on the “Raw data” tab of the “Options” dialog.

## Peak detection issues

If some **peaks are not detected**, this may be caused by the fact that when detecting a new peak (based on a second-derivative minimum), Match! searches for a maximum in the raw data within two times the FWHM. This can cause shoulder peaks to be neglected if the default FWHM value is relatively large. You should adjust the default FWHM value on the “Raw data” tab of the “Options” dialog (maybe you have to deactivate the corresponding “Automatic” option in order to be able to modify the default FWHM value).

If **peak positions are not determined exactly**, this may be caused by a relatively large step width in your raw / profile data. To fix this problem, you could try to increase the resolution (i.e. decrease the step width) by interpolation, using the menu command “Pattern/Increase resolution...”. You should start by trying a small factor (e.g. 2 or 3) first, because otherwise the noise may be “fixed” (i.e. fluctuations are described by too many data points, so they are no longer detected as “random noise” but as a “signal”). Repeat the peak detection after increasing the resolution.

If far **too many diffraction peaks** are frequently determined during peak searching, we recommend enabling the raw data smoothing for the automatic raw data processing in the corresponding “Options” dialog page. Start with a single “Number of repetitions” and maybe increase this number if the result is not sufficient.

If there really is a lot of noise present in your raw data (so that raw data smoothing can hardly be avoided if you would like to keep the number of detected peaks at an acceptable rate), please apply the raw data smoothing gently and carefully!

## Peak editing

Note that the following hints on peak editing are usually **not required** if you use **profile fitting search-match** for qualitative analysis!

### Peak editing in the diffraction pattern

Now it is time to closely inspect your data: Match! offers a variety of keyboard shortcuts and mouse operation options for zooming and tracking; they are described<sup>15,16</sup> in the chapter “Zooming and tracking” on p. 18. Zoom into the left-

<sup>15</sup> These features are also demonstrated in our tutorial video “Working in Match!’s Pattern Graphics” ([https://www.crystalimpact.de/match/video\\_working\\_in\\_graphics.htm](https://www.crystalimpact.de/match/video_working_in_graphics.htm)).


<sup>16</sup> You should also have a look at the chapter “Table of mouse button and key combinations” on p. 82 in the Appendix.

hand side (low 2theta region) of the pattern and inspect or edit peaks and their positions while slowly moving to the right (high 2theta region).

You can edit the peaks directly in the diffraction pattern using the mouse. Add, edit or delete peaks while scrolling through the enlarged pattern, and maybe fit individual peaks to the profile data to obtain accurate intensity values. Peaks can easily be added or edited using the mouse in combination with certain keyboard buttons<sup>15,16</sup>.

**Please note:** Before you can start to edit the peaks in the pattern graphics using the mouse, you need to give the input focus to the diffraction pattern first, e.g. by clicking on it.

Take care that all maxima in the raw data that you estimate as being “real” diffraction peaks are “covered” by peaks, while at the same time using as few peaks as possible. **Always keep in mind that the “empty” spaces between the peaks are as important to exclude non-matching phases as the peaks are important to find the matching ones!** Hence, by only using the peaks you are certain about you can increase the separating power of the search-match calculation.

**Add peak:** If you would like to add a peak, please press the <Ctrl> button (<Cmd> on a Mac) first; the mouse cursor will change to . Keep the button pressed, move the mouse pointer to the corresponding 2theta position, and click the **right** mouse button. A peak will be inserted at the corresponding position. Once you have finished adding peaks, you can release the <Ctrl> keyboard button.





Depending on the (de-)activation of the profile fitting settings (2theta, intensity and/or FWHM, see below), the 2theta, intensity and/or FWHM value(s) of the new peak will be instantly optimized by **automatic profile fitting**, right after you have clicked the mouse button. If all three profile fitting options (2theta, intensity and FWHM) are active, it is enough to (right-)click somewhere in the peak area below the profile curve in order to add the peak.

If the calculated profile is currently displayed, the new peak data will be included in the profile and  $R_p$ -factor calculation automatically.


If **no profile data** are present, the top of the peak (i.e. the peak intensity) will be taken from the position of the mouse cursor. The FWHM of the peak will be set to the corresponding default value that can be defined on the “Raw data” tab of the “Options” dialog.

**Please note:** After adding the strongest peak you may want to run the “Scale relative intensities” command from the “Peaks” menu, in order to adjust the maximum relative peak intensity to a value of 1000.0 .


**Mark peak(s):** There are several options to mark one or more peak(s):


- **Mark single peak:** Move the mouse cursor to a peak at or below the top of a peak (must be visible!). The mouse cursor will change to  or . Now, simply click the **left** button in order to mark the peak below the mouse cursor; marks at other peaks will be removed.
- **Mark selected peaks:** Move the mouse cursor to a peak at or below the top of a peak (must be visible!). The mouse cursor will change to  or . Press the <Ctrl> button on your keyboard (<Cmd> on the Mac), and keep it pressed while clicking on one or more peaks using the **left** mouse button in order to mark them, in addition to the peaks that are already marked. Finally, release the <Ctrl> button.
- **Mark range of peaks:** First, move the mouse cursor to the left of the left-most peak in the range you would like to mark. Press the <Ctrl> button on your keyboard (<Cmd> on the Mac), and keep it pressed while moving the mouse to the right until you have selected the range of peaks you would like to mark. Finally, release the mouse button and the keyboard button.

Marked peaks are indicated by a small triangle displayed at the top of the peaks in the pattern graphics. In the peak list, the corresponding lines are inverted.

**Edit peak position:** If you would like to edit a peak position (i.e. shift a peak on the 2theta axis), please move the mouse cursor close to the peak position (below the peak top), so that the mouse cursor changes to . Afterwards, press the **right** mouse button and move the mouse to the position inside the current viewing region where you would like to

place the peak. Finally, release the mouse button. If the calculated profile and the  $R_p$ -factor are currently displayed, they will be updated with regard to the new peak position.

**Edit peak position and/or intensity:** You can also modify both peak position and intensity at the same time: Please move the mouse cursor close to the top of the corresponding peak until the mouse cursor changes to , then press the **right** mouse button and move the mouse to the intensity /  $2\theta$  position where you would like to place the peak. Finally, release the right mouse button. If the calculated profile and the  $R_p$ -factor are currently displayed, they will be updated with regard to the new peak position.

**Edit peak FWHM:** You can modify the FWHM (Full Width at Half Maximum) of marked peaks using the mouse: Mark one (or more) peaks as described above, then move the mouse over one of the marked peaks until the mouse cursor changes to , and finally turn the **mouse wheel** in order to modify the FWHM of the marked peak(s).

**Invert peak mark(s):** If you would like to mark all but a few peaks, you should use the "invert peak marks" facility: First, mark the few peaks you do **not** want to mark (see above), then press the **right** mouse button within the diffraction pattern (which will open the context menu), and select "Invert selection" from the menu.

**Delete peak(s):** To delete one or more peaks, you first have to mark the corresponding peaks in the diffraction pattern (see above). Once you have marked one or more peaks, there are several options to delete them:

- Press the **"Del"** button on your keyboard
- Press the **right mouse button** within the pattern graphics, and select the "Delete" command from the context menu
- Select the "Delete" command from the **"Peaks" menu**

If the calculated profile and the  $R_p$ -factor are currently displayed, they will be updated with regard to the remaining peaks.


**Deactivate peak(s):** You can deactivate individual peaks of the unknown sample's pattern so that they are not taken into account during the search-match (i.e. figure-of-merit) calculation. This is e.g. useful if you are not sure about a certain peak and would like to check what would be the result of the search-match without this peak.

To deactivate one or more peaks, you first have to mark them (see above). Afterwards, please press the **right mouse button** within the diffraction pattern and select "Deactivate" from the context menu (or use the corresponding command from the "Peaks" menu). The candidate list will immediately reflect the change in the FoM-values of the entries. However, you should perhaps perform a completely new search-match operation to check if there are new matching entries! Please note that **deactivated peaks are displayed in light grey** in the diffraction pattern.

**Activate peak(s):** You can reactivate individual peaks of the unknown sample's pattern you have deactivated earlier. Please mark the corresponding peaks (see above), then press the **right mouse button** within the diffraction pattern and select "Activate" from the context menu (or use the corresponding command from the "Peaks" menu).

### Peak editing in the peak list

You can edit the peaks directly in the peak list using the keyboard. (If the peak list is currently not displayed, please select the "peak list" command from the "View" menu or press <Ctrl+L>).

**Add peak:** If you would like to add a peak, please select the "Add peak(s)" command from the "Peaks" menu or press the corresponding button  in the toolbar at the top. The "Add Peak" dialog will be displayed.

Please select if your data are  $2\theta$ , d-values or  $1/d$  on the right-hand side of the dialog first. Afterwards, write the peak  $2\theta$ /d-value, the intensity and the FWHM in the corresponding fields. If you do not want to provide the FWHM value for each separate peak, you can activate the corresponding option below.

If you press the **"Add peak"** button afterwards, the peak will be added to your peak list, however, the dialog will remain open so that you can enter the next peak.



If you realize that you have accidentally entered a wrong peak after you have pressed the “Add” button, you can remove the corresponding peak again by pressing the “Delete previous” button.

Once you have finished entering peaks, please press the “Quit” button. The dialog will be closed.

**Edit peak position:** If you would like to edit a peak position of the experimental pattern, please activate the corresponding field in the **first** column of the peak list by double-clicking on it. The field will switch to the “Edit” mode. You can now enter the new value for the peak position. When you are finished, press <Return> or click on another field. Both the diffraction pattern and the candidate list will be updated immediately.

**Edit peak intensity:** This works similar to the editing of the peak positions: Activate the corresponding field in the **second** column of the peak list by double-clicking on it; the field will switch to the “Edit” mode. You can now enter the new value for the peak intensity. When you are finished, press <Return> or click on another field. Both the diffraction pattern and the candidate list will be updated immediately.

**Edit FWHM:** This works similar to the editing of the peak positions and intensities: Activate the corresponding field in the **third** column of the peak list by double-clicking on it; the field again in order to switch to the “Edit” mode. You can now enter the new FWHM value for the peak. When you are finished, press <Return> or click on another field. Both the diffraction pattern and the candidate list will be updated immediately.

**Mark peak(s):** You can mark individual peaks simply by clicking on the corresponding line(s) in the peak list using the left mouse button. If you keep the <Shift> or <Ctrl> button (<Cmd> button on the Mac) on your keyboard pressed while doing this, you can select more than one individual peak. The lines of the marked peaks are displayed inverted. Note that marked peaks are also indicated in the diffraction pattern by a small triangle displayed at the top of the peaks.

**Invert peak mark(s):** If you would like to mark all but a few peaks, you should use the “invert peak marks” facility: First, mark the few peaks you do **not** want to mark, then press the right button to open the peak list's context menu, and select the “Invert selection” command from this menu.

**Delete peak:** In order to delete one or more peaks, you first have to mark the corresponding peaks (see above). Once you have marked one or more peaks, please execute the “Delete” command from the “Peaks” menu, or right-click in the peak list (in order to open the context menu) and select the command from the context menu.

**Deactivate peak(s):** You can deactivate individual peaks of the unknown sample's pattern so that they are not taken into account during the search-match (figure-of-merit) calculation. This is e.g. useful if you are not sure about a certain peak and would like to check what would be the result of the search-match without this peak.

To deactivate one or more peaks, you first have to mark them (see above). Afterwards, please open the peak list's context menu (by pressing the right mouse button on one of the marked peaks), then select the “Deactivate” command from this menu. The candidate list will immediately reflect the change in the FoM-values of the entries. However, you should perhaps perform a completely new search-match operation in order to check if there are new matching entries! Please note that **deactivated peaks are displayed in light grey** color.

**Activate peak(s):** You can reactivate individual peaks of the unknown sample's pattern you have deactivated earlier. Please mark the corresponding peaks, then open the context menu (press the right mouse button on one of the marked peaks) and select the “Activate” command from this menu.

**Please note:** After editing the strongest peak you may want to run the “Scale relative intensities” command from the “Peaks” menu, in order to adjust the maximum relative peak intensity to a value of 1000.0 .

## Profile fitting

While the peak searching algorithm is very fast and produces peak data appropriate for many “routine” problems, there may be cases where more accurate peak parameters (d-value/2theta, intensity and peak width (FWHM)) is required, e.g. for crystallite size estimation (p. 73). In these cases, profile fitting may be applied.




Do not mismatch profile fitting search-match (PFSM) with profile fitting as described in this chapter! PFSM fits the profile calculated from **reference database entries**, while profile fitting is operated on the **experimental peak data**.

During the profile fitting calculation, Match! tries to optimize the peak parameters (2theta, intensity and FWHM (= "Full Width at Half Maximum")) to obtain a reasonably good agreement between calculated and experimental diffraction pattern (profile data). This is achieved by **using the peak data as parameters in a constrained least-squares refinement**.

Profile fitting requires the presence of peak parameters (2theta, I, FWHM). If no peaks are present yet when the profile fitting command is executed, peak searching will be run first automatically.

If **no peaks are currently marked** / selected, the parameters of **all peaks will be fitted automatically**. Match! will **not** use the user-selected parameters to be fitted (2theta, intensity, FWHM; see below) but refine its own parameter combinations in a multiple step procedure. This **automatic profile fitting calculation** is by default also performed immediately **after peak searching** (see "Options / Raw data").


If on the other hand one or more **peaks are marked when profile fitting is run**, only the parameters of the **marked peaks will be refined**. Besides this, the user can select which parameter(s) (2theta, I, FWHM) shall be varied in the profile fitting. This can be achieved by clicking the corresponding buttons in the toolbar, by pressing the corresponding function keys <F6>, <F7> and <F8>, or alternatively by selecting the corresponding options in the "Pattern/Profile fitting" submenu:

<i>Peak parameter to be fitted</i>	<i>Toolbar button</i>	<i>Keyboard shortcut</i>
2theta		F6
intensity		F7
FWHM		F8

In other words: It is not only possible to perform a peak search followed by profile fitting for all peaks, but you can also **fit individual parameters of individual peaks**.

The **default setting** is to optimize intensity and FWHM values, and to leave the 2theta values resulting from the peak searching untouched. The reason is that the peak positions (2theta values) obtained by the second-derivative method for peak searching are generally extremely accurate.

If a **mixed radiation** (containing alpha1 and alpha2 contributions) has been used in the diffraction experiment, Match! will by default add the alpha2 contribution (peak) automatically and refine it along with the corresponding alpha1 peak. This behavior can be turned off by deactivating the option "Operate alpha2 peaks automatically" on the "Raw data" page of the "Options" window.

The actual profile fitting calculation can be executed once the peaks and / or the parameters which shall be fitted have been selected. This is achieved simply by pressing the <F5> key on your keyboard, by pressing the corresponding button  in the main toolbar, or by selecting the corresponding command in the "Pattern/Profile fitting" submenu. When the calculation is finished, the success is announced in the status bar at the bottom. Besides this, the  $R_{wp}$  value which has been reached is shown.

When a combined peak searching / profile fitting calculation is carried out for the first time, a default **sensitivity** is used which takes the "noise" found in the raw diffraction data into account. This default sensitivity has been chosen to obtain good results with a large variety of diffraction patterns.

If you have the impression that the calculation either yielded too many or too few peaks, you might want to adjust the peak searching sensitivity for profile fitting on the "Raw data" tab of the "Options" dialog for your special data.

Normally, the intensity values resulting from the profile fitting procedure are **integrated intensities**, taking into account both the height as well as the FWHM of each peak. You can view the integrated intensity values in the peak list on the upper right-hand side. An exception to this is the relative intensity scaling of the vertical axis, in which case the integrated intensity values are scaled to a maximum value of 1000.0.


## Correction of 2theta errors

Once you have investigated the whole pattern and have settled on a set of peaks, check and (if necessary) correct the specimen displacement error as well as the zero point, using the corresponding commands in the "Pattern" menu. Use the histograms to decide on a certain correction value, and do not hesitate to come back and try a different

correction if the search-match calculation did not give a reasonable result. Match! also offers a variety of tools for correcting 2theta errors using the mouse:

In addition to the 2theta correction functions “Zero-point” and “Specimen-displacement” that are available in the “Pattern” menu, it is also possible to directly adjust the experimental diffraction pattern manually using the mouse.

### Zero-point correction


To shift the experimental diffraction data on the 2theta (x-) axis (zero-point correction), move the mouse into the diffraction pattern graphics, then press the <Ctrl> as well as the <Alt> buttons on your keyboard (<Cmd> and <Alt> on the Mac). The mouse cursor will now change into .

While keeping the <Ctrl> (<Cmd>) and <Alt> buttons pressed, turn the mouse wheel away from you in order to shift the experimental data to higher 2theta values, or towards you in order to shift to lower angles. The changes will be automatically applied to the candidate list as well as the peak correlations to reference diffraction patterns.

In order to restore the original 2theta values, simply press the mouse wheel button while keeping the <Ctrl> and <Alt> buttons pressed.

### Specimen-displacement correction

The procedure to apply a specimen-displacement correction to the experimental pattern is pretty similar to the zero-point correction:

In order to shift the experimental diffraction data on the 2theta (x-) axis with  $\cos(\theta)$ - (Bragg-Brentano geometry) or  $\sin(2\theta)$ - (asymmetric geometry) dependence (specimen-displacement correction), move the mouse into the diffraction pattern graphics, then press the <Shift>, the <Ctrl> and the <Alt> buttons on your keyboard (<Shift>, <Cmd> and <Alt> on the Mac). The mouse cursor will now change into .

While keeping the <Shift>, <Ctrl> (<Cmd>) and <Alt> buttons pressed, turn the mouse wheel away from you in order to shift the experimental data to higher 2theta values, or towards you in order to shift to lower angles. The changes will be automatically applied to the candidate list as well as the peak correlations to reference diffraction patterns.

In order to restore the original 2theta values, simply press the mouse wheel button while keeping the <Ctrl> and <Alt> buttons pressed.

### Specimen-displacement correction for asymmetric geometry

In addition to the specimen-displacement correction for Bragg-Brentano geometry just mentioned, a correction for asymmetric geometry is also available. The geometry (as well as the parameter  $\Omega$  for the asymmetric geometry) can be adjusted at the bottom of the “Raw data” processing tab of the “Options” dialog.

### Correction of 2theta errors in Match! and Rietveld refinement (FullProf)

If you perform Rietveld refinement calculations using FullProf, please note that the **zero point** as well as the **specimen displacement error corrections** are implemented in **opposite directions in Match! and FullProf**. In other words, the absolute values of the corrections using Match! and FullProf will be similar, but the sign will be different (opposite).

The background is that **Match! tries to remove potential errors** (like a zero point deviation) **from the experimental data** right away **before performing the actual analysis**, just like stripping of the  $\alpha_2$  radiation part, background subtraction and raw data smoothing.

In **FullProf** (or Rietveld refinement in general), the concept is rather to **leave the experimental diffraction data in their original state** and try to **include corrections for potential errors** (like the zero point) **in the model function**.

### Correction of 2theta errors using internal standard

To correct potential 2theta errors, you can also use an internal standard if you know that a certain phase is present in the sample. Simply press <Ctrl+F> (<Cmd+F> on the Mac) (or click into the corresponding field “Find phases/entries” to the right of the toolbar at the top), then type the name, the formula sum or the entry number of the known compounds, and finally press <Return>. Match! will make sure that the corresponding entries are displayed in the candidate list at the bottom of the screen, and then automatically highlight the first entry matching



your criterion (e.g. name or formula sum). As a result, the corresponding diffraction pattern will be displayed in the pattern graphics above. You can now adjust the 2theta axis according to the highlighted internal standard, simply by pressing <Ctrl+T> (<Cmd+T> on the Mac).

## Qualitative phase analysis

Once the raw data processing (p. 20) of your powder diffraction data has been accomplished, you are ready to determine the phases that are present in your sample.

“Qualitative analysis” means the determination of the phases that are present in your sample. For this, any additional information about the sample that you may have should be applied first before we start to analyze your diffraction pattern.

For example, if you already know in advance that one (or even more) specific compounds are present in your sample, you should first read the chapter “Search for specific phase/entry” (p. 40) below to find out how to directly enter and use this information.

If you already know that certain elements are present or can be excluded, you should first follow the guidelines given in the chapter “Instant usage of additional information (“restraints”)” on p. 43 to define them.

Once you have entered this additional information, please return here to learn how to determine the remaining phases in your sample. Typically, you will apply the so-called “search-match” functions (available in the menu “Search”) for this purpose.

These functions compare the diffraction pattern of your sample to the patterns of known compounds stored in the reference pattern database (p. 92), by calculating a numerical value for the degree of agreement (the so-called “Figure-of-merit” (FoM)) for each of these “candidates”. Afterwards, Match! presents a ranked list of these candidates in the candidate list at the bottom left, with the most likely phases (the ones with the best FoM values) at the top.

There are two different functions implemented in Match! for this purpose:

1. The conventional (but proven) **peak-based search-match**
2. The innovative **profile fitting search-match (PFSM)** that Match! offers since version 4

For automatic operations, Match! can select the search-match method to be used (peak-based or profile fitting search-match) on its own, depending on the number of entries in the current reference database (or answer set) and the number of available CPU cores. You can activate this option at the top of the “Search-Match” page of the “Options” window.


### Peak-based search-match

This analysis is based on the Bragg peaks (positions and intensities) found in your sample’s powder diffraction pattern. Hence, the most important prerequisite for a successful application of this method is to first determine all diffraction peaks (and the background curve!) in the raw (profile) data as accurately as possible.

The quality of your analysis strongly depends on the quality of the peak data that are derived from your initial raw data: On the one hand, it is important not to miss any peaks, to identify all (even minor) phases in the sample. On the other hand, any surplus peaks might bring up wrong phases (“false positives”) to the top of the candidate list.

As a guide, you can use the diffraction profile calculated from the experimental peak data as well as the background: It should be in reasonable agreement with the experimental diffraction pattern/profile throughout the whole pattern. You may want to display the difference plot in the pattern graphics to check for remaining differences between experimental and calculated diffraction data.

During the “search-match” calculation, Match! compares the Bragg peak data (d-values and intensities) of your sample’s diffraction pattern to a so-called “reference database” (like the PDF or the COD) in which peak data of a large number of compounds are stored. Afterwards, the results are sorted according to their “similarity” (figure-of-merit (“FoM”) values) and presented in the candidate list.

You can run the search-match calculation e.g. by pressing <Ctrl+M> (<Cmd+M> on the Mac), by pressing the  button in the toolbar, or by running the “Search-match” command from the “Search” menu. Match! will now

calculate figure-of-merit (FoM) values for all entries in the current answer set (i.e. for the whole reference database if you did not enter any selection criteria, like elements etc.)<sup>17</sup>.


### Figure-of-merit calculation

As has already been mentioned, the qualitative analysis in Match! is based on the so-called “figure-of-merit” (FoM), a numerical value describing the quality of the agreement between a certain reference database pattern and the pattern of the unknown sample.

The calculation of the figure-of-merit is to a large degree based on the peaks found in the unknown sample's diffraction pattern. In a first step, Match! tries to correlate the database pattern's peaks to the peaks in the unknown sample's pattern. Depending on the command used to run the search-match, Match! will either try to correlate **all peaks** (menu command “Search/Search-Match”, shortcut <Ctrl+M>) or the **marked peaks only** (menu command “Search/Search-Match (marked peaks only)”; shortcut <Ctrl+Shift+M>).

Afterwards, it calculates the FoM as a weighted sum of a variety of different pattern agreement criteria:

- 2theta-value differences of correlated peaks
- Intensity differences of correlated peaks
- Difference between the number of correlated peaks and the total number of peaks in the unknown pattern.
- Difference between the number of peaks which have been correlated in relation to the number of peaks which should have been correlated.
- Intensity scaling factor for the database entry's peaks which gives the best agreement with the unknown pattern regarding the peak intensities.

Depending on the kind of problem, some of these factors should be weighted to a larger or smaller degree. For instance, the “difference between the number of correlated peaks and the total number of peaks in the unknown pattern” favors entries which cover as much of the unknown pattern's peaks as possible, thus favoring single phases. The corresponding weighting factor should be reduced in the search-match options (which can e.g. be displayed by pressing the  button in the toolbar) if the possibility that the unknown sample contains more than a single phase cannot be excluded.

### Search-match results evaluation

When the search-match calculation has finished, you should investigate the resulting entries in the candidate list, and finally select the matching phases, just as it has been described in the “Quick start” chapter. Typically, the phases that are more likely to be present can be found close to the top of the candidate list, as indicated by their higher FoM-values. However, there may be reasons to disregard entries despite they have a large FoM-value, e.g. if they contain elements that cannot be present in the sample.

### Search-match based on marked peaks only




Normally, the search-match calculation in Match! is based on all diffraction peaks (at least on those that are not located in excluded ranges or that are disabled). However, it is also possible to run the search-match based on marked peaks only, by first marking one or more peaks and then running the “Search-Match (marked peaks only)” command in the “Search” menu (or pressing the keyboard shortcut <Ctrl+Shift+M>). Typically, the intention for this is to find/prefer phases who show a diffraction peak close to the marked peaks.

### Workflow for qualitative analysis using peak-based search-match

A common **strategy for qualitative analysis** using individually marked peaks goes like this:

1. Import your raw (profile) diffraction data, e.g. by pressing on the '+' button on the upper right-hand side of the pattern graphics.
2. Process your raw diffraction data carefully, until the profile calculated from the experimental peak data as well as the background is in reasonable agreement with the experiment. It is also essential to eliminate any potential 2θ axis errors (e.g. zero point or specimen displacement error) in this step.

<sup>17</sup> If no peak data but profile data are available when you run the “Search-match” command, Match! will automatically perform the raw data processing and determine the peak data.

3. Start with a full search-match calculation (menu command "Search/Search-Match", shortcut <Ctrl+M>, toolbar button  and the selection of a first (typically major) phase. The latter can e.g. be performed by double-clicking on the corresponding line in the candidate list.
4. Afterwards, a common strategy is to focus on experimental peaks that are not covered by identified phases yet. In order to make this easier, you can activate the "Show uncorrelated peaks" option, e.g. by pressing <Ctrl+Shift+U> or by using the menu command "View / Pattern / Uncorrelated peaks" .
5. Mark (click on) a peak that cannot be "explained" with the already selected phase(s), i.e. which has not been correlated to an identified phase yet.
6. Run the menu command "Search/Search-Match (marked peaks only)" (or press the keyboard shortcut <Ctrl+Shift+M> or the toolbar button ). Wait until the update of the candidate list (figure-of-merit values) has been completed.

If the result is not satisfactory, try to deactivate the options "Residual searching" and "Downgrade entries with low intensity scaling factors" on the "Search-Match" tab of the "Options" window.


7. Investigate the entries / phases at the top of the candidate list as usual and select one (or more) phases that you assume to be present, based on the results for the marked peak(s).
8. Match! will automatically run a new full search-match calculation (for all peaks) at this point, in order to update the figure-of-merit values for all reference database entries with regard to the new "situation" (list of selected phases as well as the peak intensities covered by them).
9. Repeat the steps 4-7 until the profile calculated from the selected phases (and the background) is in reasonable agreement with the experimental diffraction profile, so that it is rather likely that all phases in the sample have been identified.

If no reasonable phase is found when running a search-match calculation for one (or more) marked peaks, this could be due to one of the following reasons:

- Check if potential 2 $\theta$ -errors (e.g. zero point or specimen displacement) have been eliminated.
- Check the value of the parameter "2theta window for peak correlation" in the search-match options. This parameter value is used to determine if a certain reference diffraction pattern contains a peak at the position of the marked peak(s) or not.
- Consider that there may be no suitable phase (entry) present in the current reference database.
- The phase may be still unknown.

Please pay attention to the following hints, too:

- You can mark all peaks that have not been correlated to known phases yet using the menu command "Peaks/Mark uncorrelated peaks".
- If only raw (profile) but no peak data are present when a (full) search-match calculation is run, Match! will automatically execute the automatic raw data processing before the actual search-match is started.
- If you mark more than a single peak and run the command "Search-Match (marked peaks only)", the entries that contain one or the other marked peak(s) will be united (logical OR), because you cannot estimate if several peaks belong to the same or different phases at this stage.
- If the current FoM-values (ranking) in the candidate list is based on a search-match for marked peaks only, this is indicated by the following means:
  - The data of the corresponding peaks are displayed in **bold font** in the peak list.

- A '\*' character will be added to the column headers "P(2theta)", "P(I/I0)", "I scale fct." and "FoM" in the candidate list.
- The peaks that were used in this calculation are displayed in the pattern graphics with an increased line width.
- A blue button  is displayed in the status bar at the bottom. If you click on this button, the search-match calculation will be repeated for all peaks.
- The user can restrict the comparison with the pattern of the unknown sample to certain groups of database entries, by applying additional restraints (like chemical composition, color, density, crystallographic data, quality marks, PDF subfiles etc.), to keep the number of possible candidate phases as low as possible.
- A variety of options and parameters can be adjusted which affect the FoM-calculation. If your search-match calculation does not give a reasonable result, you should "play around" with the parameters a little bit to check how the results could be influenced (e.g. by reducing the effect of intensity differences in order to compensate for textural effects).
- You can clear the FoM values and all other results of a search-match calculation by running the "Reset search-match results" command from the "Search" menu. This might be useful e.g. if you are applying restraints and would like to check which entries would be present without the minimum figure-of-merit criterion.
- The FoM should only be one guide for the user to select the matching entries from the list of candidate entries, however, it should not be the only one. With most "real-live" samples it is necessary to also visually compare the diffraction patterns using the diffraction pattern graphics and the peak list.

### Profile fitting search-match (PFSM)

Match! offers the innovative profile fitting search-match (PFSM) as an alternative to the classical search-match based on peak data. PFSM fits the profile calculated from every candidate entry in the reference database to your experimental profile diffraction pattern. Afterwards, it creates a ranking list (candidate list) so that the entries/phases which fit best (i.e. have the highest FoM value) are located at the top. Finally, the user can evaluate the entries at the top of the list and select those which are most likely to be present in the sample ("matching entries/phases").

Additional information and more details about PFSM can be found in the chapter "Details about profile fitting search-match" below (p. 36).

### Workflow for qualitative analysis using profile fitting search-match

In general, there are only few steps to be taken for using PFSM in your qualitative phase analysis:

1. Import your raw (profile) diffraction data, e.g. by pressing on the '+' button on the upper right-hand side of the pattern graphics.
2. If required, adjust the background (orange curve) that has been calculated from the profile data automatically at pattern import, by dragging around the background control points (squares) with your mouse. It is rather **important that the background is defined correctly in advance** because it is currently **not refined during PFSM!**
3. If you have any information about the **elements that may be present** (e.g. from XRF or chemical analysis), **press the "Toggle" button** below the periodic table on the upper right-hand side (tab "Restrains / Composition"). This will mark all elements in red ("to be excluded").

Afterwards, **click on the elements that may be present** according to your knowledge about the sample. This will mark them in yellow color ("optional", "maybe present"), while the rest will remain excluded. You can also use other selection criteria (e.g. subfiles, like "Cement materials"), of course.

Here is an example:

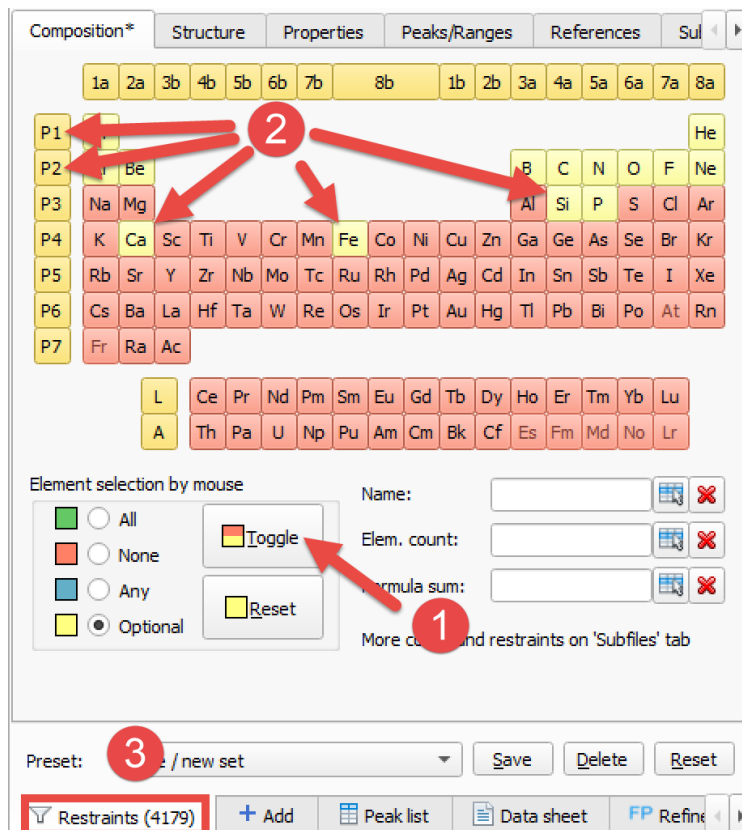



Fig. 9: Selection of elements that may be known e.g. from XRF: After pressing "Toggle" (1), click on "P1" and "P2" ("light elements" (LE)) as well as "Ca", "Fe", "Si" and "P" (2) (for example "advanced\_example.dat"). Only 4179 entries are left (3) for being investigated in PFSM.

4. Run profile fitting search-match, e.g. by pressing <Ctrl+Alt+M> (<Cmd+Alt+M> on the Mac), by running the command "Search-match using profile fitting" from the "Search" menu, or by pressing the toolbar button .
5. Select the matching phase(s). Match! will by default run another PFSM calculation after the selection of a phase ("residual searching").

Here is a screenshot that shows profile fitting search-match in action:

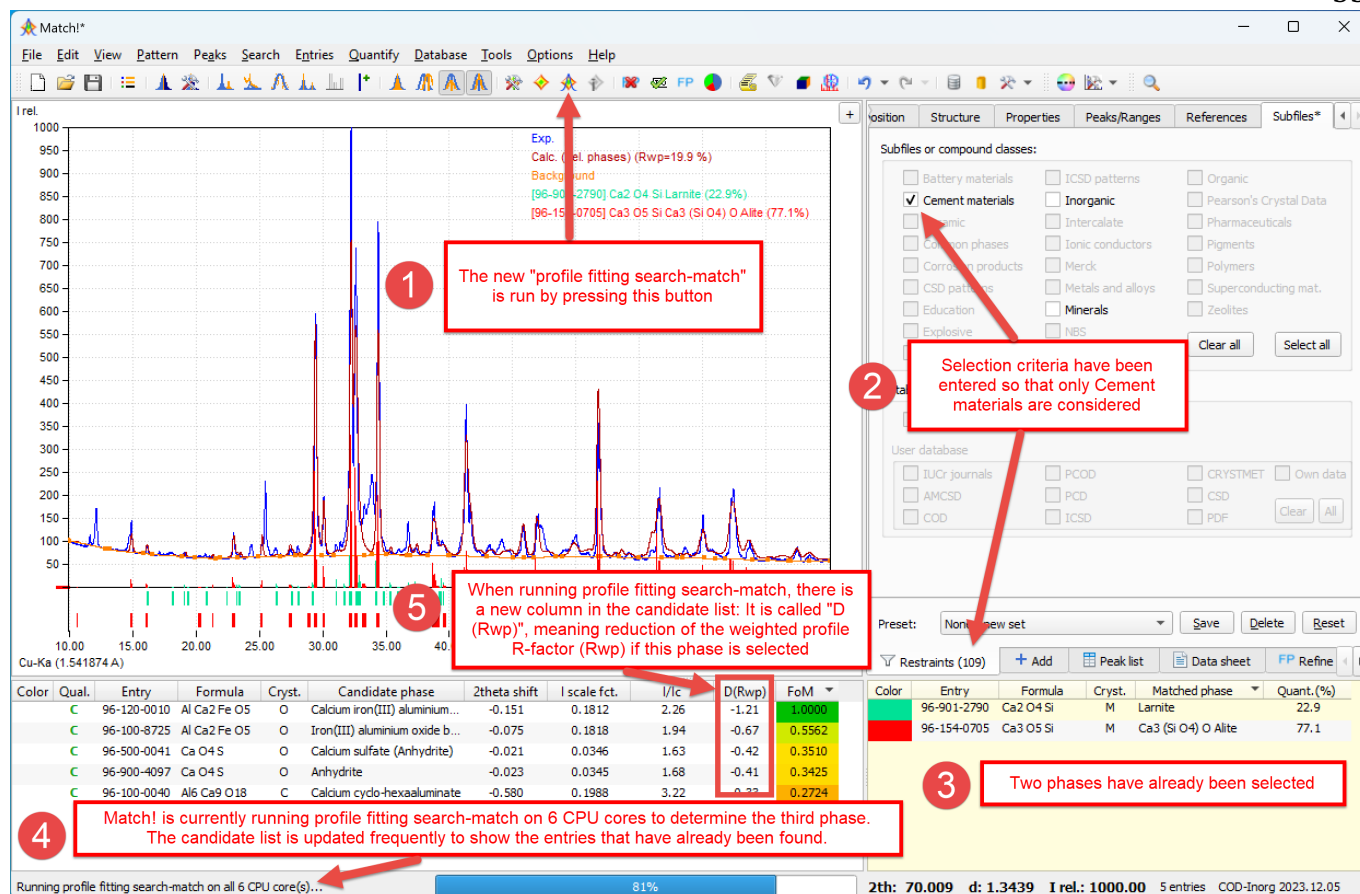


Fig. 10: Profile fitting search-match in action, working on a Cement sample

#### Explanations:

1. PFSM can be run using the menu command "Search / Search-match using profile fitting", by pressing <Ctrl+Alt+M> (<Cmd+Alt+M> on the Mac), or by pressing the toolbar button
2. We strongly recommend restricting the PFSM calculation to certain groups of phases, if you have additional information about the sample. In this example (Fig. 10), it was known a-priori that the sample was a Cement material. In other cases, it may be known that certain elements may be present or can be excluded (Fig. 9). In general, additional knowledge about the sample is applied by selecting **restraints** (p. 40).
3. Selected phases are collected in the **match list** as usual, along with their amounts if a quantitative analysis could be run automatically. Once you have selected a phase, PFSM is run again automatically by default, to find the next matching phase.
4. During the PFSM calculation, you can watch the progress in the status bar at the bottom. Here, you can also see how many CPU cores are used. If you would like to **stop the PFSM calculation**, simply **press <Esc>** on your keyboard.
5. During and after a PFSM calculation, the results that have already been obtained are collected and displayed in the **candidate list**. A few columns in the candidate list will be different compared to the normal (peak-based) search-match.

#### Please note:

- You should always keep in mind that **"false positives"** may result from profile fitting search-match if the **background is not marked properly**, i.e. if it is too low. On the other hand, **phases may be not detected** if the **background is too high**.
- Selecting reasonable elements helps to reduce the calculation time required for PFSM pretty much!
- **Include the first two rows of the periodic table (P1 and P2)** as "optional" (yellow) if you are using **results from XRF spectroscopy** where these "light elements" (LE) are usually not detected.



- If no reasonable phase is found when a search-match calculation has finished, you should check the following:
  - A variety of options and parameters can be adjusted on the "Search-Match" tab of the "Options" window which affect the FoM-calculation. If your search-match calculation does not give a reasonable result, you should "play around" with these parameters to check how the results could be influenced (e.g. by reducing "Min. Rwp reduction required" if minor phases are not detected).
  - Maybe you have already selected all phases that are present in your sample?
  - Consider that there may be no suitable phase (entry) present in the current reference database, or that the phase may even be still unknown.
- After a profile fitting search-match calculation has been run, the FoM values in the candidate list are relative, with the best-matching entry (the one that reduces the Rwp most) being attributed FoM=1.0. Therefore, there **still may be candidate entries with a "promising" high FoM value even if all phases in the sample have been selected!**

To avoid selecting "false positives" in this situation, please also check the values (columns) "I scale fact." and "D(Rwp)" in the candidate list. If these values are rather low (close to zero), it is not very likely that these phases are present.

- You can adjust both the **minimum intensity scale factor** as well as the **minimum Rwp reduction** required for entries being **displayed in the candidate list** on the "Search-Match" tab of the "Options" window (section "Profile fitting search-match (PFSM)").
- Once a PFSM calculations has been finished, the following options will be activated automatically:
  - Graphics / Display profile calculated from selected phases
  - Candidate list / Include marked candidate list entries in profile calculation
- The FoM can be a good guide for the user to select the matching entries from the list of candidate entries, however, **it should not be the only one**. With most "real-live" samples it is necessary to also compare the diffraction patterns using the diffraction pattern graphics visually.
- You can **clear the FoM values** and all other results of a search-match calculation by running the "**Reset search-match results**" command from the "Search" menu.

### Details about profile fitting search-match

"Profile fitting search-match" (PFSM) is a powerful, innovative alternative to the proven peak-based search-match functionality for qualitative phase analysis (p. 30). PFSM **fits the profile** calculated from each candidate entry of the current reference database (or answer set) to the experimental profile on the fly.

### Advantages of PFSM

One of the main advantages of PFSM is that the sometimes-ambiguous peak searching is no longer required for qualitative phase analysis, thus avoiding the ambiguities that may arise from this.

Due to this, the success rate of PFSM is higher than the "classical" (peak-based) approach (especially with minor or trace phases), **provided that the background is set correctly before running the calculation**.

Another important advantage (compared to the Rietveld refinement search-match approaches cited below) is that PFSM in Match! can use **common peak data reference databases**, like the COD, ICDD PDF-2, PDF-4, PDF-5+, own diffraction patterns etc. **The knowledge of atomic parameters for the candidate phases is not required!**

### How it works

PFSM in Match! works without additional software, i.e. no Rietveld software (like FullProf) is required. To be clear, **no Rietveld refinement is performed**, because **no crystal structure parameters are refined**.

Instead, Match! calculates a profile pattern for every entry of the reference database (or answer set), fits both the **intensity scale factor** as well as the **2theta shift** in order to get an optimum agreement with the experimental profile



diffraction pattern, and finally stores the Rwp value reduction that could be achieved (along with the corresponding intensity scale factor and 2theta shift parameter values).

The **background is not refined** during the PFSM calculation, to avoid any ambiguities that may result when doing so. Hence, it is rather **important** to make sure that the **orange background curve in the pattern graphics is in perfect agreement with the background** that you estimate "by eye" before running the PFSM calculation!

### Display of results

During the PFSM calculation, all candidate entries for which the profile fitting has already been performed are displayed in the candidate list (at least if the corresponding option is active). The candidate entries are ranked according to decreasing reduction of the Rwp value (D(Rwp)) that could be achieved during the corresponding fit (taking into account the already selected phases).

Since the results are ranked according to decreasing reduction of the Rwp value, the **phases are normally identified in the same order as they contribute to the diffraction profile**. Usually, the phase with the highest amount is selected first and the phase with the lowest amount last (also depending on their scattering power, of course).

### Calculation times

While the success rate of PFSM is higher than the "classical" (peak-based) approach (especially with minor or trace phases), there is certainly one main drawback: The calculation time is significantly longer.

To compensate for this to a certain degree, **PFSM is by default run in parallel** on all available cores of your CPU<sup>18</sup>.

Here are a few hints what you can do to speed-up the calculation:

- **Use any additional information available** about the sample, e.g. by selecting elements that may be present or can be excluded (known e.g. from XRF), and / or by selecting a suitable application context (e.g. "Cement materials") as subfiles.
- Calculations may also be sped-up by **removing (trimming) the high-angle part of your diffraction pattern** (e.g. the range beyond 70-80 degrees 2theta), especially if it contains only small or even no peaks.
- If available, **use a computer with more CPU cores**.

Please note though that the improvement that may be achieved by this can be lower than expected, especially if the individual profile fitting calculations take only a very short time. The main reason is that in these cases the calculation time will be dominated by the internal administrative tasks to distribute the calculations to the individual cores and collecting the results afterwards.

- Although we do not generally recommend it, you can also speed-up the PFSM calculations by **reducing the resolution of your diffraction data**. You can do so by running the "Decrease resolution..." command from the "Pattern" menu.

### Some important facts and hints

- During PFSM, the intensity scale factor and 2theta shift parameters of already selected (match list) entries are refined along with each individual candidate entry, **but the resulting values** (intensity scale factor and 2theta shift) **are not retained in the match list entries**. The background is that these values may only be reasonable for the current but not for other candidate entries.
- Due to the inclusion of the already selected phases (match list entries) in the profile fitting calculation, PFSM takes longer when more entries are present in the match list.
- The FoM values in the candidate list obtained from PFSM are relative, with the best-matching entry (the one that reduces the Rwp most) being attributed FoM=1.0.

Therefore, there still may be candidate entries with a "promising" high FoM value even if all phases in the sample have been selected! To avoid selecting "false positives" in this situation, please also check the values

<sup>18</sup> It is also possible to restrict the calculation to a lower number of CPU cores (or even to a single core), to keep your computer more "responsive" for other tasks. You can do so in the section "Profile-fitting search-match (PFSM)" on the "Search-Match" tab of the "Options" window.

(columns) "I scale fact." and "D(Rwp)" in the candidate list. If these values are rather low (close to zero), it is not very likely that these phases are present.

The background is that especially after all phases present in the sample have been selected, there may remain entries in the candidate list with low intensity scale factor but a lot of peaks that "mimic" the background and the noise in the diffraction data.

- Do not mismatch PFSM with profile fitting! **PFSM** uses the profile calculated from **reference database entries**, while **profile fitting** is operated on the experimental peak data.

### References for profile fitting search-match

Profile fitting search-match as it is now implemented in Match! has not been invented "out of the blue" but has been inspired by other approaches, most of which use Rietveld refinement for qualitative phase analysis:

- Döbelin, N., Kleeberg, R., "Profex: a graphical user interface for the Rietveld refinement program *BGMN*", Journal of Applied Crystallography **48** (2015), 1573-1580. doi:10.1107/S1600576715014685
- Luca Lutterotti: "Full Profile Search Match (FPSM)": Lutterotti, L. et al., "Full-profile search-match by the Rietveld method", J. Appl. Cryst. **52** (2019).
- SNAP-1D:  
C. J. Gilmore, G. Barr and J. Paisley, "High-throughput powder diffraction. I. A new approach to qualitative and quantitative powder diffraction pattern analysis using full pattern profiles", J. Appl. Cryst. **37**, 231-242 (2004).

and

Barr, G., Gilmore, C. J. & Paisley, J., "SNAP-1D: a computer program for qualitative and quantitative powder diffraction pattern analysis using the full pattern profile", J. Appl. Cryst. **37**, 665-668 (2004).

### Direct searching for individual peaks

As an alternative to the peak-based or profile fitting search match functions just described, you can also directly search the reference database for entries that have peaks at certain  $2\theta$  (or d-value) positions (or in ranges). This can be achieved on the "Peaks/Ranges" page of the **Restraints** tab. There are two different tabs/approaches available for this:

- **Ranges:** You can define  $2\theta$  ranges in which accepted diffraction patterns (entries) must have at least one peak, or in which accepted entries **must not have** a peak (depending on "Mode").
- **Strong lines:** Here you can define one or more peak positions for up to three strongest peaks, similar to the well-known Hanawalt- or Fink-searching.

All this can be accomplished on the "Peaks/Ranges" sub-tab of the "Restraints" tab on the right-hand side of the windows. See also the chapter "Searching for entries (restraints and additional entries)" below.

### Ranges

On this tab you can select entries that contain one or more peaks in certain ranges. For example, it is possible to search for entries that contain at least one peak in each of the ranges  $23.07..23.09^\circ$ ,  $43.1..43.3^\circ$  and  $50.1..50.2^\circ$  (Fig. 11). This is sometimes useful if e.g. a few experimental peaks are still uncorrelated after you have run a search-match calculation and identified the matching phases based on the FoM-values.

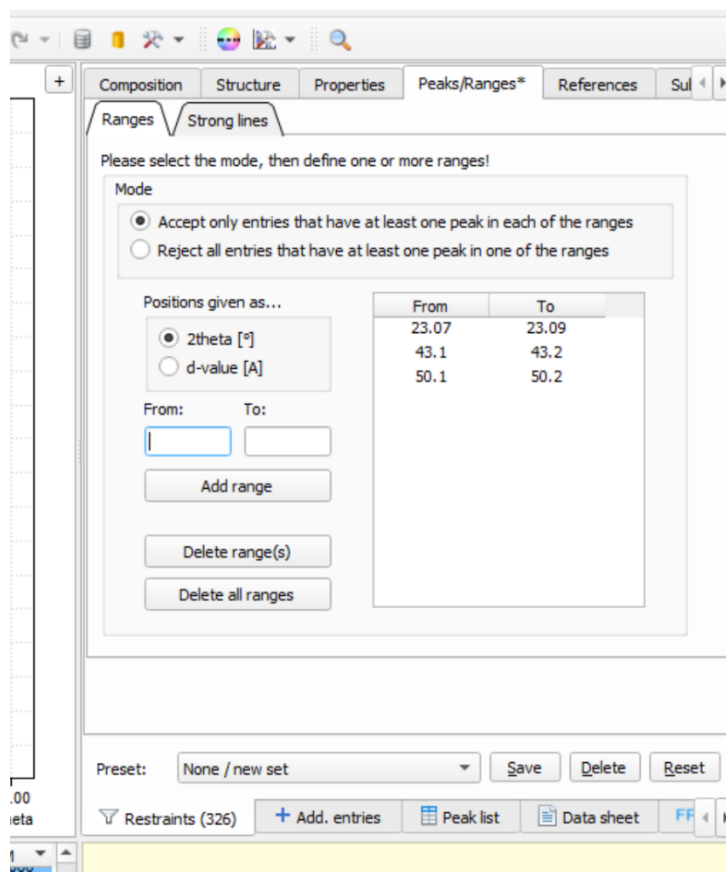


Fig. 11: You can search for entries containing peaks in certain ranges on the “Peaks/Ranges” sub-tab of the “Restrains” tab. In this case, 354 entries contain at least one peak in each of the range 23.07..23.09°, 43.1..43.3° and 50.1..50.2°.

In a similar manner, it is also possible to exclude all entries that contain at least one peak in one of the ranges given (using the “Mode” option at the top of the “Peaks/Ranges” sub-tab).

### Strong lines

On the “Strong lines” tab you can enter positions of peaks (“lines”) that must be present among the three strongest peaks in a diffraction pattern. In addition to the peak position (given as d-value) you can define a tolerance and select if you would like to search for this peak as the strongest (1.), second-strongest (2.) and/or third-strongest peak (or any combination of them) (Fig. 12).

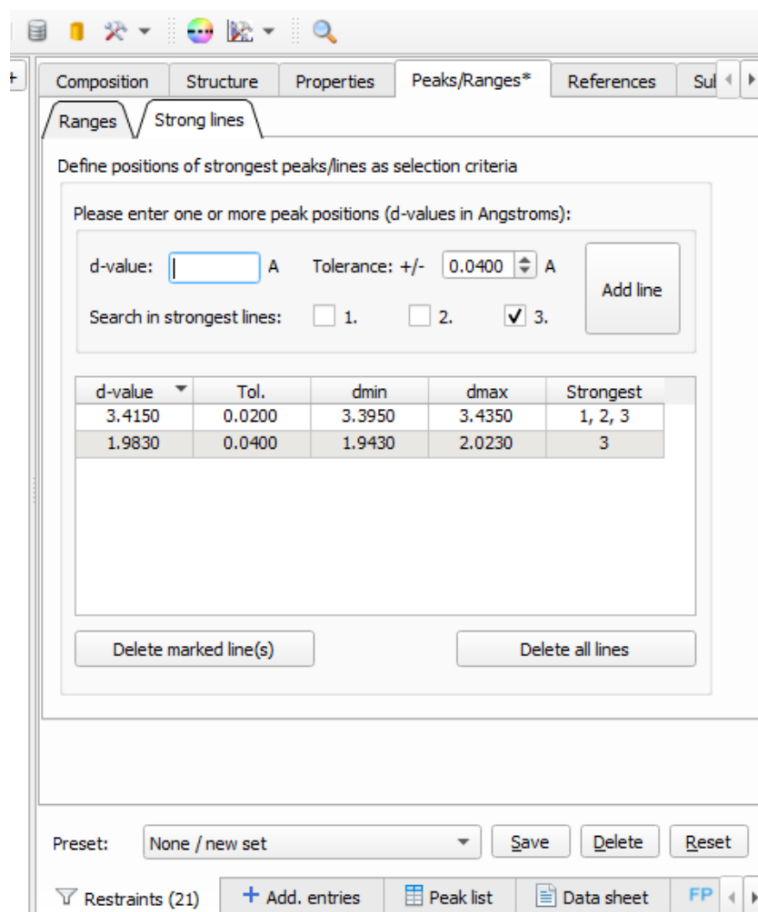


Fig. 12: Searching for strongest lines (Hanawalt- or Fink-index searching)

Once you have entered the d-value to be searched for (and maybe the tolerance and strongest lines order), please press the **Add line** button in order to add this line position to the table below and apply it as selection criterion.

You can of course enter more than a single line position, so that you can work with this feature similar to the Hanawalt- or Fink-indices.

**Please note:** You can quickly open the “Strong lines” selection criteria page by pressing <Ctrl+H> (<Cmd+H> on the Mac) and entering the first line position straight away.

## Searching for entries (restraints and additional entries)

### Search for specific phase/entry

Sometimes you would like to quickly view a certain entry/phase from the reference database, e.g. if you know that this phase is present in your sample.

The easiest way to do so is to press <Ctrl+F> (<Cmd+F> on the Mac), type the name (formula sum or entry number) of the phase you are looking for in the small window that opens, and press <Return>. Match! will instantly display and mark the best-matching entry in the candidate list at the bottom left, and at the same time display its diffraction pattern in the graphics pane.

You can now use the commands from the “Entries” menu e.g. in order to select this entry as “matching” (by pressing the <Space> bar), to use it as an internal 2theta standard (by pressing <Ctrl+T>), to **load it as an additional experimental pattern** (by pressing <Ctrl+Shift+T>), or to display the complete entry data (data sheet) by pressing <Ctrl+D>.

The “search for specific phase” feature is extremely useful in a variety of situations:

- Sometimes you already know that one or more phases are present in your sample and would like to quickly select these phases before getting into the details of determining the remaining phases.

- In other cases, you have the suspicion that a certain compound might be present and would like to quickly view a corresponding reference pattern to check it.
- Maybe you would like to quickly find and highlight a certain phase, to use it as an internal standard for the correction of 2theta-errors?
- Finally, this is also a convenient way to quickly display the data sheet of a certain compound.

Here is a quick example: Suppose that you have imported your experimental diffraction data, run the raw data processing, and performed a first search-match run, to calculate the figure-of-merit (FoM) values of the candidate entries. Now you are ready to perform your actual phase analysis. Your screen might look like Fig. 13:

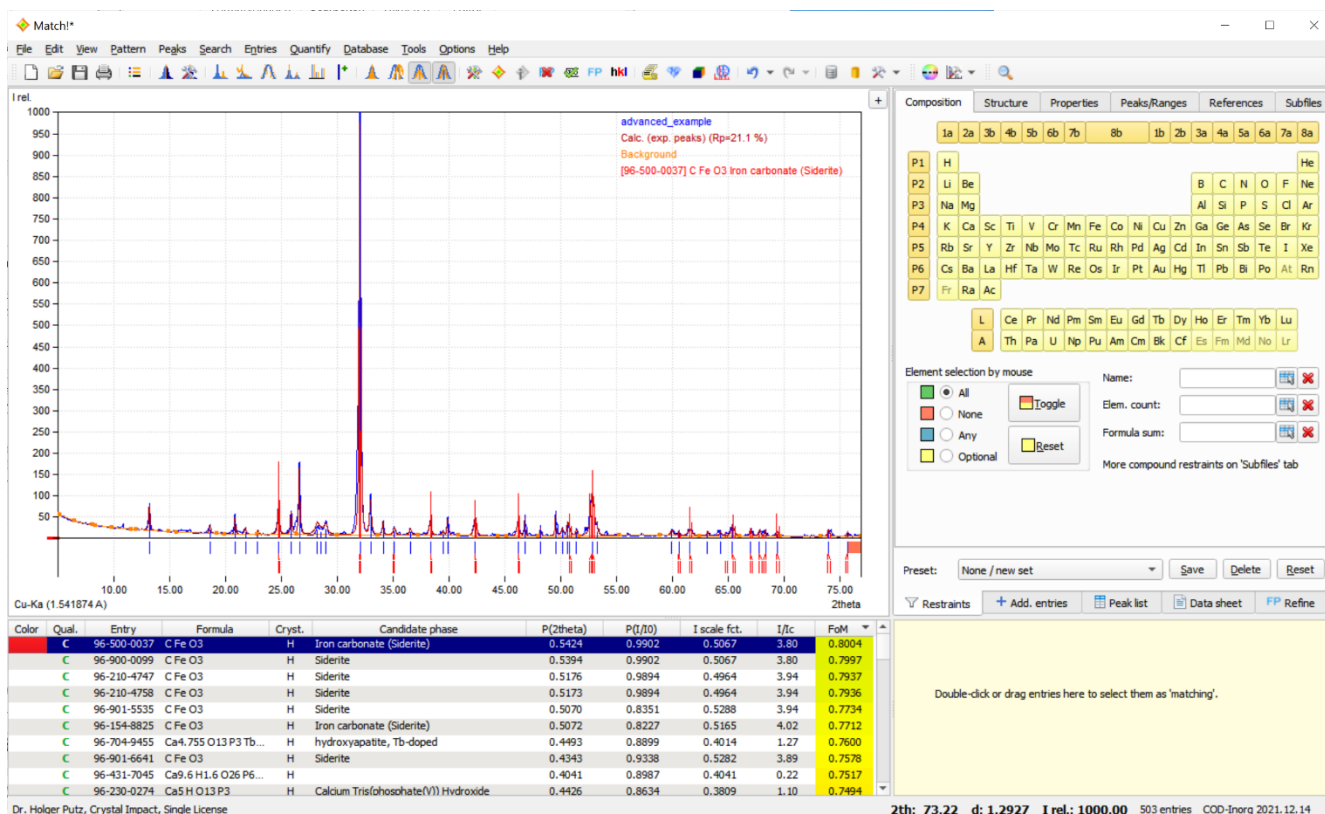


Fig. 13: That's what the screen looks like having imported and processed the raw data, as well as run the search-match calculation.

Now, you would like to find and display the diffraction pattern of quartz. In order to do so, simply press <Ctrl+F> on your keyboard (<Cmd+F> on the Mac), type 'quartz', and press <Return>. The best matching 'quartz' entry will automatically be highlighted in the candidate list and displayed in the diffraction pattern (Fig. 14).

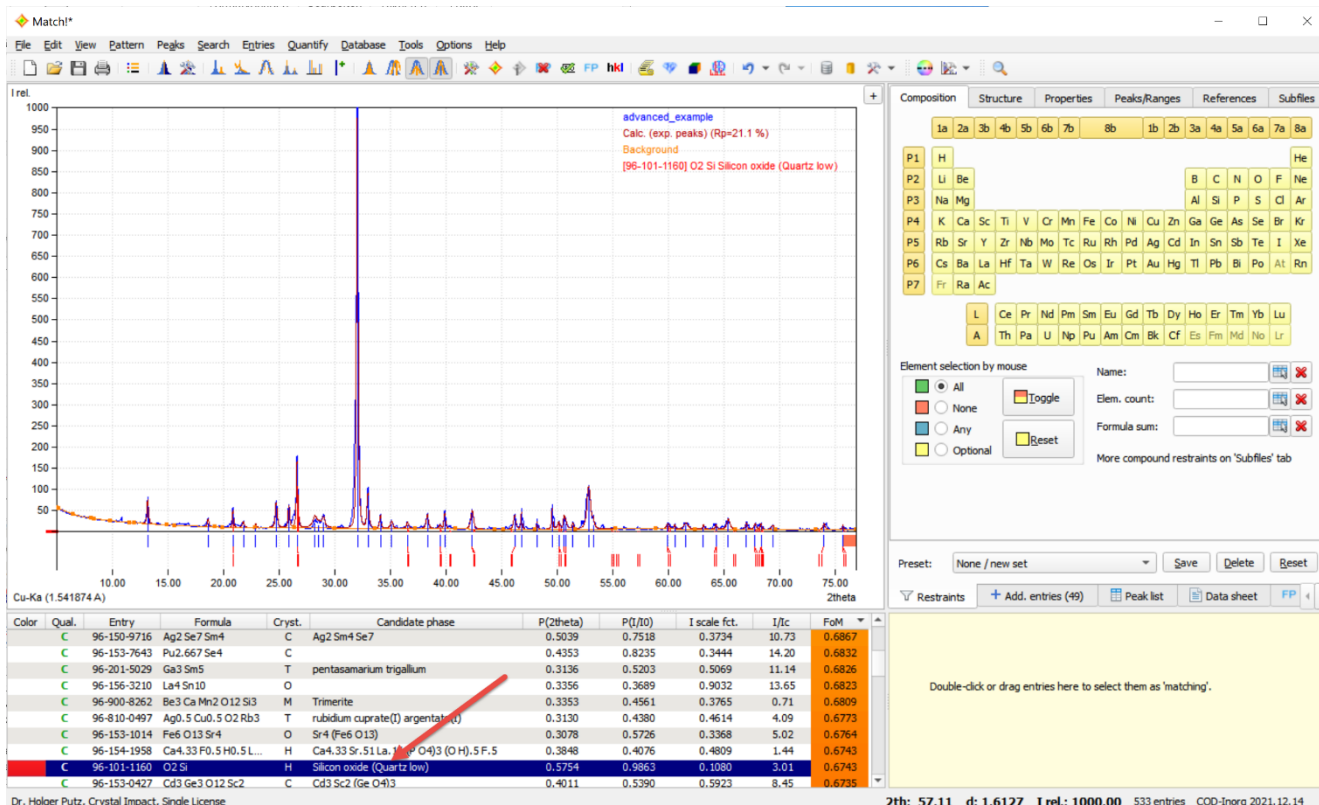


Fig. 14: Once you have pressed <Ctrl(Cmd)+F> and entered your selection criterion ("quartz" in this case), the best-matching corresponding entry will automatically be highlighted in the candidate list.

The best matching entry for 'quartz' has already been marked in the candidate list, so you can instantly use it as an internal standard for the correction of the 2theta-error. In order to do so, simply press <Ctrl+T>. The new (corrected) 2theta values of the experimental peaks will be taken into account automatically in all 'views' of the data, resulting for example in an automatic update of the candidate list.

Due to the correction, the overlap between the experimental and the 'quartz' reference pattern has become better, resulting in an increased figure-of-merit (FoM) value for this phase/entry. As a result, it will now be displayed closer to the top of the candidate list (Fig. 15).

Color	Qual.	Entry	Formula	Candidate phase	P(2theta)	P(I/I0)	I scale fct.	I/Ic	FoM
	C	96-700-1907	Ca10 Cu H O26 P6	Alkaline-earth Apatite	0.4749	0.8499	0.4336	1.60	0.8202
	C	96-900-2217	Ca5 H2 O13 P3	Hydroxylapatite	0.5421	0.9543	0.2254	1.59	0.8202
	C	96-901-0053	Ca5 H2 O13 P3	Apatite-(CaOH)	0.5421	0.9543	0.2254	1.59	0.8202
	C	96-710-3015	O2 Si		0.8166	0.9991	0.1662	4.46	0.8191
	C	96-500-0036	O2 Si	Silicon oxide (Quartz)	0.8162	0.9992	0.1661	4.66	0.8189
	C	96-901-3551	Ca4.961 F O12 P3 Th0.039	Fluorapatite	0.5641	0.9561	0.2379	1.77	0.8187
	C	96-901-3556	Ca4.961 F O12 P3 Th0.039	Apatite-(CaF)	0.5641	0.9561	0.2379	1.77	0.8187
	C	96-101-1098	O2 Si	Silicon oxide $\beta$ -alpha (Quart...	0.8150	0.9993	0.1658	4.43	0.8186
	C	96-101-1173	O2 Si	Silicon oxide $\beta$ -alpha (Quart...	0.8113	0.9992	0.1661	4.64	0.8180
	C	96-901-3322	O2 Si	Quartz	0.8096	0.9993	0.1660	4.74	0.8176
	C	96-101-1160	O2 Si	Silicon oxide (Quartz low)	0.8047	0.9990	0.1664	4.82	0.8168

Fig. 15: In the candidate list, the best-matching entry corresponding to the criterion "quartz" has been marked automatically.

Now you can easily select the 'quartz' entry as matching: Since it is still marked in the candidate list, simply press the space bar to do so. Once the entry has been transferred to the Match list on the right-hand side, the candidate list will instantly be updated, and the next best matching entry (Siderite in this case) will be highlighted (Fig. 16).

Color	Qual.	Entry	Formula	Candidate phase	P(2theta)	P(I/I0)	I scale fct.	I/Ic	FoM	Color	Entry	Formula	Matched phase	Quant.(%)
C	96-900-0099	C Fe O3		Siderite	0.8715	0.8174	0.7931	4.13	0.8676		96-500-0036	O2 Si	Silicon oxide Quartz	100.0
C	96-500-0037	C Fe O3		Iron carbonate (Siderite)	0.8675	0.8173	0.7931	4.13	0.8668					
C	96-900-1233	Ca5 F O12 P3		Fluorapatite	0.7871	0.9598	0.2311	1.63	0.8662					
C	96-900-1346	Ca4.825 Ce0.165 F0.74 H2 Na0.01 O12.26 P2.8		Fluorapatite	0.7079	0.9639	0.2387	1.82	0.8569					
C	96-210-4747	C Fe O3		Siderite	0.7986	0.8178	0.7935	4.14	0.8536					
C	96-210-4758	C Fe O3		Siderite	0.7979	0.8178	0.7935	4.14	0.8535					
C	96-900-1673	Ca4.331 F Na0.257 Nd0.409 O12 P2.841 Si0.159		Fluorapatite	0.6653	0.9671	0.2455	2.09	0.8524					
C	96-900-2214	Ca5 H O13 P3		Hydroxylapatite	0.6797	0.9601	0.2295	1.62	0.8504					
C	96-700-1906	Ca10 Cu0.20 H1.28 O26 P6		Alkaline-earth Apatite	0.6559	0.9585	0.2287	1.66	0.8436					
C	96-900-1879	Ca5 F O12 P3		Fluorapatite	0.6607	0.9607	0.2302	1.65	0.8436					
C	96-100-8828	Ca9 F1.5 Nd O24.25 P5 Si		Calcium neodymium phosph...	0.6434	0.9673	0.2531	2.25	0.8428					

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2th: 63.94 d: 1.4548 I rel.: 1000.00 1858 entries COD-Ingva REIV40301 2015.07.0

Fig. 16: The best-matching entry for "quartz" has been selected as "matching".

In practice, you could now compare and select the next best matching entry as well, simply by pressing the space bar again and so on, until you have identified all phases in the sample.



## Instant usage of additional information (“restraints”)

It is very easy to directly use any kind of additional information about the sample (like the elements that can or must be present). The aim is to restrict the entries in candidate list to those that match certain criteria (“restraints”).

All corresponding selections are made on the “Restrains” or “Additional entries” tabs on the upper right-hand side, and the results are instantly reflected in the candidate list at the bottom of the screen (and of course also apply to the entries that are investigated during the search-match calculation). This technique is called “perpetual restraining” and is also used in other software products, e.g. “Pearson’s Crystal Data”.

For example, if you would like to keep only compounds (i.e. entries) that contain the elements Si and O, simply click on these two elements on the “Composition” sub-tab of the “Restrains” tab, so that the color of these elements switches to green. Your candidate list at the bottom will instantly be updated accordingly.

You can also use other selection criteria, like the name, the formula sum, crystallographic data, physical properties, peak positions, bibliographic data etc.

For example, suppose that you know that the element oxygen (O) must be present in all matching phases. In order to use this information, simply click on the corresponding button in the periodic table on the upper right-hand side; Match! will instantly apply this additional information to the current answer set (table “candidate list” at the bottom; Fig. 17).

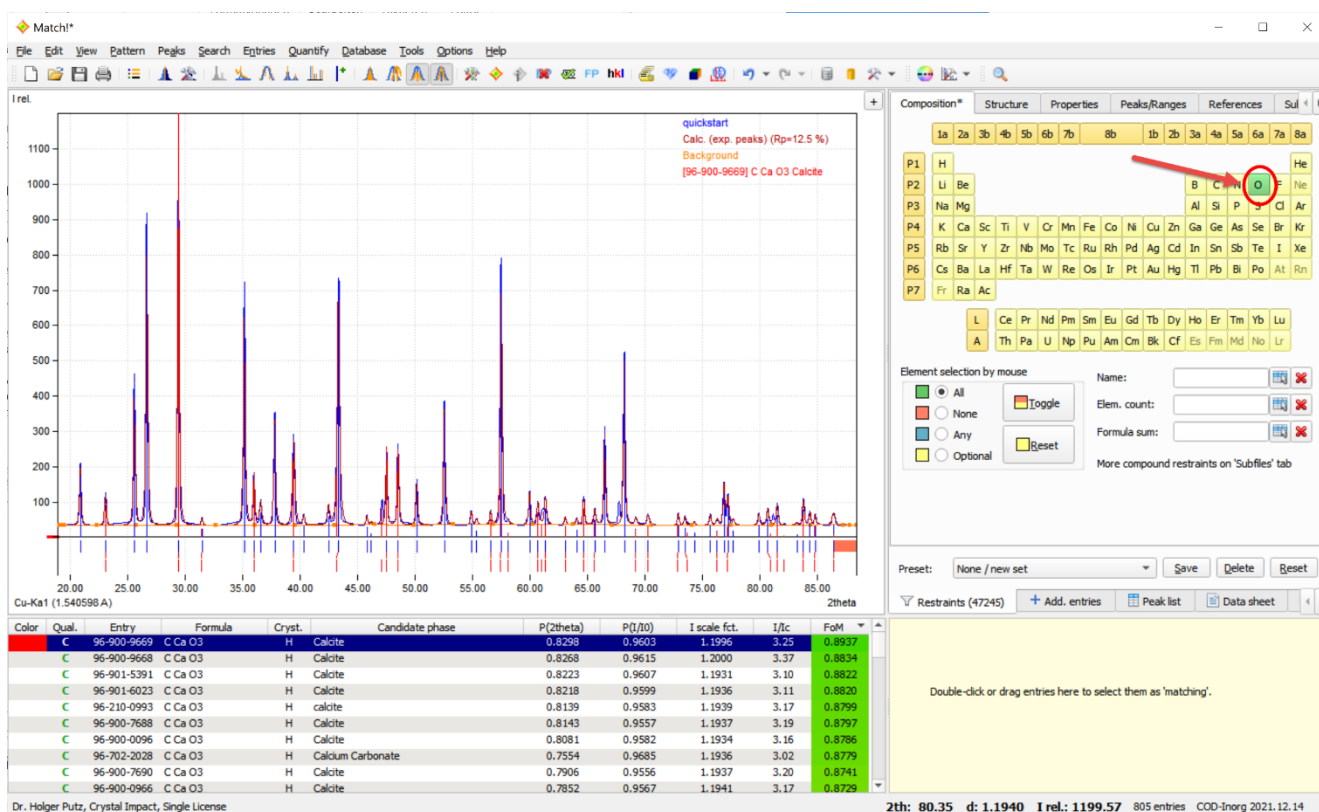


Fig. 17: Once you have pressed the “O” button in the periodic table on the upper right-hand side, the corresponding selection criterion will instantly be used in the candidate list on the left.

As you see, Match! uses the same perpetual restraining mechanism that you may already know from “Pearson’s Crystal Data”: While entering your selection criteria, any modification will instantly be reflected e.g. in the table of resulting entries and the entry count.

As an example, we assume that you would like to enter the additional information that the element Si must be present. In order to do so, simply press on the element “Si” in the periodic table on the upper right-hand side. The candidate list at the bottom is instantly modified: All entries for CaCO3 (Calcite) that were present before are now gone, and the number of entries matching your selection criteria (displayed to the right of “Restrains” on the tab control) has been significantly reduced (from 1632 to 399; Fig. 18).



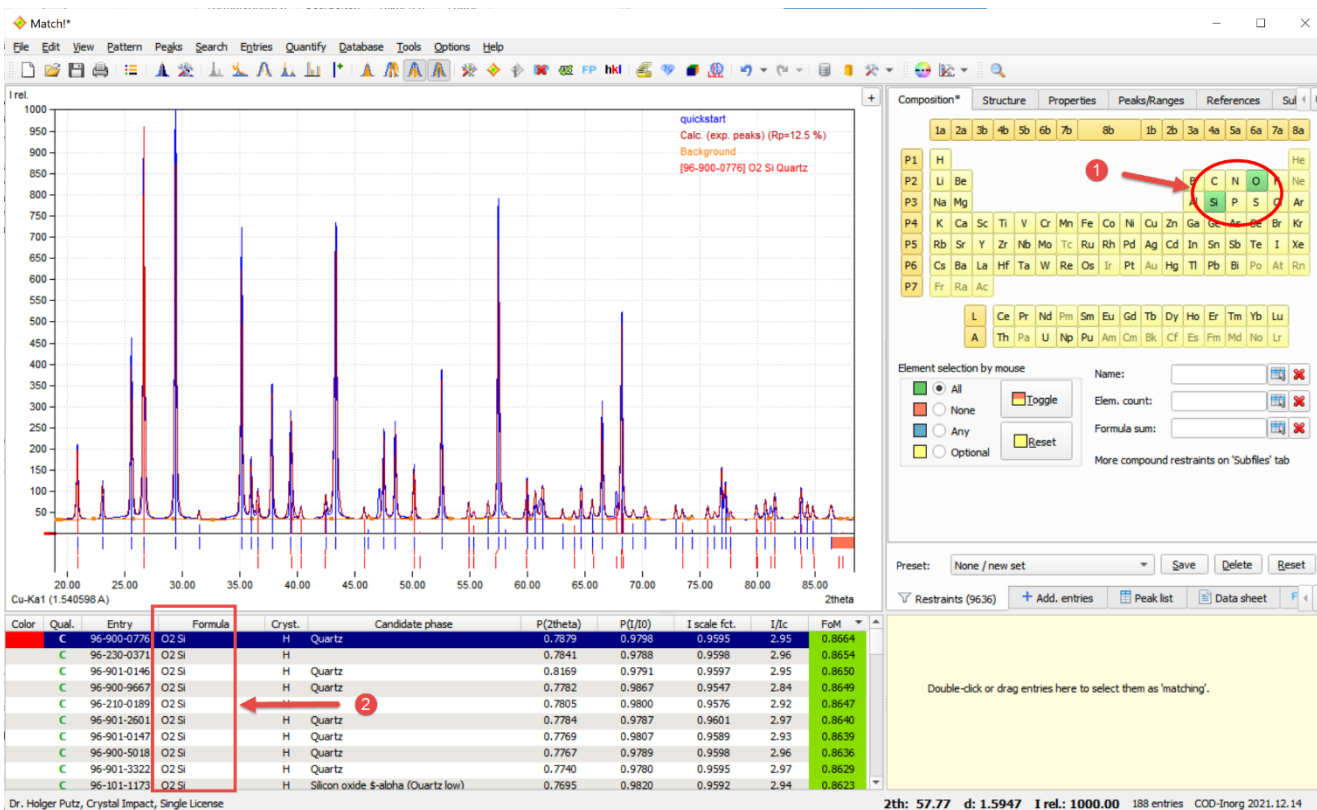


Fig. 18: After you have clicked on a second element "Si", only compound containing both Si and O remain in the Candidate list.

In a similar manner, it is also possible to add specific entries to the table of candidate entries (candidate list): Simply click on the tab "Additional entries"; this will bring up a totally equivalent set of tab sheets like the "Restrains" set. You can now define precisely which entries you would like to add to the candidate list even though they do not match the "Restrains" criteria.

### Add entries that match certain criteria to candidate list ("additional entries")

If you are missing certain phases in the candidate list, you can add them using the "Add, entries" tab on the right-hand side. Similar to the restraints just mentioned, the selection criteria are entered on sub-tabs of the "Add. Entries" tab on the right-hand side. The same selection criteria are available for restraining and adding of entries.

Note that adding specific entries does not necessarily mean that they are immediately marked/displayed in the candidate list (like it would be the case when using the "Find phases/entries" functionality mentioned above)! Adding entries just makes sure that they are present in the current answer set. If the number of entries in the current answer set is sufficiently low (i.e. below the "Max. number of entries" which can be defined on the "candidate list" tab of the "Options" dialog), the additional entries are present somewhere in the candidate list, typically at its bottom because their figure-of-merit is normally rather low.

### Add entries that match certain criteria to match list ("select as matching")

If you already know right from the beginning of an analysis that one or the other phase is present in your sample, you can select these phases directly, without having to detect them using the normal search-match procedure. To do so, simply press <Ctrl+E> (<Cmd+E> on the Mac). This will open a small window where you can enter the mineral name(s), entry number(s) or formula sum(s) of the compounds you would like to add directly. If you would like to give multiple names or numbers, please separate them by semi-colon (;).

If multiple entries from the reference database are in agreement with the information you have entered, another window will open in which you can mark the actual entries to be selected in the column "Select". Once you have marked all entries (phases) you know to be present, please press "OK". They corresponding entry(s) will be added to the match list.

### Saving of selection criteria (presets)

If you are frequently using the same restraints (selection criteria), you will instantly know what this feature is about: You can easily save the current selection criteria and recall them later on with just two mouse clicks. Of course, it is possible to save several sets of selection criteria.

You will find the corresponding control elements at the bottom of the “Restrains” (and “Additional entries”) tab to the right of “Preset:” (Fig. 19).

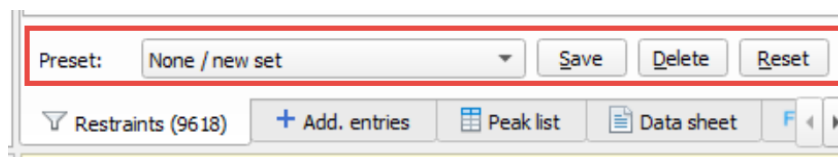


Fig. 19: Using these buttons at the bottom of the periodic table, you can easily save and recall all kinds of restraints/additional entry settings.

In order to save the current selection criteria, simply press the “Save” button. Afterwards, you have to enter a name using which you can easily identify this set of selection criteria later on (“Silicon compounds” in our example).

Your selection criteria will then be stored in your personal settings (e.g. Windows registry). If another person is using the same computer, he can store his own selection criteria independent from yours (of course assuming that he is using his own account on this machine...).

If you would like to recall a certain set of selection criteria, simply press the “arrow down” button of the combo box to the left of the “Save” button and select the name of the desired selection criteria from the list that opens.

That’s it! The selection criteria that have been loaded will instantly be applied to the table of candidate entries (candidate list), and of course also to the entries that are investigated during the search-match calculation.

### Background information on searching and restraining


Using the entry searching and restraining facilities of Match! is rather straight forward in most cases, however, there may be circumstances in which an in depth knowledge of the logical concepts behind the “Restrains”, “Additional entries” and “Find phases/entries” functionality may be helpful:

First of all, the **candidate list** in the bottom left corner of the Match! program window displays a list of all entries in the **current answer set**, the entry number of which is always displayed in the status bar at the bottom to the left of the reference database name (in the corner on the lower right-hand side).

Right after you have started Match! or run the “File/New” command, the “current answer set” contains all entries from the current reference database. Typically, these are 40.000 to 400.000 entries, so it would take a lot of time and memory (and wouldn’t even make much sense) to load and display the entry data of all reference database entries into the candidate list. Hence, Match! displays a message instead, asking you to do something in order to delimit this large amount of entries in order to find out which entries you are interested in, e.g. to import diffraction data and run a search-match, or to enter selection criteria (restraints).

For example, if you import diffraction data and run a search-match calculation, a figure-of-merit value (FoM) is calculated for each entry, so the criterion “Minimum FoM” (which can be adjusted in the lower left-hand corner of the “Search-Match” tab of the “Options” dialog) can be applied to restrict the answer set to only those entries whose figure-of-merit is above this user defined value, in order to select the entries that best match your diffraction pattern.

Another possibility to delimit the full amount of reference database entries to the ones you are interested in is to enter selection criteria (e.g. name) on the “**Restrains**” tab on the right-hand side. This tab offers a large amount of selection criteria like elements that must or must not be present.

Some of these selection criteria are text fields, like e.g. “Name”. If you enter some text here, only reference database entries that **exactly** contain this text in the corresponding database field are accepted to be included in the answer set. In order to help you here, Match! can display a list of all corresponding values in the reference database so that you can directly select from this list. This “List selection box” is displayed by pressing the corresponding button  to the right of a text field input line. You can also use the wild card character “\*” to tell Match! to disregard text before and/or after the fragment you have entered (e.g. “\*corundum\*”), however, Match! still distinguishes between capital and small characters within the fragments (case-sensitive comparison).

Once you have delimited the full amount of reference database entries in one or the other way, you have obtained an answer set (a set of selected entries below the full reference database), the entries of which can now be displayed in the candidate list. However, there is another limitation for this, i.e. the “Max. number of entries” setting at the top of the “Candidate list” tab sheet of the “Options” dialog. Normally, the candidate list will only be filled with entries if the current answer set does not contain more than this number of entries. If the number of answer set entries is

larger than this value, a corresponding message “Too many matching entries” is displayed in the candidate list instead of the entries, instructing you to further delimit the current answer set e.g. by entering additional entries.

So far for the candidate list, the current answer set and the “Restrains” tab.

The “**Add. Entries**” (additional entries) tab does something different: While normally the current answer set (→ candidate list) only contains entries that match all “Restrains” criteria as well as the “Minimum FoM” criterion (if applicable), the “Add entries” tab allows you to add specific entries regardless of these criteria. This may be useful for example if you know that a certain phase/entry is present in your sample but has not been assigned a figure-of-merit value larger than “Minimum FoM” in the last search-match calculation. Hence, you most probably would like to add this entry to the answer set/candidate list, in order to check what caused the low FoM value, like missing/undetected peaks, a strong 2theta shift, or a very low intensity scaling factor.

To do so, you can enter selection criteria (e.g. name) on the “Add. Entries” tab, just like on the “Restrains” tab. The number of entries that match these selection criteria is displayed in brackets behind “Add. Entries” on the tab; these entries are then added to the ones selected by “Restrains” and/or the “Minimum FoM” criterion. Typically, you will find these additional entries at the bottom of the candidate list because their figure-of-merit values are low (quite often close to 0.0).

As you can imagine from these explanations, the usage of the “Add. Entries” tab only makes sense if the current answer set does not already contain the full reference database (in which case there would be no more entries that could be added). Hence, the “Add entries” tab is inactive in this case in some earlier versions of Match!.

The “**Find phases/entries**” functionality in the top right corner of the Match! window is pretty much some kind of mixture between these two facilities (“Restrains” and “Add. Entries”): Once you have entered some criterion (e.g. name) in the corresponding line at the top and pressed <Return>, Match! searches for matching entries in the reference database. It then checks if these entries are present in the current answer set. If this is not the case, it adds these matching entries, using the “Add. Entries” mechanism, by automatically entering the corresponding entry numbers on the “References” sub-tab of the “Add. entries” tab.

Afterwards, Match! locates the first of these matching entries (typically the one with the highest FoM-value) in the candidate list (answer set) and makes sure that it is marked and hence displayed in the powder diffraction pattern.

Hence, this functionality is some kind of abbreviation to the much more detailed “Add. Entries” mechanism and at the same time quickly locates the entry(s) of interest in the candidate list. In order to account for this “quick searching” character of the functionality, it is not required that the name entered in the “Find phases/entries” field is matched exactly (like it is the case on the “Add. Entries” and “Restrains” tab). Instead, it is sufficient that an entry to be regarded as “matching” contains the entered name as a fragment, also neglecting small and capital letters (case-insensitive comparison, in contrast to the criterion “Name” on the “Restrains” and “Add. Entries” tabs).

This latter feature is something that might have caused some misunderstanding in some cases: For example, the current “COD-Inorg” reference database contains 26 entries with name “Corundum” and 1 entry with name “corundum”, i.e. with a small letter at first position. As has already been mentioned, this difference does not matter when using the “Find phases/entries” line, so 27 entries are added using the “Add. entries” mechanism.

However, this mechanism does not delimit the current answer set, like it would be the case if you used “Restrains”, it just makes sure the corresponding entries are present (maybe among others) in the current answer set, and marks/displays the first one of these entries. If the current number of entries in the answer set is larger than the corresponding parameter (so that normally nothing would be displayed), Match! uses an internal “work-around” mechanism to nevertheless display a subset of entries (that also contain the ones matching the “Find phases/entries” criterion) in the candidate list.

If you use the wild card expression “\*corundum\*” on the “Restrains” or “Add. Entries” tab, Match! nevertheless still distinguishes between capital and small characters. As has already been mentioned, there is only 1 entry with a small ‘c’ and 26 with a capital ‘C’ at the beginning (“corundum” vs. “Corundum”), so that’s why you find a single entry when you enter “\*corundum\*”, 26 entries when you enter “\*Corundum\*”, and 27 entries when you give “\*orundum\*” instead.

## Unification of candidate list

The “Unify phases” command (which can be executed either by selecting the corresponding command from the “Entries” menu, or by pressing <Ctrl+U> (<Cmd+U> on the Mac)) checks the candidate list for entries that describe


the same phase. If any of these “duplicate entries” are detected, Match! removes all but the best-matching entry for this phase. As comparison criteria, Match! uses the composition as well as the powder diffraction pattern similarity (R-factor).

This command is especially useful if run before the selection of matching phases, in order to prevent multiple entries for a certain phase block the candidate list or even appear in the Match list.

## Quantitative phase analysis

Once you have finished the qualitative analysis (i.e. you have found out which phases are present in your sample; see the previous chapter for details), you can determine the amounts (weight %) of the phases that are present. Depending on the method you apply, you can do so for all crystalline phases and/or (in some cases) also for the amorphous phase(s)<sup>19</sup>.

### Automatic analysis

Match! can perform a quantitative phase analysis completely on its own. All you must do is to press the corresponding button  in the toolbar at the top or the combination <Ctrl+Alt+Q> on your keyboard (<Cmd+Alt+Q> on the Mac). The program will ask for any missing information, starting from the very beginning (pattern import) if required.

Once the quantitative analysis has been performed, the quantity (weight %) of each selected phase/entry is displayed in the "Amount (%)" column of the match list as well as in the report. In addition, a pie chart representation of the phase and element amounts is displayed on the "Composition" tab on the right-hand side of the program window.

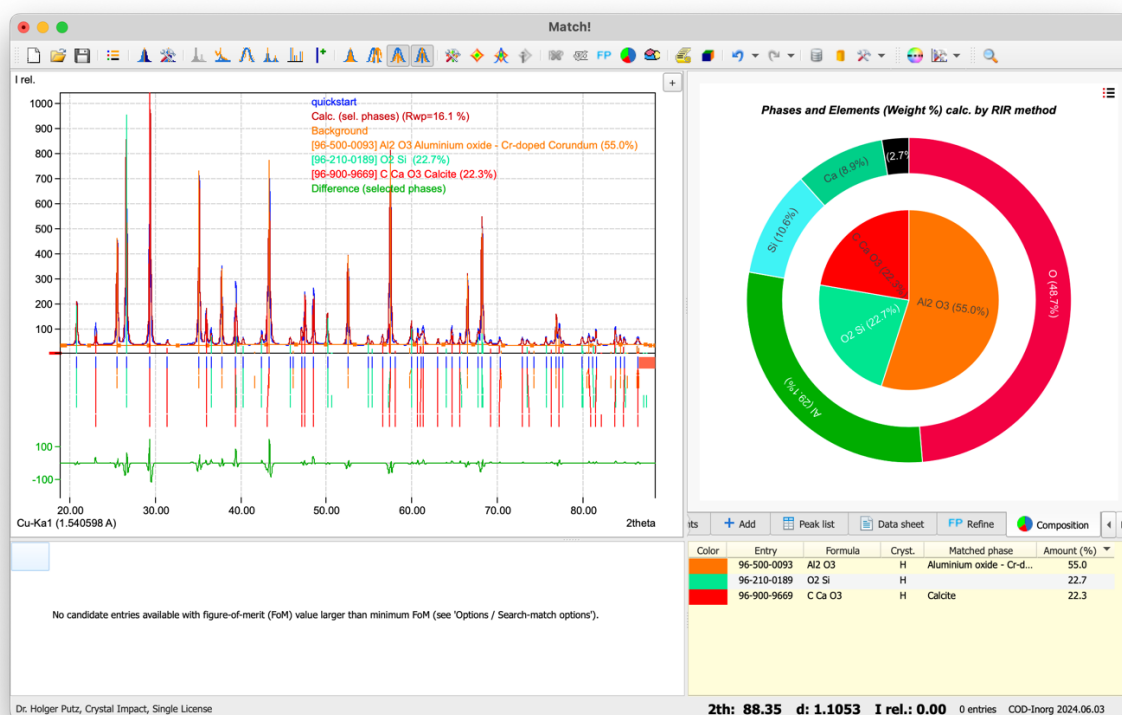


Fig. 20: Automatic quantitative analysis: Display of the result both as pie chart and table (match list).

Match! uses the **default quantitative analysis method** (RIR or Rietveld) for the automatic analysis. This can be adjusted on the corresponding tab of the "Options" window.

### Overview

Match! provides the following methods for quantitative analysis:

1. "Reference Intensity Ratio"-(RIR)-method (p. 49)

<sup>19</sup> If more than a single amorphous phase is present, you can only determine the sum of the amorphous phases.

2. Rietveld refinement<sup>20,21,22</sup> (p. 51, p. 60)
3. Degree-of-crystallinity (DOC) analysis (p. 52)
4. Internal standard (p. 56)

These methods (that can be used alone or in combination, e.g. Rietveld + internal standard) are explained and demonstrated in detail in the following sections. In addition, two commands for calculating peak/profile areas (that might be used for your own calculations) are also described in this context.

## Analysis results and pie charts

Once a quantitative analysis has been performed successfully, the quantity (weight %) of each selected phase/entry is displayed in the "Amount (%)" column of the match list as well as in the report.

In addition, a pie chart representation is available on the "Composition" tab. This tab can either be opened directly on the right-hand side of the program window or displayed by running the menu command "View / Composition".

If you have set the "Beginner" or "Automatic" user level, the "Composition" tab is also displayed automatically after each phase selection.

By default, a combined donut / pie chart representation of the elemental and phase composition is shown:

In addition to the combined display of elemental and phase composition as e.g. shown in Fig. 20, two other representations are also available:

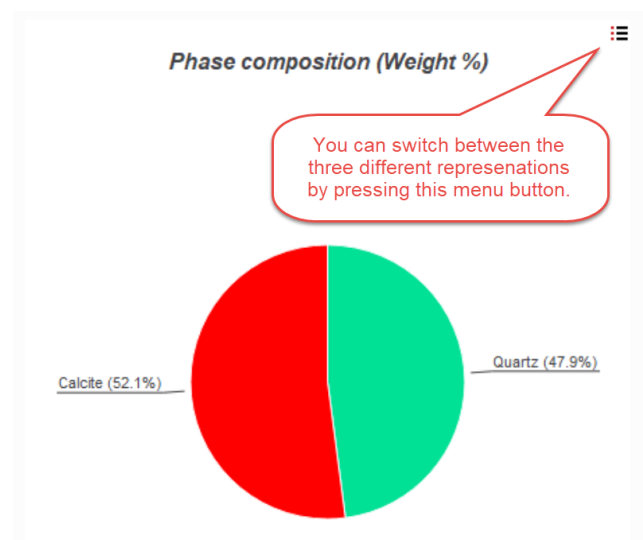


Fig. 21: Display phase composition as pie chart on composition tab

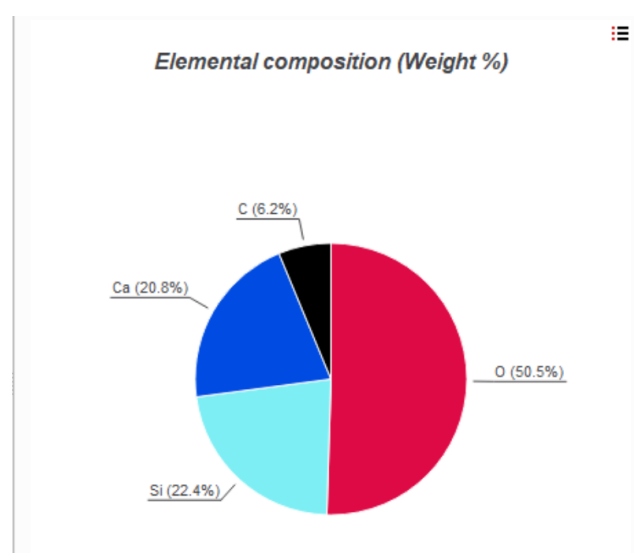


Fig. 22: The elemental composition can also be displayed as a pie chart.

Using the same menu button at the top right of the "Composition" tab, you can also copy, print or export the pie chart graphics, as well as display corresponding options and settings. The default pie chart representation can be selected on the "Quant. analysis" tab of the "Options" dialog.

## Semi-quantitative analysis using the "reference intensity ratio"-(RIR)-method

### Most suitable for...

Quick analysis

### Difficulties may arise in case of ...

High accuracy required

Preferred orientation

### Cannot be applied if...

<sup>20</sup> R.J. Hill, "Expanded Use of the Rietveld Method in Studies of Phase Abundance in Multiphase Mixtures", Powder Diffraction 6(2), 74-77 (1991).

<sup>21</sup> N.V.Y. Scarlett, I.C. Madsen, "Quantification of phases with partial or no known crystal structure", Powder Diffraction 21(4), 278-284 (2006).

<sup>22</sup> I.C. Madsen, N.V.Y. Scarlett, A. Kern, "Description and survey of methodologies for the determination of amorphous content via X-ray powder diffraction", Z. Kristallogr. 226, 944-955 (2011).



Match! can perform a (semi-)quantitative analysis of the sample using the so-called "Reference Intensity Ratio method" (RIR-method)<sup>23</sup>. This analysis is based on the comparison of the intensity scaling factors of the identified phases with reference to a "virtual" Corundum standard. "Virtual" means that Corundum must not be really present in your sample. Instead, so-called "I/I<sub>c</sub>" values for all phases are required, relating the intensity of the highest peak of a phase to the highest peak of Corundum, if both phases were present in a sample with the same amounts.

In Match!, the semi-quantitative analysis is performed automatically if at least two entries have been selected as matching. The quantity (weight %) of each selected phase/entry is displayed in the "Amount (%)" column of the match list and of course also in the report. In addition, you can display a pie-chart graphics of the result, by running the menu command "View / Composition".

### What you can do if I/I<sub>c</sub> values are missing

The RIR analysis can only be carried out if **all matching entries contain I/I<sub>c</sub> values**<sup>24</sup>. If only one of the selected entries does not contain an I/I<sub>c</sub> value, the values for the remaining selected entries cannot be calculated as well.

**All entries in the COD reference database** that is installed automatically along with Match! **contain I/I<sub>c</sub> values** that have been calculated from the crystal structure data. However, **there may be entries e.g. in ICDD PDF databases** (especially the PDF-2) that do not contain any I/I<sub>c</sub> value or at least crystal structure data that could be used to calculate I/I<sub>c</sub>.

Hence, you should **check if an entry contains an I/I<sub>c</sub> value** before selecting it, by looking at the column "I/I<sub>c</sub>" in the candidate list in which a corresponding value must be given.

If you select one (or more) entries without I/I<sub>c</sub> value as "matching", "**No I/I<sub>c</sub>**" will be displayed in the "Amount (%)" column of the match list. In this situation, "**n.a.**" is displayed for "Amount (%)" for the remaining entries even if they contain I/I<sub>c</sub> values.

Here is what to do in this situation to obtain a quantitative analysis result:

- You can **enter the I/I<sub>c</sub> value manually** that you may have obtained from other sources or **calculate I/I<sub>c</sub> from crystal structure data imported from a CIF file**. For this, either **click on the "No I/I<sub>c</sub>" cell** in the match list, or mark the corresponding line in the match list and run the menu command "Entries / Edit I/I<sub>c</sub> for quantitative RIR analysis". (This command is also available in the context menu of the match list).

A new window will open where you can either edit the I/I<sub>c</sub> value directly or press the "Calculate from crystal structure (CIF)" button to import crystal structure data and let Match! calculate I/I<sub>c</sub>.

You can also leave a note about the origin of the modified I/I<sub>c</sub> value so that you remember it later on.

Finally, press "OK" to close the window. The amounts of all entries in the match list will be recalculated accordingly.

- As an alternative, you can **create a working copy** (a so-called "**manual entry**", p. 130) of a reference database entry when selecting it. This can be achieved e.g. by marking the entry in the candidate list and pressing the keyboard combination <Alt+Space> or running the command "Select/add copy as manual "matching" entry" from the "Entries" menu.

Afterwards, you can double-click the newly created manual entry in the match list in order to edit its data.

You can then either enter I/I<sub>c</sub> manually or calculate it from imported crystal structure data (CIF) (by pressing the Import button). Both options are available (on the "Diffraction pattern" tab of the "Edit manual entry data" window).

- In "emergency" cases, you can activate an option on the "Quant. Analysis" tab of the "Options" window to let Match! **use a standard I/I<sub>c</sub> value of 1.0**. However, we do not really recommend using this option because of the extremely low accuracy of the results!

<sup>23</sup> P.M. de Wolff, J.W. Visser, "Absolute intensities", Rep. 641.109 Technische Physische Dienst, Delft 1964.

<sup>24</sup> All entries from free-of-charge COD reference database provided by Crystal Impact contain calculated I/I<sub>c</sub> values.



**Note:**

- You can also perform the RIR quantitative analysis explicitly, by running the "Reference intensity ratio (RIR)" command at the top of the "Quantify" menu.
- As an alternative to the RIR-method, you can also use **Rietveld refinement** for quantitative analysis. This approach does not depend on I/I<sub>c</sub> values and is also significantly more accurate than RIR in most circumstances.

**Manual adjustment of individual amounts for multiple-phase samples**

Normally, the (semi-quantitative) amounts of the phases are calculated based on the corresponding automatically determined intensity scale factors of the selected entries. However, it is possible to modify these intensity scale factors manually (and hence also the amounts of the individual phases). You can do so in two different ways:

- One option is to mark the phase/entry you would like to adjust the quantity of in the match list on the right-hand side. Afterwards, you can simply move the mouse cursor close to the top of one of the corresponding peaks in the diffraction pattern, press the left mouse button, and keep it pressed while moving the mouse up or down. The amount (intensity scale factor) of the marked entry/phase will now follow the mouse movements: Moving the mouse up (i.e. away from you) increases the amount of the marked phase, while moving the mouse towards you reduces the amount. The amounts of the remaining (non-marked) phases will be adjusted automatically.
- Alternatively, you can mark the phase/entry in the match list (similar to the previous option), move the mouse cursor in the match list to the column "Amount (%)" of the corresponding entry, and use the **mouse wheel** in order to adjust the amount for this phase.

**Rietveld refinement****Most suitable for...**

Careful analysis  
Increased accuracy required

**Difficulties may arise in case of ...**

Low quality data  
Quick analysis required

**Cannot be applied if...**

No crystal structure data are available for one (or more) of the selected phases

Rietveld refinement (see the chapter on p. 60) tries to mimic the experimental diffraction pattern as closely as possible, by fitting a model containing the crystal structure data of the phases, along with a large variety of other parameters. The calculation basically consists of a least-squares refinement of selected parameters like scale factors, unit cell parameters, peak shape parameters and background. In addition, potential errors can be modeled, like zero-point, specimen displacement or preferred orientation.

To **run Rietveld refinement for quantitative analysis**, you first must finish the qualitative analysis of the phases in your sample. Afterwards, simply **run the "Rietveld (FullProf)" command in the "Quantify" menu** (or press the combination <Ctrl+Alt+R> on your keyboard). Match! will run an **automatic Rietveld refinement calculation** using the parameter sequence ("preset") defined on the "Rietveld" tab of the "Options" window.

Once the Rietveld refinement was successful (has converged), the weight fractions of the individual phases are calculated from the refined scale factors, along with the density values and unit cell volumes calculated from the known crystal structures of the phases. **The resulting weight fractions will be copied to the match list** (column "Amount (%)") **automatically after each successful Rietveld refinement calculation**, replacing any values resulting from the RIR or DD calculation if present. The corresponding information will also be included in the **report** as well as the **pie-chart graphics**.

Although the main output of Rietveld refinement (at least with regard to quantitative analysis) are the scale factors of the phases (similar to the RIR-method described above), the accuracy of the amounts calculated by Rietveld refinement are much higher, because the whole profile is used for the calculation and not just the heights of 1..N peaks. In Rietveld refinement, effects like peak broadening, asymmetry, preferred orientation etc. can be investigated and considered in the quantitative analysis.

### Details

The quantitative analysis using Rietveld refinement in FullProf works by applying the equation defined by Hill and Howard<sup>25</sup>, modified by including the particle absorption contrast factor defined by Brindley<sup>26</sup> (to account for microabsorption effects), to the **scale factors** obtained from the refinement.

Hence, the better the agreement between experimental profile and the one calculated from the Rietveld model, the better (more accurate) will be the scale factors and hence also the result of the quantitative analysis.

### Degree-of-crystallinity (DOC) analysis

#### Most suitable for...

Determination of amount of amorphous compound(s)

#### Difficulties may arise in case of ...

Elemental composition of amorphous phase is not similar to crystalline compounds

#### Cannot be applied if...

No 'empty sample holder' diffraction pattern is available



This analysis requires that an additional "empty sample holder" diffraction pattern is available that has been recorded using the same experimental conditions as the sample's pattern. This additional pattern is used to subtract the background contribution caused by the instrument from the one of the sample.

The DOC analysis works best if the crystalline and amorphous parts have similar elemental composition. If the sample consists of crystalline fractions and an amorphous fraction of **different** chemical compositions, the amounts of each of the individual crystalline phases may be estimated using appropriate standard substances as described below; the amorphous fraction is then deduced indirectly by subtraction.

If this prerequisite is met, it is neither necessary to determine the experimental peaks nor to select the matching phases (qualitative analysis) for the DOC analysis. Instead, it is sufficient to subtract the instrumental background from the sample's diffraction pattern, re-determine the background, and then calculate the area below the background curve and compare it to the area of the whole pattern.

*The "Degree of Crystallinity" (DOC) submenu has been simplified (compressed to a single command in the "Quantify" menu).*

### Workflow for DOC analysis

1. Record the sample's diffraction pattern as usual; the 2theta range should be large enough to see both the start and end of the amorphous part.
2. Record an "empty sample holder" diffraction pattern with the same experimental conditions.
3. In Match!, press the **Degree of crystallinity analysis** button  in the toolbar, or run the menu command "Quantify / Degree of crystallinity (DOC)".
4. Select the sample's diffraction pattern file, then press "Open".
5. In the pattern graphics, check the background that has been determined automatically so that it clearly separates the diffraction peaks from the background (Fig. 23). If you would like to modify the background, answer "No" to the corresponding question, modify the background (p. 20), and finally press the "Degree of crystallinity analysis" button  in the toolbar again to proceed.
6. In the window that opens after you have confirmed the background, import the "empty sample holder" diffraction pattern mentioned above, by pressing the "Select..." button in the line "Import from file:". (As an alternative, you could also use an additional experimental pattern you have imported from a file as instrumental background.)

<sup>25</sup> R.J. Hill & C.J. Howard, "Quantitative phase analysis from neutron powder diffraction data using the Rietveld method", J. Appl. Cryst. **20**, 467-476 (1987). <https://doi.org/10.1107/S0021889887086199>

<sup>26</sup> G.W. Brindley, "The effect of grain or particle Size on x-ray reflections from mixed powders and alloys, considered in relation to the quantitative determination of crystalline substances by x-ray methods", Phil. Mag. **36** (256), 347-369 (1945). <https://doi.org/10.1080/14786444508520918>

7. Mark the option “Full pattern” under “Subtract full ‘empty sample holder’ pattern or background only”.
8. For a better visual comparison, you could switch over to “Counts” representation on the y-axis (e.g. by clicking on the corresponding y-axis label), so that the two patterns are scaled identically (Fig. 24).
9. Run “Quantify / Degree of crystallinity (DOC) / New analysis”
10. In the dialog that opens, make sure that the option “Use addition pattern” is marked as well as the correct additional pattern is selected.
11. Mark the option “Full pattern” under “Subtract full ‘empty sample holder’ pattern or background only”.
12. If you like to see the “real” diffraction pattern of the sample after subtraction of the instrument background, mark the option “Add result as a new experimental pattern”. Your window should now look similar to Fig. 25.
13. Press “OK”. The result of the DOC analysis will now be displayed (Fig. 26). It will also be included / displayed in the report.

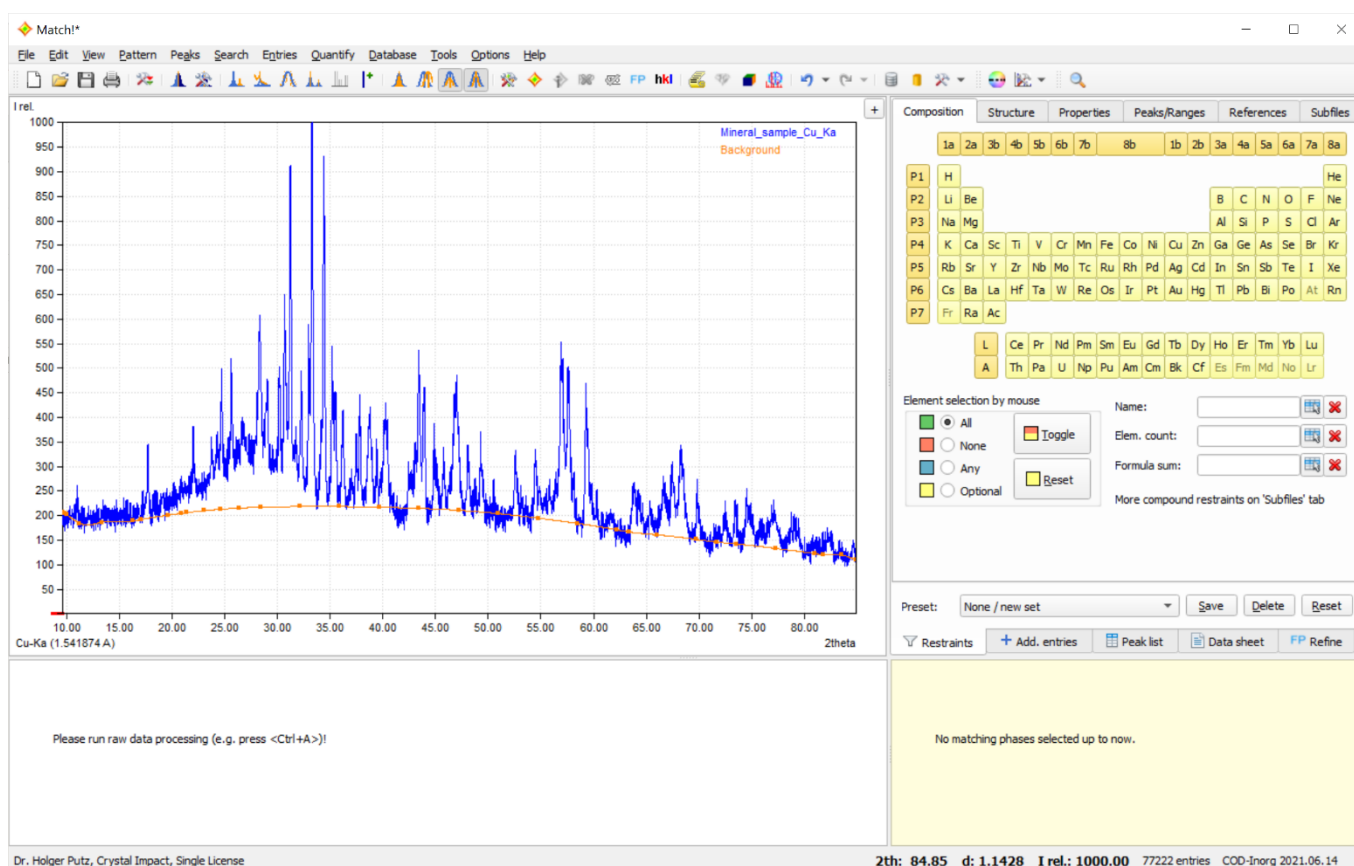


Fig. 23: Your sample's diffraction pattern has been imported for degree-of-crystallinity analysis (DOC).

### Background information for DOC analysis

The degree of crystallinity is to a large degree “affected” by the background choice:

For the degree of crystallinity (DOC) calculation to be correct, it is essential to understand that the part (the “counts”) **above** the background is attributed to the **crystalline** material, while the part **below** (the “background”) is attributed to the **amorphous** material.

The latter may contain **contributions both from your sample as well as from your diffractometer**, so you first need to remove the contribution caused by your diffractometer, the “empty sample holder pattern”.

Once you have done so, Match! can “compare” the area (counts) of the profile above the background curve with the area (counts) below it, and calculate the degree of crystallinity from the relation of the two.

Match! determines the background automatically when importing raw diffraction data files, however, the automatically determined background does not need to be correct in all cases. For example, it may happen in some cases that Match! does not include the “amorphous humps” in the amorphous background below the background curve, but rather attributes them to the “crystalline material” area above the curve.

If the automatically determined background does not seem to be “flexible” enough, you should increase the flexibility of the background determination after pattern import, by pressing <Ctrl+F2> several times until the orange curve (background) has adapted to the amorphous humps. On the other hand, you can make the background more “rigid” by pressing <Ctrl+F3>.

As an alternative, you could also define the background manually, e.g. by starting with a simple background line (menu “Pattern / Background / Two points”) and then manually adding and adjusting background control points as required.

Note that the decision what is “amorphous background” and what “broad peaks caused by very small crystallites” may not always be obvious and sometimes could be a “matter of taste” (or experience).

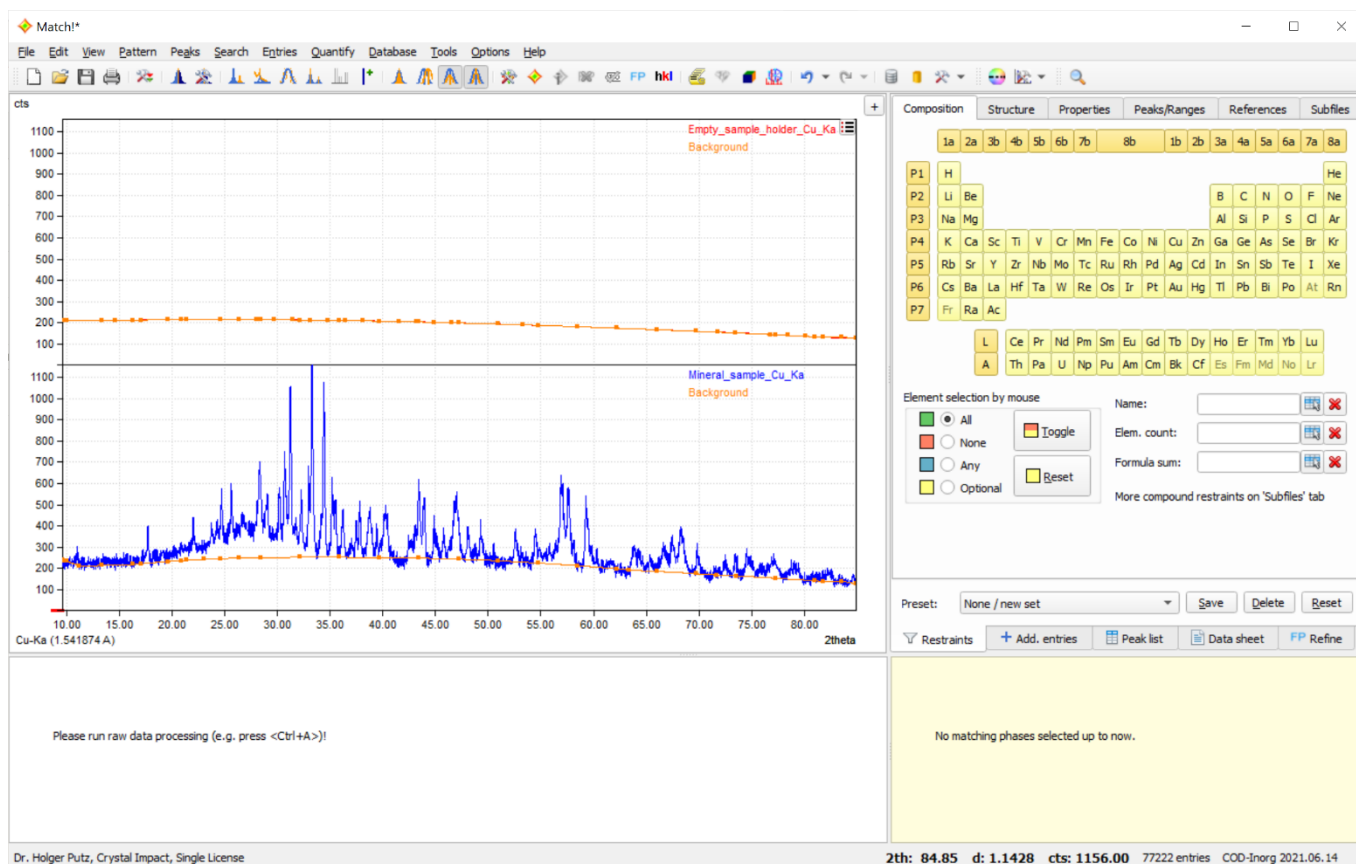


Fig. 24: The “empty sample holder” pattern (representing the instrument’s contribution to the background) has been imported as an additional experimental pattern, and the y-axis scaling has been switched over to “Counts”.

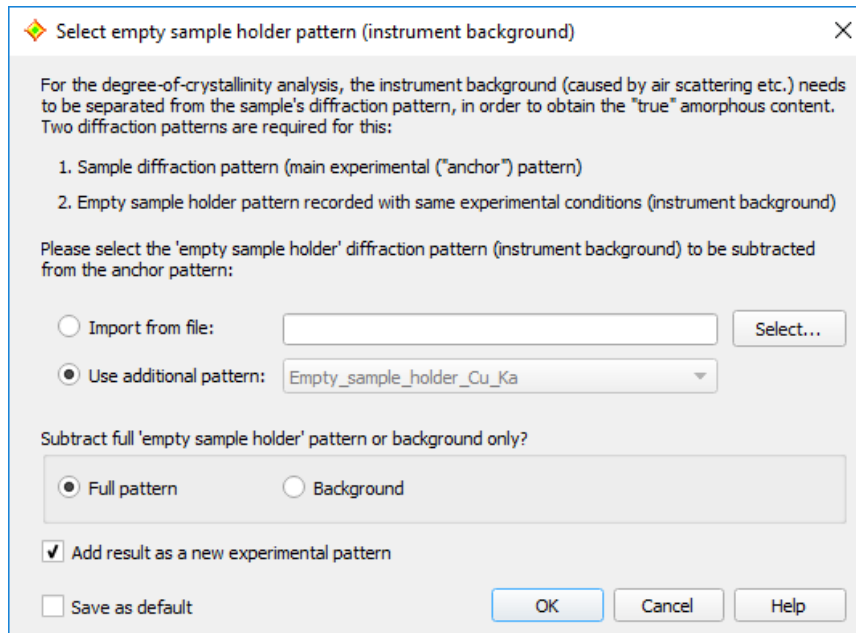


Fig. 25: Settings for DOC analysis: The “empty sample holder” data shall be taken from the additional pattern “Empty\_sample\_holder\_Cu\_Ka”, the full “empty sample holder” pattern shall be used (and not just the automatically determined background), and the result (pattern difference) shall be added as an additional experimental pattern for visual comparison.

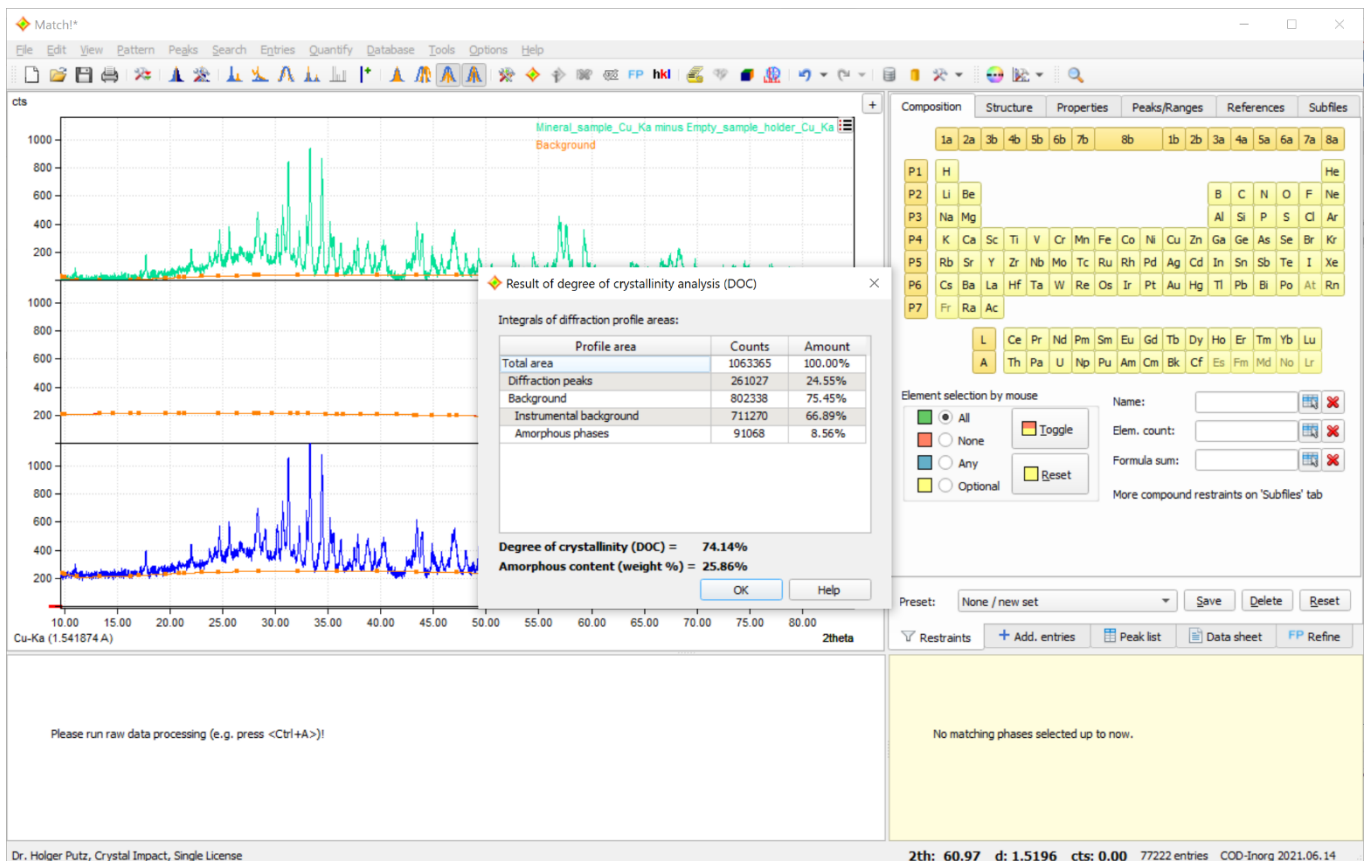


Fig. 26: Result of the degree-of-crystallinity (DOC) analysis. In this case, the degree-of crystallinity is 74.14%, and the amount of the amorphous phase(s) is 25.86%.

## Internal standard

### Most suitable for...

Careful analysis  
Increased accuracy required  
No separation of background from amorphous phases possible/required

### Difficulties may arise in case of ...

Low quality data  
Quick analysis required

### Cannot be applied if...

No known amount of a suitable standard compound can be added to the sample  
The amount of more than a single amorphous or unidentified phase shall be determined individually  
Amounts of amorphous and non-identified crystalline phases shall be determined separately

If you can add a known amount of a suitable compound (“internal standard”) to your sample before recording the diffraction pattern, this information can later be compared to the result of a Rietveld (or RIR) quantitative analysis. The corresponding correction factor (obtained from the relation “known amount of phase A added to sample” / “amount of phase A resulting from RIR- or Rietveld analysis”) can then be used to correct the amounts of the remaining phases, rather than normalizing the sum to 100%. As a result, absolute phase quantities are obtained. The difference to 100 weight-% gives the amount of amorphous (and unidentified crystalline) phases in the sample.

There are a few conditions that the internal standard compound must fulfill though:

- It must be 100% crystalline.
- It should be a highly symmetric structure generating few but intense diffraction peaks.
- The internal standard compound must not react chemically with the sample.
- The internal standard amount must not exceed the amount resulting e.g. from Rietveld refinement (or RIR analysis), because this would result in the sum of all phase amounts being larger than 100%.

When these requirements are fulfilled, a quantitative “internal standard” analysis is performed as follows:

### Workflow for “internal standard” analysis

First, add a known amount of a suitable “internal standard” compound to your sample and record its powder diffraction pattern. Import the corresponding diffraction pattern into Match! and perform the raw data processing and qualitative analysis as described above (example given in Fig. 27).



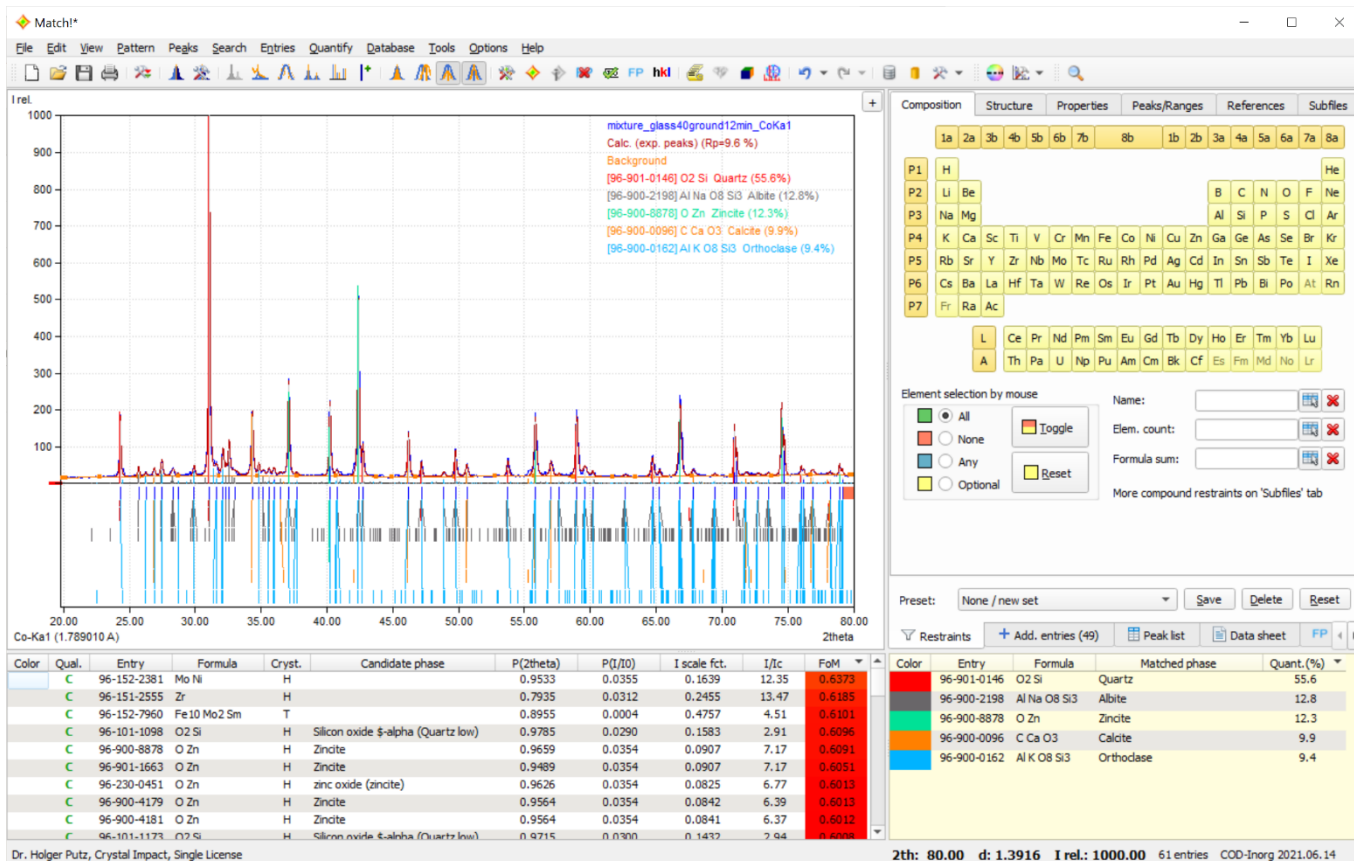


Fig. 27: A sample result from a qualitative analysis, to be used for a quantitative internal standard analysis.

Afterwards, we recommend performing a “quantitative analysis”, by running a Rietveld refinement of the scale factors, unit cell parameters, peak shape parameters and background, in order to get reasonable starting values for the amounts of the crystalline phases (Fig. 28). If you cannot run a Rietveld analysis, you can use the results of the semi-quantitative “RIR” analysis that is performed automatically by Match! (see above).

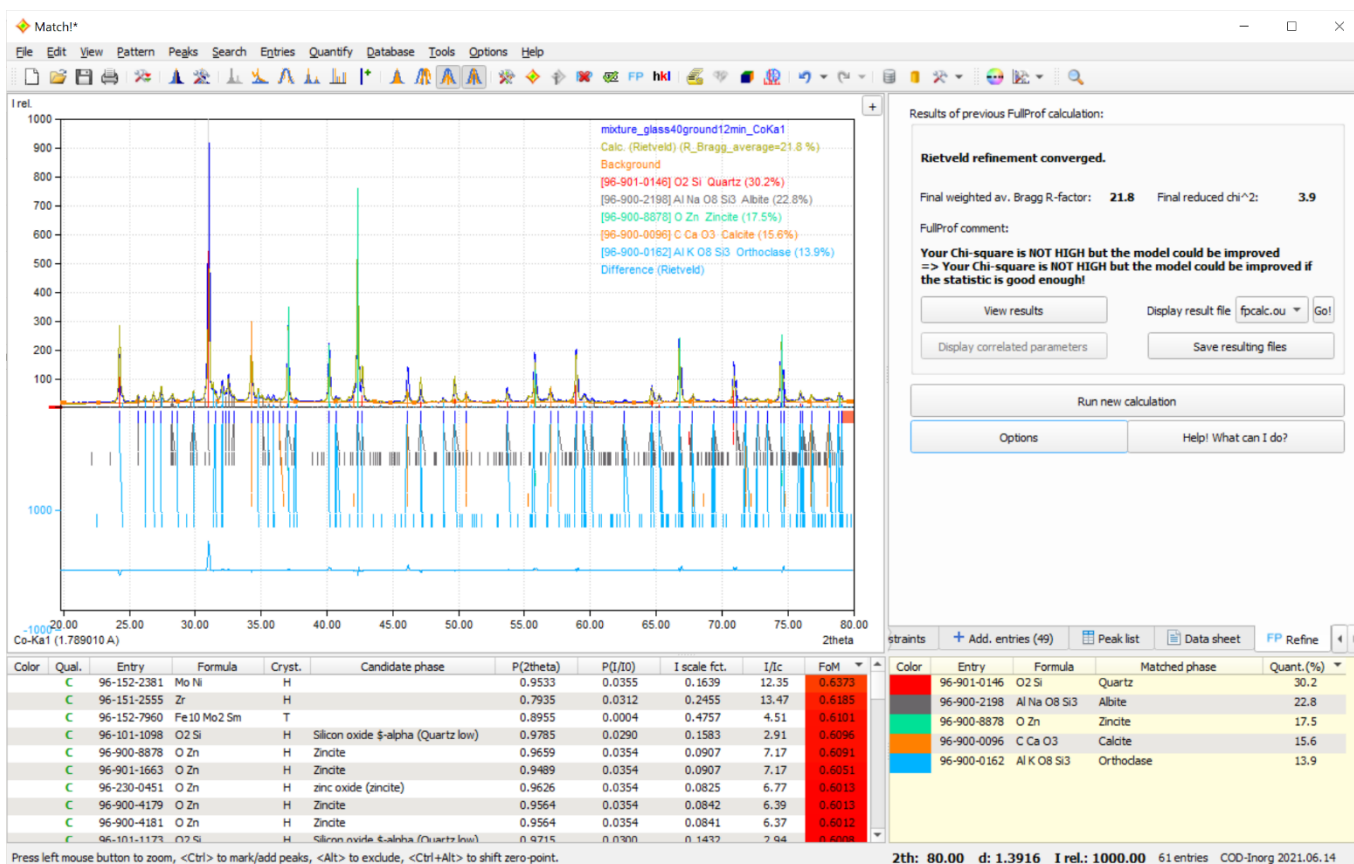




Fig. 28: A Rietveld refinement calculation of scale factors as well as unit cell, peak shape and background parameters has been run.

Verify that the amount of the internal standard compound (in this case Zincite, ZnO) is over-estimated (larger) in the Rietveld (or RIR) analysis (here 17.5%), compared to the amount added to your original sample (in this case 15%). If the latter is larger than the amount resulting from the Rietveld refinement, this would cause the amounts of the remaining phases to be increased in the calculation. As a result, the sum of all phase amounts would be larger than 100%.

Mark the phase you would like to use as internal standard in the match list (here Zincite), then run the command “Internal quant. standard” from the “Quantify” menu (or from the match list’s context menu). In the dialog that opens, please enter the amount (weight %) of the standard phase in the sample (here 15%), then press “OK”.

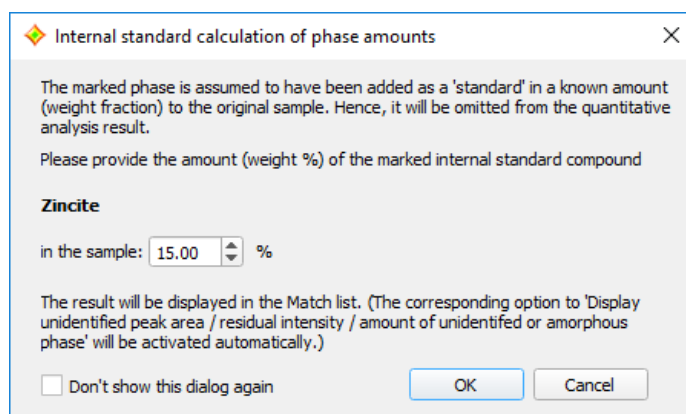


Fig. 29: In this dialog you provide the amount of the internal standard phase that you have added to your sample.

The result of the “internal standard analysis” will now be displayed both in the match list (Fig. 30) as well as in the report. In our example, the original sample (without standard) contains 30.5% Quartz, 23.0% Albite, 15.8% Calcium carbonate, 14.1% Orthoclase and 16.6% of amorphous (or unidentified) phase(s).

Color	Entry	Formula	Matched phase	Quant.(%)
Red	96-901-0146	O2 Si	Quartz	30.5
Orange	96-900-2198	Al Na O8 Si3	Albite	23.0
Yellow	96-900-0096	C Ca O3	Calcite	15.8
Blue	96-900-8878	O Zn	Zincite	15.0
Green	96-900-0162	Al K O8 Si3	Orthoclase	14.1
			Amorphous or unident. phases	16.6

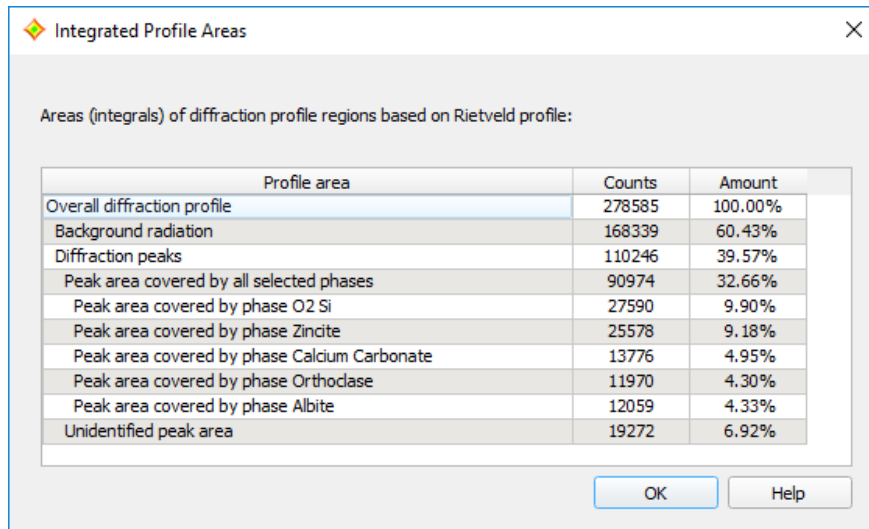
Fig. 30: The result of “internal standard” analysis is given in the match list.

If you would like to return to the “normal” quantitative analysis with the identified crystalline phases adding up to 100%, you can do so by running “Quantify / Reset internal standard”.

## Calculate profile integrals

You can instruct Match! to calculate the intensity integrals of various profile areas by selecting the command “Calculate profile integrals...” from the “Quantify” menu. A new dialog will open and display a table of the following different profile areas (Fig. 31):

- Overall diffraction profile
- Background radiation
- Diffraction peaks
- Peak area belonging to selected phases
- Peak area belonging to each individual selected phase
- Unidentified peak area



Integrated Profile Areas

Areas (integrals) of diffraction profile regions based on Rietveld profile:

Profile area	Counts	Amount
Overall diffraction profile	278585	100.00%
Background radiation	168339	60.43%
Diffraction peaks	110246	39.57%
Peak area covered by all selected phases	90974	32.66%
Peak area covered by phase O2 Si	27590	9.90%
Peak area covered by phase Zincite	25578	9.18%
Peak area covered by phase Calcium Carbonate	13776	4.95%
Peak area covered by phase Orthodase	11970	4.30%
Peak area covered by phase Albite	12059	4.33%
Unidentified peak area	19272	6.92%

OK Help

Fig. 31: You can calculate various profile areas using the “Integrated profile areas...” command in the “Quantify” menu.

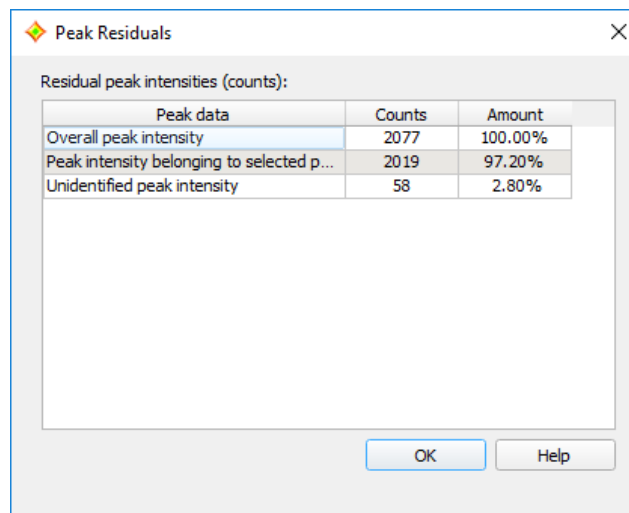
For each profile area, the **integrated counts** as well as the **relative amount** is given. The **profile integrals** are also given at the bottom of the match list as well as the report.

### Calculate peak residuals

The peak residuals are the remaining experimental peak intensities after subtracting the intensities covered by the identified phases. You can ask Match! to calculate the **residual peak intensities** by selecting the “Calculate peak residuals...” command from the “Quantify” menu. A new dialog will open and display a table of 3 different peak intensities (Fig. 32):

- Overall peak intensity
- Peak intensity belonging to selected phases
- Unidentified peak intensity

For each peak intensity type, the **integrated counts** as well as the **relative amount** is given.



Peak Residuals

Residual peak intensities (counts):

Peak data	Counts	Amount
Overall peak intensity	2077	100.00%
Peak intensity belonging to selected p...	2019	97.20%
Unidentified peak intensity	58	2.80%

OK Help

Fig. 32: Calculation of peak residual intensity values

## Refinement Calculations

Refinement calculations are frequently used to get or confirm detailed information about a micro-crystalline sample, based on powder diffraction data. Typically, these calculations work as follows:

First, a so-called “model” is set up. This “model” can be imagined as a large formula using which the intensity at every single data point of a powder diffraction pattern can be calculated. For this, the formula contains information like the crystal structure data of all identified phases as well as terms that describe all kinds of effects one could imagine to be present in the material, e.g. stacking faults or micro-strain (causing peak broadening), preferred-orientation (causing peak intensity deviations) etc.

Afterwards, the numerical parameters in this model (formula) are varied, typically using a so-called “least-squares refinement”. The aim is to determine the set of parameter values that gives the best possible agreement between the experimental diffraction profile and the profile calculated from this model (measured as “R-factor” or “chi<sup>2</sup>-value”). Finally, the obtained parameter values are critically analyzed, and conclusions about the “physical reality” in the sample are drawn.

In combination with FullProf, Match! offers the following refinement calculations:

- Rietveld refinement
- Pattern decomposition (Le Bail method)

While Rietveld refinement requires the presence of atomic coordinates in all data sets, this does not apply to pattern decomposition (also called “profile matching mode” in FullProf).

It is possible to perform mixed refinement calculations though, where some phases (where atomic coordinates are available) are refined using Rietveld and others (without atomic coordinates) by pattern decomposition. Hence, it is perfectly possible to perform refinements even if one or the other “matching entry” does not contain atomic coordinates.

**Please note:** If such a mixed calculation is performed, the entries where pattern decomposition is applied are not included in the quantitative analysis (their amounts will be displayed as zero (0.0)). In these cases it is possible to perform a full quantitative analysis if the amounts of these phases are known from other sources:

You can enter the known amount(s) manually in the match list, by double-clicking the corresponding “missing” amount value “0.0” in the match list, entering the “true” amount, and finally pressing <Return>. Match! will re-scale the amounts of the remaining phases accordingly.

### Rietveld refinement

#### Basics

Before we start: An excellent **introduction to Rietveld refinement suitable even for absolute beginners** is the very clearly structured document “Lesson 5: Rietveld Refinement” of Nicola Döbelin's **Lecture Handouts**<sup>27</sup>.

Rietveld refinement is a tool that tries to model a full powder diffraction profile based on crystal structure data, specimen and instrument effects, by fitting a large variety of corresponding functions parameters. It was first introduced by Hugo Rietveld in 1967 and 1969. The parameters are varied using a least-squares procedure, in order to minimize the difference between the calculated and the experimental powder diffraction pattern. Details of the method are available in the literature<sup>28,29,30</sup>.

One of the key issues of Rietveld refinement is that the method is rather sensitive to problems and errors in the model, resulting in non-convergence and other issues. Hence, it has become a common agreement for many scientists

<sup>27</sup> N. Döbelin, “Lecture Handouts”, Lesson 5: Rietveld Refinement, [http://profex.doebelin.org/?page\\_id=68](http://profex.doebelin.org/?page_id=68).

<sup>28</sup> H.M. Rietveld, *Acta Cryst.* **22**, 151-2 (1967).

<sup>29</sup> R.A. Young (ed.), “The Rietveld Method”, International Union of Crystallography, Oxford University Press, New York 1993.

<sup>30</sup> H.M. Rietveld, *J. Appl. Cryst.* **2**, 65-71 (1969).

that a successful phase analysis should be proven by a successful Rietveld refinement converging at low R- and  $\chi^2$ -factors.

Well, in practice things are not always that easy, but running Rietveld refinements on your diffraction pattern will at least give you a good chance to think and learn more about your experiment and sample.

### Rietveld refinement in Match!

Today a variety of excellent programs for Rietveld refinement are available, so there is little need to invent the wheel again and again. Match! uses the well-known Rietveld program “FullProf”<sup>31,32</sup> to actually perform the calculations. However, with Match! you do not have to interact with FullProf directly; instead, you can use the Match! user interface to define (“turn-on”) the parameters, setup the calculations and evaluate the results.

When you run Match! for the first time, the software tries to automatically determine the path to the FullProf software. If this is not possible, you will be asked if you would like to manually select this path. Finally, if this is not successful, you will be asked if you would like to download and install FullProf from the Crystal Impact web site.

This “checking for FullProf” procedure is carried out only once. If there is no valid path to FullProf available at its end (e.g. because you have pressed the “Cancel” buttons), you won’t be asked again until you try to run a Rietveld refinement calculation. However, you can download and install FullProf manually later by selecting the “FullProf download” command from the “Tools” menu. As an alternative, you can define or modify the path to FullProf any time on the “Rietveld” tab of the “Options” dialog (which can be opened e.g. from the “Options” menu). Once you have defined the path to FullProf, you are ready to run Rietveld refinement calculations from within Match!.

To do so, you first have to perform the normal qualitative phase analysis, i.e. import (raw / profile!) diffraction data, find the peaks, run a search-match and select one or more “matching phases”. Afterwards, please select e.g. the “Rietveld (FullProf)” command from the “Options” menu (or press “Ctrl + Shift + R” on your keyboard), to bring up the “Parameter Turn-On” dialog (Fig. 33).

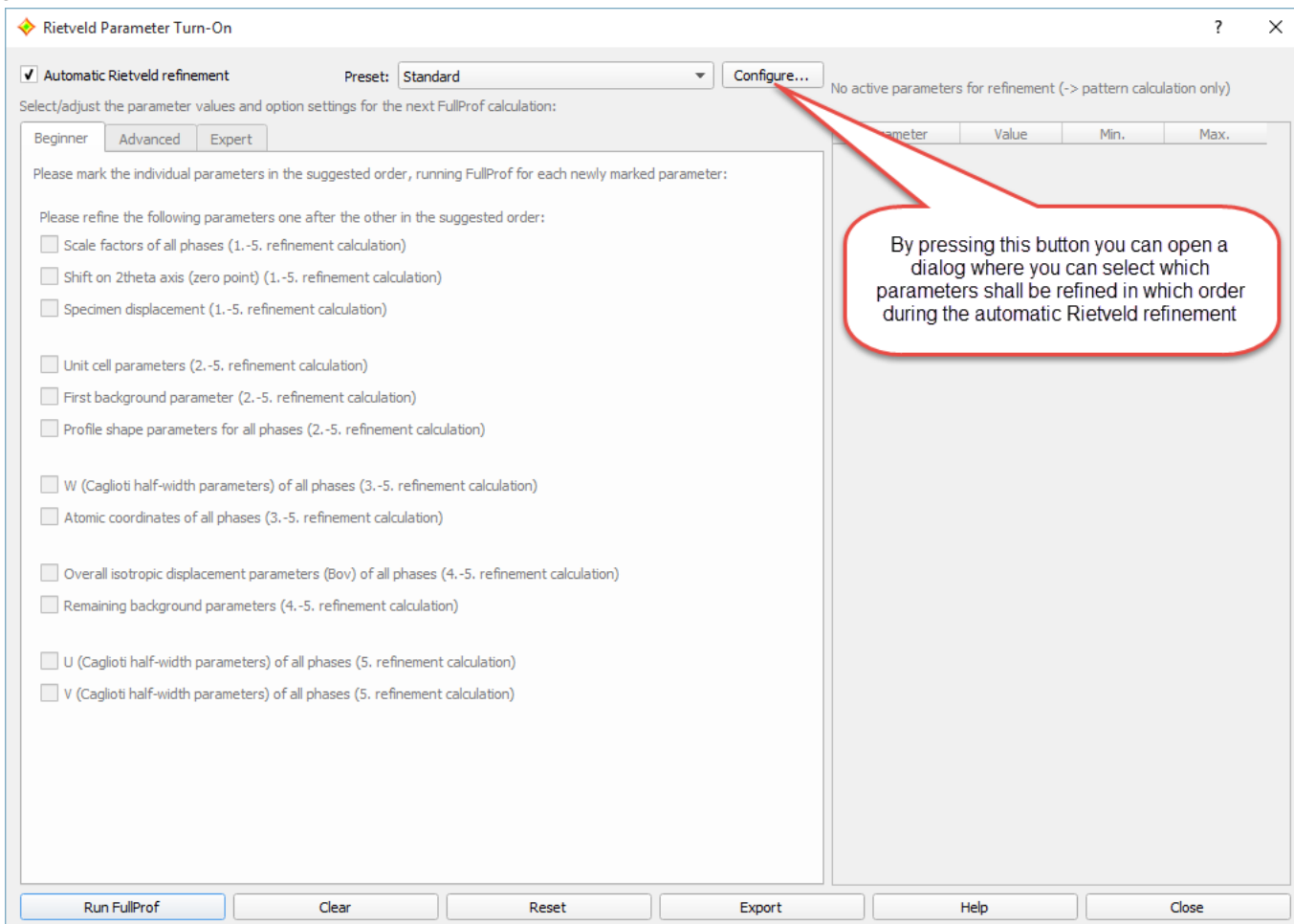
If any of the entries you have selected as “matching phases” does not contain a full crystal structure data set (e.g. if the atomic coordinates are missing), you will be prompted to import suitable crystal structure data from cif-files. The background is that it is not possible to run Rietveld refinements without complete structural models. Once complete crystal structure data sets are available for all matching phases, the “Parameter Turn-On” dialog will be displayed.

**Please note:** You can eliminate all entries that do not contain a full crystal structure description from the candidate list using the menu command “Entries/Delete incomplete entries”.

Match! will also switch to the “Rietveld” tab on the upper right-hand side of the Match! window automatically where the results and viewing options will be available after the refinement calculation.

<sup>31</sup> J. Rodriguez-Carvajal, *Physica B* **192**, 55 (1993).

<sup>32</sup> <http://www.ill.eu/sites/fullprof/index.html>



**Fig. 33: The “Parameter Turn-On Dialog” in its default state: The “Automatic Rietveld Refinement” option is active, so the Rietveld refinement can be run directly by pressing the “Run FullProf” button at the bottom left.**

In order to introduce users that are new to Rietveld refinement to this method, we have implemented four different approaches to define (“turn-on”) the options and parameters for the calculation. The method that is easiest to use (“Automatic Rietveld Refinement”) is available simply by marking the corresponding checkbox at the top of the “Parameter Turn-On” dialog, while the three remaining facilities “Beginner”, “Advanced” and “Expert” are present as tabs in the main part of the dialog. The parameters on the three tabs are linked to each other, so that you can start turning on parameters e.g. on the “Beginner” tab and finish as an “Expert”.

We will now discuss the four approaches of using the “Parameter Turn-On” dialog in more detail:

### 1. Automatic Rietveld refinement

The easiest way to setup a Rietveld refinement calculation is to activate the “Automatic Rietveld refinement” option at the top of the “Parameter Turn-On”-dialog. If this option is active, all remaining options are disabled. Afterwards, you can run the automatic refinement calculation by pressing the “Run FullProf” button on the lower left-hand side. The calculation(s) will be run automatically; at the end, the result will be displayed on the “Rietveld”-tab on the upper right-hand side of the Match! window.

You can create own parameter sequences to be used in automatic Rietveld refinement; this will be described in the chapter “Configuring automatic Rietveld refinement calculations” below.

### 2. Beginner

The next step for learning how to do Rietveld refinement is to deactivate the “Automatic Rietveld refinement” option, and to use the options (checkboxes) on the “Beginner” tab. On this tab, a selection of Rietveld parameters is available, along with a suggested order in which they shall be turned on in successive calculations (Fig. 34).

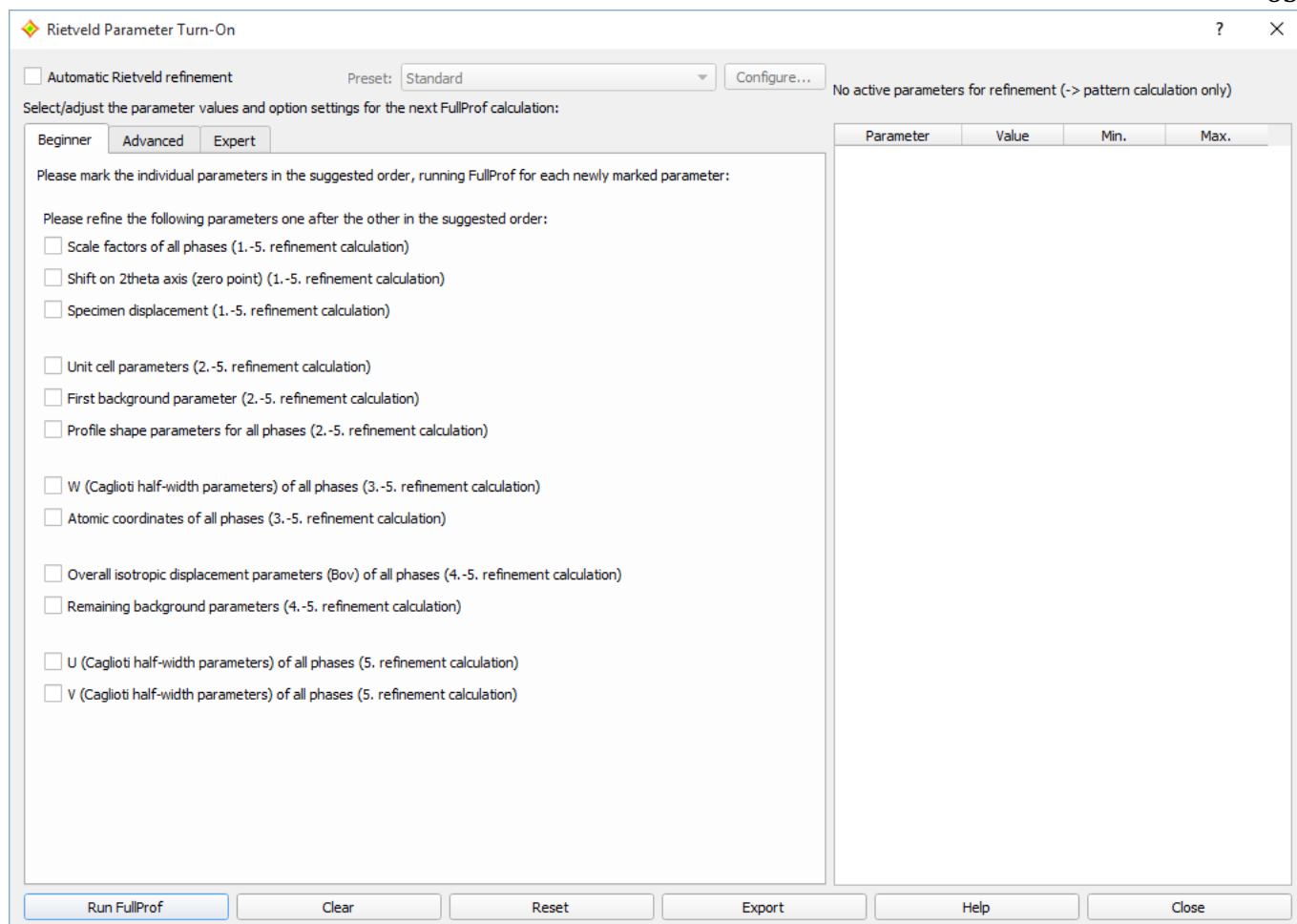


Fig. 34: On the “Beginner” tab of the “Parameter Turn-On” dialog, the available parameters are grouped according to the suggested order in which they shall be included in the refinement.

For example, in the first calculation only the scale factors and specimen displacement parameters are recommended for refinement. If this first refinement calculation is successful, the unit cell and first background parameters can be activated in addition to the first parameters, and another refinement calculation is performed. If this is successful, the W and atomic coordinate parameters are added etc.

In fact, this is just the order in which the calculations are carried out during the automatic refinement. However, you now have more control and can stop at certain points or repeat steps if you like. This order is taken from the excellent book edited by R. A. Young<sup>29</sup>.

### 3. Advanced

Once you are familiar with the principal procedure and main parameters, you are ready for more detailed options and parameters. Hence, we have introduced the “Advanced” tab, on which a reasonable number of parameters is grouped according to their effect: “Peak positions”, “Peak intensities” and “Profile shape”.

You can e.g. address specific problems e.g. concerning the positions of the peaks by marking one or the other parameter on the “Peak positions” tab for refinement (Fig. 35).

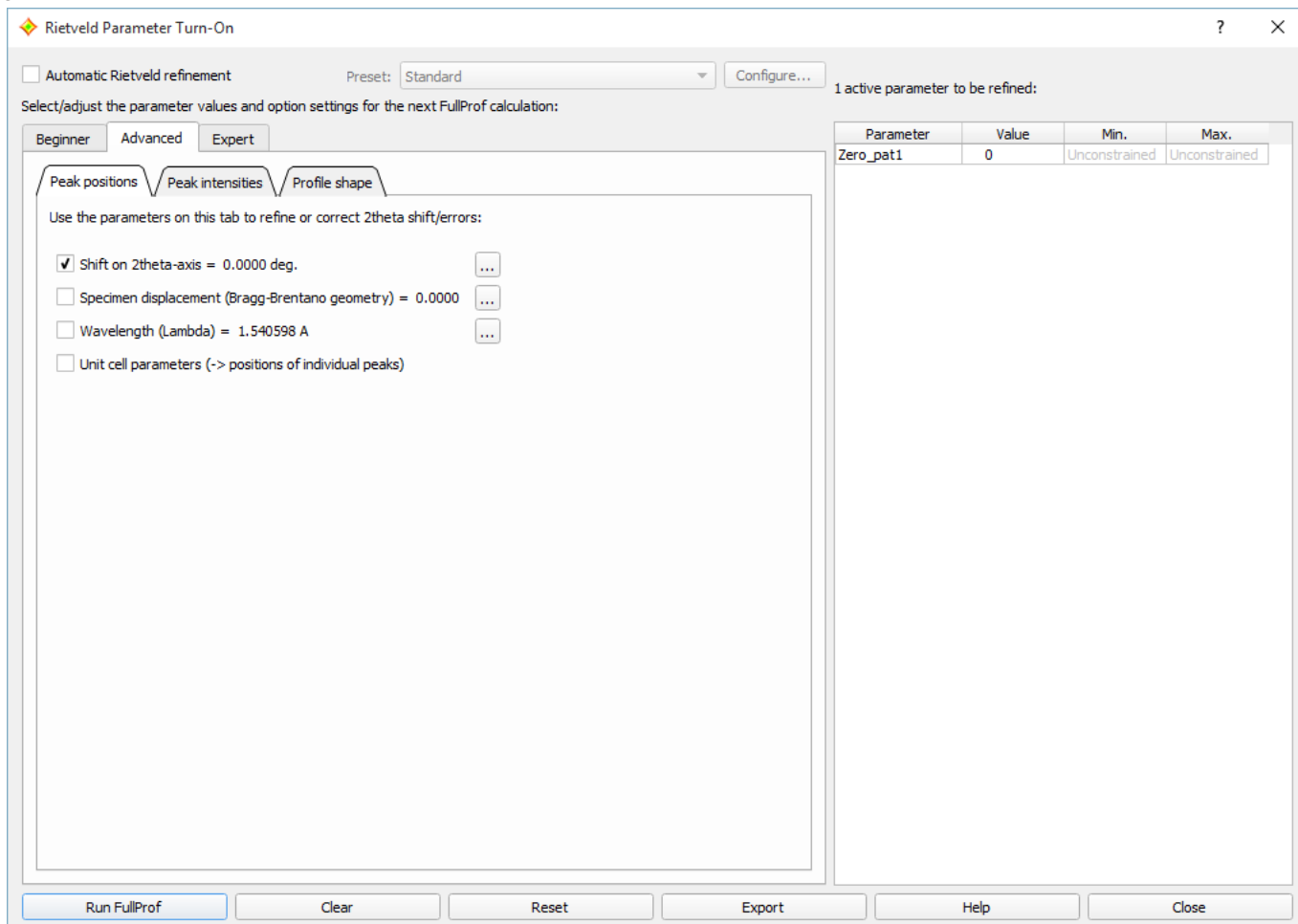


Fig. 35: On the “Advanced” tab of the “Parameter Turn-On” dialog the available parameters are grouped according to the topic they take an effect on, like peak positions, peak intensities and profile shape.

Another new feature on the “Advanced” tab (that is also available on the “Expert” tab) is the possibility to define constraints for a certain parameter. In order to do so please press the “...” button to the right of the corresponding parameter (e.g. “Shift on 2theta-axis”). A new dialog window will open (Fig. 36) in which you cannot only modify the parameter value or mark the parameter for being optimized, but also define constraints by entering the limiting numerical values in the “Minimum value” and/or “Maximum value” fields.

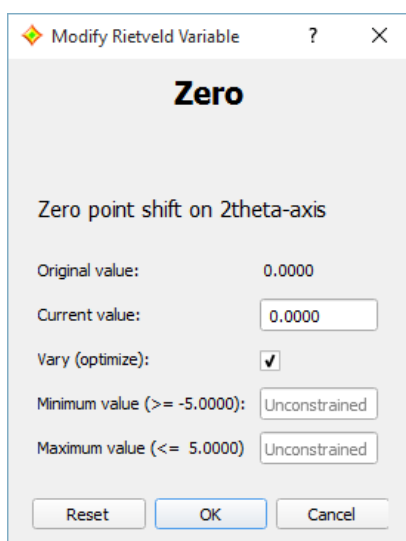


Fig. 36: Using this dialog (which can be opened by pressing the “...” button to the right of a certain numerical parameter) you can modify the value of the parameter as well as define constraints for it.

At this stage you should also note the table of “Active parameters” on the right-hand side of the “Parameter Turn-On” dialog: Here you can get an overview over the parameters that are currently marked for being varied in the next refinement calculation. Please note that the parameter names given in the left-most column are the original full



parameter identifiers used in FullProf. If you double-click on a certain line of the table, the parameter modification dialog just mentioned will be opened, so that you can modify parameter settings directly without having to search for the corresponding “...” button or tab.

Once you have defined the parameters you would like to refine, please press the “Run FullProf” button at the bottom in order to run the Rietveld refinement calculation.

#### 4. Expert

This is the most comprehensive but also the most demanding option for setting up the Rietveld refinement parameters. All FullProf parameters that are currently supported by Match! are available here. You can adjust global settings like “Zero” or “Lambda” on the “Global” tab, as well as select or modify parameters for individual phases (e.g. unit cell parameters or atomic coordinates). For each phase of the Match list, a separate tab is available. All parameters belonging to a certain phase are distributed to subtabs like “Quant.”, “Profile” or “Crystal structure”.

#### Pattern calculation

Before we leave the “Parameter Turn-On” dialog please note that there is a fifth way of using the “Parameter Turn-On” dialog: If you do not mark any of the “vary” checkboxes (i.e. if the table of “Active parameters” on the right-hand side is empty), you can instruct FullProf to calculate the powder diffraction pattern (based on the current settings and parameter values) simply by pressing the “Run FullProf” button. When the calculation has finished, you can e.g. export the calculated pattern using the menu command “File/Export/Profile data (Rietveld)”.

#### Buttons in “Parameter Turn-On” dialog

There are a couple of buttons located at the bottom of the “Parameter Turn-On”-dialog:

- **Run FullProf:** Once you have selected the parameters you would like to optimize, the Rietveld refinement calculation is started by pressing this button.
- **Clear:** By pressing this button you can turn off all parameters, i.e. uncheck the “vary” checkboxes of all parameters. This will also erase the “Active parameters” table.
- **Reset:** You can reset all parameters to their original values (the ones before the first Rietveld refinement) by pressing this button.
- **Export:** Match! offers a large variety of FullProf variables and options. Nevertheless, it may be useful in special situations to use FullProf directly (without Match!). For this purpose you can export the input files required (\*.pcr, \*.dat and \*.bac) as a starting point for the FullProf calculation by pressing this button. You will be asked to provide the path where the FullProf input files shall be stored. Afterwards, the files will be created in the specified directory.

#### Running the calculation

When you have selected all parameters you would like to refine, the Rietveld refinement calculation is started by pressing the “Run FullProf” button at the bottom left of the “Parameter Turn-On” dialog. As soon as the calculation has finished, the results (e.g. R-factor,  $\chi^2$ , FullProf comment) will be displayed in the “Rietveld” tab to the right of the Match! window. You will also be informed if the calculation was successful (reached convergence) or not.

#### Results viewing

When the FullProf calculation has finished there are several facilities to view and evaluate the results of a refinement calculation:

First of all, the convergence, the weighted average Bragg R-factor, the final reduced  $\chi^2$  and the comment from FullProf are displayed at the top of the “Rietveld” tab. Below, there are several buttons using which more detailed information is available:

The “**View results**” button displays a table in which you can compare the parameter values before and after the refinement calculation. If FullProf has detected correlated parameters during the calculation, you can display them by pressing the “**Display correlated parameters**” button below.

To the right, you can display the original FullProf files resulting from the calculation, simply by selecting the file you would like to view in the “**Display result file**” combobox. A window will open where you can view and maybe copy the contents of the selected file. This facility is especially useful if the result of a calculation is not to your satisfaction and you would like to view more details of the calculation.

Finally, you can copy the FullProf result files to a user-defined directory by pressing the “Save resulting files” button. **If you do not save the FullProf files using this button, they will be deleted when you open or create a new Match! document.**

### Configuring automatic Rietveld refinement calculations

Using the "Define Parameter Sequence for Automatic Rietveld Refinement" dialog (Fig. 37) you can select which parameters shall be refined in which order (cycle) during the automatic Rietveld refinement procedure.

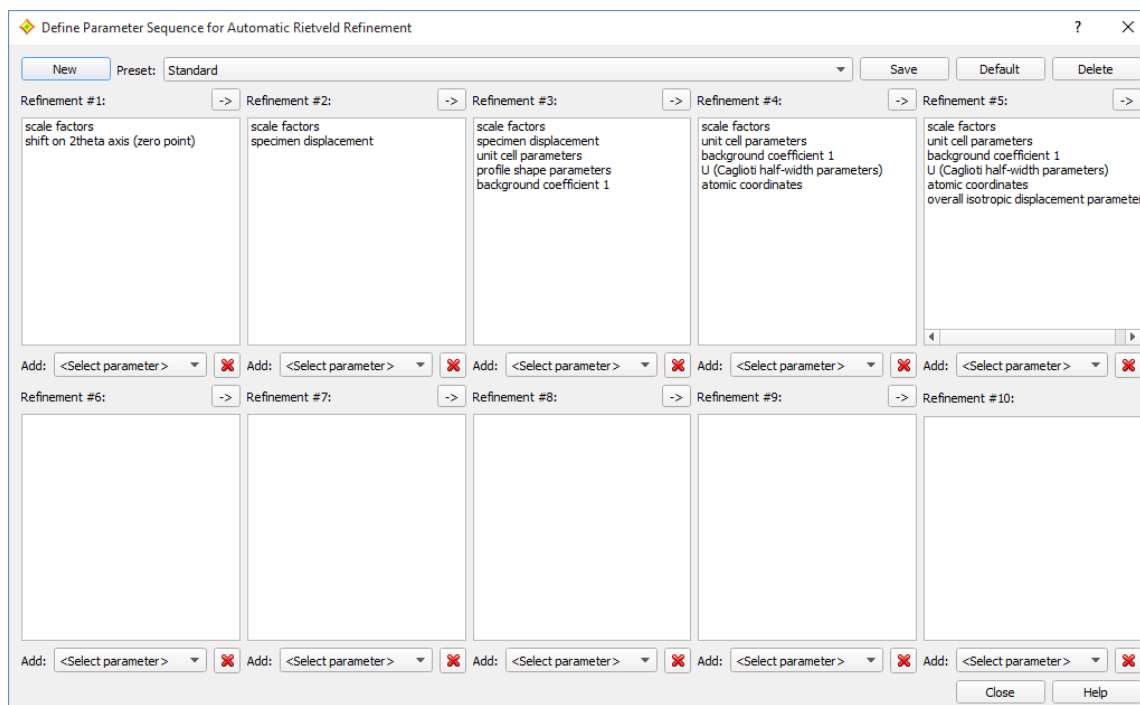


Fig. 37: In this dialog you can select which parameters shall be refined in which Rietveld refinement calculation

You can define parameters for a maximum of 10 subsequent refinement cycles.

The dialog can be opened by pressing the “Configure...” button at the top of the "Rietveld Parameter Turn-On" dialog (Fig. 33). In the top row of the dialog window, the dialog elements for the control of the current parameter sequence are placed:

- **New:** By pressing this button, the parameter sets for the 10 refinement cycles are erased, so that you can start from scratch to create a new parameter sequence. You will be asked if you would really like to do so after pressing the New button.
- In the **Preset** combo box, you can access all parameter sequence sets that you have already created. Simply click on the combo box and select the name of the parameter set you would like to open.


The "Standard" parameter set is always present in this combo box. This set contains the default/factory automatic refinement procedure; it cannot be deleted.

- By pressing the **Save** button you can store the current parameter sequence set using a user-defined name, so that you can recall this setting later on in the "Preset" combo boxes both of the "Define Parameter Sequence..." as well as the Rietveld Parameter Turn-On" dialog. After pressing the button, you will be asked to enter a reasonable name for the parameter set. Once you have pressed "OK", the new parameter sequence preset will be added to the "Preset" combo box.
- If you press the **Default** button, the current parameter sequence set will be selected as the new default parameter sequence for automatic Rietveld refinements. The current parameter sequence must have been saved in advance for this purpose; otherwise a corresponding hint/message will be displayed.
- Pressing the **Delete** button removes the current set from the "Preset" list. Hence, if you would like to remove a parameter set, you have to select it from the "Preset" combo box first, and then press the "Delete" button.

**Please note:** The parameter set called "Standard" contains the factory parameter set; it cannot be deleted.

In the **10 boxes (parameter lists)** (labeled "#1", "#2" etc.) below, you can select which parameters shall be varied separately for each refinement cycle. Match! runs the Rietveld refinements in the order as they are indicated at the top of the boxes, i.e. it starts with "Refinement #1", then runs "Refinement #2" etc. In each refinement cycle, all parameters that are present in the corresponding list (box) will be varied.

For every refinement cycle parameter box, a set of associated dialog elements is available:

- The "->" (arrow right) button at the top right of each parameter box copies the parameters of the corresponding box into the next box. This may be useful if you would like to add more and more parameters in each subsequent cycle, which is a common strategy in Rietveld refinement.
- In order to **Add** a new parameter to a parameter box, simply select it from the combobox at the bottom of the corresponding parameter list. It will instantly be added to the list.
- By pressing the  button at the bottom right of each parameter box you can delete the marked parameters from the corresponding parameter box. If no parameter is currently marked, all parameters will be removed from the box.

Once you have finished editing the Rietveld refinement parameter sets, please press the **Close** button to return to the "Rietveld Parameter Turn-On" dialog.

### Rietveld options

On the "Rietveld" page of the "Options"-dialog you can make some adjustments for Rietveld refinement. First of all, you can define the directory in which the FullProf Suite is installed. In addition, you can select which tab ("Rietveld user level"; Beginner, Advanced, Expert or Previous) you prefer for being displayed first when the "Parameter Turn-On"-dialog is opened. It is also possible to make the "Automatic Rietveld refinement" option default. In addition, you can instruct Match! to keep the previous selection of parameters to be refined when you open the parameter turn-on dialog the next time ("Save parameter selection for next calculation"). Finally, you can decide if you would like to automatically display the profile data resulting from the Rietveld refinement (as well as the corresponding difference plot) when a refinement calculation has converged.

The Rietveld options page can also be displayed directly from the "Rietveld"-tab on the right-hand side of the Match! window by pressing the "Options" button.

### Tips for Rietveld refinement

With Match! we have tried to get you into Rietveld refinement as gently as possible by offering different approaches with increasing difficulty level, from the "Automatic refinement" option to the "Expert" facilities. Nevertheless, Rietveld refinement is a complex subject that can require quite some experience. We would like to provide you with some hints and facts you should keep in mind in order to avoid running into problems at an early stage.

### General remarks

First of all, Rietveld refinement uses a **local** optimization method (least-squares refinement). This means that the method will try to reach the next minimum available from the starting point. You cannot expect from the method to investigate large parts of the cost function hypersurface! In practice this means that your starting model (e.g. crystal structure data, scaling factors, profile parameter values etc.) should be as close to the final model as possible, in order to reach convergence. You should avoid to give the system any "room" for getting stuck in a false minimum or being blown up by a singular matrix.

### Strategy for refinement

A reasonable strategy for performing a Rietveld refinement is not to vary all parameters straight away from the beginning, but to introduce them one after the other in a certain reasonable order. For example, there is little sense in trying to refine your atomic coordinates as long as the scaling factors of the phases are far off their optimum values!

On the "Beginner" tab of the "Parameter Turn-On" dialog you can see "our" suggestion<sup>33</sup> for the order of parameter introduction into the calculation: You start by refining the scale factors of the phases and maybe the specimen

<sup>33</sup> The strategy has been adapted from the suggestion described in R.A. Young (ed.), "The Rietveld Method", International Union of Crystallography, Oxford University Press, New York 1993, p. 32-36.

displacement. Once you have run the corresponding Rietveld refinement and reached convergence, you can add the unit cell parameters and the first background parameter, and perform the second Rietveld refinement etc.

### Check of refinement result

It is always advisable to take a look at the pattern graphics and compare the profile resulting from the Rietveld refinement (which has light-green color by default) to the experimental profile. Quite a lot of problems can be identified by this approach:

- Wrong scaling factor(s)
- Background is not correct
- Wrong or unidentified phase(s)
- Missing or surplus peaks
- 2theta error (e.g. zero point and/or specimen displacement)
- One or more unit cell parameters do not match
- Profile shape is not described correctly by the profile function applied, e.g. due to asymmetry

### Preferred orientation

If you observe that the intensities of one (or more) peaks of a certain phase are way off their expected values, this may be an indication that the crystallites in your sample are not oriented completely at random, but that there is a certain “accumulation” of a certain crystallite orientation with regard to the incident beam (a so-called “preferred orientation”, also called “texture”). This may happen for example if your crystallites have the shape of needles or plates, so that they prefer to be oriented along the axis of a capillary or the surface of a flat plate sample.

In Rietveld refinement using FullProf, this can be taken into account (at least to a certain degree) by refining the parameters of a corresponding preferred orientation function (“exponential” or “March” function). Please follow these instructions in order to do so:

1. Run Rietveld refinement of at least the scaling factors.
2. Display the contents of the result file “fpcalc.hkl”, by selecting this file in the “Display result file” drop-down box on the “Rietveld” tab and pressing the “Go!” button.
3. Examine the list of intensities and locate the preferred orientation, indicated by a series of harmonic reflections with  $I_{\text{obs}}$  systematically quite larger than  $I_{\text{calc}}$ . If you cannot locate a clear preferred orientation, you may try some possibilities like 001, 100, 010, 110, etc.
4. Press “Run new calculation” (open the “Rietveld Parameter Turn-On”-dialog), then enter the preferred orientation vector just mentioned on the “Stress/strain/pref. orientation” sub-tab of the corresponding phase’s page on the “Expert” tab.
5. On the same tab, mark “Pref1” for refinement.
6. Press “Run FullProf” in order to run the refinement.
7. If you have achieved a significant drop of the R-factor, you may have found the preferred orientation. If not (or if the refinement calculation did not even converge at all), you should try another preferred orientation vector as described above.
8. By default, Match!/FullProf uses the “Exponential function” for preferred orientation. You could also try the “Modified March’s function”, by changing the corresponding value of “Nor” on the “Global” sub-tab of the “Expert” tab.

### Convergence problems

If a calculation does not converge, you should go back and try to find out which parameter causes the problem. Maybe you can keep it fixed or introduce some constraints for it.

If you encounter convergence problems if only the scaling factor(s) of one or more phases are refined, you should check the crystal structure descriptions of the match list entries, especially the space group, setting and atomic coordinates. You could e.g. try to use a different entry describing the same phase, or display and investigate the crystal structure in the "Diamond" software (only available on Windows platforms).

### **Refinement of atomic parameters**

If your successive Rietveld refinement calculations do no longer converge after activating the option/parameter "Atomic coordinates of all phases" on the "Beginner" or "Advanced" tab of the "Parameter Turn-On" dialog, you should try to activate the atomic coordinates of the atoms individually one after the other instead. This can be achieved on the separate "Crystal structure" tabs for each individual selected phase (tab "Expert").

### **Correlated parameters**

Another typical origin for convergence problems are parameter correlations. Correlated parameters can e.g. prevent a refinement calculation from converging by switching between two states, or by endless variations of one or more parameters that do not have any effect on the cost function (R-factor,  $\chi^2$ ). As has already been mentioned above, you can press the "Display correlated parameters" button on the "Rietveld" tab to the right to display the correlated parameters detected by FullProf.

### **Original FullProf output checking**

In addition, it might be extremely helpful to take a look at the FullProf output files (e.g. fpcalc.out, fpcalc.sum and fplog.log), especially at their lower part. Here you can normally locate the origin of severe problems. In order to display one of these files, simply select the corresponding file from the "Display result file" combobox on the right-hand side of the "Rietveld" tab, and/or press "Go!".

If you really get stuck with your refinement, you might consider to **vary individual parameters manually** until you have reached a reasonable agreement between the pattern calculated by FullProf and the experimental pattern.

The background is that if the starting values of one or more important parameters (like the scaling factors) are too far off their optimum values, there may be little to no "contact" between the experimental diffraction pattern and the one calculated by FullProf. As a result, it may be very difficult for the Rietveld refinement to modify these parameters into the right "direction", because there may be no real improvement when varying these parameters one or the other way. Keep in mind that "Rietveld refinement" is a local optimization, i.e. it tries to reach the next minimum!

In order to improve this situation, it may be necessary to run a **"manual refinement"**, i.e. to adjust some parameters manually until a reasonable agreement between calculated and experimental has been reached that may then be used as a starting point for the Rietveld refinement.

First of all, run some basic Rietveld refinement varying e.g. the scaling factors, and compare the resulting calculated pattern to the experimental one afterwards in the diffraction pattern graphics. Try to figure out which parameter should be changed in order to get a better agreement between the two curves. Afterwards, open the "Parameter Turn-On dialog", disable the "Automatic Rietveld refinement" option at the top if necessary, and search for the parameter to be changed on the "Advanced" or "Expert" tab. Click on the "..."-button to the right of the corresponding parameter, and modify the "Current value" of the parameter in the dialog that is displayed. Do **not** activate the variation of this or any other parameter!

After you have modified the parameter(s) according to your assumptions, check again that no parameters are activated for Rietveld refinement (the "Table of active parameters" on the right-hand side must be empty), then press the "Run FullProf" button on the bottom left in order to instruct FullProf to recalculate the diffraction pattern based on the new parameter values. When the calculation has finished, compare the two curves mentioned above again, and think again of any parameters that may need some adjustment for a better agreement.

Repeat these steps until a reasonable agreement between calculated and experimental diffraction pattern has been achieved, then continue by running a normal Rietveld refinement starting at this point.

If all these hints do not help to obtain a reasonable refinement, or if you have special requirements, you might consider to **move on to using FullProf directly**, so that you really have all possibilities this program package offers. In order to do so, you can press the "Export" button in the "Parameter Turn-On" dialog to export FullProf files (pcr, dat and bac), so that you have a starting point for your journey into the world of FullProf.



## Pattern decomposition (Le Bail method)

### Basics

Pattern decomposition<sup>34,35</sup> aims at obtaining **reflection intensities  $I(hkl)$**  from powder diffraction data. The method is pretty similar to Rietveld refinement, in the sense that it tries to mimic an experimental powder diffraction profile by refining certain parameters of a model (function). However, in contrast to Rietveld refinement, pattern decomposition does not require the availability of full crystal structure data. Instead, it just needs unit cell parameters and maybe the space group (if available) for all phases that are present in the sample. Hence, you can also apply it in cases where no atomic coordinates are available.

This is possible because in pattern decomposition using the Le Bail method the reflection (or peak) intensities  $I(hkl)$  are not calculated from the given crystal structure data, but are obtained directly from an **iterative partitioning of the experimental intensities according to the intensities calculated from the model**.

There are basically three purposes for pattern decomposition:

1. Obtain reflection intensities  $I(hkl)$ , e.g. for crystal structure solution
2. Determine the lowest possible R-factor (or  $\chi^2$  value) that can be expected from a corresponding Rietveld refinement. The background is that in pattern decomposition the  $I(hkl)$  values are not constrained by the atomic coordinates. Instead, they can be freely adapted to the experimental peak intensities, in order to mimic them as closely as possible, thus leading to the best possible agreement between calculated and experimental diffraction pattern (lowest possible R-factor).
3. Verify the space group selection, by comparing the results of two (or even more) calculations in different space groups

### Pattern decomposition in Match! using FullProf

For pattern decomposition, Match! uses the well-known Le Bail method, as it is implemented in the Rietveld program FullProf (J. Rodriguez-Carvajal, Physica B **192**, 55 (1993)) in its so-called "Profile matching" mode. You do not have to interact with FullProf directly though; instead, you can use the Match! user interface to define ("turn-on") the parameters, setup the calculations and evaluate the results.

### Prerequisites

Before you start your actual pattern decomposition calculations in Match!, please check the following requirements:

- The path to FullProf must be defined: Normally, Match! determines the path to the FullProf software on your computer automatically. If this is not possible, you will be asked if you would like to manually select this path. Finally, if this is not successful (e.g. if you pressed the "Cancel" button), you will be asked to download and install FullProf from the Crystal Impact website ([https://www.crystalimpact.de/match/download.htm#download\\_fp](https://www.crystalimpact.de/match/download.htm#download_fp))
- Experimental diffraction pattern (profile) must have been imported.
- The qualitative analysis must have been completed, i.e. the match list must contain a list of all phases in the sample. All experimental peaks should have been assigned either to known phases or to the compound you would like to investigate by pattern decomposition.
- All entries in the match list must at least contain unit cell parameters and preferably space group. If the unit cell is still unknown for the compound under investigation, you have to run indexing first (p. 73).

### Setting up and running pattern decomposition calculations

Once you have checked the prerequisites mentioned above, you are ready to setup and run pattern decomposition calculations. This is achieved by running the menu command "Tools / Pattern decomposition (Le Bail fit) using FullProf..." or by pressing the corresponding button **hkl** in the toolbar. This will open the so-called "Parameter Turn-

<sup>34</sup> A. Le Bail, "Whole powder pattern decomposition methods and applications: A retrospection", Powder Diffraction, Volume 20, Issue 4, December 2005, pp. 316 - 326; DOI: <https://doi.org/10.1154/1.2135315>

<sup>35</sup> Advanced Certificate in Powder Diffraction on the Web, School of Crystallography, Birkbeck College, University of London, 1997-2006; <http://pd.chem.ucl.ac.uk/pdnn/solve1/lebaill.htm>



On" dialog, just like in Rietveld refinement (p. 61). Please follow the instructions given there in order to learn how to operate this dialog and run refinement calculations.

We recommend to refine the following parameters in subsequent refinement calculations (although you can use your own scheme, of course!):

- Shift on 2theta axis (zero point)
- Unit cell parameters
- U, V, W (Caglioti half-width parameters)
- Profile shape parameters
- Asymmetry parameters Asym1, Asym2
- Background parameters

Just like in Rietveld refinement, try to reduce the R-factor ( $\chi^2$  value) as much as possible, while selecting only reasonable parameters for refinement.

### Results viewing and exporting

When the FullProf refinement calculation has finished, there are several facilities to view and evaluate the results of a refinement calculation:

First of all, the convergence, the weighted average Bragg R-factor, the final reduced  $\chi^2$  and the FullProf comment are displayed at the top of the "Rietveld" tab on the upper right-hand side of the screen. Below, there are several buttons using which more detailed information is available:

- The **View results button** displays a table in which you can compare the parameter values before and after the refinement calculation.
- If FullProf has detected correlated parameters during the calculation, you can display them by pressing the **"Display correlated parameters" button** below.
- To the right, you can display the original FullProf files resulting from the calculation, simply by selecting the file you would like to view in the **Display result file** box. A window will open where you can view and maybe copy the contents of the selected file.
- This facility is especially useful if the result of a calculation is not to your satisfaction and you would like to view more details of the calculation.
- Finally, you can copy the original FullProf result files to a user-defined directory by pressing the **Save resulting files button**. Note that if you do not save the FullProf files using this button, they will be deleted when you open or create a new Match! document!
- In order to **export the resulting I(hkl) data**, please run the menu command "File / Export / Reflection data I(hkl) or |F(hkl)|".

If the peak data of a match list entry result from a pattern decomposition calculation, this is indicated by a "[PD]" in the legend of the pattern graphics.

### Quantitative Analysis

Once a pure Rietveld refinement calculation using FullProf has converged, the amounts of the individual phases resulting from the calculation are copied back into the match list, so that the results of the quantitative analysis are available there. Hence, the values in the "Amount (%)" column in the match list may change when a Rietveld/FullProf calculation has been run successfully (i.e. convergence was reached).

However, if a mixed (Rietveld and pattern decomposition) or a pure pattern decomposition refinement has been performed, the entries where pattern decomposition has been applied are not included in the quantitative analysis

(their amounts will be displayed as zero (0.0)). In these cases it is possible to perform a full quantitative analysis if the amounts of these phases are known from other sources:

You can enter the known amount(s) manually in the match list, by double-clicking the corresponding "missing" amount value "0.0" in the match list, entering the "true" amount, and finally pressing <Return>. Match! will re-scale the amounts of the remaining phases accordingly.

## Crystallite size estimation

### Basics

The average crystallite size(s) are calculated from the peak widths (FWHM values) using the Scherrer equation (Equation 1). The peak widths can be obtained e.g. by profile fitting (p. 26) or Rietveld refinement (p. 60).

Since the observed peak widths contain contributions not only from your sample but also from your instrument (diffractometer), it is important to determine and "subtract" the instrumental contribution before the actual analysis can be performed. You need the diffraction pattern of a suitable standard material (e.g. LaB<sub>6</sub> or Si) recorded at the same conditions as your sample's pattern for this purpose.

### Instructions

#### 1. Check Instrumental Standard

"Standard material patterns" (also called "instrumental standards") can be stored in Match! for multiple usage. If you don't know for sure if a suitable instrumental standard is already available in your Match! environment, you can check it e.g. by running the "Add/edit instrumental broadening standard" command from the "Quantify / Crystallite size estimation" menu:

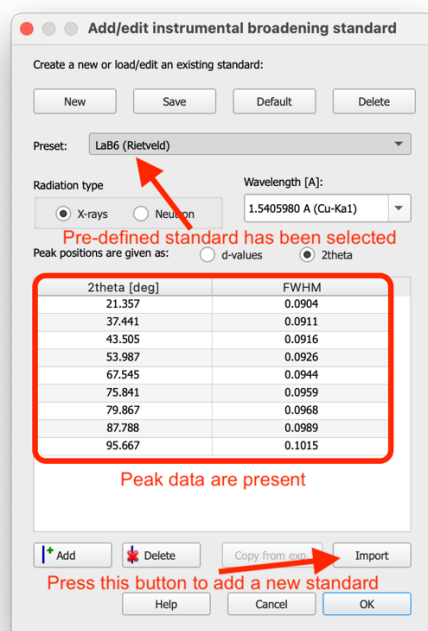


Fig. 38: In the "Instrumental Standard" window you can create, modify and delete standards for the peak broadening caused by your instrument.

If no standard peak data are displayed in the corresponding table (meaning that at least no standard has been selected as "default" up to now), please check the "Preset" drop-down list at the top for available pre-defined standards on your computer.

If no (reasonable) standard is currently available, please read the chapter below to get more information about the various methods to create an instrumental standard in Match!. Afterwards, please return here and move on.

#### 2. Import Diffraction Data


If your sample's powder diffraction pattern has not been imported so far, please do so now (p. 20).

#### 3. Process your Diffraction Pattern and Determine Peak Widths

Now the choice is your's:

- If you just want to get an estimate of the average crystallite size in your sample (without determining crystallite sizes of individual phases), you can simply run profile fitting (p. 26) by pressing <F5> and then move on.
- However, if you would like to calculate average crystallite sizes for each individual phase, please run a qualitative analysis first and preferably a Rietveld refinement afterwards, e.g. by pressing <Ctrl+Alt+R> (Mac: <Cmd+Alt+R>) (p. 51). Finally, return here and move on.

#### 4. Automatic Crystallite Size Estimation

Press the button  in the toolbar (or run the "Crystallite size estimation..." command from the "Quantify / Crystallite size estimation" menu). A new window will open in which the average crystallite sizes that have been calculated automatically are presented:

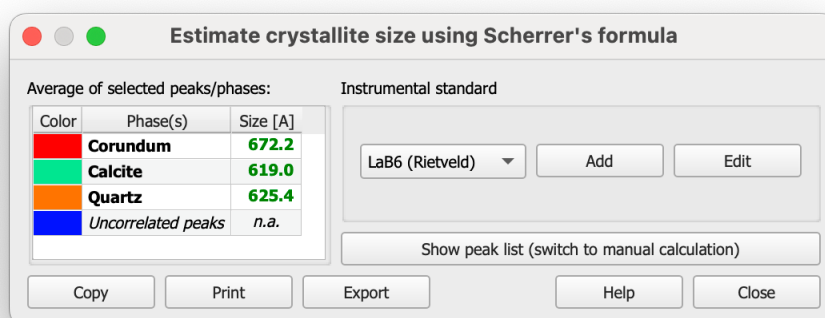


Fig. 39: The result of the automatic crystallite size estimation calculation is present in the table on the left-hand side

The font color of the values in the column "Size [Å]" indicates the reliability of the peak width source used for the calculation: From **green** (Rietveld refinement) over **blue** (profile fitting of **correlated** peaks) and **purple** (profile fitting of closest peaks) down to **red** (default FWHM value or unknown source).

If experimental peaks are present that could not be correlated to any matching phase (or if no phases have been selected as 'matching' up to now), the corresponding peak widths are used to calculate the crystallite size shown in the line "Uncorrelated peaks".

You can now **copy**, **print** or **export** the results by pressing the corresponding buttons. The crystallite size values will also be included in the **report**.

#### 5. Manual Calculations

If you would like to go more into detail, you should press the button "Show peak list (switch to manual calculation)". This will enlarge the window, now also displaying a table of the individual experimental peaks, the corresponding FWHM values as well as the assigned phases:

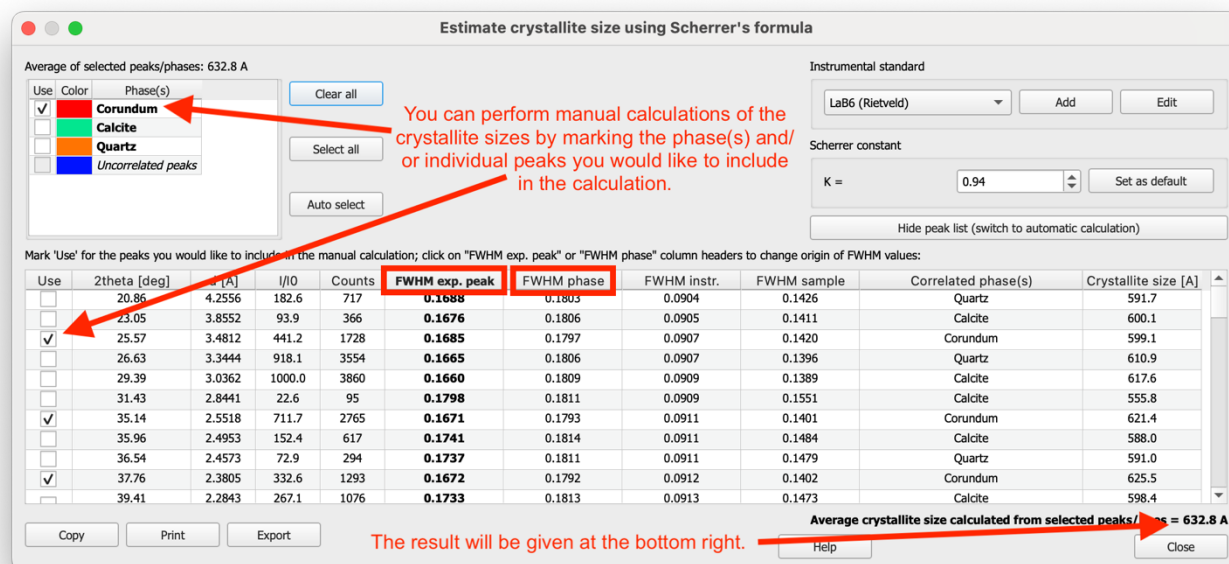


Fig. 40: When using manual calculation you can control which peaks and which FWHM source shall be used for crystallite size estimation

You can include or exclude experimental peaks from being included in the crystallite size calculation by (un-)marking the box in the column "Use" on the left-hand side.

To switch between using the widths of the experimental peaks ("FWHM exp. peak") or the ones stored for the individual phases ("FWHM phase"; e.g. from Rietveld refinement), please click on the corresponding column headers in the peak table (red frames in the screenshot above). The currently used FWHM source is indicated by the bold characters.

If you mark (click on) one or more line(s) in the peak list of the Crystallite size estimation window, the corresponding experimental peaks will also be marked in the main window (e.g. pattern graphics, peak list).

## Background Information

### Scherrer Equation

The widths of the peaks are given as FWHM values (FWHM = Full Width at Half Maximum). The crystallite sizes are calculated from the given peak widths FWHM using the Scherrer equation<sup>36,37</sup>:

$$L = \frac{K \times \lambda}{FWHM \times \cos \theta}$$

Equation 1: The Scherrer equation is used to calculate the average crystallite size  $L$  (in Å) from the given peak widths (FWHM) and diffraction angle  $\theta$

where  $K$  is the so-called "Scherrer constant" (typically =0.94 for FWHM of spherical crystals with cubic symmetry),  $\lambda$  is the wavelength of the radiation and  $\theta$  is the diffraction angle of the peak.

### Instrumental Peak Broadening Contribution

Before the peak width (FWHM) values can be used to calculate crystallite size(s), it is necessary to remove the instrumental contribution to the peak broadening. To do so, you first must create a so-called **instrumental standard** that contains your instrument's contribution to peak broadening. Further information can be found here.

<sup>36</sup> P. Scherrer, "Bestimmung der Größe und der inneren Struktur von Kolloidteilchen mittels Röntgenstrahlen", Nachr. Ges. Wiss. Göttingen **26** (1918), 98-100.

<sup>37</sup> J.I. Langford and A.J.C. Wilson, "Scherrer after Sixty Years: A Survey and Some New Results in the Determination of Crystallite Size", J. Appl. Cryst. **11** (1978), 102-113.

The instrumental contribution to the peak broadening is removed from the observed peak width using the formula

$$FWHM_{sample}^2 = FWHM_{observed}^2 - FWHM_{instrumental}^2$$

**Equation 2: Removal of the instrumental contribution to peak broadening from the observed / experimental peak widths**

The background why not the simple difference  $FWHM_{sample} = FWHM_{observed} - FWHM_{instrumental}$  is used is that peak broadening contributions from different sources combine in a quadratic manner, not linearly. This is because the broadening from different factors (such as crystallite size, strain, and instrumental effects) is typically considered to be independent and additive in terms of variance rather than in terms of simple widths.

The "observed peak widths" ( $FWHM_{observed}$ ) just mentioned may either result from simple profile fitting of the diffraction peaks, or they may be calculated using the Caglioti equation

$$FWHM_{observed}^2 = U \cdot \tan^2 \theta + V \cdot \tan \theta + W$$

**Equation 3: Caglioti formula for the calculation of peak widths FWHM for given diffraction angle  $\theta$ . The parameters U, V and W can be determined e.g. by Rietveld refinement.**

## Instrumental Standards

### Basics and Background

The crystallite size estimation in Match! is based on the analysis of the peak widths, given as the FWHM values (FWHM = Full Width at Half Maximum). However, before the FWHM values of e.g. the experimental peaks can be used in this calculation, it is necessary to separate the contribution of the instrument to the peak broadening from the actual contribution of the sample that we are interested in.

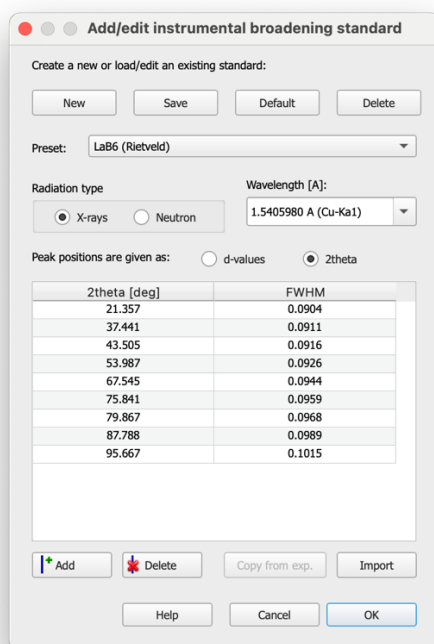
To do so, you first must create a so-called "instrumental standard" that contains your instrument's contribution to peak broadening. This can be achieved by recording, importing and analyzing the powder diffraction pattern of a suitable standard material, using the same setup and experimental conditions as have been used for your sample.

Typically, an instrumental standard consists of a list of peaks found in the diffraction pattern of the standard material, namely the peak positions and their widths (FWHM values). Both can be obtained e.g. from a profile fit of the peak data to the standard's raw (profile) diffraction pattern.

### Instructions

Instrumental standard data can be worked on in the "Add/edit instrumental broadening standard" window that can be opened e.g. using the corresponding command from the "Quantify / Crystallite size estimation" menu.





**Fig. 41: In this window that can be opened from the "Quantify / Crystallite size estimation" sub-menu, you can create, modify or delete an instrumental peak broadening standard**

There are several ways to add a new instrumental standard:

#### Add New Standard with Automatic Analysis

The fastest way to add a new instrumental standard is to use automatic analysis. Before you start, make sure that you have the raw (profile) diffraction data file of the standard material mentioned above available.

Run the "Quantify / Crystallite size estimation / Add/edit instrumental broadening standard" menu command, then press the "Import" button in the window that opens. Select the standard material's diffraction pattern file just mentioned, then press "Open".

Match! will import the diffraction data file and analyze it automatically, i.e. search for the diffraction peaks and perform profile fitting. The resulting peak data will then be displayed in the table.

Finally, please press "OK" at the bottom right. Match! will ask you to save the new standard under a user-defined name, and then close the window. You are now ready to use this standard in your analyses.

#### Add New Standard using Rietveld Refinement

Using a standard with peak widths obtained from Rietveld refinement is highly recommended because of the typically high accuracy of the data. The drawback is that the creation of the standard in Match! can be a little bit more demanding than the other options.

The first step is to import the powder diffraction pattern of a suitable standard (see above). Afterwards, please perform a qualitative analysis, and select an appropriate entry belonging to the known standard material as "matching".

Now that the match list contains the standard material phase, please perform a Rietveld refinement, e.g. by running the menu command "Quantify / Rietveld (FullProf)". This will run an automatic Rietveld refinement calculation (normally intended for quantitative analysis) during which also the so-called "Caglioti parameter"  $U$  (and maybe also  $V$  and  $W$  if possible) are refined. Afterwards, Match! will calculate peak width (FWHM) values for the peak positions  $\theta$  by applying the Caglioti formula, using the parameter values  $U$ ,  $V$  and  $W$  obtained from Rietveld refinement. Finally, Match! will store the resulting peak data ( $2\theta$  and FWHM values) in the match list entry.

You are now ready to run the "Quantify / Crystallite size estimation / Add/edit instrumental broadening standard" menu command. Match! will detect that peak data have been calculated using the Caglioti formula, and will ask if you would like to add these peak data (stored in the match list entry) as a new instrumental standard. Please confirm

by clicking "Yes". The "Add/edit instrumental broadening standard" window will open where the resulting peak data are displayed in the table.

Finally, please press "OK" at the bottom right. Match! will ask you to save the new standard under a user-defined name, and then close the window. You are now ready to use this standard in your analyses.

**Please note:** If you have performed a Rietveld refinement on an arbitrary sample in which you have also refined at least the Caglioti parameter U for a certain phase, you can add it as a new instrumental standard straight away. To do so, right-click on the corresponding phase (line) in the match list, then select the command "Add as instrumental broadening standard" from the menu that opens.

The "Add/edit instrumental broadening standard" window will open where the resulting peak data are displayed in the table. Finally, please press "OK" at the bottom right. Match! will ask you to save the new standard under a user-defined name, and then close the window. You are now ready to use the new standard in your analyses.

### Add New Standard with Manual Analysis

It is also possible to import and process the diffraction pattern of a suitable standard material manually without Rietveld refinement but using profile fitting instead. For this, the first thing you must do is to import the powder diffraction pattern of a suitable standard (see above). Afterwards, run the peak searching and profile fitting calculation (if they are not performed automatically). Make sure that the agreement between the experimental diffraction profile and the one calculated from the experimental peaks is good. You can display the resulting peak parameters in the peak list if you like.

Now you are ready to add these peak data as a new instrumental standard for crystallite size estimation: Run the "Quantify / Crystallite size estimation / Add/edit instrumental broadening standard" menu command. Match! will detect that experimental peak data are currently present, so it will ask if you would like to add these peak data as a new instrumental standard; please confirm by clicking "Yes". The "Add/edit instrumental broadening standard" window will open where the resulting peak data are displayed in the table.

Finally, please press "OK" at the bottom right. Match! will ask you to save the new standard under a user-defined name and then close the window. You are now ready to use this standard in your analyses.

### Add New Standard Data Manually

You can also enter the standard's peak data manually, by pressing the "Add" button below the peak data table. At least one peak position and FWHM value must be entered to create a valid standard.

To edit the peak data, please double-click on the corresponding cell in the table, then type the new value.

When you have finished, please press "OK" at the bottom right. Match! will ask you to save the new standard under a user-defined name, and then close the window. You are now ready to use this standard in your analyses.

### Additional Options and Functionality

There are some other buttons and options in the "Add/edit instrumental broadening standard" window (Fig. 41) that have not been mentioned so far:

By pressing the **New** button you can delete all current peak data and start from scratch. If peak data are already present (e.g. if you have copied them from the current experimental pattern), you will be asked if you would like to save the current data/standard. If you click "Yes", you can enter a reasonable name (e.g. the formula sum) for the new standard. Afterwards, the peak data table in the dialog will be erased.

Using the **Save** button you can save the current peak data as a new standard, or update the standard currently given as "Preset" (see below). Please enter a reasonable name (e.g. the formula sum) for the new standard if you do not want to overwrite the current standard ("Preset").

If you press the **Default** button, the standard currently given as "Preset" (see below) will be made the default instrumental standard for future crystallite size estimation calculations.

By pressing the **Delete** button you can remove the standard currently given as "Preset" (see below) from the settings, so it won't be available in the future anymore.

In the **Preset** line the instrumental standard for which the peak data are currently displayed is given. If you press the "drop down" arrow on the right-hand side, a list of all instrumental standards that are currently available in the settings is provided, so that you can select the standard for which you would like to see or modify the peak data, or which you would like to make the new default standard.

Below, you can define the **radiation type** and the **wavelength** for the current standard.

The **peak positions** in the table can either be displayed as **d-values** or **2theta**, depending on the corresponding selection.

In the lower half of the dialog, the **peak data table** is given, where you can view or edit the peak data for the current instrumental standard given in the "Preset" line.

Below the peak data table you can use the **Add** or **Delete** buttons to either add a new peak or delete the peaks (lines) that are currently marked in the peak data table.

By pressing the button **Copy from exp.** you can copy the experimental peak data from the current Match! document, in order to add them as a new standard.

It is also possible to **Import** a diffraction data file and extract the information to create a standard from it, by pressing the corresponding button. If the selected diffraction data file contains raw (profile) diffraction data, Match! will automatically process them right away, by running peak searching and profile fitting automatically. Data from peak data files (3-column peak list files (2theta/d intensity FWHM) or Stoe peak list files (\*.pks) are used straight away.

Once you have finished editing your instrumental standard peak data, please press **OK** to close this dialog. You may be asked to save your current standard data if you have not already done so. Help will display the corresponding page in the online help.

### Instrumental Standard Materials

Materials suitable as 'instrumental standard' are compounds for which it is known that they do not contribute to the diffraction peak profile (so that the peak broadening is almost entirely caused by the instrument). In an ideal standard material, the crystallite size should be larger than 500 nm while the particle size should be less than 10  $\mu\text{m}$ .

In addition, the standard material should be free of defects and strain. Finally, the standard should have a similar mass absorption coefficient than the nanocrystalline specimen as well as a similar atomic weight and packing density<sup>38</sup>.

**Typical standard materials** for the determination of the instrumental peak broadening are **LaB<sub>6</sub>**, **CeO<sub>2</sub>** or **Si**.

### Important facts to keep in mind

- Peak widths of a certain phase cannot take arbitrary values as a function of the diffraction angle  $\theta$ , in contrast to the peak widths obtained by simple profile fitting of the experimental data. It should be possible to describe the peak widths  $\text{FWHM}_i$  of a certain phase  $i$  as a function of  $\theta$  using the Caglioti formula (Equation 3).
- Peak widths of individual phases may be different, even when their peaks are assigned to the same experimental peak(s). You need to run Rietveld refinement of the Caglioti parameters  $U$ ,  $V$  and  $W$  to account for this.
- Please do not mismatch the **average crystallite size** with the **grain size**! A grain may be composed of several crystallites with different sizes.
- You should always keep in mind that effects other than domain size may contribute to the peak broadening as well, e.g. strain!
- It is extremely important to make sure that the "standard's diffraction pattern has been recorded on the same diffractometer and using the same experimental conditions than your sample's pattern. Do not use a

<sup>38</sup> Scott A Speakman, "Estimating Crystallite Size Using XRD", <http://prism.mit.edu/xray/documents/5a%20Estimating%20Crystallite%20Size%20Using%20XRD.pdf>

"standard material" diffraction pattern obtained from another source that has nothing to do with your own sample!

- The automatic calculation result may deviate from the result of a manual calculation for the same phase, because the automatic calculation uses all peaks from the corresponding match list entry for the crystallite size calculation, while the manual calculation uses the correlated experimental peaks. There may be match list entry peaks not correlated to experimental peaks, or multiple match list entry peaks that are correlated to the same experimental peak!

## Unit cell determination (indexing)

### Basics

Within Match!, “indexing” means the derivation of unit cell parameters from given peak positions in a powder diffraction pattern. It is a mandatory step in crystal structure solution from powder diffraction data, e.g. using our software package “Endeavour”. Knowing the unit cell can also be very useful in qualitative phase analysis, considering that cell parameters can be used as restraints.

Quite a lot of indexing programs are available today<sup>39</sup>; Match! can use two of the most prominent: **Treor90** and **Dicvol**.


### Prerequisites

In principle, you can download and install Treor and/or Dicvol separately on your PC, however, these programs are also included in the FullProf Suite<sup>40</sup>. Hence, there is no need to bother with this if you have already installed FullProf on your computer (e.g. for Rietveld refinement, p. 90). Match! will automatically locate the Treor90 and Dicvol06 programs included in this package, so you are ready to setup and run indexing calculations straight away. If this does not apply, you should take a look at the indexing options, in order to learn how to setup, the paths to the indexing programs.

### Setting up and running indexing calculations

All that is required to run an indexing calculation are either experimental peaks or raw diffraction data. If only raw (profile) but no peak data are present when the indexing command is run, Match! will automatically execute the raw data processing before the actual indexing calculation is started.

Before running the “Indexing” command, you should mark the peaks to be taken into account in the indexing calculation. If you do not mark any peaks, Match! will automatically use the 20 strongest peaks (if present) that are not yet covered by selected phases for indexing, and whose relative intensity is larger than the corresponding minimum value (which can e.g. be adjusted using the red bar on the y-axis of the diffraction pattern graphics)<sup>41</sup>.

You can run indexing either using the corresponding command from the “Tools” menu, or simply by pressing the corresponding button  in the main toolbar. Depending on the current settings and situation, this will either bring up a dialog asking which indexing method (Treor or Dicvol) you would like to use, run the default indexing program, or display the table of indexing results that are already present (and from which also new calculations can be run).

Once you have run the indexing command and maybe selected an indexing program, the corresponding parameter settings dialog will be displayed. The available parameters are different for Treor and Dicvol, so please see the corresponding chapters below for a detailed description of the two programs and their parameters.

#### Please note:

- Indexing can only be successful if all peaks that are considered belong to a single phase.
- It is strongly recommended to check (and maybe correct) 2theta errors (p. 27) before trying indexing.
- Criterion for the best cell: Maximum figure-of-merit, minimum number of unindexed lines

### Results viewing

When the calculation has finished, you may be presented with one (or even a table of) potential solution(s). Please mark and/or confirm the solution(s) you would like to accept. You will then be taken to the “Indexing results” dialog (see below) where you can evaluate the solutions (i.e. unit cells), inspect peak data, select crystal system and space group, and maybe add the solution as a new manual entry to the match list (e.g. to proceed with structure solution (p. 90)).


### Indexing results dialog

The “Indexing results” dialog (Fig. 42) presents the solutions (e.g. unit cells) of all indexing calculations that have been accepted for the current experimental pattern up to now. It will either be displayed after an indexing calculation

<sup>39</sup> <http://www.ccp14.ac.uk/solution/indexing/>

<sup>40</sup> <http://www.ill.eu/sites/fullprof/index.html>

<sup>41</sup> You can also adjust the corresponding parameter “minimum relative intensity for automatic peak usage” on the “Indexing” tab or the parameter “minimum relative intensity for peak correlations” on the “Search-Match” of the “Options” dialog. The values of these two parameters are identical.

has been run, or if the "Tools/Indexing" command is run (or the corresponding toolbar button  is pressed) when at least one indexing solution is already present for the current experimental pattern.

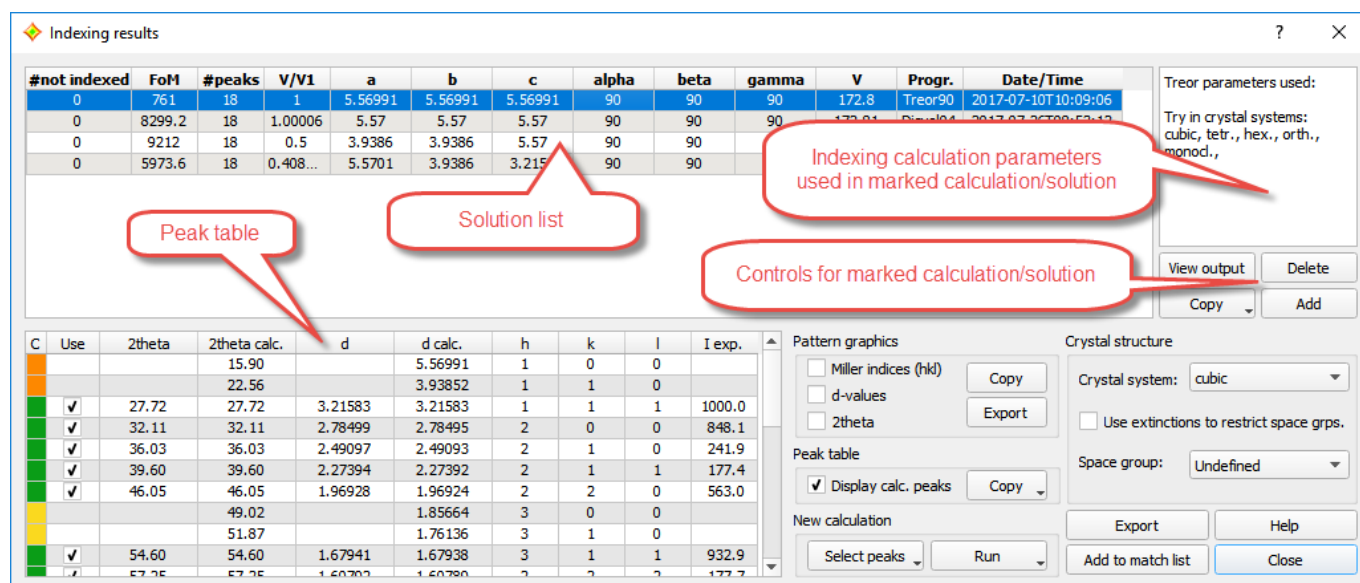


Fig. 42: The "Indexing results" dialog provides an overview over all unit cells that have been found for the current experimental pattern so far, along with the corresponding peak data.

The "Indexing results" dialog is organized as follows:

The table at the top (the so-called "**solution list**") displays the main results of the indexing calculations (e.g. unit cell parameters, cell volume, number of (un-)indexed peaks, figure-of-merit, name of the indexing program used etc.). To its right, the parameters that were used for the marked indexing calculation are displayed. Below the parameter listing, a couple of buttons allow the refinement of the unit cell parameters, viewing of the original output files, the copying and export of the solution list, deleting marked solutions as well as adding solutions (unit cells) manually.

If a solution (unit cell) is marked in the solution list, the corresponding calculated peak positions are displayed as vertical bars in the main pattern graphics. (Depending on your screen size and resolution, you may have to adjust the position of the "Indexing solutions" dialog window to view the important parts of the pattern graphics.)

In the lower half of the dialog, the most prominent dialog element is the **peak table** on the left-hand side. Here, all peaks that are somehow involved (both experimental as well as calculated) in the indexing calculation marked in the solution list are listed. A color-coding on the left provides a quick overview regarding the influence of each peak, e.g. if it has been indexed (green) or not (red).

The main controls are located on the lower right-hand side of the dialog. Here, you can adjust, copy and export the pattern graphics and the peak table, setup and run new indexing calculations, select crystal system and space group, export or add a solution to the match list. Both peak table and control elements refer to the solution that is currently marked in the solution list at the top.

### Solution list and its controls

The so-called "solution list" provides an overview over the unit cells (indexing calculation results, "solutions") that have been found so far for the current experimental diffraction pattern ("anchor pattern"). When a line in the solution list is marked, the peak data involved in this solution are displayed in the peak table at the bottom left. At the same time, the peak positions calculated from the current unit cell (and space group) will be displayed as vertical bars in the main diffraction pattern graphics. By default, these bars will have a light-orange color; you can change this color on the "Pattern graphics" page of the "Colors and line styles" dialog. The peak positions just mentioned are only displayed as long as a solution is marked or the "Indexing solutions" dialog is displayed; they will vanish when the dialog is closed.

The parameters that have been used in the indexing calculation resulting in the marked solution are displayed in the **parameters panel** on the top right-hand side of the window.

Below, you can **refine the unit cell** by pressing the **Refine** button. A least-squares refinement of the currently marked unit cell parameters will be performed, based on all marked, indexed or at least correlated peaks. The result will be added as a new line to the solution list.



The **View output** button can be used to display the original Treor or Dicvol output file for the currently marked solution/calculation.

The **Add** button allows the user to manually add a “solution” (i.e. set of unit cell parameters) to the solution list. This can be useful e.g. to check how a certain unit cell you may have in mind relates to the experimental data or the solutions resulting from the indexing calculations. When you press the “Add” button, a new dialog will be displayed in which the unit cell parameters as well as the crystal system can be entered. After accepting the parameters by pressing <OK>, the new unit cell will be added to the table of solutions and can be handled just like the results from the “normal” indexing calculations.







By pressing the **Del(ete)** button you can remove the currently marked solution from the solution list. The **Copy** button (for copying the current solution list into the clipboard) gives also access to the **Export** and **Print** functionality for the solution list.

If you would like to **edit the parameters of a manually added unit cell**, you can do so by double-clicking on the corresponding line in the solution list.

### Peak table

In the peak table, all peaks that are currently present in the experimental data as well as the marked solution are listed. For each peak, the following information is given as separate columns:

The “C(olor)” represents the status of each peak in the currently marked indexing solution:

-  Indexed peak
-  Experimental peak correlated to calculated peak, not used for indexing
-  Unindexed peak
-  Experimental peak not used for indexing, not correlated to calculated peak (maybe impurity phase)
-  Calculated peak, not observed in experimental data
-  Calculated peak, outside exp. 2theta range

The meaning of the individual colors is also displayed as a tooltip if you keep the mouse pointer over one of the colored panels.

If the checkbox “Use” is marked, the corresponding peak will be marked and included in the next indexing calculation.

In addition, the following peak parameters are given: “**2theta**” value of the experimental peak, “**2theta calc.**” 2theta value of the peak calculated from the current unit cell (solution), “**d**”-value of the experimental peak, “**d calc.**” d-value of the peak calculated from the current unit cell (solution), “**h, k, l**” Miller indices of the peak, referring to the current unit cell (solution), “**I exp.**” intensity value (I rel.) of the experimental peak.

### Pattern graphics

Using this panel you can control some displaying options of the main pattern graphics: If you mark any of the three checkboxes **Miller indices (hkl)**, **d-values** and/or **2theta**, the corresponding information will be displayed at the top of each calculated (or reference database) peak.

By pressing the **Copy** button you can copy the current contents of the main pattern graphics to the clipboard (e.g. to paste it into some Word or PowerPoint document). You can also **Export** the current pattern graphics to a file by pressing the corresponding button.

### Peak table control panel

In the “Peak table” panel you can toggle the **display of the calculated peaks** in the peak table on the lower left-hand side. Disabling the calculated peaks may sometimes be useful if a large number of them prohibits the inspection of the (un-)indexed peaks.

You can **Copy**, **Export** or **Print** the peak table: Pressing the “Copy” button gives access to all three commands.

### New calculation

Here you can quickly setup and run a new indexing calculation: First, use the **Select peaks** button to mark the experimental peaks you would like to use for indexing (if you have not already marked the peaks otherwise, e.g. in the "Use" column of the peak table or directly in the pattern graphics or peak list). Afterwards, start the indexing calculation by clicking on **Run**.

If you click on the "Run" button, either the default indexing program will be run or the "Select indexing program" dialog will be displayed, depending on the corresponding options setting. If you **keep the "Run" button pressed for about 1-2 seconds**, you can directly select if you would like to run Treor or Dicvol.

### Crystal structure

Using the dialog elements in this panel you can add more information about the crystal structure of the marked indexing solution (unit cell): You can select the **crystal system** and the **space group** from corresponding drop-down boxes.

If you mark the checkbox **"Use extinctions to restrict space grps."**, only space groups that are in agreement with the observed peaks in the current experimental pattern are available in the "Space group" drop-down box.

This procedure works using systematic absences as follows: First, Match! calculates the powder diffraction pattern for all space groups that are in agreement with the current crystal system. Afterwards, Match! checks for every calculated pattern if there are peaks for which the intensity value in the calculated pattern is zero while there is a correlated experimental peak with an intensity  $> 0.0$  (i.e. for which the correlated experimental peak is observed). If this applies, the space group does not fit to the experimental data and is removed from the list.

### Export

By pressing this button, you can export the current solution (unit cell parameters and space group) to a cif-file, e.g. for importing it in some other program for crystal structure solution or visualization.

### Add to match list


By pressing this button, you can add the current solution (unit cell parameters and space group) as a new manual entry (p. 125) to the match list. From there, you can e.g. run a crystal structure solution calculation (p. 90) using Endeavour.

Since an indexing calculation only reveals the peak positions that are in agreement with the resulting unit cell parameters but not the peak intensities, you have to select which peak intensity values shall be copied to the manual entry in the match list:

- **Full exp. intensities:** The full relative intensity values of the indexed experimental peaks will be used, i.e. the peaks that have been used for indexing or have been correlated to the indexing result.
- **Residuals:** The peak residuals are calculated by subtracting the peak intensities covered by the matching entries from the experimental peak intensities. Like with the previous option, the remaining intensity values will be used both for the 'indexed' peaks (i.e. the peaks that have been used for indexing) as well as those that have been correlated to the indexing result.
- **No intensity values:** The peak intensities in the new manual entry will be left undefined.

### Close

This button closes the "Indexing results" dialog. At the same time, the peak positions of the marked solution will vanish from the pattern graphics.

You can display the dialog again either by running the "Indexing" command from the "Tools" menu, or pressing the corresponding button  in the main toolbar. Your indexing results will still be present, of course.

## Indexing using Treor90


### Basics

Treor90<sup>42, 43</sup> is a well-known program for indexing powder diffraction patterns. Treor can be used by Match! to derive unit cell parameters from the peak positions of marked experimental peaks. As an alternative to Treor, Dicvol (see below) can also be used for this purpose.

### Setting up and running Treor90 indexing calculations

All that is required to run an indexing calculation are either experimental peaks or raw diffraction data. If only raw (profile) but no peak data are present when the indexing command is run, Match! will automatically execute the raw data processing before the actual indexing calculation is started.

Before running the “Indexing” command, you should **mark the peaks** to be considered in the indexing calculation. If you do not mark any peaks, Match! will automatically use the 20 strongest peaks (if present) that are **not yet covered by selected phases** for indexing, and **whose relative intensity is larger than the corresponding minimum value** (which can e.g. be adjusted using the red bar on the y-axis of the diffraction pattern graphics)<sup>41</sup>.

You can run indexing either using the corresponding command from the “Tools” menu, or simply by pressing the corresponding button  in the main toolbar. Depending on the current settings and situation, this will either bring up a dialog asking which indexing method (Treor or Dicvol) you would like to use, run the default indexing program, or display the table of indexing results that are already present (and from which also new calculations can be run).

Once you have run the indexing command and selected Treor as the indexing program to be used, the Treor90 parameter settings dialog will be displayed (Fig. 43).

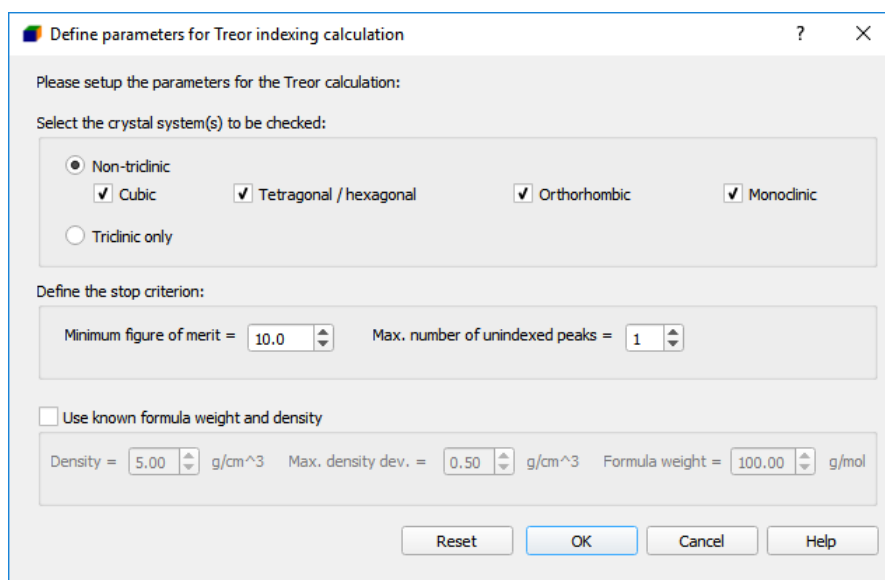


Fig. 43: In this dialog, you can define unit cell and parameter limits for the Treor90 indexing calculation.

The following parameters are available:

**Crystal system(s) to be checked:** You can select if you would like to investigate either triclinic or non-triclinic crystal systems. If you mark “non-triclinic”, you can include or exclude cubic, tetragonal/hexagonal, orthorhombic and/or monoclinic cells.

**Unit cell parameter restrictions:** In this section, you can define maximum value for the cell lengths as well as the maximum unit cell volume.

**Additional limits:** You can define the minimum figure-of-merit as well as the maximum number of unindexed peaks for a solution to be accepted. Increasing the maximum number of unindexed peaks will increase the probability to

<sup>42</sup> P.-E. Werner, “Trial-and-error computer methods for the indexing of unknown powder patterns”, *Z. Krist.* **120**, 375-387 (1964).

<sup>43</sup> P.-E. Werner, L. Eriksson and M. Westdahl, “Treor, a semi-exhaustive trial-and-error powder indexing program for all symmetries”, *J. Appl. Cryst.* **18**, 367-370 (1985).

get a solution (unit cell), so this may be a way out if you do not get a reasonable result with the standard settings. You should keep in mind though that you must check afterwards why the unindexed peaks are present in your pattern (maybe they belong to an impurity phase or are just artifacts). **Note** that by ignoring unindexed peaks it is quite easy to get artificial unit cells that have nothing to do with reality!

**Known formula weight and density:** If you know the arbitrary formula weight and density of your compound, and if the expected number of molecules or formula units in the unit cell is integer, you can enter the corresponding values as well as the max. density deviation as additional criteria to restrict the cell volume and hence the search space of the program. The value for the max. density deviation should be the maximum expected density deviation plus about 5-10%. The choice of the value should also take the quality of your diffraction data into account.

### Results viewing

When the calculation has finished, Treor will select the most promising indexing result (unit cell) automatically. Match! will display the result and ask you to confirm or reject this solution. You will then be taken to the "Indexing results" dialog (p. 81) where you can evaluate the solutions (i.e. unit cells) that you have found up to now, inspect peak data, select crystal system and space group, and finally export the solution or add it as a new manual entry to the match list (e.g. in order to proceed with structure solution).

If you would like to take a look at the **original Treor90 output file**, you can do so by marking the corresponding solution in the solution list and clicking the "View output" button on the upper right-hand side.

### General hints on indexing from the Treor documentation

- The standard procedure is to start with the high symmetries: cubic, tetragonal, hexagonal and orthorhombic (in one job). Next the monoclinic symmetry should be tried (more than one job may be needed). Successively increasing the number of base line sets and cell volume.
- The cell volume parameter may be estimated from the d-value of the 2th line (cf. keyword TRIC)
- Warning: If the true unit cell has a small volume, for example 250 Å<sup>3</sup> and VOL=2000 is used, the correct solution may be lost in the trial process.
- Warning: Estimation of the unit cell volume from the relations  $VOL(\text{monoclinic cell})=20 \cdot D(20)^3$  ( $D(20)$ =the d-value of the 20th line) and  $VOL(\text{orthorhombic})=31 \cdot D(20)^3$  are much less reliable than the corresponding relation for the triclinic symmetry  $VOL(\text{TRICLINIC})=13.39 \cdot D(20)^3$ . Reason: Triclinic structures have no systematic extinctions!
- Generally, the first 20-30 lines should be used. Remaining lines may be used in later final refinements.
- You should not accept unindexed lines unless you are able to explain them.
- On the other hand, you should not put in uncertain (doubtful) lines in this program. They may be tested later by any refinement program.
- The output list will be interrupted as soon as a unit cell that will satisfy the criteria 'minimum figure-of-merit' and 'maximum number of unindexed lines' are fulfilled.
- Although the trial cells will be ordered according to priority rules (max. number of indexable lines and min. volume), it is not a guarantee that the first refined cell gives a correct solution.
- The main rule is that if all the first twenty lines are indexed and the de Wolff figure-of-merit  $M(20)$  is greater than 9, then the indexing problem is in principle solved. This does not mean that the cell is reduced, that a cell axis may not be double etc.
- Unit cells obtained by this program should be carefully checked...
  - if the de Wolff figure of merit  $M(20)$  is less than 10 or more than one line is unindexed within the 20 first observed lines, the solution is probably meaningless. Try next step in the strategy (see above).
  - for common factors in the quadratic forms. For example, a tetragonal pattern may have  $H^2H + K^2K = 5 \cdot N$ , i.e. the a-axis is 2.3607 (square root of 5) times shorter than given on the output list. Obviously, if for example all H,K or L are even, the corresponding cell axis should be divided by two. This may occur if a too large VOL parameter has been given.
  - if the unit cell obtained is centered, derive a primitive cell.
  - reduce the primitive cell and derive the conventional cell.
  - Hexagonal and tetragonal cells are sometimes indexed as orthorhombic. For example:  $a = b \cdot 1.7321$ , i.e. a possible hexagonal cell.
  - Check for geometrical ambiguities (see reference list). It is also strongly recommended to check cubic, tetragonal and hexagonal solutions by an orthorhombic test.

## Indexing using Dicvol


### Basics

Dicvol06<sup>44</sup> is a well-known program for indexing powder diffraction patterns. Dicvol can be used by Match! to derive unit cell parameters from the peak positions of marked experimental peaks. As an alternative to Dicvol, Treor (see above) can also be used for this purpose.

### Setting up and running indexing calculations

All that is required to run an indexing calculation are either experimental peaks or raw diffraction data. If only raw (profile) but no peak data are present when the indexing command is run, Match! will automatically execute the raw data processing before the actual indexing calculation is started.

Before running the “Indexing” command you should mark the peaks to be considered in the indexing calculation. If you do not mark any peaks, Match! will automatically use the 20 strongest peaks (if present) that are **not yet covered by selected phases** for indexing, and **whose relative intensity is larger than the corresponding minimum value** (which can e.g. be adjusted using the red bar on the y-axis of the diffraction pattern graphics)<sup>41</sup>.

You can run indexing either using the corresponding command from the “Tools” menu, or simply by pressing the corresponding button  in the main toolbar. Depending on the current settings and situation, this will either bring up a dialog asking which indexing method (Treor or Dicvol) you would like to use, run the default indexing program, or display the table of indexing results that are already present (and from which also new calculations can be run).

Once you have run the indexing command and selected Dicvol as the indexing program to be used, the Dicvol parameter settings dialog will be displayed (Fig. 44).

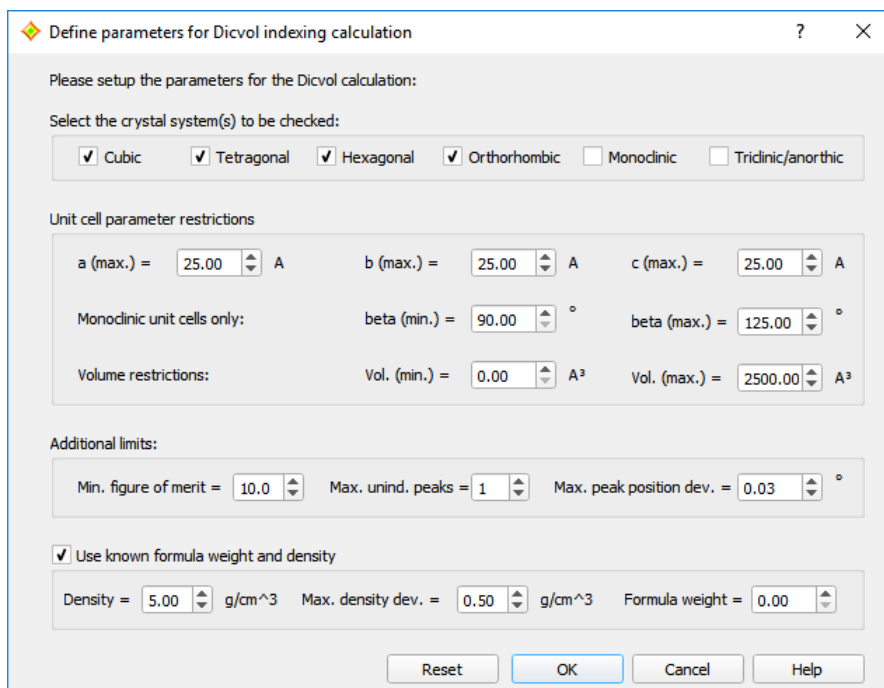


Fig. 44: In this dialog, you can define unit cell and parameter limits for the Dicvol indexing calculation.

The following parameters are available:

**Crystal system(s) to be checked:** You can include or exclude cubic, tetragonal, hexagonal, orthorhombic, monoclinic and/or triclinic cells. Normally, you should **start by excluding monoclinic and triclinic** crystal systems.

**Unit cell parameter restrictions:** In this section, you can define maximum values for the cell lengths, minimum and maximum monoclinic cell angle, as well as minimum and maximum unit cell volume.

**Additional limits:** You can define the minimum figure-of-merit as well as the maximum number of unindexed peaks (in the Dicvol manual also called "impurity tolerance"  $N_{IMP}$ ) for a solution to be accepted. Increasing the maximum

<sup>44</sup> A. Boulton & D. Louer, "Program for the Automatic Indexing of Powder Diffraction Patterns by the Successive Dichotomy Method", J. Appl. Cryst. 37, 724-731 (2004).



number of unindexed peaks will increase the probability to get a solution (unit cell), so this may be a way out if you do not get a reasonable result with the standard settings. You should keep in mind though that you must check afterwards why the unindexed peaks are present in your pattern (maybe they belong to an impurity phase or are just artifacts). Note that by ignoring unindexed peaks it is quite easy to get artificial unit cells that have nothing to do with reality!

In addition, you can define the max. peak position deviation (in degrees  $2\theta$ ), i.e. the maximum  $2\theta$  difference between an experimental and its corresponding calculated peak. If the  $2\theta$  difference is larger than this value, peaks are not regarded as being correlated (i.e. indexed).

**Known formula weight and density:** If you know the arbitrary formula weight and density of your compound, and if the expected number of molecules or formula units in the unit cell is integer, you can enter the corresponding values as well as the max. density deviation as additional criteria to restrict the cell volume and hence the search space of the program. The value for the max. density deviation should be the maximum expected density deviation plus about 5-10%. The choice of the value should also take the quality of your diffraction data into account.

### Results viewing

When the calculation has finished, a table of the unit cells (solutions) found by Dicvol will be displayed. Please mark one or more solutions you would like to keep, then press <OK>. You will then be taken to the "Indexing solutions" dialog (p. 81) where you can evaluate the solutions (i.e. unit cells) that you have found up to now, inspect peak data, select crystal system and space group, and finally export the solution or add it as a new manual entry (p. 125) to the match list (e.g. in order to proceed with structure solution (p. 90)).

The **crystal system and space group suggested by Dicvol** are also copied to the individual solution(s) in Match!. They can be seen in the corresponding dialog elements on the right-hand side of the "Indexing results" dialog if a corresponding line is marked in the solution list at the top. You can of course modify these suggestions using the corresponding dialog elements.

If you would like to look at the **original Dicvol output file**, you can do so by marking the corresponding solution in the solution list and clicking the "View output" button on the upper right-hand side.

### General hints on indexing from the Dicvol documentation

- Be careful in using the impurity tolerance: spurious lines increases the risk to miss the correct solution!
- It is recommended to use a two- or three-stages procedure (i.e. triclinic lattices should preferably be studied separately), for example:
  1. search in high symmetries down to orthorhombic: Line 2: n,itype,1,1,1,1,0,0
  2. search in monoclinic symmetry: Line 2: n,itype,0,0,0,0,1,0
  3. if necessary, search in triclinic symmetry: Line 2 : n,itype,0,0,0,0,0,1

Note that for solutions with Monoclinic and Triclinic symmetries the program provides the reduced cell. If various equivalent solutions are found, only one of them is listed in the output file.

- Trigonal symmetry case with rhombohedral lattice: the pattern is indexed with an hexagonal lattice, having a unit cell volume three times greater.
- Please, spend time to ensure the quality of your collected data. With accurate data, the success rate of Dicvol06 is very high. Peak positions should be extracted with a profile fitting software. An interactive program should be preferred, since automatic extractions can miss lines (low intensity, shoulder, ...).
- With bad data, the chance to obtain the correct solution is small and the calculation can be time-consuming.
- With modern X-ray powder diffractometers (the use of monochromatic radiation is recommended), absolute errors on peak positions lower than 0.02 degrees  $2\theta$  can be routinely obtained. For indexing purposes, errors should not (ideally) exceed 0.03 degrees in  $2\theta$ .
- With high resolution powder diffraction data (conventional or, particularly, synchrotron X-ray sources), the absolute error is usually less than 0.02 degrees (or even 0.01 degrees with ultra-high resolution) in  $2\theta$ ;



consequently, a maximum peak position deviation of 0.02 (or even 0.01) is recommended; the convergence of the dichotomy procedure will be improved. However, be sure that this condition is true for all lines used as input data. (Remember that all mathematical solutions within the input limits and error bounds are found, the greater they are the greater is the number of mathematical solutions).

- The maximum number of unindexed lines (also called "number of impurity lines",  $N_{IMP}$ ) can be used in case of expected spurious lines (i.e. impurity lines, as well as observed lines out of the input error).  $N_{IMP}$  acts at all successive levels of the dichotomy algorithm. As soon as an indexing solution is retained, a least-squares refinement of lattice parameters is carried out. For this refinement a larger error on observed lines is considered. Then, a line rejected at the last dichotomy level can, by chance, be accepted with the refined lattice parameters.
- Note that the program Dicvol06 is executable from 7 lines- 8 lines if the 'zero-shift' is refined - (though it is not recommendable since LS refinement instabilities can be expected).
- Long and short axis cases (dominant zone cases): if such cases are expected, the number  $N$  of lines used for searching the solution should, generally, be greater than 20.
- The minimum value for a linear lattice parameter has been fixed to 2.5 angstroms.
- Reliability of indexing solutions: read paragraph 8 of ref. 5 and refs 7 and 8.
- Note that with the option Dicvol04 (option =0), as soon as a solution is found, only solutions with smallest volumes will be subsequently retained. If (for some reasons!) you are not satisfied by the solution, you can run again the program with an input lower volume limit slightly greater than that of the found solution (the exhaustive search is then extended to a higher volume).
- Note that the search is exhaustive within the limits on the input data. In particular, the search is constrained by the higher and smaller bounds on parameters, volumes, selected FoM and absolute errors on peak positions. Please act on these parameters when using Dicvol06.
- A lattice metric singularity occurs when unit cells defining two lattices have an identical set of calculated d-spacings. This can be observed with high symmetry lattices, simple relations exist between the parameters of the two cells, as well as particular cell-volume ratios. A typical case is: an hexagonal cell [ $a$ ,  $c$ , volume  $v$ ] can be indexed with an orthorhombic cell [parameters:  $a/2$ ,  $a\sqrt{3}$ ,  $c$ , volume  $v/2$ ]. Due to the strategy used in Dicvol, based on an analysis through decreasing symmetry, all cells should be, in principle, displayed in the output file (except if a solution is rejected by the input maximum volume).
- Possible space groups: look at the hkl conditions in the output list of the reviewing of the complete input data provided after a solution is found from the first  $N$  lines.

## Crystal structure solution using Endeavour

### Basics

After collecting a set of peaks belonging to a presumably unknown phase in your sample/diffraction pattern, you should first try to index them (p. 60). Once you have been successful and obtained a promising set of unit cell parameters, you can store the result (peak data and unit cell parameters) in a manual entry (p. 125) in the match list. Afterwards, you can try to **solve/complete the crystal structure** (i.e. determine the atomic parameters) based on this manual entry, e.g. using our software Endeavour<sup>45,46</sup> (which is available for Windows only, unfortunately).

Match! can forward the data you have collected (peak data, unit cell parameters and maybe space group) from the manual entry to Endeavour and run it. Once the calculations have finished and a promising structural model has been found, you can export the resulting crystal structure from Endeavour to a cif-file, and then re-import this into the manual entry just mentioned, e.g. in order to run a Rietveld refinement (p. 60).

### Method

Endeavour uses a so-called “direct-space method” to solve a crystal structure: It starts by placing the atoms at random positions in the unit cell and then moves them around, trying to minimize the R-factor (difference between experimental and calculated diffraction pattern) and the potential energy (details can be found in ref. 45 and 46). For this, it needs to know which atoms (elements and maybe oxidation states/charges) are present in the unit cell.

Hence, in order to be able to apply Endeavour, you should at least know the composition (formula sum or molecule structure) of the unknown compound, e.g. from XRF experiments or chemical analysis. In addition, you also need the number of formula units per unit cell (*Z*). Endeavour can help you with the latter if you have at least a rough idea of the density of the material and/or of the space filling percentage.

### Space group determination

What is still missing for a full description of the crystal structure is the space group:

Before adding a solution as a new manual entry to the match list in the “Indexing results” dialog, you can ask Match! to determine potential space group candidates, by activating the checkbox “Use extinctions to restrict space grps.” in the “Crystal structure” section of the dialog.

Once you have done so, only space groups that agree with the observed peaks in the current experimental pattern are available in the “Space group” drop-down box. This function works by checking systematic absences as described on p. 84.

Depending on the type of compound (individual atoms or molecules) and the symmetry it is sometimes advantageous to already use the space group information in the Endeavour crystal structure solution calculation. In other cases, it is better to run the crystal structure solution without space group restrictions (i.e. in space group *P* 1) and determine the space group from the resulting structural model afterwards. Endeavour can do the latter using the SFND/RGS function in the program KPLOT<sup>47,48</sup> developed by R. Hundt and co-workers.

### Running Endeavour

If you are running a Windows version of Match! and have installed Endeavour on your computer, Match! will determine the path to the software automatically; you can also select it manually on the “General” tab of the “Options”-dialog.


To run an Endeavour calculation, please mark the corresponding entry in the match list that contains the data to be used (at least peak data and unit cell parameters) first. Afterwards, you can either run the “Structure solution

<sup>45</sup> H. Putz, J.C. Schoen, M. Jansen, “Combined Method for ‘Ab Initio’ Structure Solution from Powder Diffraction Data”, *J. Appl. Cryst.* **32**, 864-870 (1999).

<sup>46</sup> Crystal Impact GbR, Endeavour 1.7, Internet: <https://www.crystalimpact.de/endeavour>, E-mail: [info@crystalimpact.com](mailto:info@crystalimpact.com), Bonn 2009.

<sup>47</sup> A. Hannemann, R. Hundt, J.C. Schoen, M. Jansen, “A New Algorithm for Space-Group Determination”, *J. Appl. Cryst.* **31**, 922-928 (1998).

<sup>48</sup> R. Hundt, J.C. Schoen, A. Hannemann, M. Jansen, “Determination of Symmetries and Idealized Cell Parameters for Simulated Structures”, *J. Appl. Cryst.* **32**, 413-416 (1999).

(Endeavour)..." command from the "Tools" menu (or the context menu of the match list), or press the corresponding button  in the Match! toolbar.

A new windows will open showing some instructions how to run the structure solution calculation in Endeavour, and how to get the resulting crystal structure data back into Match!. You can disable the future displaying of this information window by marking the corresponding option.

After confirming the dialog window by pressing <OK>, Endeavour will be run, and the current crystal structure and diffraction data will be transferred to it.

When the Endeavour program window is displayed, please press the "F7" button (or run "Structure/Start solution...") to open Endeavour's structure solution wizard. It will take you step by step through the input of any missing information (like the elements and composition) and finally run the actual structure solution calculation.

### Reimporting Endeavour result into Match!

Once the structure solution calculation(s) has finished and a promising solution has been found, you can transfer it back to Match!, e.g. in order to run a Rietveld refinement. To do so, please mark the solution in the configuration list on the upper right-hand side of the Endeavour program window, then click into the structure picture to shift the focus. Run the "File/Save As/Save Structure As..." command, select the file type "CIF (\*.cif)", and choose/enter an appropriate directory and file name.

In Match!, please right-click on the manual entry you would like to import the crystal structure to, select "Edit manual entry" from the context menu, and finally press the "Import from cif-file" button on the upper right-hand side of the dialog that opens.

As an alternative, you could also run the command "File/Import/Crystal structure (CIF)", in order to add the solved structure as a new manual entry to the match list.

## Reference pattern database

### Overview

Match! identifies phases in a sample by comparing its powder diffraction pattern to reference patterns of known phases. Hence, it needs a so-called "reference database" in which these reference patterns are provided. Match! is extremely flexible in this context, with several options for obtaining/using a reference database:

- A free-of-charge reference database for inorganic compounds is by default installed automatically along with Match!<sup>49</sup>; it can be used straight away after the installation. This reference database contains powder diffraction patterns calculated from crystal structure data taken from the "Crystallography Open Database" (COD)<sup>50,51,52,53,54,56</sup>, which itself provides crystal structure data published by the IUCr journals<sup>55</sup>, the "American Mineralogist Crystal Structure Database" (AMCSD)<sup>56</sup>, and various other sources.

**In this context, we would like to thank Pete Strickland (IUCr), Armel Le Bail and Saulius Grazulis (COD), as well as Bob Downs (AMCSD) for their kind permission to download and distribute their data free-of-charge!**

All entries taken from the COD reference database contain atomic coordinates, based on which the corresponding powder diffraction patterns have been calculated. Besides this, for all entries,  $I/I_c$ -values have been calculated, so that a semi-quantitative analysis can be carried out.

You can download additional or updated reference databases free-of-charge from

<https://www.crystalimpact.de/match/download.htm#refdb>

- The classical reference pattern database is the so-called "PDF" database provided by the ICDD<sup>57</sup>. There are several PDF database products available (e.g. PDF-2, PDF-5+, PDF-4/Minerals), all of which can be used with Match!<sup>58</sup>.  
According to our knowledge, the PDF is the largest and most comprehensive source of reference diffraction patterns.
- Many users also have diffraction patterns of own compounds that are not (yet) present in the COD or PDF databases. Hence, it is desirable to use these patterns in phase analysis in addition to the "normal" patterns. This can be achieved using the so-called "user database" (p. 103).
- You can use an ICSD/Retrieve version released between 1993 and 2002 that you might have available<sup>59</sup>. Match! can import the ICSD/Retrieve entries into a normal Match! user database and calculate reference powder diffraction patterns in a single step (p. 120).

<sup>49</sup> The Match! installer contains only data from the "Inorganics" subset of the COD. You can download and install the full COD reference database from the Match! web page <https://www.crystalimpact.de/match/download.htm#refdb>.

<sup>50</sup> Merkys, A., Vaitkus, A., Butkus, J., Okulič-Kazarinas, M., Kairys, V. & Gražulis, S. (2016) "COD::CIF::Parser: an error-correcting CIF parser for the Perl language". *Journal of Applied Crystallography* 49.

<sup>51</sup> Gražulis, S., Merkys, A., Vaitkus, A. & Okulič-Kazarinas, M. (2015) "Computing stoichiometric molecular composition from crystal structures". *Journal of Applied Crystallography* 48, 85-91.

<sup>52</sup> Gražulis, S., Daškevič, A., Merkys, A., Chateigner, D., Lutterotti, L., Quirós, M., Serebryanaya, N. R., Moeck, P., Downs, R. T. & LeBail, A. (2012) "Crystallography Open Database (COD): an open-access collection of crystal structures and platform for world-wide collaboration". *Nucleic Acids Research* 40, D420-D427.

<sup>53</sup> Gražulis, S., Chateigner, D., Downs, R. T., Yokochi, A. T., Quiros, M., Lutterotti, L., Manakova, E., Butkus, J., Moeck, P. & Le Bail, A. (2009) "Crystallography Open Database – an open-access collection of crystal structures". *J. Appl. Cryst.* 42, 726-729.

<sup>54</sup> <http://www.crystallography.net/cod/>

<sup>55</sup> International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, United Kingdom. <http://journals.iucr.org>

<sup>56</sup> R.T. Downs, M. Hall-Wallace, "The American Mineralogist Crystal Structure Database", *American Mineralogist* 88, 247-250 (2003). <http://rruff.geo.arizona.edu/AMS/amcsd.php>

<sup>57</sup> International Centre for Diffraction Data, 12 Campus Boulevard, Newtown Square, PA 19073-3273, U.S.A. Phone: +1-610-325-9814; Fax: +1-610-325-9823; E-mail: [info@icdd.com](mailto:info@icdd.com), Internet: [www.icdd.com](http://www.icdd.com)

<sup>58</sup> Please note that ICDD's relational database products (PDF-4, PDF-2) are currently only available for the Windows platform. However, on Mac OS X or Linux, you can use the "old" PDF-2 database releases before 2005, if you have a valid license for it.

<sup>59</sup> Of course, you must have a valid license for ICSD/Retrieve! Please contact FIZ Karlsruhe (Germany) (e-mail: [crysdata@fiz-karlsruhe.de](mailto:crysdata@fiz-karlsruhe.de)) if you are in doubt whether your license is still valid!

You cannot only use one or the other of the above-mentioned reference databases but also **combinations** of them. For example, you can combine diffraction patterns of your own compounds with the COD database that is installed with Match! (p. 101).

When selecting your reference database, you should always keep in mind that there may be unforeseen phases in your samples, in which case it is extremely useful to have a large pattern database available in which even diffraction patterns of “strange” phases are present.

We recommend to **use an ICDD PDF database as reference database** (if you have one available), either stand-alone **or in combination with the COD database** that is installed along with Match!. The background why we recommend the PDF is that we have found that at least in case of **natural samples** (e.g. minerals, rocks etc.), the PDF sometimes gives better qualitative analysis results than e.g. the COD. This seems to be caused by the fact that certain phases show a certain variation of peak positions and intensities, e.g. caused by the insertion or replacement of atoms (leading to different unit cell parameters and hence peak positions) or preferred-orientation effects (causing the intensities of certain peaks to be different from the ones calculated just from the given crystal structure).

In contrast to the COD (which only contains calculated powder diffraction patterns), the PDF also contains a large variety of experimental patterns with very different origin and quality, some of which may also show the “variations” just mentioned. As a result, the probability that the PDF contains a reference pattern that is similar to the one of your sample maybe higher than when using the COD.

## Reference Database Library

If you would like to apply a different reference database than the one that is installed along with Match! (typically, the COD or the “Inorganics” subset of the COD), you first have to add it to the so-called “Reference Database Library”. This is a table (in fact two tables) of all reference databases that are currently available to the user. Each row in the table corresponds to one reference database, for which the name, the number of entries, and the location/path of the database/index files are displayed. There are two tables, one for reference databases that are available to all users, and another one that can only be accessed by the current user (Fig. 45).

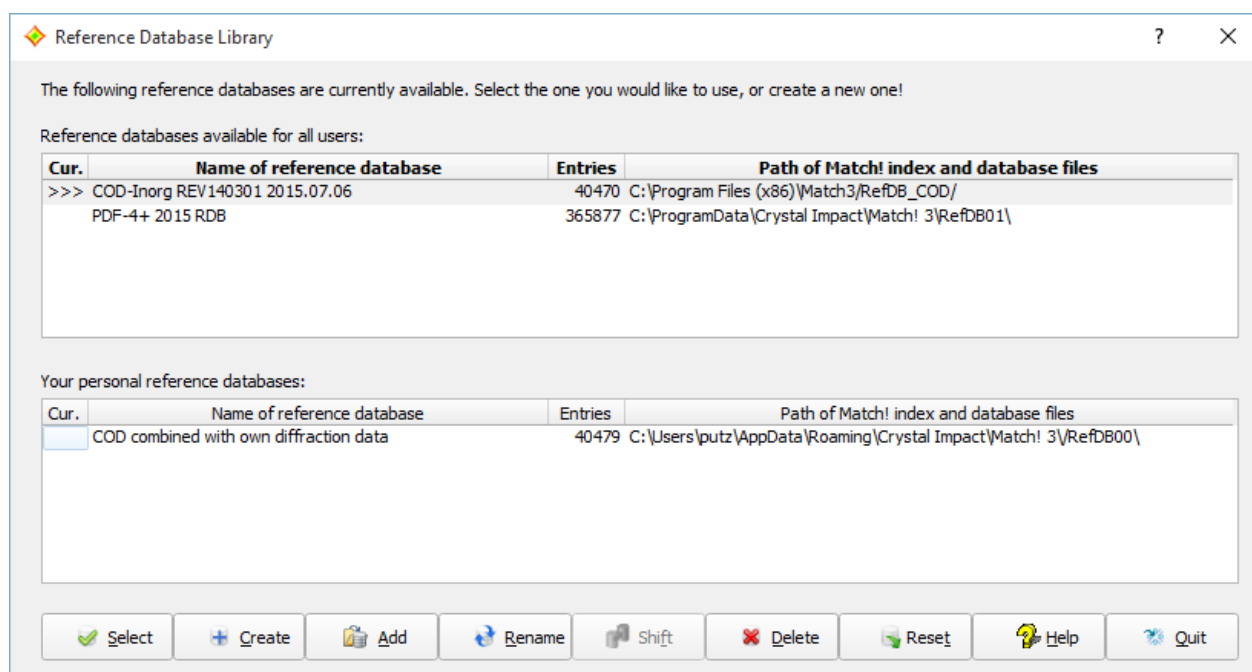


Fig. 45: Using the “Reference Database Library”, you can manage the various reference pattern databases on your PC. In this case, a COD “Inorganics” database (REV140301) is installed for all users on this PC (upper table) and has been selected for being used in phase analysis (column “Cur.”). Besides this, the PDF-4+ Release 2015 is also available for all users. In addition, there is another COD version that has been combined with user data; this reference database is only available to the current user.

Thanks to the “Reference Database Library”, Match! is capable of handling more than a single reference pattern database at a time: You can switch between all reference databases you have created (i.e. created index files for) while keeping your diffraction data in memory, thus enabling you to compare phase analysis results from various reference databases. Of course, it is not necessary to perform a re-indexation of a reference database when switching between them!

The “Reference Database Library” dialog is opened automatically at program start if you did not install a reference database along with Match!. It can also be opened by selecting the “Select/create reference database”



command from the “Database” menu, or by pressing the corresponding button in the toolbar.

As has already been mentioned, the “Reference Database Library” contains a list of all reference databases that are available for the current user (see below). For each available reference database, the name, the number of entries, and the directory in which it is stored are displayed. The database you are currently using is identified by an “>>>”-arrow to its left.

On a multi-user machine, each user may have individual reference database(s). It is perfectly possible to create a new reference database as a normal (standard) user, i.e. it is not necessary to have administrator privileges for this task. However, please note that a standard user can create reference databases only for himself, while an administrator can create databases also for all users. If a database is available to all users, it is listed in the upper table. Note that databases in this table cannot be modified or deleted by normal (standard) users!

You can manage your reference databases using the buttons at the bottom of the “Reference Database Library” dialog:

- **Select** another reference database for search-match or database retrieval purposes (of course without the need to perform a complete new indexation!). Please note that the current contents of the candidate list will be updated if you select a new reference database, in order to avoid problems like a certain entry being present in one reference database while missing in another one.
- **Create** a new reference database (e.g. as a working-copy of the COD, from an existing Match! user database<sup>60</sup>, or by importing entry data from cif-files or the ICSD<sup>60</sup>).
- **Add** a reference database that is stored “ready for usage” in a certain directory<sup>60</sup>.
- **Rename** an existing reference database<sup>60</sup>.
- **Shift** the position of a classical PDF-2 database that is used in the marked reference database to a new directory.
- **Delete** an existing reference database.
- **Quit** the Reference Database Library.

## Create a new reference database

Match! cannot use pattern sources like the PDF or COD database directly; it requires the presence of so-called “index files”. These files contain sorted extracts of the original data, thus enabling a much faster processing of diffraction pattern comparison and database retrieval tasks. In other words, creating a new reference database basically means to create index files for an existing source database.

If you would like to create a new reference database, please press the “Create” button in the Reference Database Library dialog. This will bring up the “Create Reference Database” dialog in which you can select the source(s) of the reference powder patterns. You can either mark one source or create combined reference databases by marking more of them, e.g. the “COD” and “User database”. It is also possible to define a name for the new reference database, and to select the directory in which all files of this new reference database shall be stored (Fig. 46).

<sup>60</sup> Not yet available in current beta version!



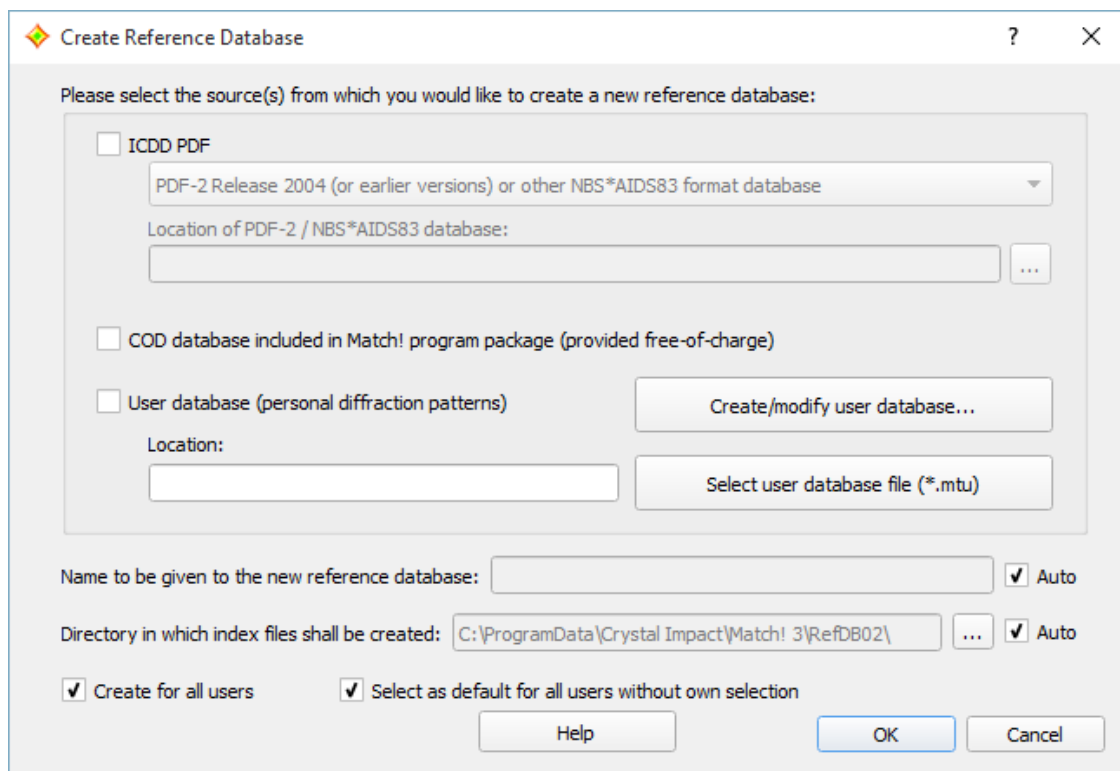


Fig. 46: Using this dialog you can create a new reference database for Match!.

The way how to proceed depends on the kind of database you would like to create index files for; please continue with the corresponding chapter below.

### PDF-5+, PDF-4 or PDF-2

Using the ICDD PDF database products with Match! is easy<sup>61</sup>: Simply install the PDF database on your Windows PC according to the instructions given by ICDD, then launch Match!.

Match! will **automatically detect newly installed PDF database products** at program startup (at least if the corresponding option is set) and ask if you would like to index one of them straight away. If you agree by clicking “Yes”, the database indexing will be performed immediately. You will then be asked if you would like to use the new reference database straight away. You can do so by clicking “Yes” again. That's it!

#### Please note:

- Even if you click “No” in the last step, you can switch over to the new PDF reference database later in the **Reference Database Library**.
- You can also check for new/updated PDF database products from within Match!, by running the “Database/Check for new PDF databases...” menu command.

You can also perform the indexing of a PDF database manually, of course. In the following, we will demonstrate how to apply an existing ICDD PDF-5+, PDF-4 or PDF-2 database as a Match! reference database:

Let us assume that you would like to add the ICDD PDF-4+ Release 2015 database (which must have been installed on your PC in advance, of course); the procedure for using the PDF-5+ or the PDF-2 is the same.

Once you have pressed the “Create” button in the Reference Database Library as just described, Match! will automatically check for available PDF relational database products (like the PDF-5+ or the PDF-2). If at least one PDF RDB is found, the checkbox “ICDD PDF” in the upper part of the dialog will be checked automatically, with the first PDF that has been found already selected in the drop-down box below “ICDD PDF”. If you would like to select a different PDF version, you have to click on the drop-down box and mark the corresponding line. In our case, we

<sup>61</sup> The ICDD PDF relational database products (like PDF-4+, PDF-2 starting with release 2005 etc.) are currently only available for the Windows platform. Hence, you cannot use these databases if you are running Match! on a Mac or Linux machine.

would like to use the PDF-4+/Release 2015, with the corresponding line already having been selected automatically (Fig. 47).

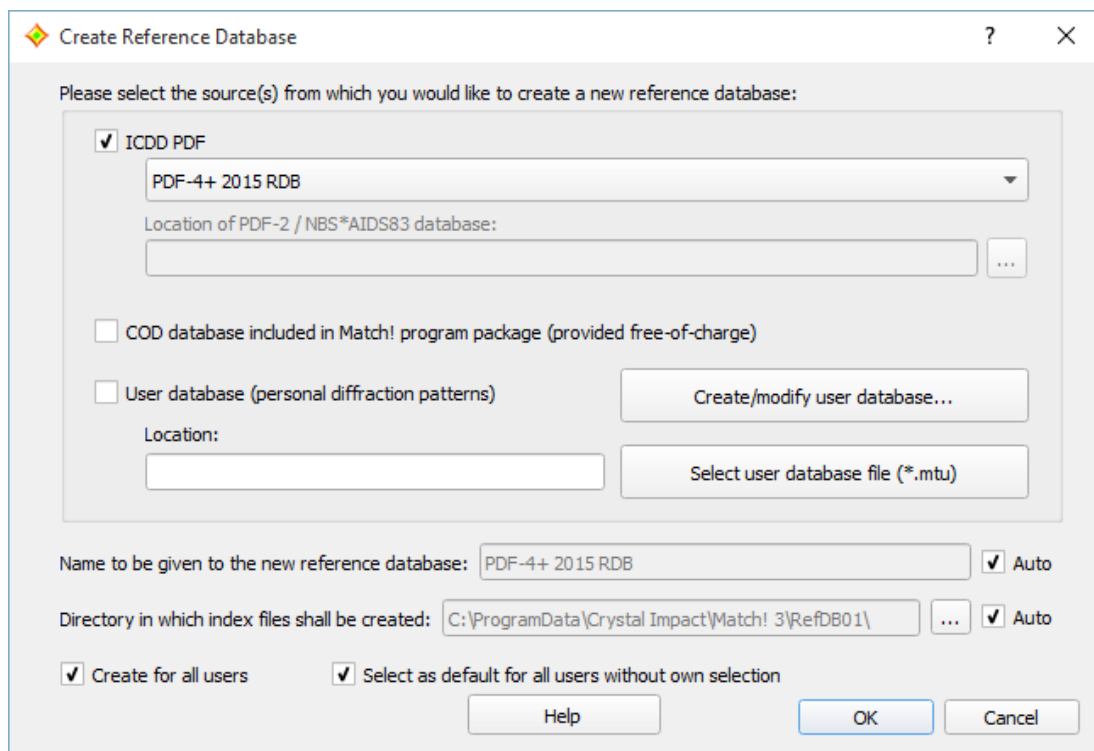


Fig. 47: You have selected to apply the ICDD PDF-4+ Release 2015 database as Match! reference database.

If you like, you can change the name of the new reference database at the bottom of the dialog (deactivate the corresponding "Automatic" checkbox first!), and/or change the location (directory) in which the index files for the new reference database shall be stored. Normally, Match! will automatically create a suitable name and select an appropriate directory.

In case you have administrator privileges, you can also select if you would like to make the new reference database available to all users (or only to you), and if you would like to make it the default Match! reference database for new users on your PC.

Please note that on **Windows** it is **not** sufficient to run Match! from an administrator account; you have to explicitly use the command "**Run as administrator**" (which is available e.g. in the context-menu (click right mouse button)) in order to enable the two options "**Create for all users**" and "**Select as default for all users without own selection**". On **Linux**, you have to use "su" or "sudo" in order to run Match! with "root" privileges and enable these two options.

Once you have made your selections, press the "OK" button at the bottom to start the creation of the index files. A small window will be display the progress of the indexation (Fig. 48). Due to the large amount of data which have to be read and sorted<sup>62</sup>, the creation of index files is a rather time-consuming process. The procedure may take between about 30 minutes to an hour or even more, depending especially on the drive access and processing speed of your computer. When the indexation has finished, a corresponding message will be displayed. Afterwards, the new reference database will appear in the list of the Reference Database Library, ready for being selected (Fig. 49).

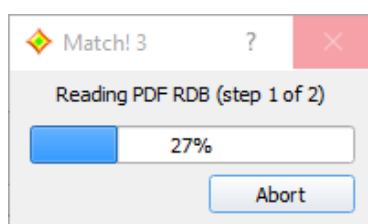


Fig. 48: This window shows the progress of the index file creation.

<sup>62</sup> The PDF-4+ Release 2010 contains more than 300,000 entries !

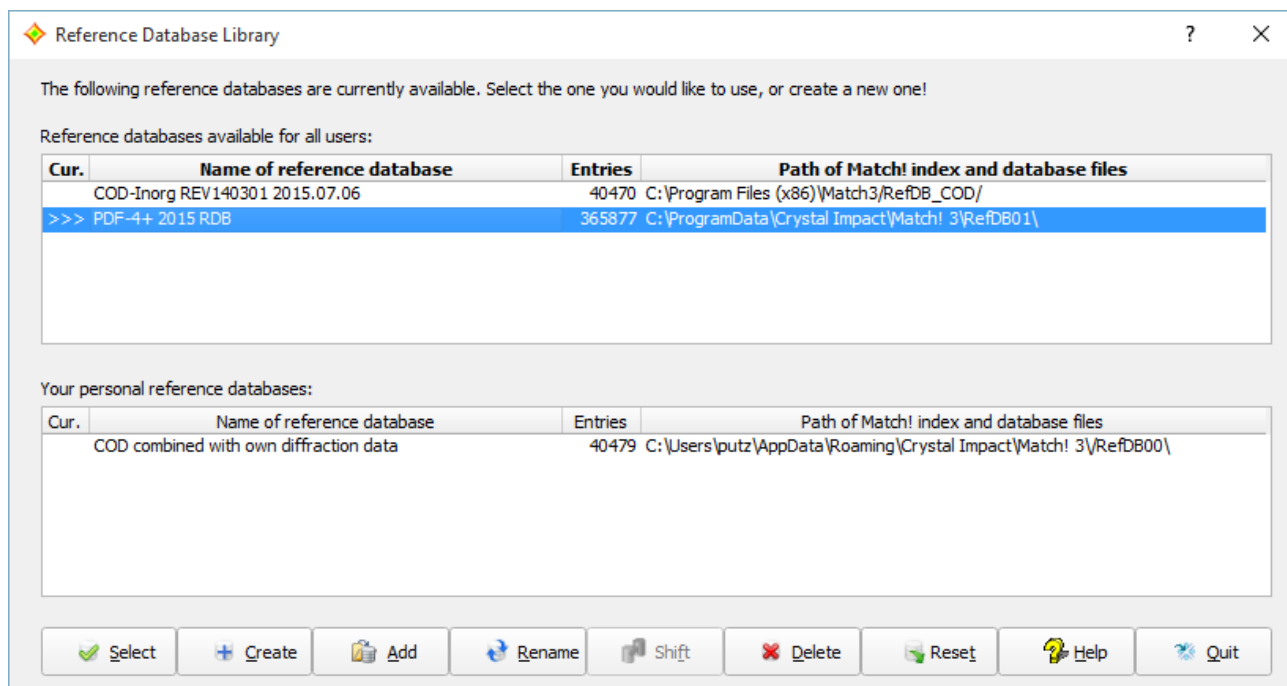


Fig. 49: The “PDF-4+ 2015 RDB” reference database is now available in the list for all users

If the new reference database is the only one available in the Reference Database Library, it is selected for being used automatically. Otherwise, you have to select the new reference database manually: Simply mark (click) on the corresponding line in the table, then press “Select”. The license for the PDF database is checked, then the new reference database is marked as selected, indicated by the “>>>” arrow on the left-hand side of the corresponding line.

You can now leave the Reference Database Library by pressing “Quit” and apply the PDF-4+ reference database in phase analysis and database retrievals.

If you would like to use the PDF-5+, the PDF-2 or any other current ICDD PDF database product, this can be done in a similar way than the procedure just described for the PDF-4+. Starting with **version 4.2**, Match! is able not only to use local (fixed) PDF licenses but also **supports floating PDF server licenses**.

### Old format PDF-2

If you would like to use a ICDD PDF-2 database in the old format (i.e. release before 2005) as reference database, you can do so as follows:

Similar to current PDF-2, PDF-5+ or PDF-4 versions, you first have to tell Match! that you would like to use an ICDD PDF database, by marking the checkbox “ICDD PDF” in the upper part of the “Create Reference Database” dialog. Afterwards, please mark (click on) the line “PDF-2 Release 2004 (or earlier versions)” in the list below “ICDD PDF” (Fig. 50).

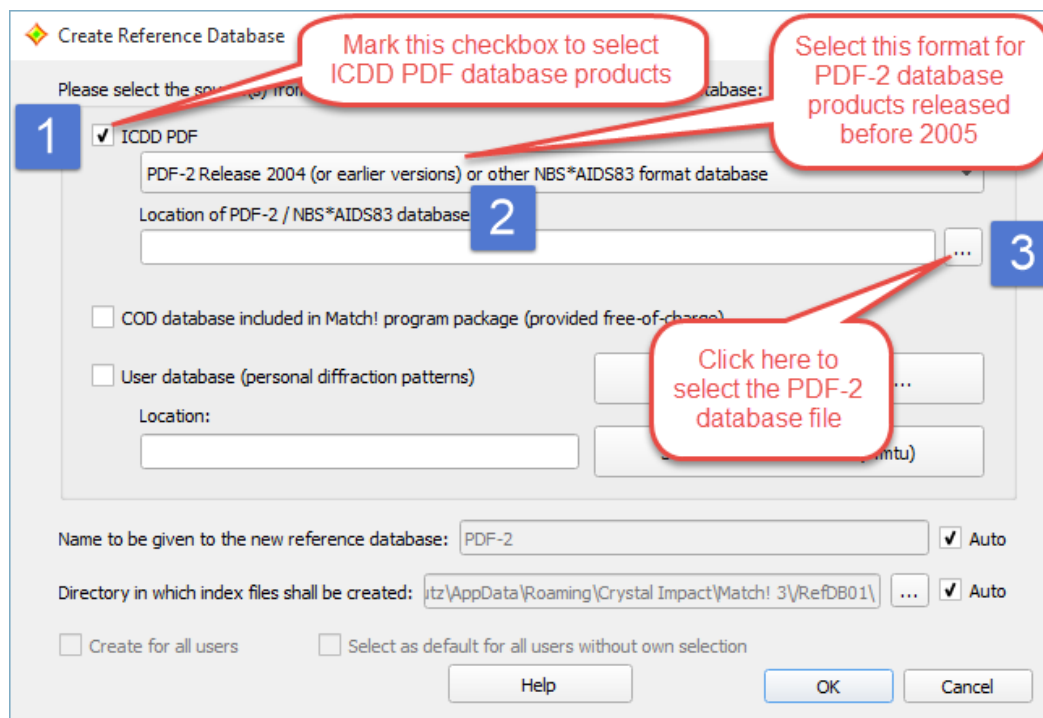


Fig. 50: You have selected to apply an ICDD PDF-2 database released before 2005 as Match! reference database.

You now have to give the directory in which the PDF-2 database (to be exact: the file named "pdf2.dat" or similar) is stored in the input box below "Location of PDF-2 / NBS\*AIDS83 database". You can easily select this file / directory by clicking on the "..." button to the right of this input line.

A "File Open" dialog will be displayed in which you have to select the file "pdf2.dat" (or similar) in the directory where your PDF-2 database is stored. Afterwards, press "Open" to select the file / directory. A new dialog will open in which you have to explicitly confirm that you have a valid license for the PDF-2 database you are about to use. If you confirm the validity of the license, the location of the PDF-2 database file will be displayed in the corresponding input box.

If you like, you can now change the name of the new reference database at the bottom of the dialog (deactivate the corresponding "Automatic" checkbox first!), and/or change the location (directory) in which the index files for the new reference database shall be stored. Normally, Match! will automatically create a suitable name and select an appropriate directory.

In case you have administrator privileges, you can also select if you would like to make the new reference database available to all users (or only to you), and if you would like to make it the default Match! reference database for new users on your computer.

Please note that on **Windows** it is **not** sufficient to run Match! from an administrator account; you have to explicitly use the command "**Run as administrator**" (which is available e.g. in the context-menu (click right mouse button)) in order to enable the two options "**Create for all users**" and "**Select as default for all users without own selection**". On **Linux**, you have to use "su" or "sudo" in order to run Match! with "root" privileges and enable these two options.

Once you have made your selections, press the "OK" button at the bottom to start the creation of the index files. A small window will display the progress of the indexation (Fig. 51). The procedure will take a few minutes, depending especially on the drive access and processing speed of your computer. When the indexation has finished, a corresponding message will be displayed. Afterwards, the new reference database will appear in the list of the Reference Database Library, ready for being selected.

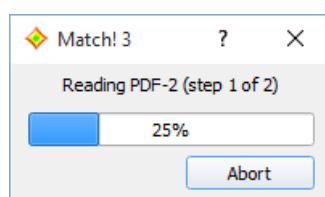


Fig. 51: This window shows the progress of the index file creation.

If the new reference database is the only one available in the Reference Database Library, it is selected for being used automatically. Otherwise, you have to select the new reference database manually: Simply mark (click) on the corresponding line in the table, then press the “Select” button at the bottom. The new reference database will be marked as selected, indicated by the “>>>” arrow on the left-hand side of the corresponding line.

You can now leave the Reference Database Library by pressing “Quit”, and apply the PDF-2 reference database in phase analysis and database retrievals.

### Create a working-copy of the COD

If you would like to apply modifications to the COD reference database that is installed along with the Match! software, you first must create a working-copy of it, because as a standard user you do not have write permission to the original database.

In order to do so, please click the “Create” button in the “Reference Database Library” dialog first. In the dialog that opens, please make sure to only mark the “COD database” checkbox (remove the hook in front of “ICDD PDF” if required), and adjust all settings according to Fig. 52.

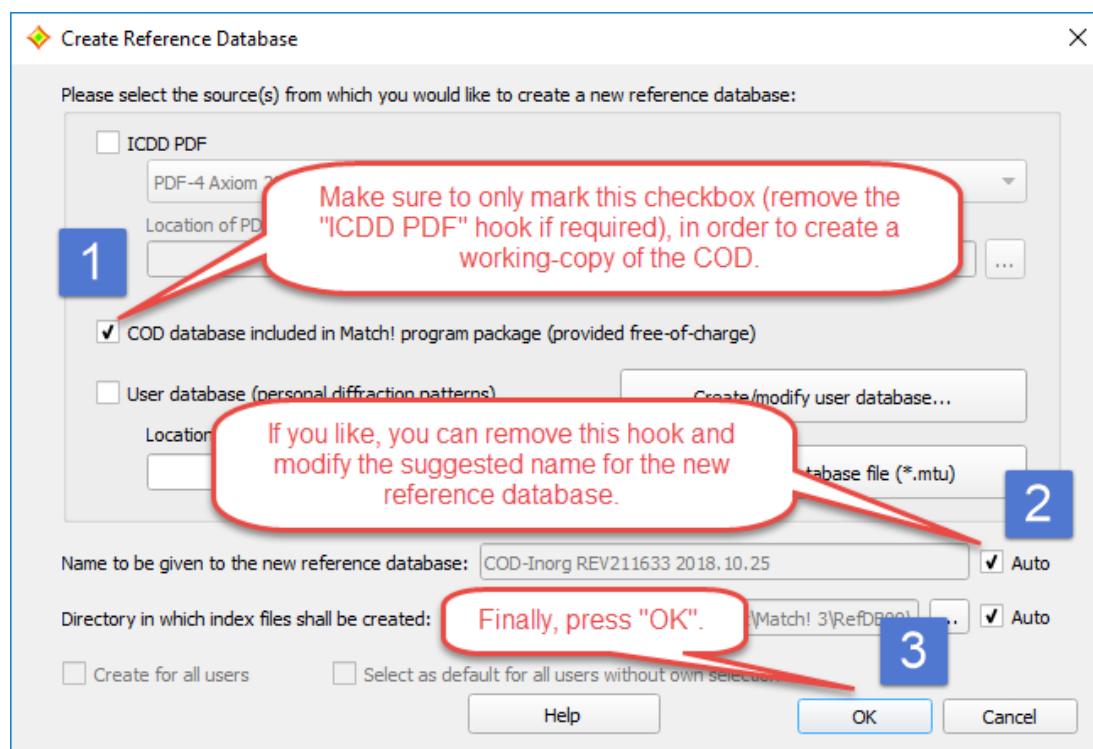


Fig. 52: Instructions to create a working-copy of the COD-Inorganics reference database installed with Match!

Once you have finished and clicked “OK”, a copy of the COD reference database will be created. A small window will display the progress of the process (that will typically take only a few seconds to complete). Afterwards, a corresponding message will be displayed, and the new reference database will appear in the list of the Reference Database Library, ready for being selected.

### Create reference database from user data or ICSD/Retrieve

As has already been mentioned, it is also possible to use own diffraction patterns or the ICSD/Retrieve database in phase analysis. Before you can do so, you have to store/convert the corresponding diffraction patterns and/or crystal structure data sets into a so-called “user database” file (file extension \*.mtu), using the so-called “User Database Manager” dialog<sup>63</sup>.

If you have not already done so, please follow the instructions on p. 103 first, in order to create the mtu-file from your data. Afterwards, please return to this point and continue reading.

<sup>63</sup> You can open the “User Database Manager” directly from the “Create Reference Database” dialog by pressing the “Create/modify user database...” button. Alternatively, the “User Database Manager” can also be invoked from the “Database” menu.

The procedure to use an existing user database file (\*.mtu) as reference database is pretty similar to the one using an old PDF-2 version: First, you have to tell Match! that you would like to apply a user database, by marking the corresponding option in the middle of the “Create Reference Database” dialog. Afterwards, you have to select the location of the \*.mtu file, by pressing the button “Select user database file (\*.mtu)” to the right of the corresponding input line “Location:”.

A “File Open” dialog will be displayed in which you have to select the mtu-file in which your user data are stored. Afterwards, press “Open” to select the file/directory and return to the “Create Reference Database” dialog. The location of the mtu-file will now be displayed in the corresponding input box (Fig. 53).

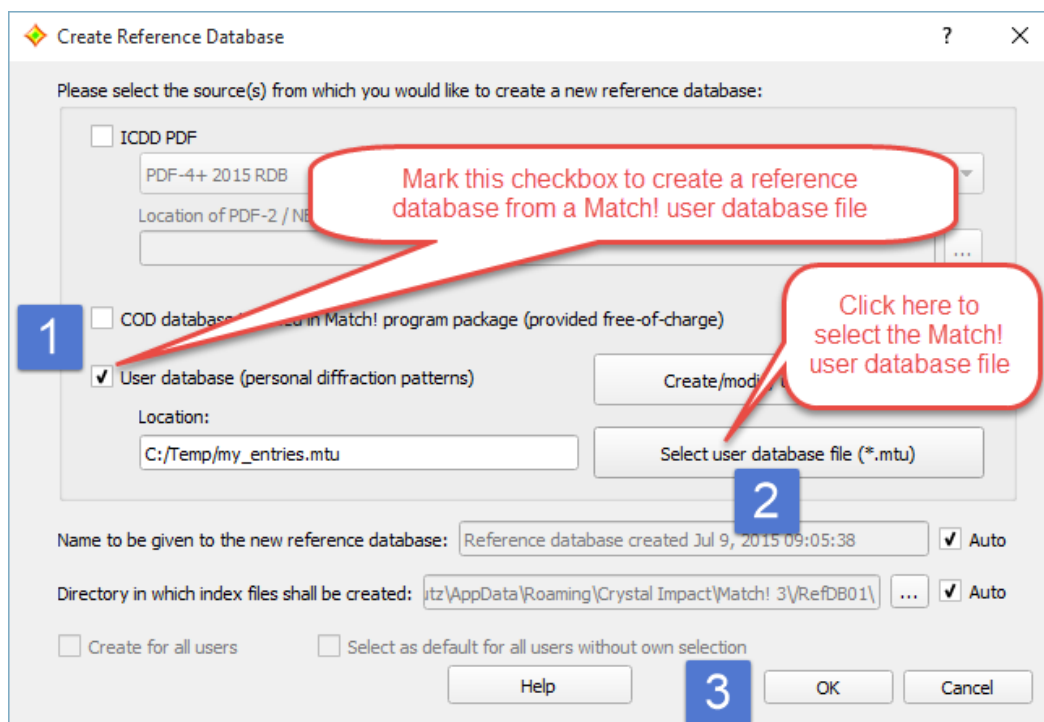


Fig. 53: The Match! user database file based on which a new Match! reference database shall be created has been selected.

If you like, you can now change the name of the new reference database at the bottom of the dialog (deactivate the corresponding “Automatic” checkbox first!), and/or change the location (directory) in which the index files for the new reference database shall be stored. Normally, Match! will automatically create a suitable name and select an appropriate directory.

If you create a new reference database for an existing user database (mtu-file), the selected mtu-file will be copied to the directory in which also the index files are stored. Hence, it does not matter if you change or delete the original user database file later on; this will not affect the reference database.

In case you have administrator privileges, you can also select if you would like to make the new reference database available to all users (or only to you), and if you would like to make it the default Match! reference database for new users on your PC.

Please note that on **Windows** it is **not** sufficient to run Match! from an administrator account; you have to explicitly use the command “**Run as administrator**” (which is available e.g. in the context-menu (click right mouse button)) in order to enable the two options “**Create for all users**” and “**Select as default for all users without own selection**”! On **Linux**, you have to use “su” or “sudo” in order to run Match! with “root” privileges and enable these two options.

Once you have made your selections, press the “OK” button at the bottom to start the creation of the index files. A small window will display the progress of the indexation (Fig. 54). The procedure will take a few minutes, depending especially on the number of entries as well as the drive access and processing speed of your computer. When the indexation has finished, a corresponding message will be displayed. Afterwards, the new reference database will appear in the list of the Reference Database Library, ready for being selected.



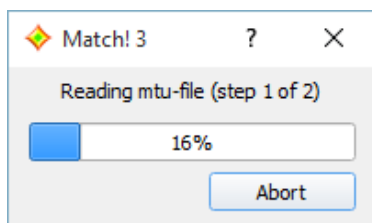


Fig. 54: This window shows the progress of the index file creation process.

If the new reference database is the only one available in the Reference Database Library, it is selected for being used automatically. Otherwise, you have to select the new reference database manually: Simply mark (click) on the corresponding line in the table, then press "Select". The new reference database will be marked as selected, indicated by the ">>>" arrow on the left-hand side of the corresponding line.

You can now leave the Reference Database Library by pressing "Quit" and apply the new reference database in phase analysis and database retrievals.

### Creating combined reference databases

You can create combined reference databases that e.g. contain diffraction patterns of your own compounds along with the COD or PDF data. To do so, simply mark the corresponding checkboxes in the "Create Reference Database" dialog (Fig. 53, p. 100).

If you would like to use a suitable name for the new reference database instead of the one that is suggested by Match! automatically, you can remove the hook in the checkbox "Auto" to the right of the line "Name to be given to the new reference database", then edit the name.

### Select reference database

In order to select another existing reference database for being used in future search-match and restraining operations, please mark (click on) the corresponding line in the Reference Database Library dialog. Afterwards, press the "Select" button at the bottom of the dialog. If the selected reference database is a PDF-2 (Release after 2004), PDF-5+ or PDF-4 database, the validity of the license will be checked. Afterwards, the reference database will be marked as selected, indicated by the ">>>" arrow on the left-hand side of the corresponding line.

#### Please note:

- If your candidate list contains entries when you open the Reference Database Library, it will be updated if you select a different reference database. This is because the entries present in one reference database will most probably not be present in another database.
- The name of the currently selected reference database is displayed in the status bar at the bottom of the Match! window. This name is updated when the Reference Database Library is closed.

### Add reference database

You can create backup copies of complete reference databases, simply by copying the complete contents of a reference database index directory. The name of a current reference database directory is given in the right-most column in the Reference Database Library dialog.

If you would like to use/restore a backup copy later on, you can simply copy it to an appropriate directory on your computer. Afterwards, click the "Add" button in the Reference Database Library. A "File Open" dialog will be displayed in which you can select the "Match! Reference Database" file (MatchRefDBInfo.mtn) that contains the information required to use the index files in the same directory. Please mark the file "MatchRefDBInfo.mtn", then press "Open".

In case you have administrator privileges, you will now be asked if you would like to make the new reference database available to all users (or only to you). Afterwards, the new reference database will appear in the corresponding table of the Reference Database Library, ready for being selected for usage.

## Rename reference database

If you would like to rename an existing reference database, please mark (click on) the corresponding line in the Reference Database Library dialog. Afterwards, press the “Rename” button at the bottom of the dialog, and enter the new name in the input window that is opened. Once you press “OK”, the name of the currently marked reference database will be updated in the Reference Database Library list.

### Please note:

- If you are a standard user (i.e. do not have administrator privileges), you can only rename reference databases that are listed in the table “Your personal reference databases”!
- The name of the currently selected reference database is displayed in the status bar at the bottom of the Match! window. This name is updated when the Reference Database Library is closed.

## Shift PDF-2 reference database

If the reference database that is currently marked contains a PDF-2 database in the “old” format, you can shift the corresponding PDF-2 database file to a new location: First move or copy the corresponding file “pdf2.dat” (or similar) to the new location (e.g. using the Windows Explorer or file manager), then press this button, and select the file “pdf2.dat” at the new location. Match! will update the internal reference to this file, so that it knows where to find it when reading data e.g. for displaying them in an entry data sheet.

## Delete reference database

In order to remove an existing reference database from the current computer, please mark (click on) the corresponding line in the Reference Database Library dialog. Afterwards, press the “Delete” button at the bottom of the dialog. Once you have acknowledged the warning message, you will be asked if you would also like to “physically” remove the corresponding index files. If you answer “No”, you can reactivate the corresponding reference database later on using the “Add” command. Once you press “OK”, the name of the currently marked reference database will be removed from the Reference Database Library list.


If you are a standard user (i.e. do not have administrator privileges), please note that you can only delete reference databases that are listed in the table “Your personal reference databases”!

## User database

### Overview

As has already been mentioned earlier in this manual, phase analysis using powder diffraction data generally requires the availability of a so-called “reference pattern database”. In many cases, this is one of the PDF database products provided by the ICDD. However, there are also alternative sources of reference patterns, like the COD database delivered with Match!, your own diffraction data, or even data from the literature. The latter is especially appropriate when e.g. new compounds have been synthesized in a laboratory whose diffraction patterns and/or crystal structures have not yet been published.

While the COD reference database can be downloaded “ready-to-use” from the Crystal Impact web page free-of-charge, your own diffraction patterns (or other suitable data) must first be imported into a so-called “user database” (a file with extension “\*.mtu”) before they can be used with Match!. Once you have created this user database file, you can select it in the “Create Reference Database” dialog.


User databases are typically created and maintained in the so-called “User Database Manager” which can e.g. be opened using the “User database manager” command in the “Database” menu, or simply by pressing the corresponding button  in the toolbar.

The contents of user database entries may originate from a variety of sources:

- Own diffraction patterns
- Crystal structure data (typically CIF-files)
- Data published in the literature
- Your colleague's user database
- ICSD/Retrieve database (released 1993-2002)

These user diffraction patterns have to be stored in a so-called “user database” (file with extension “\*.mtu”) which can then be selected in the “Create Reference Database” dialog (p. 99). In the following, we will demonstrate how a user database (\*.mtu-file) can be created using any of the data sources mentioned above.

### Creating a user database

The central tool for the creation and maintenance of the user database is the so-called “User Database Manager”. It can be opened either by clicking on the corresponding toolbar button  (in the main toolbar at the top), by selecting the command “User Database Manager” from the “Database” menu, or by pressing the Create/modify user database...” button in the “Create Reference Database” dialog.

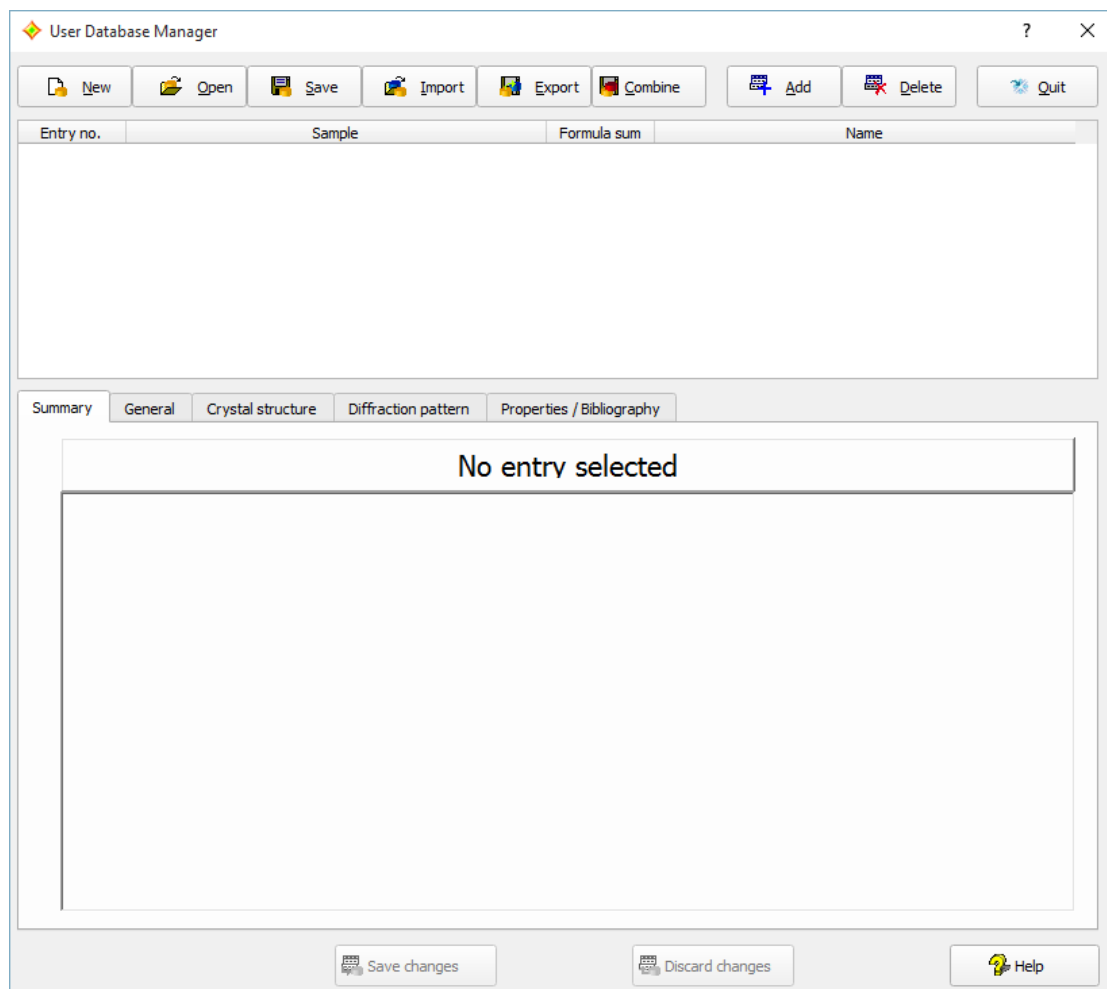


Fig. 55: User Database Manager: The new user database is still empty.

The user database manager window (Fig. 55) consists of three parts: At the top, there are nine buttons using which the basic actions (e.g. import or adding of entries) can be initiated. Below, in the upper half of the window, is the list of entries currently present. Finally, in the lower part of the window there is a set of so-called “tab sheets” in which the details of any entry marked in the entry list above are displayed and edited. You can switch between the individual tab sheets by clicking on the corresponding tab sheet header.

The first tab sheet (called “Summary”) contains an extract of the database fields on the remaining tab sheets; the data can just be viewed here, but not edited. The second tab sheet “General” contains data required for the description of the phase, like formula sum, chemical name etc. On the third tab sheet “Crystal structure”, crystal structure data can be entered in order to calculate the corresponding diffraction pattern on the subsequent tab sheet “Diffraction pattern”. Here, it is not only possible to calculate and view the pattern, but also to import (or export) diffraction data as peak list files, or to enter the diffraction data manually. Finally, the “Properties / Bibliography” tab sheet provides access to the physical property (e.g. density) as well as bibliographic database fields.

In the following subsections, we will create a small user database in order to demonstrate the various ways in which data can be entered into the database. Once you have entered your data, the modified user database has to be saved to a mtu-file before it actually can be used. You will be asked automatically to save your user database when you leave the User Database Manager dialog by pressing the “Quit” button. Alternatively, you can also press the “Save” button at the top of the dialog window.

### Import of Diffraction Data

You can use your own diffraction patterns as reference for phase analysis. For this you must import them into a Match! user database file first.

This is possible in two different ways:

- You can add the current experimental diffraction pattern (to be exact: the peak data) to a user database file (\*.mtu).

- In the User Database Manager, you can create a new entry and import the diffraction peak data from a peak list file.

These two methods are described in detail in the following:

### Add current experimental peaks to user database file

In order to add the current experimental peaks as a new entry to a user database file (\*.mtu), please run the command “Add peaks to user database” from the “Peaks” or the “Database” menu. A dialog will open in which you can select the user database file (\*.mtu) to which the new entry shall be added to. (It is also possible to create a new user database file at this point, simply by entering a new file name in this dialog.)

Once you have selected the name of the user database file, a new dialog will open in which you can enter additional information for the new entry, like formula sum of the compound, chemical and/or mineral name etc. Please enter your data on the appropriate tab sheets following the guidelines given for the manual addition of entries in the chapter “Manual input and editing of entry data” on p. 122.

After closing the “Add New Entry Data” dialog by pressing “OK”, the entry will be added to the selected user database file.

### Please note:

- If experimental peaks are marked, only the marked peaks will be copied to the new user database entry. This may be useful when identifying an unknown phase in a mixture with known phases, in which the peaks of the latter are covered by selected phases (command “Peaks/Mark uncorrelated peaks”). If no peaks are marked, all peaks will be copied.
- A corresponding command to add the current experimental peak data to a user database file is also available in the “Pattern” menus of additional experimental patterns, provided that they contain peak data.

### Import peak data into new user database entry

As an alternative to adding peaks from the current experimental data as a new entry to a user database file (as described above), it is also possible to add a new entry in the User Database Manager, and to import peak data from a corresponding file into it.

When the User Database Manager is displayed, you can import the diffraction pattern of the entry you are currently editing from the following peak data file formats:

- Stoe peak files (\*.pks)
- Philips/PANalytical peak data files (\*.udi)
- Endeavour peak list files (2 columns: 2theta/d intensity; \*.dif)

Of course, peak data files normally do not contain a lot of additional information (e.g. the composition), so we have to enter these data manually. We will start with the diffraction pattern import and enter the phase information afterwards.

Suppose that you have a diffraction pattern of the mineral Aragonite available in the Philips/PANalytical peak data format (aragonite.udi), and you would like to include the data from this file into your user database. This is a rather simple task:

Make sure that the “User Database Manager” is displayed, then click on the “Add” button at its top in order to add a new entry. The “General” tab sheet will be activated automatically, with the cursor in the first input field “Sample name”. However, we will import the diffraction data first and enter the phase information details afterwards, so please click on the “Diffraction pattern” tab sheet header in order to bring the corresponding tab sheet into front (Fig. 56).

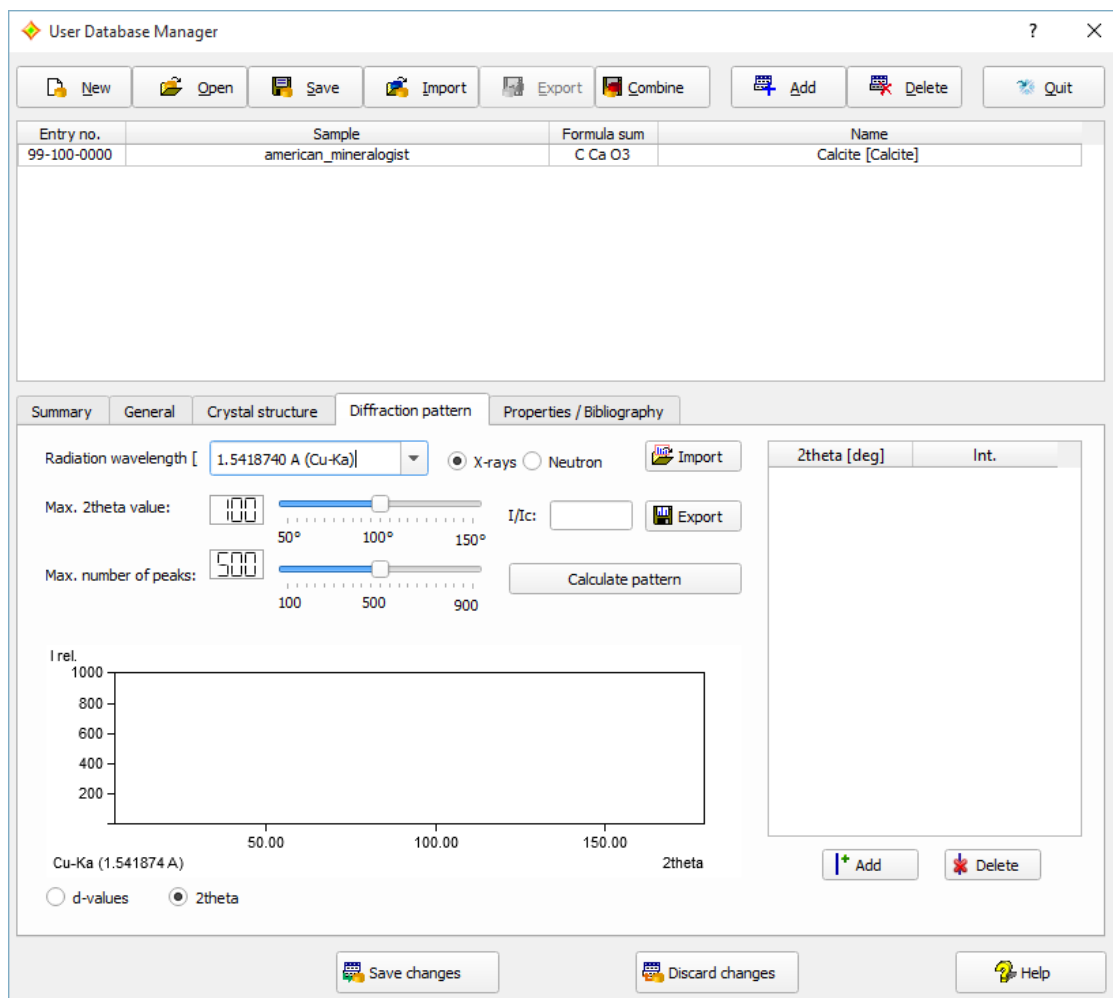


Fig. 56: The "Diffraction pattern" tab sheet is still empty.

Afterwards, please click on the "Import" button to the left of the peak data table. A dialog will open in which you have to select the diffraction data file you would like to import. Please mark "Philips/PANalytical Peak data (\*.udi)" as "File type" at the bottom of the dialog, then select the file "aragonite.udi" in the "Tutorial" subdirectory of the Match! program directory (e.g. "C:\Program Files\Match4\Tutorial"). Finally, please press "Open". The diffraction data are now present in the "Diffraction pattern" tab sheet; they are displayed both as diffraction pattern picture as well as peak list (2theta or d-values/ Intensities) in the table to the right (Fig. 57).



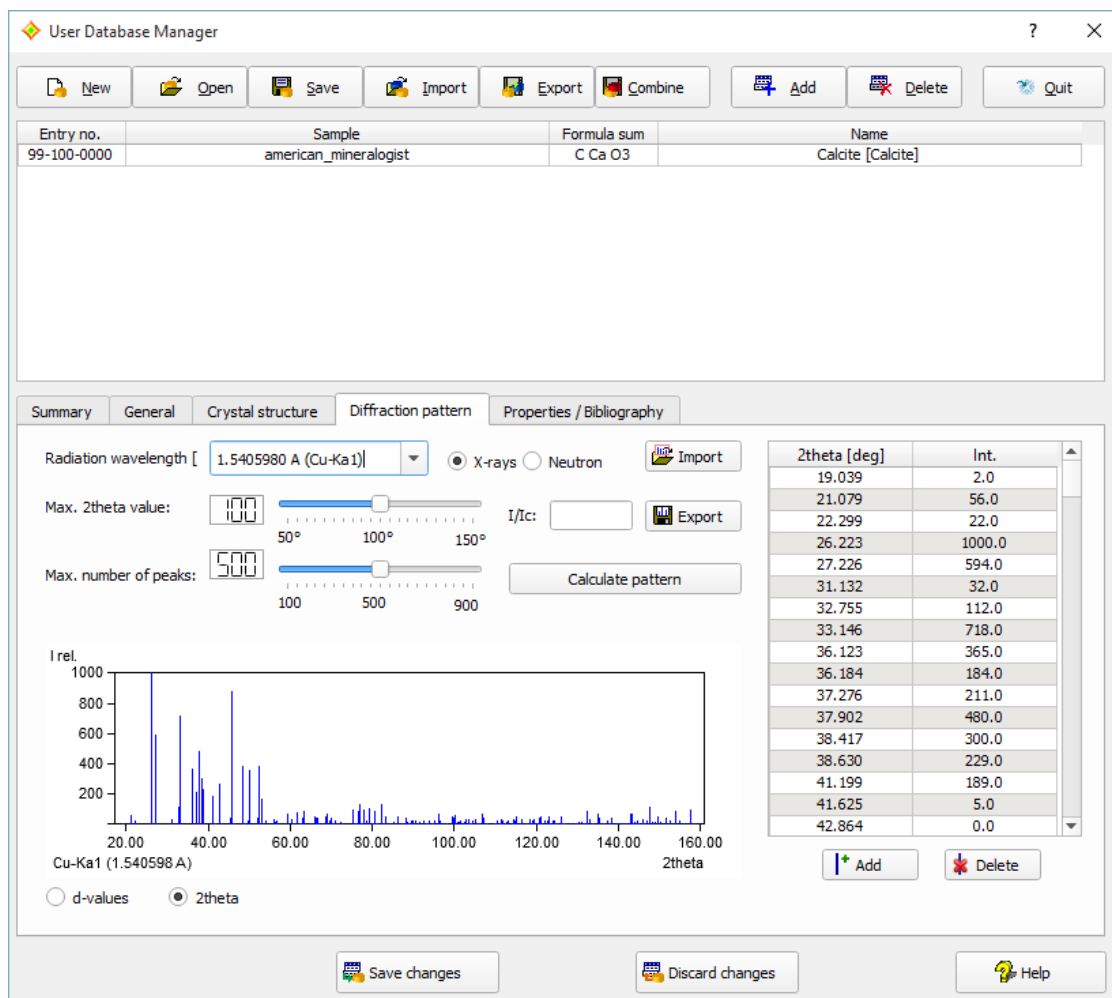


Fig. 57: Your "Aragonite" diffraction pattern has been imported from the file "aragonite.udi".

All that remains to do is to enter the phase information on the "General" tab sheet, so please activate this tab sheet now. Afterwards, please enter "Aragonite" as the "Sample name", then press <Tab> to advance to the "Formula sum" input field. Enter "Ca C O3" (mind the blank characters between the elements!). Afterwards, press <Tab> to advance. Enter "Calciumcarbonate" as "Chemical name", press <Tab> again, and give "Aragonite" as mineral name.

Finally, you might want to mark the quality of the data. In our case, the diffraction pattern is really excellent, so please click on "\*" (excellent)" in the "Quality" box on the lower left-hand side. Afterwards, press the "Save changes" button at the bottom of the tab sheet.

That's it! Your diffraction data entry has been added to the user database, as can be seen from the entry list above (Fig. 58).

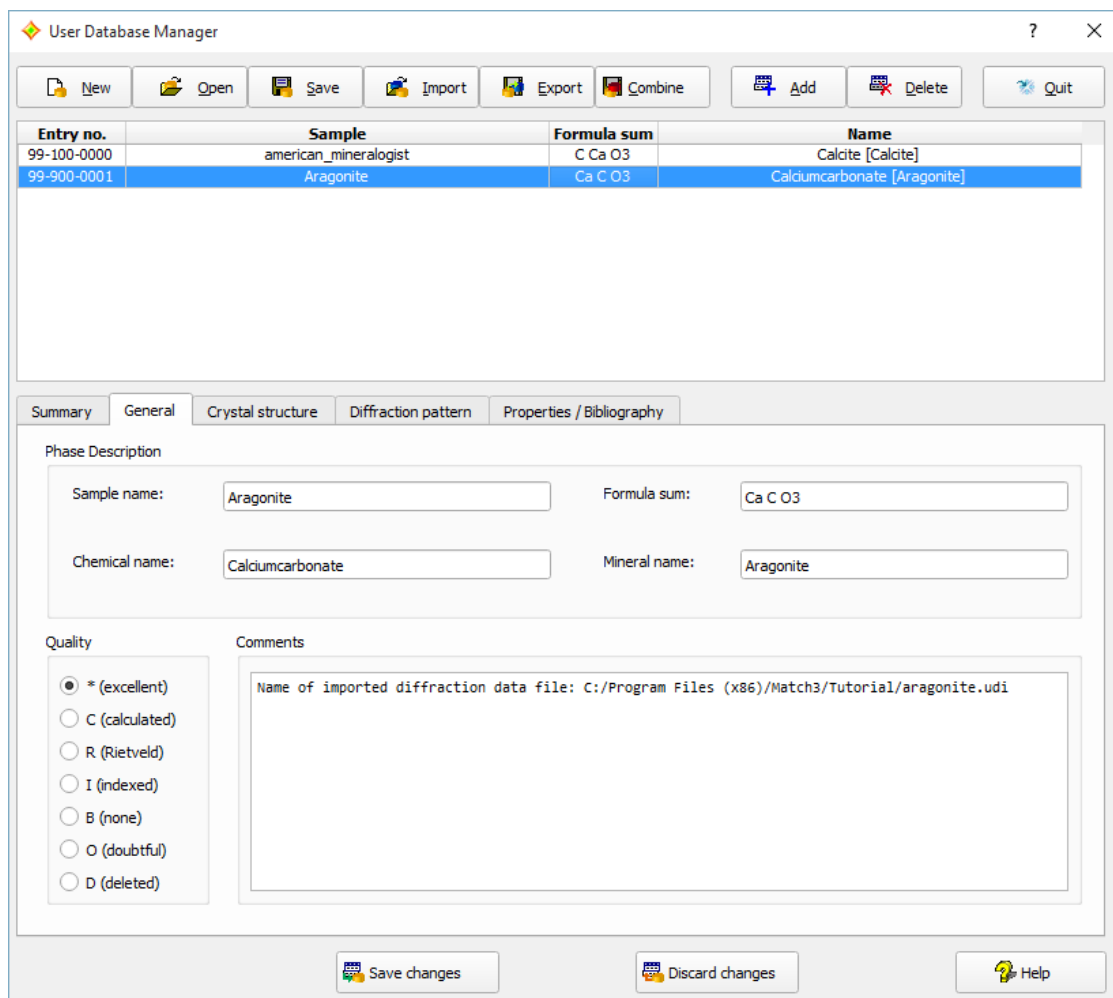


Fig. 58: Your Aragonite diffraction pattern has been successfully added to the user database.

### Calculate Patterns for Crystal Structures Imported from CIF-Files

The most convenient way to add entries to a user database is probably the import of crystal structure data from CIF-files, whereupon the corresponding powder diffraction patterns (as well as the  $I/I_c$  values required for quantitative analysis) are calculated automatically.

Please click on the “Import” button at the top of the user database manager; a dialog will be displayed in which you can select if you would like to import entry data either from cif (crystallographic information files), from some other Match! user database (mtu-file), or from the ICSD (Fig. 59).

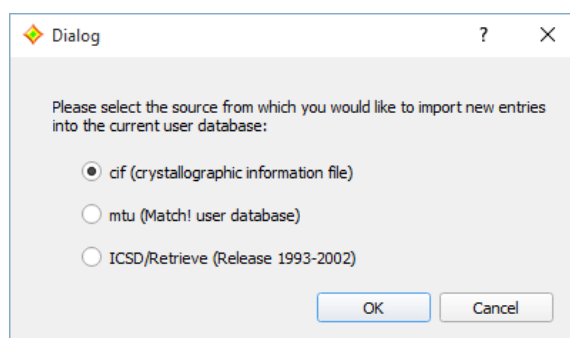


Fig. 59: In this dialog, you have to select the origin of the entry data to be imported (either CIF-files, Match! user database files or ICSD/Retrieve).

Please mark the “cif” option, then press “OK”. A new dialog is displayed in which you have to select the directory from which you would like to import CIF-files<sup>64</sup>. Please mark the “Tutorial” subdirectory of the Match! program directory (Fig. 60), then press “OK”.

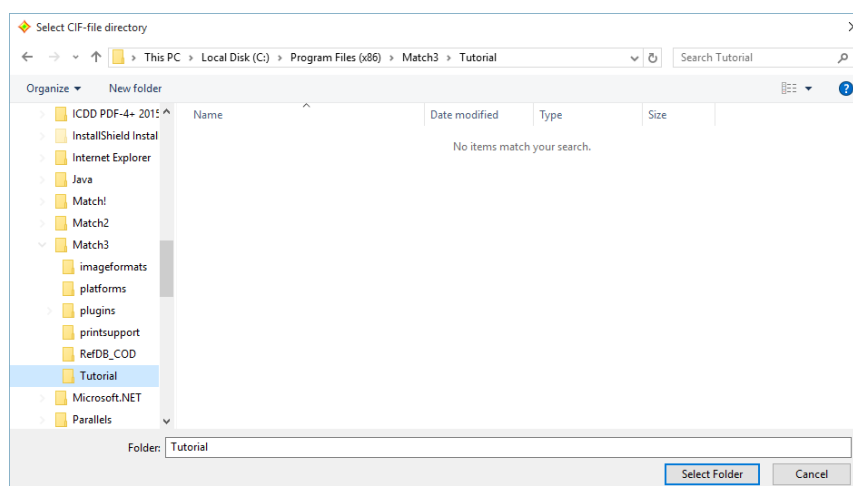


Fig. 60: Here, you have to select the directory in which the CIF-files you would like to import are stored.

Another dialog will open, presenting a list of all CIF-files present in the selected directory (as well as all cif-files from all subdirectories if present). Here, you can actually select the CIF-files you would like to import. Please mark the file “calcite.cif”<sup>65</sup>, then press “OK”.

Again, a new dialog is displayed in which you can select the origin (e.g. source database) from which the CIF-files has been taken, e.g. the COD or AMCSD. Besides this, you can also adjust some settings concerning the calculation of diffraction patterns: the radiation type (X-rays or neutron), the wavelength, the maximum 2theta angle, and the maximum number of peaks that shall be included in the database to be created. Note that this is a convenient method to create a reference database for neutron diffraction data!

In our case, the entry has been taken directly from the original AMCSD, so please mark the corresponding option (Fig. 61) and press “OK”.

<sup>64</sup> The normal “File-Open” dialog cannot be used for this task due to a well-known Windows bug when a large number of files is selected.

<sup>65</sup> The CIF-file has been taken from the American Mineralogist Crystal Structure Database (<http://rruff.geo.arizona.edu/AMS/amcsd.php>).

Fig. 61: The entry we would like to import has been taken from the AMCS D database.

That's it! Everything else will be handled automatically: A new entry will be created; the data from the CIF-file will be imported into the corresponding data fields, and the diffraction pattern, the density and the  $I/I_c$  value will be calculated from the imported crystal structure data. The new entry will be automatically added to the user database, so it will appear in the Entry list a few seconds later<sup>66</sup> (Fig. 62).

<sup>66</sup> Of course, if the unit cell is large, the calculation of the diffraction pattern may take much longer...

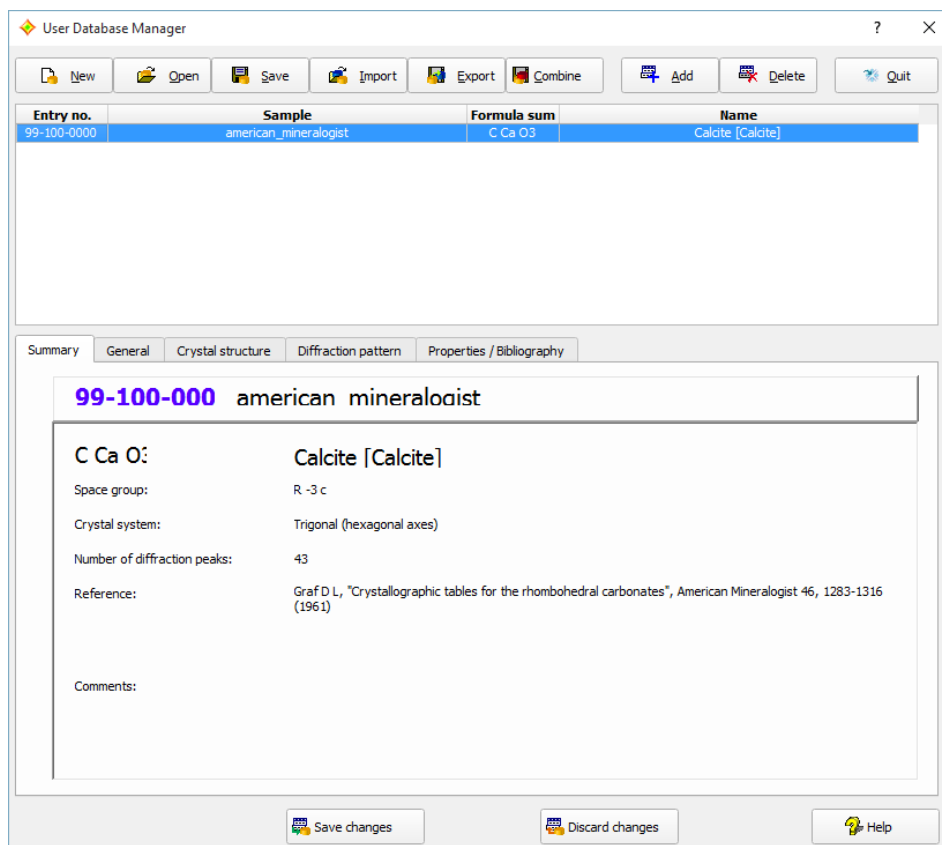


Fig. 62: The new entry "Calcite" has been imported from a CIF-file taken from the "American Mineralogist Crystal Structure Database".

As has already been mentioned, it is possible to select more than a single CIF-file for being imported at a time, e.g. by keeping the <Shift> or <Ctrl> button pressed while you click on the individual file names. In this case, all selected files will be imported automatically one after the other. If you import more than a single CIF-file at a time, a report of warnings and errors is displayed when the last file has been imported, compared to the import of a single CIF-file in which case any warnings and errors are reported directly. The "import of multiple CIF-files" functionality is rather powerful; it has been used by Crystal Impact to create the COD reference database containing about 177,000 entries from the COD CIF files.

### Manual Input of Diffraction Data

The probably most flexible (but also the most tiresome) way is to enter the diffraction data manually. However, in many cases this is the only applicable way, if e.g. the data estimate from a printed publication. We will now add a (small) entry from scratch in order to demonstrate how this can be done.

Here are the data extracted from a hypothetical scientific paper:

```
Title: Common Salt
Formula Sum: NaCl
Chemical name: Sodiumchloride
Mineral name: Halite
List of peaks (d Int.):
3.2447    82.5
2.8100  1000.0
1.9870    616.9
1.6945     17.7
1.6224    186.5
1.4050     76.8
1.2893      7.9
1.2567    192.4
1.1472    134.3
1.0816      8.1
```

We will enter this minimal data set into the user database. Please click on the "Add" button at the top of the User Database Manager window, in order to add a new entry to the user database. The "General" tabsheet will be activated automatically, with the cursor in the first input field "Sample name".

The four database fields at the top of the “General” tabsheet grouped as “Phase Description” are used later on to identify a certain entry in the Candidate list, so it is worth while to enter reasonable data here.

In our case, we will enter the publication title as sample name, so please type “Common Salt” (of course only the text between the quotation marks, not the quotation marks themselves!) and press <Tab> in order to advance to the next field “formula sum”.

Here we will enter the composition NaCl; however, it is important to **insert a blank character between the elements according to the CIF- or PDF-standard**. Hence, please enter “Na Cl” and advance to “Chemical name” by pressing the <Tab> key again.

Please enter “Sodiumchloride” as chemical name, then advance to the “Mineral name” field (<Tab>) and enter “Halite”. Finally, set the “Quality” to “\* (excellent)” by clicking on the corresponding radio button to the left. Your screen should now look similar to Fig. 63.

The screenshot shows the 'User Database Manager' window. At the top is a menu bar with icons for New, Open, Save, Import, Export, Combine, Add, Delete, and Quit. Below this is a table with the following data:

Entry no.	Sample	Formula sum	Name
99-100-0000	american_mineralogist	C Ca O3	Calcite [Calcite]
99-900-0001	Aragonite	Ca C O3	Calciumcarbonate [Aragonite]

Below the table are tabs for Summary, General (selected), Crystal structure, Diffraction pattern, and Properties / Bibliography. The 'General' tab contains the 'Phase Description' section with the following fields filled in:

- Sample name: Common salt
- Formula sum: Na Cl
- Chemical name: Sodiumchloride
- Mineral name: Halite

Below this is the 'Quality' section with radio buttons. The '\* (excellent)' option is selected. To the right of the quality options is a large empty text area for 'Comments'. At the bottom of the window are three buttons: 'Save changes', 'Discard changes', and 'Help'.

Fig. 63: The Sodiumchloride data on the "General" tab sheet have been filled in.

The only data extracted from the paper which have not yet been entered so far are the diffraction data, so please click on the “Diffraction pattern” header to bring the corresponding tab sheet into front. You will enter the d-values of the peak, so please make sure that you **click on the “d-values” radio button** in the bottom left corner first.

Afterwards, please click on button “Add” below the peak data table on the right-hand side, enter the d-value of the first peak (3.2447), then press <Tab> to advance to the second column “Int.”. Please enter the corresponding intensity value (82.5), then press <Return> in order to finish the input of the first peak. The peak will appear in the diffraction pattern to the left of the table.

In the same way, you can now enter the data of the second peak (2.81, 1000.0) right away. Please do so, and do not forget to press the <Tab> key in between to advance to the next field! The second peak will also appear in the diffraction pattern; your screen should now look like Fig. 64.



User Database Manager

Entry no.	Sample	Formula sum	Name
99-100-0000	american_mineralogist	C Ca O3	Calcite [Calcite]
99-900-0001	Aragonite	Ca C O3	Calciumcarbonate [Aragonite]

Summary General Crystal structure Diffraction pattern Properties / Bibliography

Radiation wavelength [ 1.5418740 Å (Cu-Kα) ] ☒ X-rays ☐ Neutron

Max. 2theta value:   I/Ic:

Max. number of peaks:

☒ d-values ☐ 2theta

d [Angstrom]	Int.
3.2447	82.5
2.8100	1000.0

Fig. 64: The data of the first two peaks have already been entered.

Please enter the peak data of the remaining eight peaks now in the same manner as above.

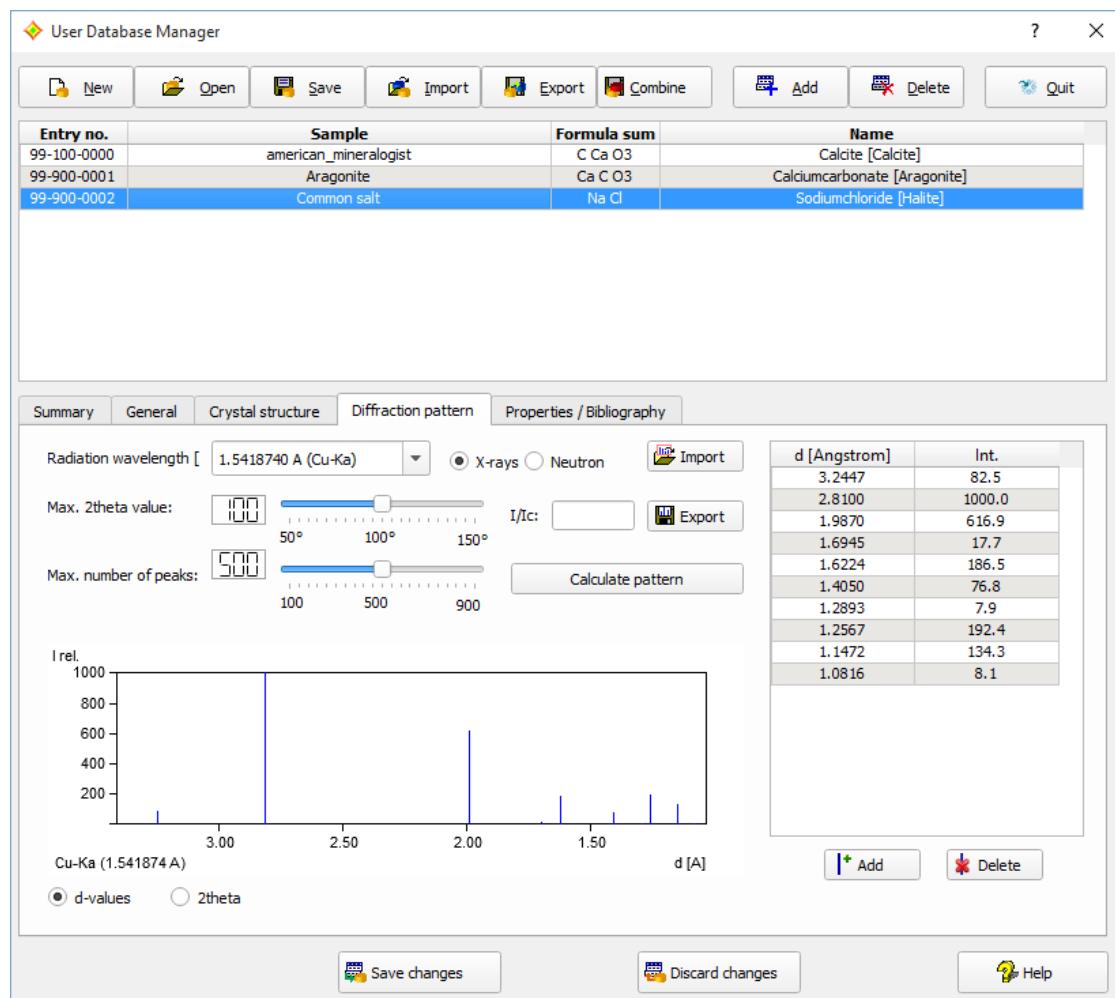


Fig. 65: All peak data have now been entered; the new entry has been saved.

So far, the data have been input but not yet saved to the database (the entry is not yet present in the list at top of the User Database Manager window). In order to do so, please click the “Save changes” button at the bottom of the User Database Manager; your entry will now appear in the entry list at the top. Your screen should now look similar to Fig. 65.

The **entry numbers** for the user database are assigned automatically according to the new ICDD PDF numbering scheme; they cannot be changed by the user.

The entry numbers depend on the origin of the data. If the entry has been imported from the COD, the entry number is calculated as 960000000 + COD file number + 1, e.g. the COD cif file 9000000.cif gets the entry number 96-900-0001. If the entry has been imported from the ICSD, the entry number is calculated as 980000000 + ICSD Collection Code (COL), e.g. the ICSD entry with COL=68860 gets the entry number 98-006-8860. Entries that have been entered manually start with the entry number 99-900-0000.

### Manual Input of Crystal Structure Data

If a publication does not contain the powder diffraction pattern of a compound but the crystal structure data, you can enter them instead and calculate the diffraction pattern from these data afterwards. We will add a new entry “Quartz” in order to demonstrate how to do this.

The data extracted from the scientific paper are:

```
Title: alpha-quartz
Formula Sum: SiO2
Chemical name: Silicondioxide
Mineral name: Quartz
Crystal structure data:
Crystal system: trigonal
Space group: P 32 2 1
Unit cell: a = 4.914 c = 5.405 alpha = 90.0 gamma = 120.0
Atomic coordinates:
Si 0.4698 0.0000 0.6667
```

O 0.4145 0.2662 0.7856

Reference: G. Smith, L.E. Alexander, Acta Cryst. 16(6), 462 (1963)

Please enter these data in the User Database Manager as follows: Click on the “Add” button at its top in order to add a new entry. Like in the previous examples, the “General” tab sheet will be activated automatically, with the cursor in the first input field “Sample name”.

Please enter the title “alpha-quartz” as sample name and advance to the “Formula sum” field by pressing <Tab>. The composition is SiO<sub>2</sub>, so please enter “Si O2” (mind the blank character between Si and O!) and press the <Tab> key again.

Afterwards, enter “Silicondioxide” as “Chemical name”, press <Tab>, and give “Quartz” as mineral name. Finally, set the “Quality” to “C (calculated)”, since the diffraction pattern will be calculated from the crystal structure data (Fig. 66).

The screenshot shows the 'User Database Manager' window. At the top, there is a table with the following data:

Entry no.	Sample	Formula sum	Name
99-100-0000	american_mineralogist	C Ca O3	Calcite [Calcite]
99-900-0001	Aragonite	Ca C O3	Calciumcarbonate [Aragonite]
99-900-0002	Common salt	Na Cl	Sodiumchloride [Halite]

Below the table are tabs for 'Summary', 'General' (selected), 'Crystal structure', 'Diffraction pattern', and 'Properties / Bibliography'. The 'General' tab contains the following fields:

- Phase Description:
  - Sample name: alpha-quartz
  - Formula sum: Si O2
  - Chemical name: Silicondioxide
  - Mineral name: Quartz
- Quality:
  - ☐ \* (excellent)
  - ☒ C (calculated)
  - ☐ R (Rietveld)
  - ☐ I (indexed)
  - ☐ B (none)
  - ☐ O (doubtful)
  - ☐ D (deleted)
- Comments: (Empty text area)

At the bottom, there are buttons for 'Save changes', 'Discard changes', and 'Help'.

Fig. 66: All data appropriate for the “General” tab sheet have been filled in.

The next information extracted from the paper is the crystal structure, so please bring the corresponding tab sheet into front by clicking on the “Crystal structure” tab sheet header. The first thing you have enter is the crystal system “trigonal”; please click on (activate) the “Trig./hexag.” radio button in the “Crystal system” group at the top left of the tab sheet.

Afterwards, you can select the space group in the corresponding combo box below. In this combo box, only space groups which belong to the crystal system selected above are displayed. The space group given in the paper is “P 32 2 1”, so please click on the “arrow down” to the right of the combo box, scroll down the list and select “P 32 2 1 (154)” (the number in brackets is the one given in the “International Tables of Crystallography”).

Once you have selected crystal system and space group, you can enter the unit cell constants. Depending on the crystal system and space group selection, only a few parameters have to be entered. In our case, please enter “4.914” for *a* and “5.405” for *c*.

You are now ready to enter the atomic parameters: Please click on the “Add” button below the atomic parameters table on the right-hand side, enter “si” and press <Tab>. The cursor will advance to the next column “X”. Enter “0.4698” for  $x$ , press <Tab>, then “0.0” for  $y$  (<Tab>), and finally “0.6667” for  $z$ . There is no information given about the isotropic displacement factor  $B_i$  and the site occupation factor “Occ.”, so please press <Enter> to finish the input of the first atom’s parameters.

Now the coordinates of oxygen have to be entered: Please press “Add” below the atomic parameters table, then give “o” as element, “0.4145” as  $x$ , “0.2662” as  $y$ , and “0.7856” as  $z$ . Finally, press <Enter> to finish the input of the atomic parameters (Fig. 67).

**User Database Manager**

Buttons: New, Open, Save, Import, Export, Combine, Add, Delete, Quit

Entry no.	Sample	Formula sum	Name
99-100-0000	american_mineralogist	C Ca O3	Calcite [Calcite]
99-900-0001	Aragonite	Ca C O3	Calciumcarbonate [Aragonite]
99-900-0002	Common salt	Na Cl	Sodiumchloride [Halite]

Tabs: Summary, General, **Crystal structure**, Diffraction pattern, Properties / Bibliography

**Crystal system**

☐ Trid. (anorthic)   ☐ Tetragonal   ☐ Cubic  
☐ Monoclinic   ☐ Trig. (rhomb.)   ☒ Trig. (hexag.)  
☐ Orthorhombic   ☐ Hexagonal

Space group: P 32 2 1 (154)   Z:

**Unit cell parameters:**

a: 4.914000 Å   alpha: 90.000000 °  
 b: 4.914000 Å   beta: 90.000000 °  
 c: 5.405000 Å   gamma: 120.000000 °

Element	X	Y	Z	Bi	Occ.
Si	0.46980	0.00000	0.66667	1.000	1.000
O	0.41450	0.26620	0.78560	1.000	1.000

Buttons: Add, Delete, Save changes, Discard changes, Help

Fig. 67: The complete crystal structure description has been entered: crystal system, space group, unit cell constants and atomic parameters.

Now that the crystal structure information is complete, we can advance to the diffraction pattern calculation: Please click on the “Diffraction pattern” tab sheet header, then press the “Calculate pattern” button. After a short moment, the diffraction pattern will be displayed (Fig. 68). Note that the  $I/I_c$  value required for semi-quantitative phase analysis has also been calculated automatically.

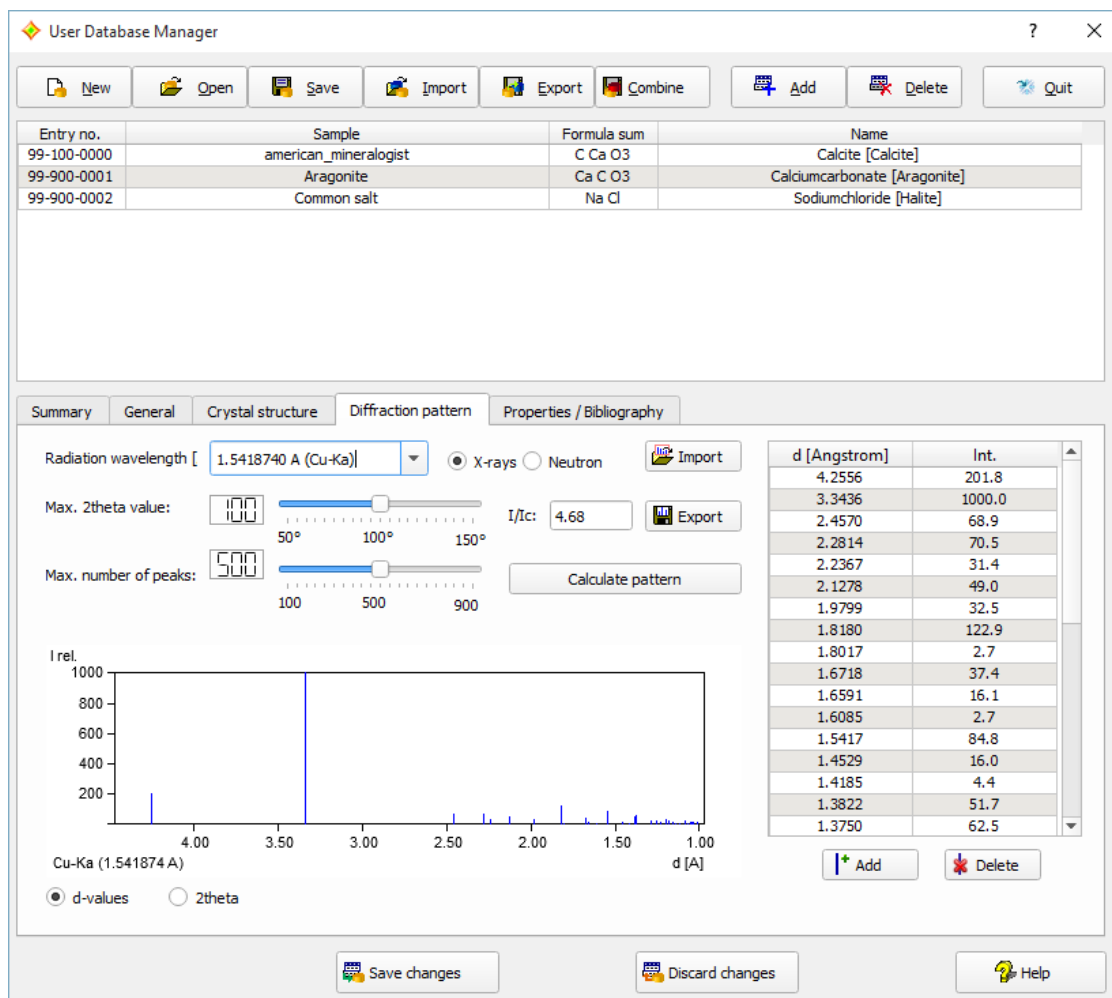


Fig. 68: The powder diffraction pattern (as well as the  $I/I_c$  value and the density) has been calculated from the crystal structure data you have entered.

Finally, you have to enter the bibliographic data: Please select the "Properties / Bibliography" tab sheet, click in the input line to the right of "Authors", and enter "G. Smith, L.E. Alexander". Afterwards, press <Tab> two times to advance to the "Journal" input line, and type "Acta Crystallographica ("). Your input will be automatically expanded to the next matching journal name. Once you have typed the "(" , the correct journal "Acta Crystallographica (1,1948-23,1967)" will be displayed.

Please press <Tab> two times (the CODEN will be set automatically to "ACCRA9") to advance to the "Volume" input line, then enter "16(6)". Press <Tab> again, and enter "462" as "Page(s)". Finally, advance to "Year" (<Tab>) and give "1963".

At this point, you have entered all data extracted from the scientific paper; your tab sheet should now be equivalent to Fig. 69.

The screenshot shows the 'User Database Manager' window. At the top is a toolbar with buttons: New, Open, Save, Import, Export, Combine, Add, Delete, and Quit. Below the toolbar is a table with four columns: Entry no., Sample, Formula sum, and Name. The table contains three entries:

Entry no.	Sample	Formula sum	Name
99-100-0000	american_mineralogist	C Ca O3	Calcite [Calcite]
99-900-0001	Aragonite	Ca C O3	Calciumcarbonate [Aragonite]
99-900-0002	Common salt	Na Cl	Sodiumchloride [Halite]

Below the table are tabs: Summary, General, Crystal structure, Diffraction pattern, and Properties / Bibliography. The 'Properties / Bibliography' tab is active. It contains two sections: 'Physical properties' and 'Bibliography'.

**Physical properties:**

Density (calc.): 2.648144 g/cm<sup>3</sup>      Density (meas.):  g/cm<sup>3</sup>      Color:

**Bibliography:**

Authors:

Title:

Journal:

CODEN:       Volume:       Page(s):       Year:

At the bottom are three buttons: Save changes, Discard changes, and Help.

Fig. 69: You have successfully entered the bibliographic data; besides this, the density has been calculated from the given crystal structure data.

All that remains to do is to actually add the entry data to the user database. Like in the previous examples, this is achieved by clicking the “Save changes” button at the bottom of the tab sheet. The new entry will be added to the entry list at the top.

### Add Entries from other User Databases

If you are more than one Match! user in an institution, it is reasonable to share the own reference diffraction patterns, or, in other words, the user database entries. Match! is able to append another user's user database entries to your own. In fact, this is a rather simple task:

Simply copy your colleague's user database file (\*.mtu) to your computer, then click the “Import” button at the top of the User Database Manager window. A dialog will be displayed in which you can select if you would like to import entry data either from cif (crystallographic information files) or from some other Match! user database (mtu-file). Please mark the “mtu (Match! user database)” option (Fig. 70), then press “OK”; a “File Open” dialog will be displayed.

For your convenience, we have prepared a (small...) user database in the “Tutorial” subdirectory of the Match! program directory, so you can import it right away.



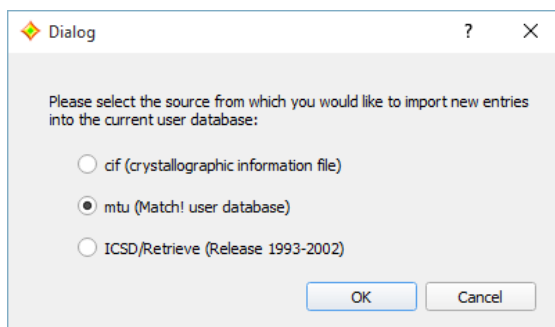


Fig. 70: In this dialog, you have to select the origin of the entry data to be imported (either CIF-files, MATCH! user database files or ICSD/Retrieve).

Please select the file "colleague\_database.mtu" in the "Tutorial" subdirectory of the Match! program directory (e.g. "C:\Program Files\Match4\Tutorial"). Afterwards, please press "Open".

A message will appear indicating that 9 entries have been imported. Once you acknowledge by pressing "OK", the new entries will appear in the entry list (Fig. 71).

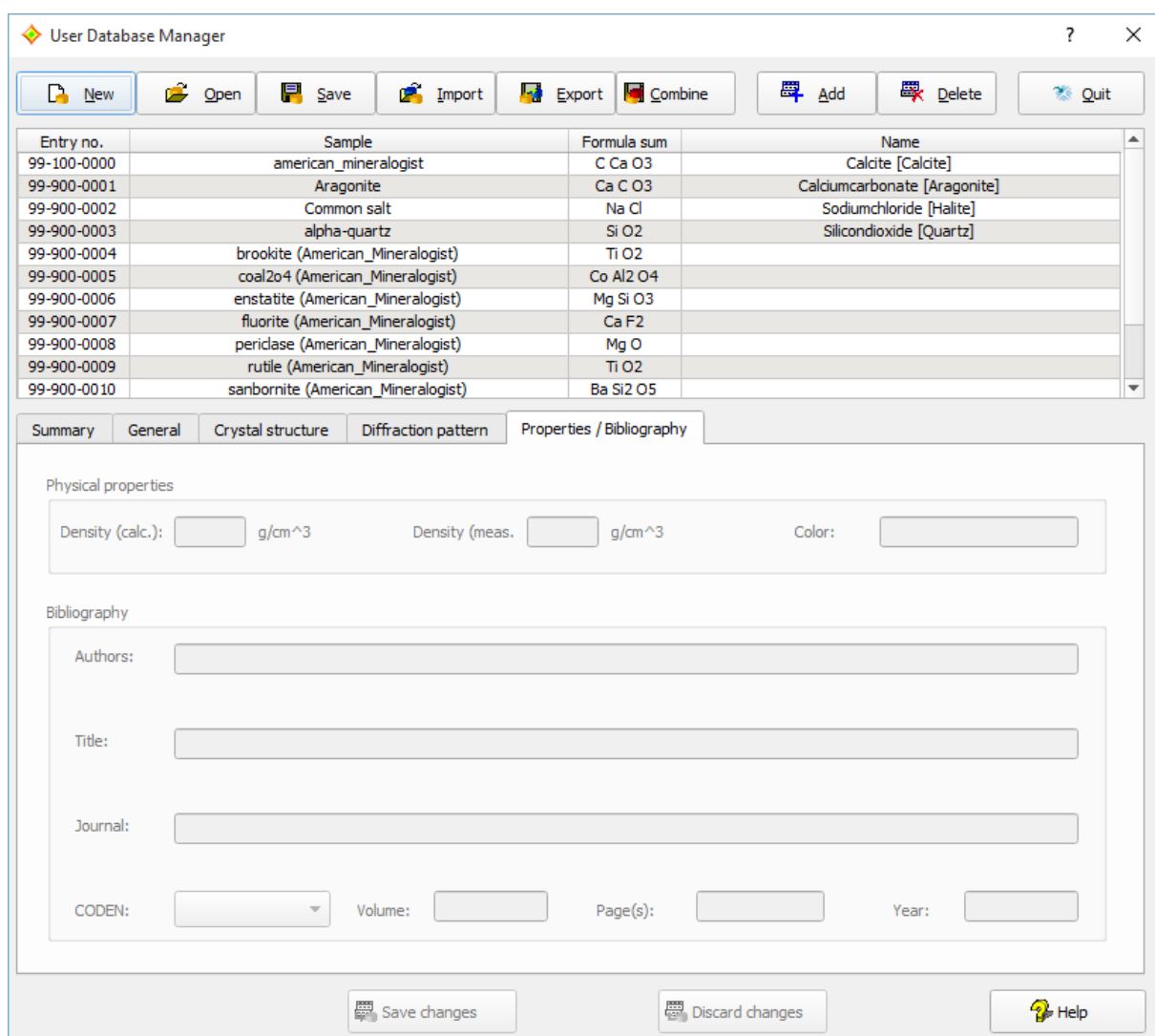


Fig. 71: The 9 entries from your colleague's user database have been added to your user database.

Once you have finished adding or modifying entries<sup>67</sup> to/in your Match! user database, please press the "Quit" button at the top of the User Database Manager. You will be asked if and where you would like to save your modified

<sup>67</sup> If you would like to **modify an entry in the user database** that is currently loaded / displayed in the User Database Manager, please mark the corresponding entry line in the table at the top, then edit the entry data at the bottom. Once you have finished, do not forget to press the "Save changes" button at the bottom to make the changes permanent.

user database. Please select/enter an appropriate file name and path and press "Save". Once the user database has been saved, the User Database manager dialog will be closed.

Please note that new entry numbers are assigned automatically to the entries imported from your colleague's user database. It is not possible to keep your colleague's entry numbers when importing; this is necessary in order to avoid duplicates.

### **Calculate Patterns for Crystal Structures Imported from ICSD/Retrieve**

If you have a valid license<sup>68</sup> for an ICSD/Retrieve version released between 1993 and 2002, you can create a powerful reference database without additional costs, simply by importing the crystal structure data from the ICSD. During the import procedure, the corresponding powder diffraction patterns as well as the  $I/I_c$  values required for quantitative analysis are calculated automatically.

If you would like to do so, please click on the "Import" button at the top of the user database manager; a dialog will be displayed in which you can select if you would like to import entry data either from cif (crystallographic information files), from some other Match! user database (mtu-file), or from the ICSD (Fig. 72).

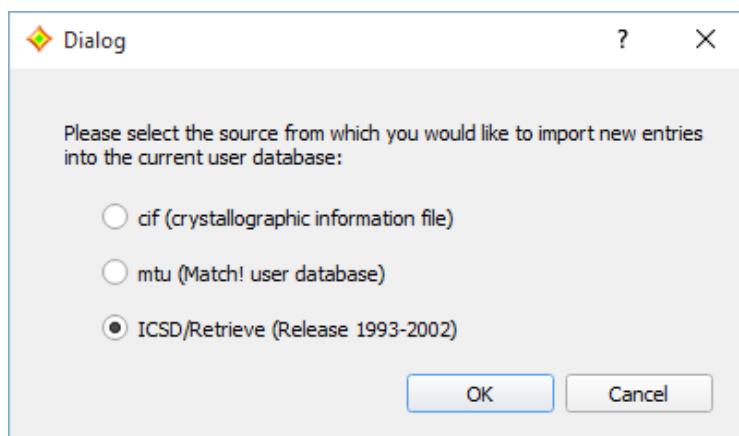


Fig. 72: In this dialog, you have to select the origin of the entry data to be imported (either CIF-files, Match! user database files or the ICSD).

Please mark the "ICSD/Retrieve" option as in Fig. 72, then press "OK". You now have to give the directory in which the ICSD/Retrieve database (to be exact: the file "ICSD.NEW") is stored. A "File Open" dialog will be displayed in which you have to select the file "ICSD.NEW". Normally, this file is located in the "INDEX" subdirectory of your ICSD/Retrieve program directory. Once you have found and marked the file "ICSD.NEW", please press "Open".

A new dialog is displayed in which you have to confirm that you have a valid license for the ICSD/Retrieve version you are about to import (Fig. 73). The confirmation will be written to a protocol logfile.

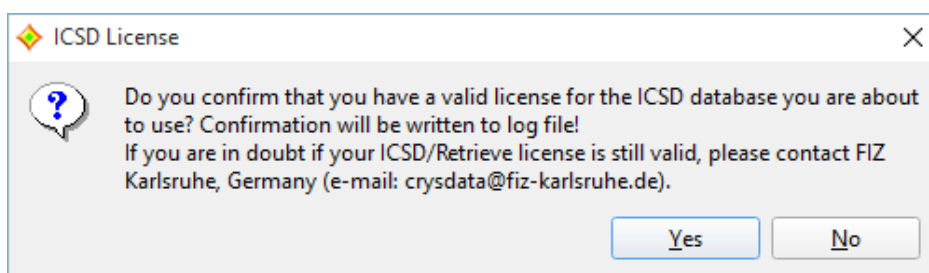


Fig. 73: Before you can use/import an ICSD/Retrieve database, you have to confirm that you have a valid license for it.

If you have confirmed that you have a valid license, a new dialog is displayed in which you can adjust some settings concerning the calculation of diffraction patterns: the radiation type (X-rays or neutron, the wavelength, the maximum 2 $\theta$  angle, and the maximum number of peaks that shall be included in the database to be created (Fig. 74). Note that this is a convenient method to create a reference database for neutron diffraction data!

<sup>68</sup> If you are in doubt whether your license is still valid, please contact FIZ Karlsruhe (Germany) (e-mail: crysdata@fiz-karlsruhe.de).

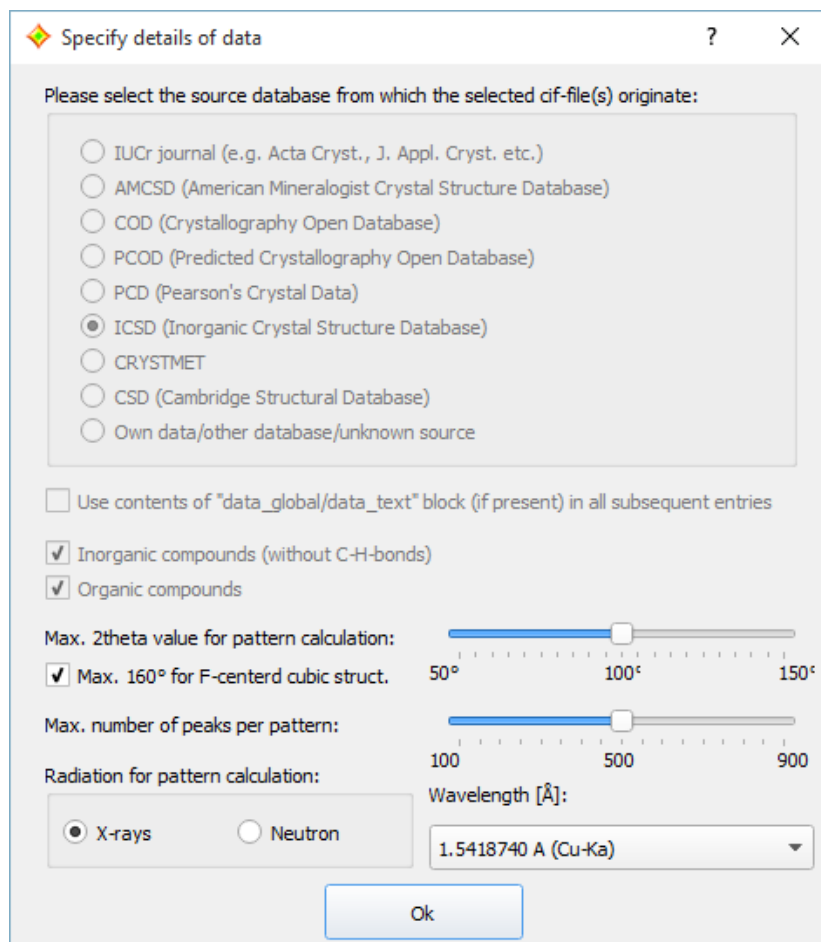


Fig. 74: There are several options that can be adjusted for the calculation of the reference powder diffraction pattern, like the radiation type, the wavelength or the upper 2theta limit.

When you have made your selections (if any), please press “OK”. That’s it! The import of the entries from the selected ICSD/Retrieve database will now begin. The progress will be displayed in a small window.

Depending both on the number of entries in the ICSD/Retrieve database as well as the processing speed of your PC, the import procedure may take a day or even longer. When the import has finished, the new entries will be automatically added to the current user database, so they will appear in the Entry list a few seconds later. Any errors that might have occurred during the import will be displayed in your text editor.

Once the import has finished, please don’t forget to press the “Save” button at the top of the user database manager, in order to save the entries imported from the ICSD/Retrieve to a so-called “user database file” (file extension \*.mtu). As has already been mentioned, this user database file can then be selected in the “Create Reference Database” dialog to create a new “ICSD/Retrieve” reference database, probably in combination with the COD reference database that is shipped along with Match!.

### Add entry to reference database directly

It is also possible to add a new entry to the current reference database directly, i.e. without having to use the User Database Manager and/or to run a new reference database indexing in the Reference Database Library. The corresponding command “Add to reference database” is available in the “Database” menu; it can also be run using the keyboard shortcut <Ctrl+Shift+A>. Both will open the “Add New Entry Data” dialog in which you can enter the entry data.

#### Please note:

- You must have **write access** to the directory in which the current reference database is stored. If this does not apply, a corresponding error message will be displayed.
- If you are currently using a pure ICDD PDF reference database, Match! will add a user database (i.e. create a combined reference database) automatically in which the new entry data will be stored. The original PDF database itself will not be affected by this, of course.

- Once you have added one or more entries to a reference database, it can no longer be used by Match! version 1. However, you can copy the actual user database file (user\_database.mtu) from the reference database directory and create a new reference database from it in Match! version 1.
- If the current anchor pattern (bottom-most experimental pattern) contains peak data when the "Add to reference database" command is run, they will be copied to the new entry automatically.

Once the "Add New Entry Data" dialog is displayed, you can enter the information to be stored in the new entry:

### Import entry data from cif-file

The easiest way to enter the new entry data is to import them from a cif-file. In order to do so, please click the corresponding button in the top right corner of the dialog, select the cif-file and finally press "Open". The entry data will be imported from the cif-file and displayed in the corresponding dialog elements afterwards. Afterwards, you can edit them using the dialog elements described below

### Manual input and editing of entry data

You can enter or edit the entry data on the "General", "Crystal Structure", "Diffraction pattern" and/or the "Properties / Bibliography" tabs. The only mandatory information that needs to be given is the *Formula sum* on the "General" tab. However, we recommend to at least also enter the *Chemical name* and / or the *Mineral name* information, because they will be displayed in the "Candidate phase" column in the Candidate list later on.

### General information

The four database fields at the top of the "General" tab sheet grouped as "Phase Description" are used later on to identify a certain entry in the Candidate list, so it is worthwhile to enter reasonable data here. As has already been mentioned, the *Chemical name* and/or the *Mineral name* information will be displayed in the "Candidate phase" column in the Candidate list later on.

**Please note:** When you enter the *Formula sum* in the corresponding field on the "General" tab sheet, please keep in mind that you have to **use upper and lower-case characters in the element symbols**, like in "Ca Si O<sub>3</sub>" (do not use "ca si o<sub>3</sub>" or "CA SI O<sub>3</sub>"). We also recommend inserting a **blank character between the elements** according to the CIF- or PDF-standard. Hence, please enter e.g. "Cu S O<sub>4</sub> (H<sub>2</sub> O)<sub>5</sub>" (and not "CuSO<sub>4</sub>(H<sub>2</sub>O)<sub>5</sub>").

You can add a *Quality* qualifier in the lower left corner if you can estimate the quality of your diffraction data (e.g. 'C' if they are calculated).

### Crystal structure data

If you do not have a diffraction pattern available but crystal structure data, you can enter them on the "Crystal structure" tab sheet, so that the diffraction pattern can be calculated by Match!. The first thing you have to enter is the crystal system in the upper left corner. Once you have selected a crystal system, the "space group" combo box below will be filled with appropriate space groups, so that you can select your space group afterwards.

Please note:

- In the "space group" combo box only space groups which belong to the crystal system selected above are displayed.
- You can get additional information about the space group currently selected in the combo box by placing the mouse cursor over the combo box.

Once you have selected crystal system and space group, you can enter the unit cell parameters. Depending on the crystal system and space group selection, only a few parameters have to be entered.

You are now ready to enter the atomic parameters:

Please click in the atomic parameter table to the right in the first line directly below "Element", enter the first element and press <Tab>. The cursor will advance to the next field "X". Enter the coordinate x of the first atom, press <Tab>, enter y, press <Tab> again, and finally enter z. If there is any information given about the isotropic displacement factor B<sub>i</sub> and the site occupation factor "Occ.", you can enter them in the corresponding remaining two columns; otherwise, please press <Tab> until the cursor has advanced to the next line. Once you have entered all atomic coordinates given in the described manner, you should press the <Return> on your keyboard to finish the input of the atomic parameters.

## Diffraction data

There are four alternate ways in which the "Diffraction pattern" tab sheet can be filled:

1. **Copy of current peak list:** If the current anchor pattern (bottom-most experimental pattern) contains peak data, they will be copied to the new entry automatically when you run the "Add to reference database" command.
2. **Calculation of diffraction pattern from crystal structure data:** If a complete set of crystal structure data is present on the "Crystal structure" tab sheet (e.g. imported from a cif-file), Match! will automatically calculate the diffraction pattern from the given crystal structure data when you open the "Diffraction pattern" tab sheet. After a few seconds, the diffraction pattern will be displayed. Of course, you can also (re-)calculate the diffraction pattern by clicking on the corresponding button.

### Please note:

- If diffraction data are already present (e.g. copied from the anchor pattern) when crystal structure data are imported from a cif-file or entered manually, the original diffraction data will be kept at first. You can overwrite them with the calculated data by pressing the "Calculate pattern" button on the "Diffraction pattern" tab.
  - Along with the diffraction pattern, also the  $I/I_c$  value (required for semi-quantitative analysis) as well as the density are calculated from the crystal structure data.
3. **Import of diffraction pattern:** If you have a peak data file (Stoe (\*.pks), Philips PANalytical (\*.udi) or Endeavour (\*.dif)) available, you can import it by clicking on the "Import" button to the left of the peak data table.
  4. **Manual input of diffraction data:** In order to enter the diffraction pattern (peak data) manually, you should first check the appropriate settings of the "Radiation wavelength" and "Abscissa" fields on the upper left hand side of the tab sheet. Afterwards, click on the "Add" button below the table to the right. Now enter the 2 $\theta$  value (or d-value, depending on "Abscissa") of the first peak, then press <Tab> to advance to the second column and enter the corresponding intensity. Finally, press <Return> or <Tab> again in order to finish the input of the first peak; the peak will appear in the diffraction pattern to the left of the table. Continue entering the remaining peak data in a similar manner until you have finished.

## Physical properties and bibliographic data

On the "Properties / Bibliography" tab sheet, both physical property data (density, color) and bibliographic information can be entered. If a complete set of crystal structure data is present on the corresponding tab sheet, you can (re-)calculate the density (which is an additional useful information for qualitative phase analysis) simply by clicking on the "Calculate pattern" button on the "Diffraction pattern" tab sheet. We also strongly recommend to enter measured density and color if available.

Below, you can enter the bibliographic details, e.g. if the entry data originate from a scientific paper. When you enter the journal name, your input will be automatically expanded to the next matching journal name in the internal CODEN table. At the same time, the CODEN will be automatically set. This works also the other way round: If you know the CODEN for the journal, you can select it in the corresponding combo box in the lower left corner; the corresponding journal name will be set automatically.

Once you have finished editing the new entry data, please press "OK", in order to add the new entry to the reference database. After a few seconds, a message will be displayed indicating that the new entry has been added to the current reference database.

The new entry is now available for search-match and retrieval operations straight away.

## Edit reference database entry

In order to edit an entry, please mark it in the candidate list first. Afterwards, you can either run the "Edit reference database entry" from the "Database" menu, or select the corresponding command from the context menu of the candidate list (which can be opened by right-clicking on the corresponding line/entry to be edited). This will open the "Edit Entry Data" dialog in which you can modify the entry data.

### Please note:

- You must have **write access** to the directory in which the current reference database is stored. If this does not apply, a corresponding error message will be displayed.
- You cannot edit ICDD PDF database entries.
- You can only edit a single entry at a time, i.e. only a single line must be marked in the candidate list in order to enable this command.
- Once you have edited one or more entries in a reference database, it can no longer be used by Match! version 1. However, you can copy the actual user database file (user\_database.mtu) from the reference database directory and create a new reference database from it in Match! version 1.
- If the current anchor pattern (bottom-most experimental pattern) contains peak data when the "Add to reference database" command is run, they will be copied to the new entry automatically.

After the "Edit Entry Data" dialog is displayed, you can modify the entry information just like adding a new entry (see above). Once you finished editing the entry data, please press "OK". After a few seconds, a message will be displayed indicating that the modified entry has been saved in the current reference database.

When an updated entry is saved to the database, Match! in fact only updates the index files and appends the modified entry data as a new entry to the end of the database file. The original entry is still kept within the database file, in order to avoid shifting/copying a lot of data while the software is still in use. When the user closes Match!, the program checks if entries have been edited or deleted, and removes the surplus entry data from the database file before finally closing. This procedure may take a few seconds.

### Delete reference database entry

You can delete one or more entries that is/are currently marked in the candidate list from the reference database under the following conditions:

- You must have **write access** to the directory in which the current reference database is stored. If this does not apply, a corresponding error message will be displayed.
- You cannot delete ICDD PDF database entries from the corresponding reference database.
- Once you have deleted one or more entries from a reference database, it can no longer be used by Match! version 1. However, you can copy the actual user database file (user\_database.mtu) from the reference database directory and create a new reference database from it in Match! version 1.

In order to delete one or more entries, please mark them in the candidate list first, e.g. by keeping the <Ctrl> (or <Cmd>) button pressed while clicking on them. Afterwards, you can either run the "Delete reference database entry" from the "Database" menu, or select the corresponding command from the context menu of the candidate list (which can be opened by right-clicking on the corresponding line/entry to be deleted). You will be asked for confirmation. After a few seconds, a message will be displayed indicating that the entry has been deleted from the current reference database.

When one or more entries are deleted from a reference database, Match! in fact only updates the index files and appends the modified entry data as a new entry to the end of the database file. The original entries are still kept within the database file, in order to avoid shifting/copying a lot of data while the software is still in use. When the user closes Match!, the program checks if entries have been edited or deleted, and removes the surplus entry data from the database file before finally closing. This procedure may take a few seconds.

### Copyright issues

With Match!, it is perfectly possible to use data from various sources (e.g. ICSD/Retrieve or cif-files downloaded from the internet) as sources for creating an own reference pattern database. However, please note that before doing so, you have to check if this does not violate the copyright of the original data! **Crystal Impact shall not be liable for any copyright violations of Match! users!** In order to prevent copyright violations, **user databases created by Match! can only be used/read on PCs on which the same Match! license is installed.**

If you know about potential sources of reference data that might be interesting for other users, please contact Crystal Impact (p. 156)!



## Advanced operations

### Multiple diffraction patterns


In addition to the first (so-called “main” or “anchor”) pattern, it is possible to add more experimental diffraction patterns and display them on top of the main experimental pattern (Fig. 75). For example, this can be useful if you have collected several data sets and would like to use these different patterns to decide if a certain peak is present or not.


For this, you can either import additional patterns, by pressing <Ctrl+I> or clicking the ‘+’-button in the top right-corner of the pattern graphics, or mark a candidate list or match list entry and run the “Load as experimental” command from the “Entries” menu. The latter will calculate profile data from the peak data given in the marked entry, and add profile and peaks as a new “experimental” pattern to the pattern graphics.




Fig. 75: Six experimental diffraction patterns are stacked on top of each other.

By default, multiple diffraction patterns are stacked on top of each other. However, you can reduce the stacking distance between diffraction patterns manually step by step up to a complete overlap with the anchor pattern at the bottom. To do so, press the Ctrl- (Cmd-) key along with '-' (or '+' vice versa), run the corresponding command(s)

from the View / Pattern menu, or move the mouse cursor to the right of the diffraction pattern until it changes to , then turn the mouse wheel up or down.

Using the menu command “Pattern / Experimental patterns...” (or by pressing the corresponding button  in the main toolbar at the top) you can display a table of all currently loaded experimental diffraction patterns, along with options to display / edit their sample ID, date/time, temperature, color, line style etc..

### Table of Experimental Diffraction Patterns

Using the menu command “Pattern / Experimental patterns...” (or by pressing the corresponding button  in the main toolbar at the top) you can display a **table of all currently loaded experimental diffraction patterns**, along with options to display / edit their sample ID, date/time, temperature, color, line style etc..

The various usage options are shown in Fig. 76.



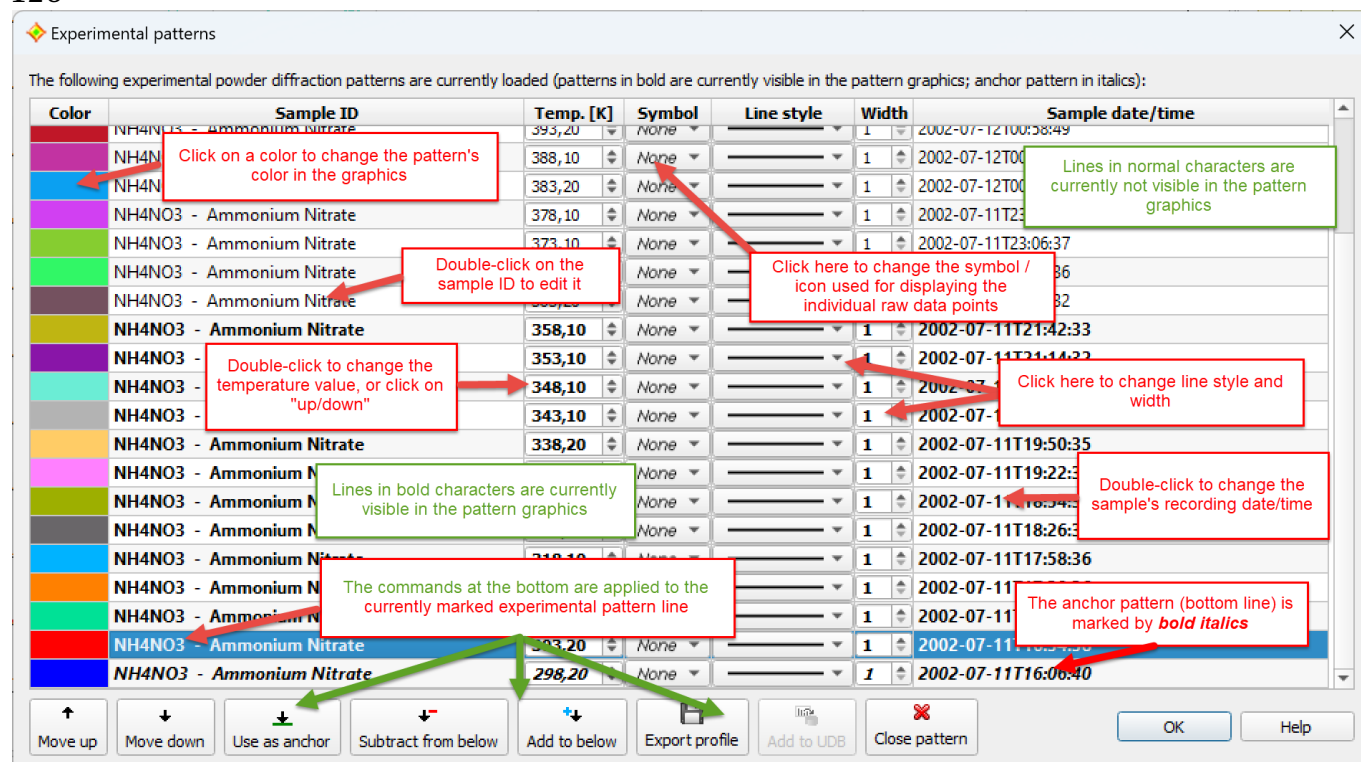


Fig. 76: The “Experimental patterns” window provides an overview over all ‘experimental’ diffraction patterns that are currently loaded, along with options to change their display color, sample ID, temperature etc.

**Please note:** This new window replaces the “Additional patterns” sub-menu at the bottom of the “Pattern” menu that was available in earlier versions of Match!.

### Adjust multiple patterns viewing distance or angle (“3D-View”)

If multiple diffraction patterns are displayed, they are displayed with maximum vertical and minimum horizontal distance by default, or, in other words, they are stacked on top of each other. You can **adjust the horizontal and vertical distance** between them as follows:

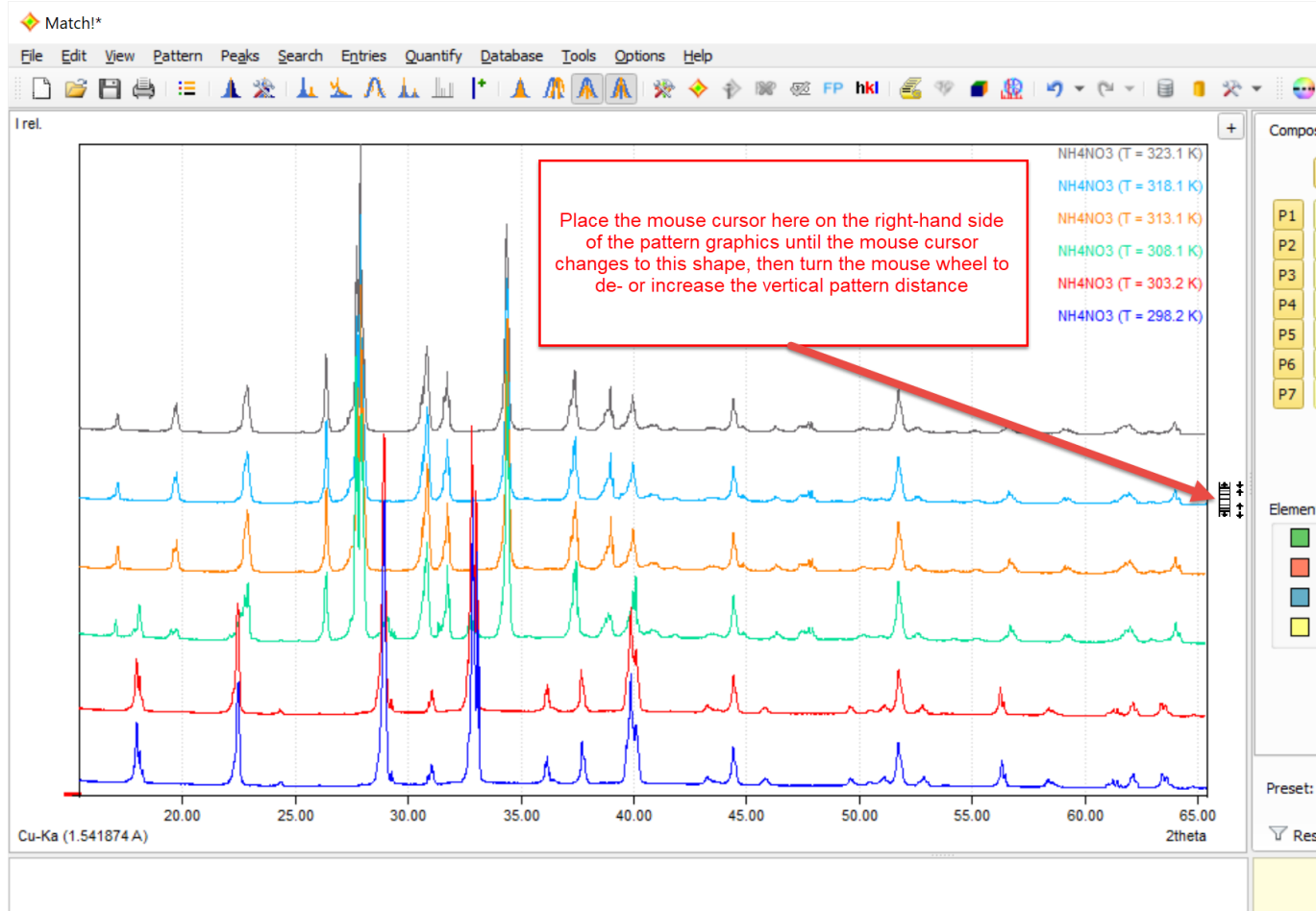



Fig. 77: Change the vertical distance between multiple experimental diffraction patterns, from “stacked on top of each other” to complete overlap.

In order to decrease the vertical distance between multiple experimental patterns in the graphics, place the mouse cursor to the right of the diffraction pattern until the mouse cursor changes to  , then turn the mouse wheel up or down in order to decrease or increase the vertical distance between the experimental diffraction patterns. As an alternative, you can increase or decrease the pattern distance using the <Ctrl+'+'> or <Ctrl+'-'> shortcuts.

You can also toggle between full and zero pattern distance by pressing the mouse wheel (center button) if this cursor is displayed.

If the vertical distance between multiple experimental diffraction patterns is at maximum or minimum value, the corresponding y-axis scale(s) are displayed on the left-hand side. However, if the pattern distance is somewhere between these two extrema, the y-axis scale is hidden.

In order to get a “3D-like” representation of multiple diffraction patterns, you can also **increase the horizontal distance** between the patterns. The option to increase the horizontal distance is **only available if the vertical distance has already been reduced** (see last paragraph). Increasing the horizontal distance will lead to a “3D-like” view of the different experimental diffraction patterns.

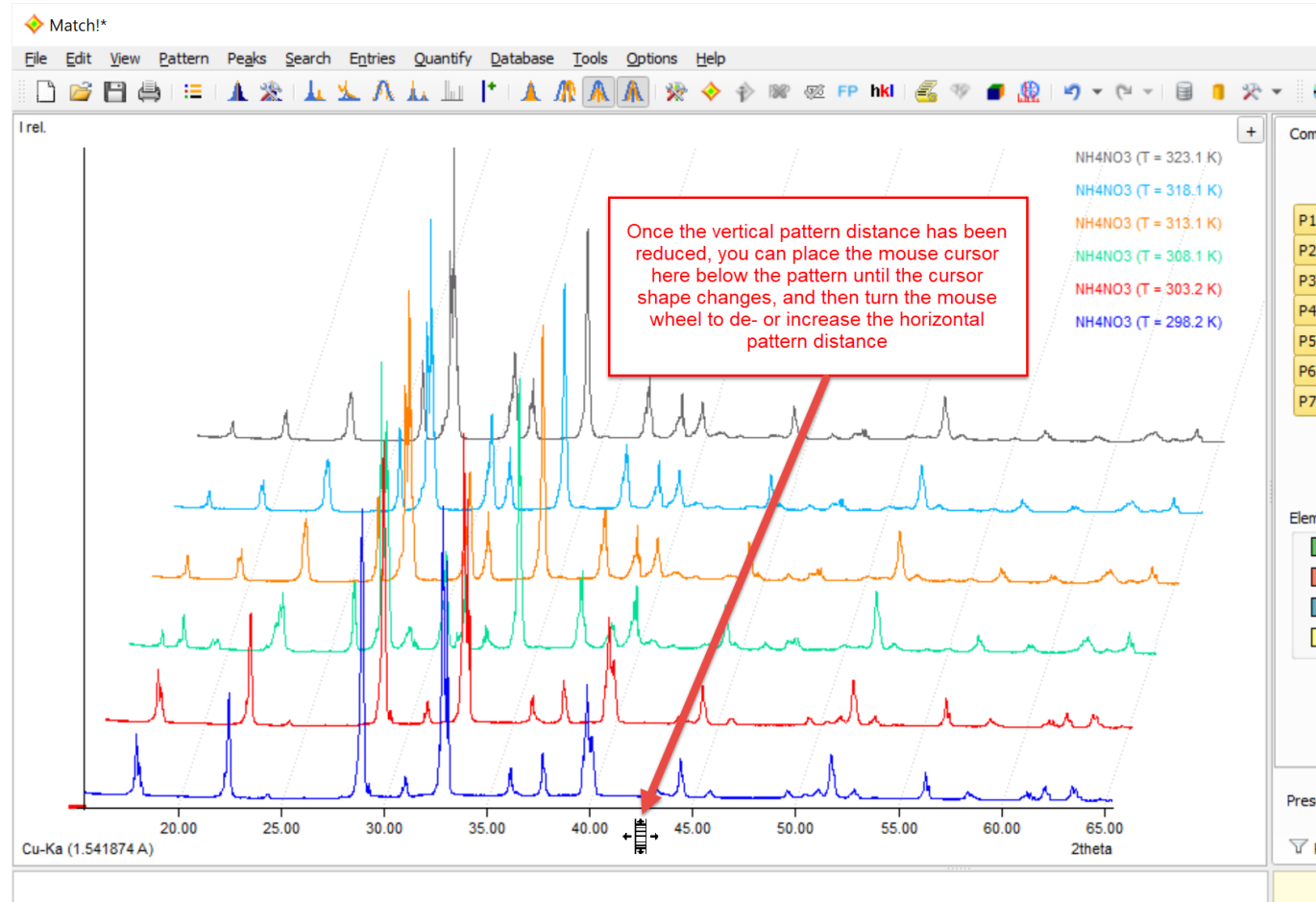



Fig. 78: By increasing the horizontal pattern distance (available once the vertical distance has also been reduced) you can create a “3D-like” view.

In order to increase the horizontal distance between multiple experimental patterns in the graphics, please **make sure that the vertical pattern distance has been reduced first**. Afterwards, place the mouse cursor in the space **below**

**the diffraction pattern** until the mouse cursor changes to , then turn the mouse wheel up or down in order to decrease or increase the vertical distance between the experimental diffraction patterns. As an alternative, you can increase or decrease the pattern distance using the <Ctrl+'+'> or <Ctrl+'-'> keyboard shortcuts.

Like with the vertical distance, you can toggle between full and zero pattern distance by pressing the mouse wheel (center button) if this cursor is displayed.

### Vertical Line at Mouse Cursor Position

It is also possible to display a vertical line following the mouse cursor (by pressing <Ctrl+X>), so that you can compare e.g. peak positions between several stacked patterns very accurately.

If the horizontal pattern distance is increased (“3D-like” view) when this option is active, a so-called “string of pearls” is displayed at the mouse cursor position. This means that colored circles are displayed at the corresponding intensity value at the cursor position for each individual pattern:

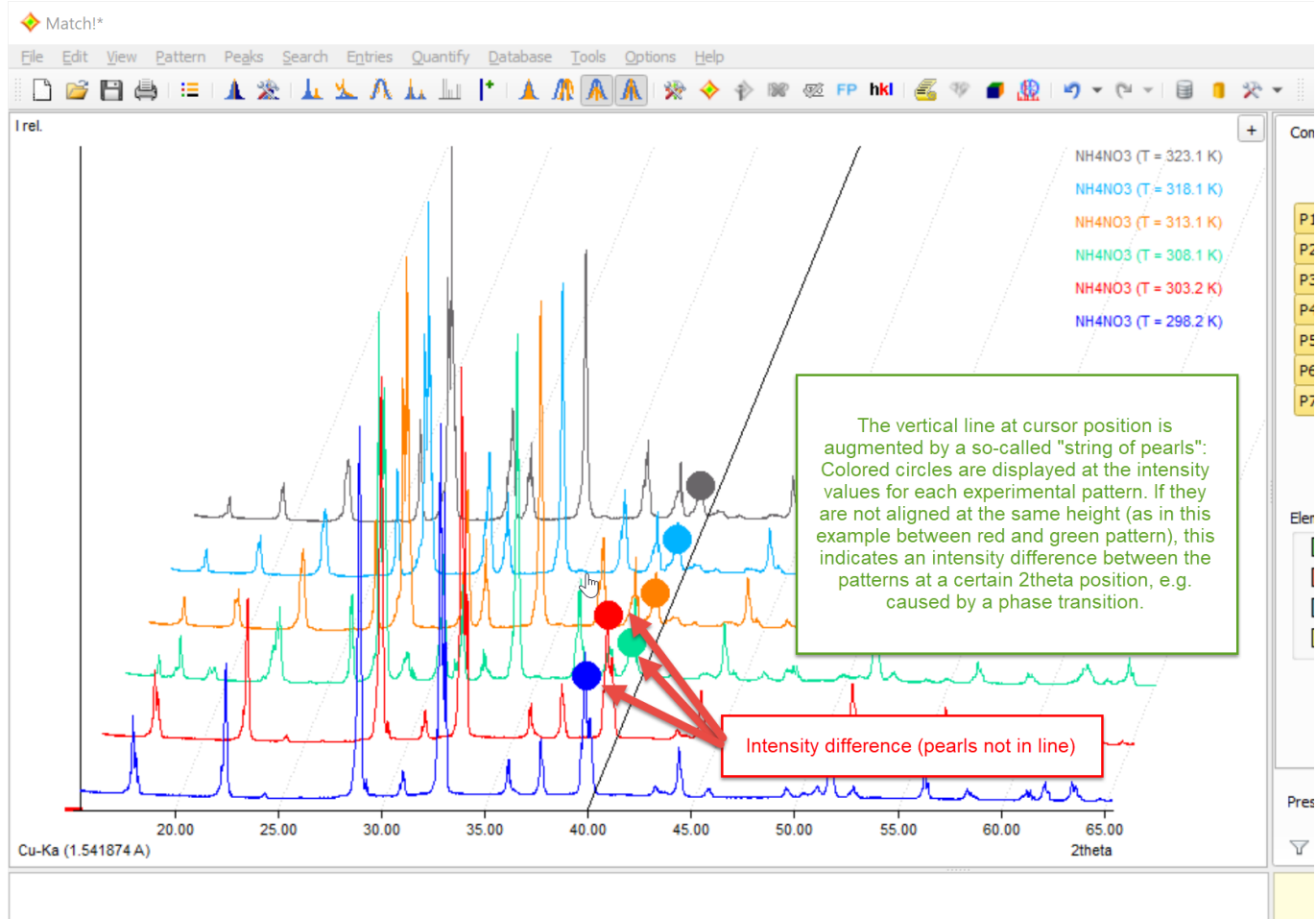



Fig. 79: The "string of pearls" is displayed at the "vertical cursor" position if the horizontal pattern distance is increased.

When moving the mouse cursor to the left or right, you can now determine intensity differences between the individual experimental patterns more easily. This can be helpful e.g. to detect phase transitions etc.

**Note:** The mouse cursor is always located in the xy-plane, i.e. the drawing plane of the anchor pattern at the bottom!

## Pattern menu

If you **mark an experimental pattern** in the graphics (e.g. by clicking on the profile curve or legend entry), it is displayed in **bold**, and the so-called pattern menu button  becomes available in the upper-right corner (instead of the normal '+' button for importing diffraction data).

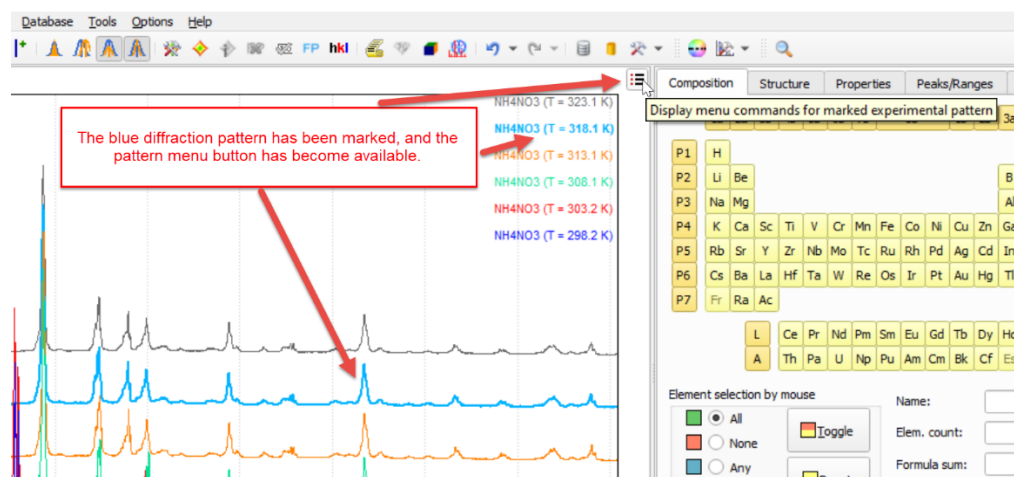


Fig. 80: After marking (clicking on the) blue diffraction pattern curve, the "pattern menu" button becomes available in the corner on the upper right-hand side.

Once you press it, the pattern menu for the marked experimental pattern is displayed:

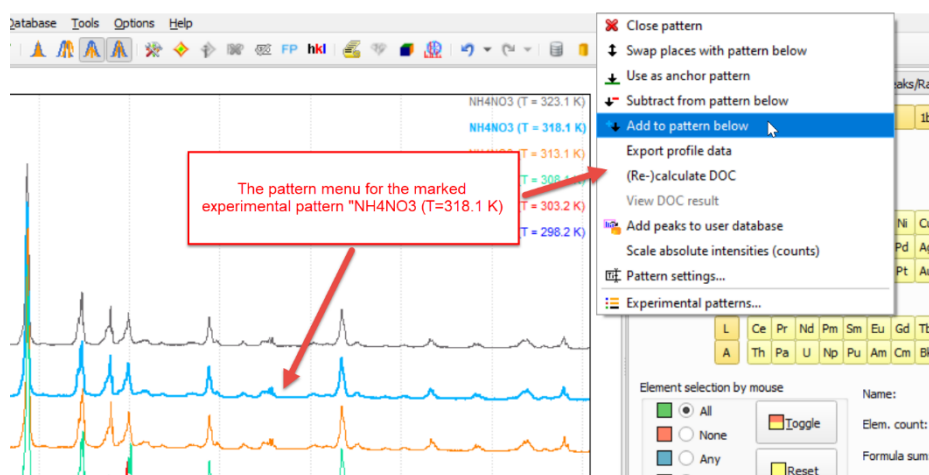


Fig. 81: The pattern menu for the marked (blue) diffraction pattern is displayed.

In the **pattern menu**, the most-common commands for experimental patterns are available. You can e.g. **exchange (swap) patterns**, **close (remove) an additional pattern**, **(re-)calculate the degree-of-crystallinity (DOC)**, change the **Pattern settings** (e.g. color, sample ID etc.), and finally also open the “**Experimental patterns**”-window that provides access to all experimental patterns that are currently loaded.

## Manual phases/entries

The **match list** on the lower right-hand side of the Match! window contains those entries/phases that are currently selected as “matching”, i.e. that have been decided on as being present in the sample. Normally, match list entries correspond to entries in the current reference database. However, it is also possible to add so-called “**manual entries**” (or phases) directly from scratch, e.g. by **importing crystal structure data** or entering them manually. It is even possible to enter only partial crystal structure data sets (e.g. containing only unit cell parameters but no space group or atomic coordinates).

To **add a new manual entry** to the match list, please run the command “Add new manual entry” from the “Entries” menu, or use the corresponding command from the match list’s context menu (which can be opened by right-clicking in the match list).

The procedure that follows is completely equivalent to adding a new entry to the reference database (p. 120), with the same dialog being used for data editing and the import of cif-files. The only differences are that for adding manual entries you do not need to have write permission for the reference database, and that the crystal structure data are accepted even if they are incomplete.

If you add **incomplete manual entries** to the match list (entries that contain peak positions but not intensities), the intensities of correlated experimental peaks will be occupied completely by these peaks if the “residual searching” option is active.

The **entry numbers of manual entries** are only virtual, of course, because manual entries are not added to the reference database normally. The numbers start with “99-999-9900” for the first manual entry. They are displayed in bold characters in the match list, so that you can distinguish them from the normal reference database entries. Manual entries are displayed just like normal match list entries in the pattern graphics. If only peak positions (but no peak intensities) are available (e.g. due to missing atomic parameters), the peaks will be displayed as vertical bars from the top to the bottom of the diffraction pattern.

Once you have added one (or even more) manual entries to the match list, you can edit them freely, e.g. to check the effect of different unit cell parameters or space groups. To do so, please mark the corresponding manual entry in the match list, then run the “Edit manual entry” either from the “Entries” menu or from the match list’s context menu. Once you have closed the “Edit manual entry” dialog by pressing “Ok”, the corresponding peak and other data will be updated.

Another option to add manual entries to the match list is to **create a copy of the reference database entry** that is currently marked in the candidate list. To do so, please mark the corresponding entry in the candidate list, then run the command “Select/add copy as manual ‘matching’ entry” either in the “Entries” menu or in the candidate list’s context menu. Once the copy has been created in the match list, you can edit the entry data as you like.

Once you have created a manual entry in the match list, you can also **add it to the current reference database**. To do so, please mark the corresponding manual entry, then use the corresponding command either from the "Database" menu or from the context menu (click right mouse-button to open).

**Please note:** Manual entries that have not been added to the current reference database cannot be retrieved using e.g. the restraints or "find phases/entries" functionality, because their data are not present in the index files!


## User levels

In addition to the option to set the automatic options for each individual step, you can also select among several so-called "user levels" at the top of the 'Automatic' page of the "Options"-dialog. The user levels define certain sets of automatic options that have shown to be reasonable. For example, the "Automatic" level lets Match! perform the complete phase analysis procedure automatically, while on the "Expert" level you have to run every single step on your own. Of course, you can also save your own automatic processing options settings as new "user levels".

When you run Match! for the very first time, you will be asked which default user level ("Beginner" or "Expert") you prefer:

In the "Beginner" mode Match! performs a nearly complete automatic processing of the initial steps: All you have to do is to select the diffraction data file you would like to analyze (you will be prompted automatically for it once the software has been started). Afterwards, Match! will automatically process the raw data, determine the peaks, and run the search-match calculation. All that remains to do is to select the "matching" phases (e.g. by double-clicking or dragging the corresponding entries from the candidate list on the left-hand side to the Match list to the right), and finally display the report containing e.g. the list of matching phases as well as their arbitrary amounts (e.g. by selecting "View/Report").

In the "Expert" mode you have to perform nearly all actions manually. This mode is especially recommended for experienced users who would like to analyze more complicated samples.

You can customize the user level (automatic processing behaviour) on the "Automatic" tab of the "Options" window (which can quickly be opened by pressing the  button in the toolbar) also later on. In addition to selecting user levels like "Beginner" or "Expert" you can also select individual automatic processing steps according to your requirements.

## Automatic processing

Match! contains several kinds of automatic functions. You can define which steps the program should carry out if another step has been accomplished. For example, you can tell Match! to process raw data automatically immediately after they have been imported.



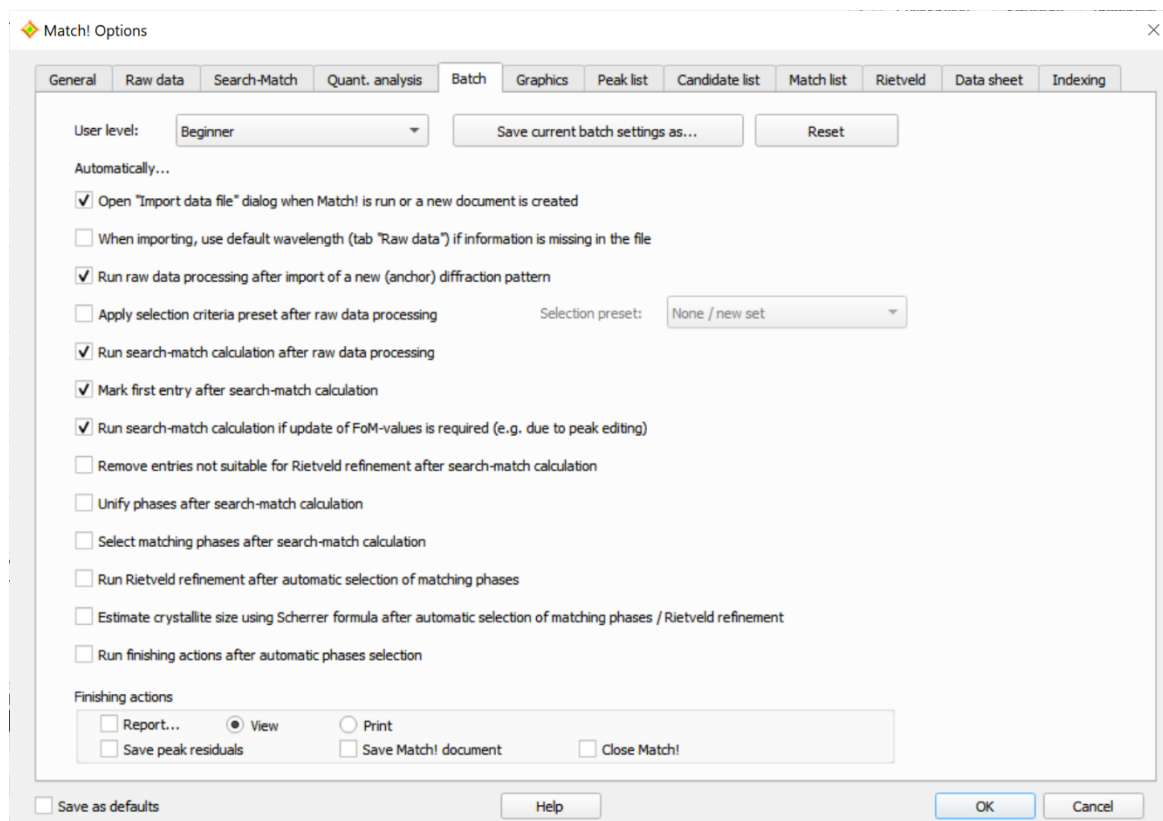


Fig. 82: On this page of the “Options” dialog (which can be opened from the “Options” menu), you can precisely define in which order automatic operations shall be carried out.

Match! is also capable of automatically selecting multiple matching phases, so the program is (at least in principle) able to automatically determine the components of a mixture of crystalline phases completely on its own. Well, from practice you will know that there may be cases in which minority phases are not identified with this approach, or that there may be other issues not recognized by the software, of course.

## Repeating similar analyzes

If you often analyze samples that contain the **same phases but in different amounts** (wt%), you can create and use predefined sets of entries (so-called "predefined selections" or "answer sets") that can be loaded into the match list straight away.

To do so, please run a first analysis, so that the match list contains all required phases. Afterwards, please run the command "File/Export/ Answer set (match list)", select an appropriate directory and file name, and finally press "Save".

As an alternative, you can also mark appropriate entries in the candidate list (maybe after using restraints or the "Find phases/entries" function). Afterwards, please run the command "File/Export/ Answer set (cand. list)" (or use the corresponding command from the context menu), select an appropriate directory and file name, and finally press "Save".

You have now created a text file containing a list of entry numbers (a so-called "Match! answer set file", extension \*.mta) that belong to the entries marked in the candidate or match list. This file can be used to directly select all matching phases during similar analyzes.

Any time you would now like to **run a similar analysis** in the future, please import the diffraction data as usual. Afterwards, please run the command "File/Import/Predefined phase selection" (or press <Ctrl+Shift+O> on the keyboard). Select the answer set file you have created in the step described above, then press "Open". The entries listed in the answer set file will be loaded into the match list straight away, with the peak searching and a single update calculation of the figure-of-merit values being performed automatically (if required). The amounts of the phases are then available in the match list straight away (if all entries contain the required  $I/I_c$  values, of course).

As an **alternative to using Match! answer set files** you can also **quickly add one (or more) specific entries** directly to the match list, by pressing <Ctrl+E> and entering either the name, the formula sum or the entry number. If more

than a single entry matches your criterion, a new dialog will be displayed in which you can select the entry(s) you would like to add to the match list.

**Please note:** If you use own diffraction patterns (user database) in addition or even instead of the COD or PDF, it is important to keep in mind that the entry numbers are specific for a certain user database. If a colleague uses an own (different) user database, it is not possible (or at least not reasonable) to exchange answer set files with her/him.

## Controlling Match! using scripts

Match! cannot be only controlled using the normal graphical user interface; it is also possible to create a list of commands in a so-called “batch script file” to be executed by Match!. Using this feature, Match! can e.g. be controlled from external programs.

The batch scripting functionality is intended to be used as follows:

First of all, you should manually optimize the relevant parameters (like the peak searching sensitivity) on diffraction patterns similar to the ones you would like to use with batch scripting. Afterwards, once you have found reasonable values for all relevant parameter values that are appropriate for your diffraction patterns and samples, you should define them as “default values”, by marking the “Save as defaults” checkbox on the lower left-hand side of the “Options”-dialog before closing the dialog by pressing “Ok”. You are now ready to use batch script files and commands for controlling the flow of the program. Match! will use the new default parameter values automatically.

A batch script file is typically created using a text editor; you can find a description of the format as well as a list of available commands below.

You can run a batch script e.g. from within Match! by selecting the corresponding command from the “File” menu. As an alternative, you can also run Match! from the command line, giving the name of the batch script file to be run as a command line parameter when the Match! program executable is invoked.

Here is a sample batch script that contains all of the commands that are currently available. You can create the corresponding file using any conventional text editor and save it e.g. as “batchscript.mbf”:

```
MATCH!_4_BATCH
!new_document
!use_ref_db("PDF-2 Release 2014")
set_default_wavelength(1.541874)
set_default_abscissa(2theta)
import("/Users/putz/Match/Samples/quickstart.rd")
!import_answerset("/Users/putz/Documents/ergebnis.mta")
!add_peak(26.62,1000.0,0.15)
strip_K_alpha2
!import_background("/Users/putz/Match/Samples/quickstart_background.bac")
subtract_background_automatic
smooth_exp_raw_data
find_peaks_normal(0.1,40.0,1)
!find_peaks_profile(0.1,96.0,1)
!correct_2theta_shift_automatic
!correct_2theta_spec_displ_automatic
!correct_2theta_shift(-0.14)
!correct_2theta_spec_displ(0.001)
!automatic_raw_data_processing
internal_standard(961011173)
!selection_preset("Silicon compounds")
search-match
!add_entry(96-900-7499)
!unify
!mark_first_entry
!import_selection_criteria("/Users/putz/Documents/selcrit.mss")
!select_matching_automatic
!select_first_entry_as_matching
!automatic_rietveld_refinement
!crystallite_size_estimation("LaB6",0.94)
!finish
!set_sample_id("TestID")
```

```
!set_sample_date_time("02.12.2010, 15:12 Uhr")
!view_report
!save_peak_residuals("/Users/putz/Documents/residuals.dif")
!save_document("/Users/putz/Documents/testdoc.mtd")
!close
!export_pattern_graphics("/Users/putz/Documents/pattern.jpg",JPG,1024,768,0)
!export_profile_data("/Users/putz/Documents/testprofile.dat")
!export_peak_data("/Users/putz/Documents/peaks.dif",DDIF2)
!export_background("/Users/putz/Documents/testbackground.dat")
!export_entry_data(96-900-7499,"/Users/putz/Documents/entry_969007499.txt",TXT)
!export_reference_pattern(96-900-7499,"/Docs/entry_969007499.pks",PKS)
!export_candidatelist("/Users/putz/Documents/resultslist.pdf",PDF)
!export_matchlist("/Users/putz/Documents/matchlist.htm",HTML)
!print_pattern_graphics(1024,768,1)
!print_peaklist
!print_entry_data(96-900-7499)
```

Note that the lines beginning with a ‘!’-character are comments and not run as commands. The keyword “MATCH!\_4\_BATCH” in the first line is mandatory; script files of the previous versions 2 or 3 (containing “MATCH!\_2\_BATCH” or “MATCH!\_3\_BATCH” in the first line) are also accepted.

You will find a complete list of commands available for batch script files along with their explanations in Match!’s online help (which can be opened by selecting the “Index” command from the “Help” menu).

## Tips & Tricks

### Identification of minor phases

The determination of minor phases will become easier if you pay attention to the following hints:

#### Peak-based search-match

- Before you run a peak searching command, please check the background (which is normally determined automatically). If the background is too high (which may e.g. be the case if there is a lot of noise in your pattern), this may prevent small peaks from being detected. If the background is not visible, please right-click in the diffraction pattern graphics and select the "Background" command from the context menu that opens.
- Please take a careful look at the peaks, especially if they have been determined automatically. It may be necessary to increase (press <F2>) or reduce (press <F3>) the peak searching sensitivity, or even to restart from scratch and determine the peaks manually.
- You may try to skip the 'alpha2 stripping' step in the raw data processing. Stripping the alpha2 part of the radiation is not necessary for qualitative phase analysis and may increase the noise in the pattern.
- The parameter "Preference for single or multiple phases" on the "Search-Match" tab of the "Options" dialog is some sort of compromise between Match!'s ability to clearly distinguish between one or two phases that are present with significant amounts (setting "Single"), and its acceptance of minor phases (setting "Multiple"). The basic influence of this parameter is the degree to which the intensity scaling factor is taken into account in the calculation of the figure-of-merit (FoM) values.
- If you are missing some minor phases, you should try to increase the value of the "Preference for single or multiple phases" parameter.
- A common problem of the conventional "residual searching" approach is that when selecting a certain phase as "matching" also other phases can be eliminated from the Candidate list, e.g. if they contain some peaks at similar positions than the selected phase. Hence, it may be easy to "overlook" these phases, especially if they are minor or even trace phases.

In these cases, try to avoid using the automatic residual searching option: Residual searching works by subtracting the peak intensities of identified phases from the experimental diffraction pattern. You can disable the automatic residual searching by removing the hook in front of the "Residual searching" option on the "Search-Match" tab of the "Options" dialog. This is also recommended if you suspect a strong peak overlap of different phases to be present.

When selecting phases as matching, you can use a "unified phases" approach instead: Please turn the search-match option "Residual searching" off (on the "Search-Match" tab of the "Options"-dialog).

Import your diffraction data, determine peak positions and run the search-match calculation as usual.

Once the search-match calculation has finished and the Candidate list has been filled with entries, please run the menu command "Entries/Unify phases" (or press <Ctrl+U>). This will quickly eliminate all duplicate or multiple occurrences of phases from the Candidate list.

Mark the best-matching entry / phase in the Candidate list and select it as "matching" as usual.

Since the "Residual searching"-option is not active, the phases selected as matching will be marked as "deleted" and hence be removed from the Candidate list.

- In certain circumstances, it may be difficult to identify minor phases if one or more of their three strongest peaks are not observed (or not found by the peak searching function). The background is that normally a reference pattern is only accepted as "candidate" if at least the three strongest peaks are observed (i.e. can be correlated to the experimental diffraction pattern).

If you are in doubt that you might be missing one or more minor phases, you should deactivate the option "Check 3 strongest peaks before running full match" on the "Search-Match" tab of the "Options" dialog.

Afterwards, please run a new search-match calculation, e.g. by selecting the "Search-Match" command from the "Search" menu. The drawback of deactivating this option is that the search-match calculation may take significantly longer.

### Profile fitting search-match (PFSM)

If you suspect that minor or trace phases have been missed by PFSM, please try the following:

- Make sure that the **background is defined accurately** (p. 20) before running profile fitting search-match!

The **background is not refined** during the PFSM calculation, to avoid any ambiguities that may result when doing so. Hence, it is rather **important** to make sure that the **orange background curve in the pattern graphics is in perfect agreement with the background** that you estimate "by eye" before running the PFSM calculation.

Once you have adjusted the background curve, run PFSM again.

- Try to adjust (reduce) the values **minimum intensity scale factor** and/or the **minimum Rwp reduction** required for entries being **displayed in the candidate list** on the "Search-Match" tab of the "Options" window (section "Profile fitting search-match (PFSM)").

You should always keep in mind that "**false positives**" may result from profile fitting search-match if the **background is not marked properly**, i.e. if it is too low. On the other hand, **phases may be not detected** if the **background is too high**.


### Large number entries resulting from search-match

If your search-match calculation gives many candidate entries, there may be two reasons for this:

- Your diffraction pattern contains many peaks. As a result, the probability that there is an acceptable agreement between reference peak positions and the experimental peaks is rather high, so many entries may have an acceptable figure-of-merit (FoM) value. Please inspect the peaks carefully one by one, and delete all those peaks that you are not really sure about. Afterwards, run the search-match again.
- The "peak correlation 2theta window" is rather large. Normally, this window is adjusted by Match! automatically before the search-match calculation, based on the average FWHM (full width at half maximum) of the experimental peaks. Therefore, broad peaks (large average FWHM) result in large peak correlation windows, so many peaks (entries) is considered as "matching". You can disable the automatic determination of the 2theta peak correlation window size on the lower right-hand side ("Delta 2theta") of the "Search-Match" page of the "Options" dialog, by deselecting the "Auto" check box below. Try to use/adjust a smaller value for "Delta 2theta", press "Ok", and run the search-match again.

### Exporting reference pattern (profile data)

In addition to the export of peak data of reference patterns, it is also possible to export them as raw (profile) data, by following these instructions:

1. Make sure that the reference database entry for which you would like to export raw (profile) data is displayed and marked in the candidate list or match list.
2. Right-click on the corresponding entry, then select the command "Load as experimental pattern (calculate profile)" from the context menu that opens (or simply press <Ctrl+Shift+T>).
3. The peak data of the marked entry will be added as an additional experimental diffraction pattern in the pattern graphics. In addition, its diffraction profile will be calculated automatically, using the default FWHM (full width at half maximum) value defined in the "Raw data processing" options.
4. If the new pattern is the first experimental pattern (anchor pattern), please run the menu command "File / Export / Profile data".
5. Otherwise (if the new pattern is added as an additional pattern on top of an already existing anchor pattern), please click on the corresponding pattern menu button  in the top right corner of the additional diffraction pattern, then select the menu command "Export profile data".

6. In the dialog that opens, please select an appropriate file type, directory and file name, then press "OK".

**Please note:**

- It is possible to export combined diffraction patterns (calculated from several reference database entries), by first adding them as new experimental patterns separately (as described above), and then combining them, using the "Add to pattern below" command from the "Pattern menus" of the additional experimental patterns. Finally, you can use the "Export profile data" command for the resulting pattern.
- You can export the profile data in the following (ASCII text) formats:
  - start, step, end, intensities
  - 2 columns (2 $\theta$  intensity)
  - 2 columns (d-value intensity)

### Difficulties with FWHM values of newly added peaks

If the FWHM values of newly added peaks are much too high (the peak profiles are too wide), you should check the automatically determined default value for FWHM on the "Raw data" tab of the "Options" dialog (which can be opened from the "Options" menu). In certain circumstances it may also be reasonable to deactivate the automatic fitting of the FWHM value, either using the menu command "Pattern / Profile fitting / Fit FWHM", or simply by pressing <F8>.

### Repeated usage/storing of restraints ("presets")

If you are frequently using the same set of restraints (e.g. elements, density, inorganics only etc.), you might get tired of selecting these restraints in the corresponding dialog repeatedly. Instead, it would be much easier if you could somehow store the entries that correspond to these restraints, to use them as a subset based on which you can run search-match operations later on.

You can easily save the current selection criteria, and recall them later with just two mouse clicks, using the so-called "selection criteria presets". You will find the corresponding control elements at the bottom of the "Restrains" (and also "Additional entries") tab to the right of "Preset". Of course, it is possible to save several sets of selection criteria.

To save the current selection criteria, simply press the "Save" button. Afterwards, you must enter a name using which you can easily identify this set of selection criteria later on. Your selection criteria will then be stored in your personal settings (e.g. Windows registry).

If another person is using the same computer, he can store his own selection criteria independent from yours (of course if he is using his own account on this machine...).

If you would like to recall a certain set of selection criteria, simply press the "arrow down" button of the combo box to the left of the "Save" button, and select the name of the desired selection criteria from the list that opens. That's it! The selection criteria that have been loaded will instantly be applied to the table of candidate entries (candidate list), and of course also to the entries that are investigated during the search-match calculation.

### List selection box handling

On the "Restrains" and "Additional entries" tab sheets, a so-called "list selection box" can be opened in each case where a manual/keyboard input of a numerical or text value is required, i.e. in each case where an edit/input line is present. In these cases, you can open a list of all available values for the corresponding field (the list selection box) by clicking on the corresponding "table" button to the right of the input line.

You can easily select the value(s) you are interested in by clicking on the corresponding lines. Besides this, you can shorten the search for a particular value/line by rapidly typing the first few letters. For instance, if you are looking for an author "Stolpovskaya V.", you can simply type stolp without pausing between the letters, and the corresponding line will instantly be displayed.

If you made a mistake by typing a wrong letter, simply wait for two seconds (which will automatically clear the input buffer) and try again.



### Creating cif-files for Rietveld refinement

If you are using a reference database that does not contain atomic coordinates for all entries, you might face the problem how to create a cif-file providing the full crystal structure data for Rietveld refinement. If you cannot export a reasonable cif-file e.g. from Pearson's Crystal Data, you might want to use a crystal structure description from a corresponding scientific paper. However, in many cases there is no cif-file available for this paper, so you have to create one on your own by manually entering the data from the paper. The problem is that the cif-syntax is far from being trivial.

Fortunately, you can use the Match! User Database Manager to create the cif-file. In order to do so, please open it e.g. by selecting the corresponding command from the "Database" menu. Once the dialog is displayed, please press the "Add" button in the toolbar at the top of the window. The tabs at the bottom of the dialog will be activated, with the "General" tab in front. Please click on the "Crystal structure" tab to make it visible, then start to enter your crystallographic data by first marking the appropriate crystal system. Afterwards, select the space group from the corresponding combo box below, and fill in the unit cell parameters. Finally, press the "Add" button below the table of atoms to the right, and enter the element and coordinates of the first atom. Finish the input of the first atom's parameters by pressing <Return>, then repeat this step for the remaining atoms. Once you have finished entering the atomic parameters, press the "Save changes" button at the bottom of the dialog.

Make sure that the new entry is marked in the table at the top, then press the "Export" button in the toolbar at the top of the dialog. Select "CIF file (\*.cif)" as "Files of type:", select an appropriate directory and file name, and press "Save".

That's it! You can now leave the User Database Manager by pressing the "Quit" button (you can save the new user database at this step if you like), and import the cif-file as a response to the corresponding question next time you try to run a Rietveld refinement.

## Software maintenance

### Installing and running Match!

You need administrator/root privileges to install Match!.

#### **Windows PCs (Windows 7, 8, 10 or 11 required)**

In order to install the most recent version<sup>69</sup> of Match!, please download and run the installer corresponding to your operating system (either 32- or 64-bit) from

<https://www.crystalimpact.de/match/download.htm>

Please note the terms of the "End User License Agreement", which will appear in the second dialog box!

Once the installation program has finished, you can run Match! e.g. by double-clicking the file "Match!.exe" in the directory where you have installed the program (e.g. "C:\Program Files\Match4"). Alternatively, you can run the software by double-clicking on the corresponding desktop symbol "Match!", or by clicking the Windows "Start" button, then on "Match4/Match!".

#### **macOS for ARM (11 "Big Sur" (or later) as well as Apple M processor required)**

If you have a Mac with an Apple Silicon processor (M1, M2, M3, ...), please make sure to use the installer for macOS for ARM, because it runs significantly faster than the one for the "old" Intel macOS.

Please download the installer disk image "Match-4-macOS-ARM-installer.dmg" from

<https://www.crystalimpact.de/match/download.htm>

Once the download has finished, please open the disk image to display its contents (e.g. by double-clicking on it), then run the installer "Match4.pkg" by double-clicking. Please follow the instructions on the screen, and note the terms of the "End User License Agreement", which will appear in the second dialog box!

Once the installation has finished, you can run Match! e.g. by double-clicking on the corresponding desktop symbol "Match!", or alternatively using the Finder (Folder "Applications/Match4").

#### **macOS (10.13 "High Sierra" or later required, runs on Intel and Apple M processors)**

Please download the installer disk image "Match-4-macOS-Intel-installer.dmg" from

<https://www.crystalimpact.de/match/download.htm>

Once the download has finished, please open the disk image to display its contents (e.g. by double-clicking on it), then run the installer "Match4.pkg" by double-clicking. Please follow the instructions on the screen and note the terms of the "End User License Agreement" which will appear in the second dialog box!

If you run the installer on macOS 10.14 "Mojave" (or later) in "dark mode", some dialog elements (especially the buttons at the bottom) are hardly visible. Please switch over to the "light" mode before running the installer, or press the button (outline visible only) in the bottom-right corner of the installer window repeatedly until the installation starts.

When the installation program has finished, you can run Match! e.g. by double-clicking on the corresponding desktop symbol "Match!", or alternatively using the Finder (Folder "Applications/Match4").

#### **Linux (Intel 64-bit system and glibc 2.27 or later required)**

Please download the corresponding compressed installer file ("Match-4-linux-x64-installer.run.zip") from

---

<sup>69</sup> Earlier versions of Match! can be downloaded and installed from

[https://www.crystalimpact.de/match/download\\_previous\\_version.htm](https://www.crystalimpact.de/match/download_previous_version.htm)

<https://www.crystalimpact.de/match/download.htm>

Once the download has finished, please decompress the zip-file into some temporary directory. Check that the file access permissions show that the file "Match-4-linux-x64-installer.run" can be executed. If this is not the case, please run the command

```
chmod a+x Match-4-linux-x64-installer.run
```

In addition, you need to install the software as "root" (administrator privileges required). To do so, either run a "su" command before running the installer, or use "sudo", e.g. by running

```
sudo ./Match-4-linux-x64-installer.run
```

When the installer is running, please follow the instructions on the screen, and note the terms of the "End User License Agreement", which will appear in the second dialog box!

If an error message "Match! cannot be run on this computer for some unknown reason" is displayed during the installation, please run the command "/opt/Match4/Match" in a terminal window and check the error messages that are displayed.

Once the installation program has finished, you can run Match! e.g. by clicking on the corresponding desktop icon that has been created during the installation, or by running the script "Match.sh" in the directory where the software has been installed (which is "/opt/Match4" by default).

### **Time-limited license**

As long as no license is installed, Match! will run in the "60 days evaluation mode", which basically means that it will stop working 60 days after it has first been installed. You have to purchase a license to continue working with Match! afterwards.

### **License purchasing**

You can get all information about the various licensing and pricing options for Match! here:

<https://www.crystalimpact.de/match/sales.htm>

Licenses can also be purchased in our online store (e.g. for credit card or PayPal payments):

<https://shop-crystalimpact.de/en/c/match>

### **License installation**

Once you have purchased and obtained a license file for Match!, you can install it as follows:

#### **You need administrator privileges to perform this task!**

If the 60 days evaluation period has already expired, Match! will ask you to install a license, otherwise please run the "Install new license..." command from the "Help" menu.

You will be asked to select the license file (either "license\_Match!.zip" or "yourlicense.lic") that you have received by e-mail after purchasing the license.

Please confirm elevation (you may have to enter your administrator password). Your license will now be installed and registered automatically.

Next time you run Match!, your license data should be displayed at the bottom of the splash screen (at program startup), in the status bar at the bottom, and finally in the "About Match!"

### **Installing FullProf**

Match! can use the well-known software "FullProf" (J. Rodriguez-Carvajal, Physica B. 192, 55 (1993); <http://www.ill.eu/sites/fullprof>) to run Rietveld refinement calculations. If you would like to use this feature, you have to install FullProf (at least if it is not already present on your machine) using one of the following options:

## Installing from installation DVD-R

If you have obtained your Match! software on DVD-R, you can install FullProf directly from this disk:

### Windows

Match! requires FullProf release January 2018 (or later) for Rietveld refinement on Windows.

To install the Windows version of FullProf, please run (double-clicking) the corresponding installer (e.g. "Setup\_FullProf\_Suite\_January2018.exe") in the "FullProf\_Suite/Windows" subdirectory of your installation DVD-R. Simply follow the instructions on your screen, keeping in mind not to use any blank or non-ASCII characters for the file and directory names!

### macOS

Match! requires FullProf release March 2018 (or later) for Rietveld refinement on macOS.

Double-click on the image "FullProf4Mac-v274.dmg" in the "FullProf\_Suite/Mac\_OS\_X" directory of your installation DVD-R in order to open it. Afterwards, copy the bundle "FullProf4Mac" from the window that opens into your "Applications" directory.

### Linux

Match! requires FullProf release February 2018 (or later) for Rietveld refinement on Linux.

First, please create a directory in which you want to store the programs of the FullProf\_Suite. e.g.: \$HOME/FullProf\_Suite

For this you must execute the following commands in a terminal window:

```
cd $HOME
mkdir FullProf_Suite
cd FullProf_Suite
```

Afterwards, copy the file FullProf\_Suite\_XXXXNNNN\_Lin.tgz (XXXX=Month NNNN=year) from the "FullProf\_Suite/Linux 64-bit" subdirectory on your installation DVD-R to the "FullProf\_Suite" directory you have just created.

Finally, decompress the file .tgz with the following command:

```
tar -xzf FullProf_Suite_XXXXNNNN_Lin.tgz
```

## Installing from download package

If you have obtained your Match! software by electronic delivery, you can download and install FullProf from the Crystal Impact web page

[https://www.crystalimpact.de/match/download.htm#download\\_fp](https://www.crystalimpact.de/match/download.htm#download_fp)

As an alternative, you can also do this directly from the FullProf web page (where you will also find detailed installation instructions):

<https://www.ill.eu/sites/fullprof/php/downloads.html>

Simply follow the download and installation instructions given there for the platform you are using.

## Adjustment of Match! User Level

When you run Match! for the very first time, you will be asked which default user level ("Beginner" or "Expert") you prefer:

In the "Beginner" mode Match! performs a nearly complete automatic processing of the initial steps: All you have to do is to select the diffraction data file you would like to analyze (you will be prompted automatically for it once the software has been started). Afterwards, Match! will automatically process the raw data, determine the peaks, and run the search-match calculation. All that remains to do is to select the "matching" phases (e.g. by double-clicking or dragging the corresponding entries from the candidate list on the left-hand side to the Match list to the right), and finally display the report containing e.g. the list of matching phases as well as their arbitrary amounts (e.g. by selecting "View/Report").

In the "Expert" mode you have to perform nearly all actions manually. This mode is especially recommended for experienced users who would like to analyze more complicated samples.

You can customize the user level (automatic processing behavior) on the "Automatic" tab of the "Options" window also later on. In addition to selecting user levels like "Beginner" or "Expert" you can also select individual automatic processing steps according to your requirements.

## Network installation on a file server

If you have a **site license** or a **campus license** for Match!, it is possible to install the software on a network drive (file server), and access the software on this drive from network-attached client computers.

For this, it is necessary though that Match! is installed at least **once on each of the client computers** before accessing the software on the network drive, because the license needs to be registered on each of the clients. **Your license file "yourlicense.lic" needs to be present in (i.e. copied into) the Match! program directory on the network drive.** Make sure that you do **not have write access on the network drive** when installing Match! on a client, so that your license file is not removed by accident (at least not before it has been registered on all client computers!)

Afterwards, you can install and use updated versions of Match! on the network drive only, without requiring further local installations on the clients. You can uninstall Match! from the clients after the license has been registered.

## Online update

By default, Match! automatically checks the Crystal Impact web server for a more recent version each time it is executed. If a new version is found, you will be informed and guided to the corresponding web page from which you can download the new version.

You can also manually check for a more recent version, simply by selecting the "Check for updates..." command from the "Help" menu. The procedure will be the same as the one described above for the automatic update.

## Reset

You can reset all settings by running Match! from the command line with the parameter "reset\_all\_settings". This can be helpful in situations where Match! does no longer run or crashes at startup. This may happen in certain rare circumstances e.g. if a reference database is no longer valid.

Running the commands below will either reset your own settings (if you run the command as normal user) or both your own as well as the system wide settings (if you run the command as administrator / super user).

In order to reset Match! and remove all settings, please do the following:

## Windows

Right-click on the Windows "Start" button, then select "Windows PowerShell (Administrator)". Confirm or enter the Administrator password.

In the "PowerShell" terminal window, please run the command

```
start-process -verb runAs "C:\Program Files\Match4\Match!.exe" -argumentlist
"reset_all_settings"
```

## macOS

Open a “Terminal” window, then enter the following command:

```
/Applications/Match4/Match\!.app/Contents/MacOS/Match\! reset_all_settings
```

Enter your “root” password if required.

## Linux

Open a terminal window, then enter the following command:

```
/opt/Match4/Match reset_all_settings
```

Enter your “root” password if required.

## Uninstall Match!

### Windows

If you would like to uninstall Match!, please open the Windows “Control Panel”, click on “Software” (“Add/Remove Programs” on more recent Windows versions). Please mark “Match! 4”, then click “Change/Remove”.

You will be asked if you would like to unregister your license from the current computer. If you click “Yes”, your license will be removed, if you click “No”, it will be kept and used automatically when installing Match! again later on.

## macOS

If you would like to remove your Match! license from the current computer, you have to unregister it before uninstalling the software itself. In order to do so, please open a Terminal window, then enter the command

```
sudo /Applications/Match4/Match\!.app/Contents/MacOS/Match\! unregister
```

If you have installed Match! in a different folder than the default “Applications” folder, you have to adapt this command accordingly.

In order to uninstall the Match! software from a macOS machine, simply delete the folder “Applications/Match4” using the Finder afterwards.

## Linux

You can uninstall Match! by running the command

```
sudo /opt/Match4/uninstall
```

Please check/correct the directory in which Match! is installed on your machine.

You will be asked if you would like to unregister your license from the current computer. If you click “Yes”, your license will be removed, if you click “No”, it will be kept and used when installing Match! on the current computer again.

## Unregister license

Normally, you unregister your license when uninstalling Match! from the computer (see above). If you would like to manually unregister your license but keep your Match! installation, please do the following:

### Windows

Right-click on the Windows “Start” button, then select “Windows PowerShell (Administrator)”. Confirm or enter the Administrator password.

In the “PowerShell” terminal window, please run the command

```
start-process -verb runAs "C:\Program Files\Match4\Match!.exe" -argumentlist  
"unregister"
```



**macOS**

Open a “Terminal” window, then enter the following command:

```
sudo /Applications/Match4/Match\!.app/Contents/MacOS/Match\! unregister
```

Enter your “root” password if required.

**Linux**

Open a terminal window, then enter the following command:

```
sudo /opt/Match4/Match unregister
```

Enter your “root” password if required.

## Update permission time model

With the previous Match! version 3, Crystal Impact has switched over to a **update permission time model for updates**, replacing the current “major/minor update model”. With the new model, **you can still use your software/license as long as you like** (if you have purchased a permanent license), just like it has been with the previous “major/minor update model”.

The major change in the new model is that **all updates and new versions that are released within a certain amount of time** (called your “**update permission time**”) will be available for download and installation **free-of-charge**, even if major improvements have been implemented. Updates of versions that are released after your update permission time has expired cannot be installed and run. If you would like to use these more recent versions, you have to purchase an extension for your update permission time.

More information about the new update permission time model as well as some frequently asked questions and their answers are available on our web page:

<https://www.crystalimpact.de/subscription.htm>









## Appendix









### Table of mouse button and key combinations





A variety of operations can be carried out directly in the diffraction pattern graphics using the mouse. In some cases, it is also necessary to keep one or the other button pressed on your keyboard, in order to invoke the appropriate command. Here is an overview what you can do inside the diffraction pattern using your mouse.







**Note:** If the mouse cursor or program does not react as expected, please make sure that the diffraction pattern graphics gets the input focus, simply by clicking into the diffraction pattern (at a position without any objects). Afterwards, please try your operation or mouse action again.

Please note that you have to replace “Ctrl” by “Cmd” if you are using a Mac!

Effect/purpose	Cursor position in pattern graphics	Keyboard button(s)	Cursor shape	Mouse action
<b>Background control point</b> <i>mod.: shift</i>	Control point (small square) in background curve	-		Press <b>left</b> button and keep it pressed while moving the mouse
<b>Background control point</b> <i>mod.: delete</i>	Control point (small square) in background curve	-		Press <b>right</b> button in order to remove the background control point below the mouse cursor
<b>Background control point</b> <i>mod.: add</i>	Background curve	-		Press <b>left</b> button to add a new background control point below the mouse cursor
<b>Mark single peak</b>	Peak below its top (must be visible!)	-		Click <b>left</b> button to mark the peak below the mouse cursor; marks at other peaks will be removed
<b>Mark selected peaks</b>	Peak below its top (must be visible!)	Ctrl		Click <b>left</b> button to mark the peak below the mouse cursor, in addition to the peaks that are already marked
<b>Shift peak on 2theta axis</b>	Peak below its top (must be visible!)	-		Click <b>right</b> button and keep it pressed while moving the mouse to the left or right
<b>Mark range of peaks</b>	To the left of the left-most peak in the range	Ctrl		Press the <b>left</b> button, then move the mouse to the right until you have selected the range of peaks you would like to mark
<b>Mark single peak</b>	Top of a peak (must be visible!)	-		Click <b>left</b> button to mark the peak below the mouse cursor; marks at other peaks will be removed

<i>Effect/purpose</i>	<i>Cursor position in pattern graphics</i>	<i>Keyboard button(s)</i>	<i>Cursor shape</i>	<i>Mouse action</i>
<b>Mark selected peaks</b>	Top of a peak (must be visible!)	Ctrl		Click <b>left</b> button to mark the peak below the mouse cursor, in addition to the peaks that are already marked
<b>Add peak</b>	Anywhere	Ctrl		Click <b>right</b> button to add a peak at the current cursor position
<b>Shift peak on 2theta axis</b>	Peak below its top - (must be visible!)	-		Click <b>right</b> button and keep it pressed while moving the mouse to the left or right
<b>Modify peak FWHM</b>	Peak below its top; peak must be <b>marked</b> and visible!	-		Mark a peak by left-clicking on it, then move the mouse over the peak (mouse cursor will change), and turn the <b>mouse wheel</b> in order to modify the FWHM (full width at half maximum) of the marked peak
<b>Modify peak intensity and/or position</b>	Top of a peak (must be visible!)	-		Click <b>right</b> button and keep it pressed while moving the mouse in any direction
<b>Select range(s) to be excluded</b>	Anywhere	Alt		Press the <b>left</b> button, then move the mouse to the right until you have selected the range you would like to exclude from FoM calculations
<b>Delete range exclusion mark</b>	Inside a range marked to be excluded (grey background color)	-		Press the <b>right</b> mouse button inside a range marked to be excluded in order to re-use this range (delete the exclusion marking / grey background color)
<b>Trim pattern on left-hand side</b>	Left border of the diffraction pattern	-		Move the mouse cursor to the left border of the diffraction pattern until the mouse cursor changes, press the left button, and move the mouse to the right until you have marked the desired area to be removed. Finally, release the mouse button.

<i>Effect/purpose</i>	<i>Cursor position in pattern graphics</i>	<i>Keyboard button(s)</i>	<i>Cursor shape</i>	<i>Mouse action</i>
<i>Trim pattern on right-hand side</i>	Right border of the diffraction pattern	-		Move the mouse cursor to the right border of the diffraction pattern until the mouse cursor changes, press the left button, and move the mouse to the left until you have marked the desired area to be removed. Finally, release the mouse button.
<i>Zoom (select range)</i>	Anywhere	-		Click <b>left</b> button at the position where you would like to start selecting your zoom range, and keep it pressed while moving your mouse, until you have selected the desired zoom range, then release the button
<i>Zoom</i>	Anywhere	-		Move the mouse cursor to a point you would like to zoom into, then turn the mouse <b>wheel</b> away from you to zoom right into this position (or vice versa)
<i>Zoom</i>	Anywhere	-	Any	Double-click the <b>left</b> button at the position you would like to zoom into (only applicable if fully zoomed out; see below)
<i>Zoom out</i>	Anywhere	-	Any	Click the <b>right</b> button to open the context menu, then select "Full pattern" or "Previous zoom"
<i>Zoom out</i>	Anywhere	-	Any	Double-click the <b>left</b> button
<i>Tracking (shifting of the zoom range)</i>	Anywhere	Shift		Once you have zoomed into the pattern, press the <b>Shift button</b> on your keyboard or the mouse <b>wheel</b> , and keep it pressed while moving the mouse around
<i>Vertical line at mouse cursor position</i>	Anywhere	Ctrl+X	Any	Press <Ctrl+X> to toggle the display of a vertical line at the cursor position, e.g. to compare peak positions

Effect/purpose	Cursor position in pattern graphics	Keyboard button(s)	Cursor shape	Mouse action
Zero point shifting	Anywhere	Ctrl+Alt		While keeping the Ctrl and Alt button pressed, turn the mouse wheel to shift the positions of exp. peaks and raw data along the 2theta-axis
Correct specimen displacement	Anywhere	Ctrl+Alt+Shift		While keeping the Ctrl, Alt and Shift button pressed, turn the mouse wheel to shift the positions of exp. peaks and raw data along the 2theta-axis according to $\Delta 2\Theta = -2s(\cos \Theta / R)$ ; $T = -s/R$
Adjustment of difference plot size/height	2theta/d-axis	-		Move the mouse cursor to the 2theta- or d-value axis (x-axis) (mouse cursor will change), press the left mouse button, and move the mouse away from you to open/increase the size of the difference plot (or vice versa)
Adjust intensity scaling factor manually	Top of a peak of an entry marked in the match list	-		Move the mouse cursor to the top of a peak of the entry that is currently marked in the match list (mouse cursor will change), then press the left mouse button, and keep it pressed while moving the mouse up or down to adjust the intensity scaling factor (-> quantity) of the corresponding selected phase
Adjust vertical pattern distance	To the right of the diffraction pattern graphics			Place the mouse cursor to the right of the diffraction pattern, then turn the mouse wheel up or down in order to decrease or increase the vertical distance between the experimental diffraction patterns. Only available if at least two diffraction patterns are present.
Adjust horizontal pattern distance	At the bottom of the diffraction pattern graphics	Ctrl+Shift+'-'; Ctrl+Shift+'+'		Place the mouse cursor at the bottom of the diffraction pattern, then turn the mouse wheel up or down in order to



<i>Effect/purpose</i>	<i>Cursor position in pattern graphics</i>	<i>Keyboard button(s)</i>	<i>Cursor shape</i>	<i>Mouse action</i>
				decrease or increase the horizontal distance between the experimental diffraction patterns ("3D-like" view). Only available if the vertical pattern distance has been reduced.

## Table of keyboard shortcuts and function keys

Many of the most common commands and procedures in Match! can also be invoked by pressing certain buttons on your keyboard. These so-called shortcuts are quite useful to speed up your work with Match!, especially if you know them by heart. Here is a list of all keyboard shortcuts in Match!.

**Please note that you have to replace “Ctrl” by “Cmd” if you are using a Mac!**

<i>Button(s)</i>	<i>Effect</i>	<i>Menu command</i>
<b>Ctrl+A</b>	Automatic raw data processing	Pattern / Automatic / Autom. raw data proc.
<b>Ctrl+Shift+A</b>	Add new entry to the reference database directly, e.g. import from cif-file, use the current peak list or enter manually	Database / Add to reference database
<b>Ctrl+B</b>	Clear the current selection criteria (restraints)	Search / Reset restraints / additional entries
<b>Ctrl+Shift+B</b>	Enables the display of the radiation background and displays instructions how to manually modify the background using the background control points	Pattern / Background / Edit background
<b>Ctrl+C</b>	Copy the current diffraction pattern graphics into the clipboard, e.g. in order to paste it into other programs like Microsoft Word or Excel	Edit / Copy
<b>Ctrl+Shift+C</b>	Correct zero-point error (2theta shift)	Pattern / Correct zero-point error
<b>Ctrl+D</b>	View entry data sheet of the entry that is currently marked in the candidates- or match list	View / Data sheet
<b>Ctrl+E</b>	Load an entry into the match list directly by specifying e.g. its name, formula sum or entry number	Search / Add entry to match list directly
<b>Ctrl+F</b>	Find and display the best entry for the selection criteria you have entered	Search / Find phase / entry(s)
<b>Ctrl+G</b>	Find next (to be applied after having used “Find” (Ctrl+F)); find the next best entry in the candidate list for your selection criteria	Search / Find next
<b>Ctrl+Shift+G</b>	Find previous (to be applied after having used “Find” (Ctrl+F)); find the previous entry for your selection criteria	Search / Find previous
<b>Ctrl+H</b>	Search for strong lines in diffraction pattern (“Hanawalt (or Fink) search”)	-
<b>Ctrl+I</b>	Import (another) diffraction pattern file	Pattern / Insert / overlay...
<b>Ctrl+J</b>	Display mouse operations and keyboard shortcuts in online help	Help / Keyboard shortcuts and mouse operations
<b>Ctrl+K</b>	Peak searching, optionally followed by automatic profile fitting	Pattern / Peak searching / Peak search
<b>Alt+K</b>	Add peaks manually by entering the peak parameters (open corresponding dialog)	Peaks / Add peak(s)

<i>Button(s)</i>	<i>Effect</i>	<i>Menu command</i>
<b>Ctrl+L</b>	View tabular summary of all experimental and reference pattern peaks	View/Peak list
<b>Ctrl+M</b>	Run a new (peak-based) search-match calculation	Search/Search-match
<b>Ctrl+Alt+M</b>	Run profile fitting search-match (PFSM; p. 33)	Search/Search-match using profile fitting
<b>Ctrl+Shift+M</b>	Run a new search-match calculation based on the currently marked peaks only	Search/Search-Match (marked peaks only)
<b>Ctrl+N</b>		
<b>Ctrl+O</b>	Open/read Match! document from file, or import first diffraction pattern file	File/Open
<b>Ctrl+Shift+O</b>	Directly define the matching entries, by loading the corresponding entry numbers from a Match! answer set file (*.mta). This is especially helpful if series of similar samples have to be investigated.	File/Import/Predefined phase selection
<b>Ctrl+P</b>	Open the "Print" dialog where you can select what you would like to print	File/Print...
<b>Ctrl+Q</b>	Close Match!	File/Quit (Mac: Match!/Quit)
<b>Ctrl+Alt+Q</b>	Perform an automatic quantitative analysis, asking for any required information automatically. Match! uses the default quantitative analysis method (RIR or Rietveld) for this purpose	-
<b>Ctrl+R</b>	Display phase analysis report	View/Report
<b>Ctrl+Shift+R</b>	Display the "Parameter Turn-On"-dialog in order to prepare and run a new Rietveld calculation	Tools/Rietveld (FullProf)
<b>Ctrl+Alt+R</b>	Run automatic Rietveld refinement to perform a quantitative analysis (p. 51)	Quantify/Rietveld (FullProf)
<b>Ctrl+S</b>	Save current session (Match! document)	File/Save
<b>Ctrl+Shift+S</b>	Save current session (Match! document) to a new file name/path	File/Save as...
<b>Ctrl+T</b>	Shift the experimental pattern on 2theta axis in order to obtain the best peak overlap with the reference pattern currently marked in the candidate list (internal standard)	Entries/Internal standard
<b>Ctrl+Shift+T</b>	Load the reference database entry that is currently marked in the candidate list as a new experimental pattern. This new pattern does not only contain the reference entry's peaks but also a profile curve that is calculated from them, using the current default FWHM value.	Entries/Load as experimental

<i>Button(s)</i>	<i>Effect</i>	<i>Menu command</i>
<b>Ctrl+U</b>	If there is more than a single entry for a certain phase present in the candidate list, remove all but the best matching entry (FoM) for each phase	Entries/Unify phases
<b>Ctrl+Shift+U</b>	Toggle graphics option "Show uncorrelated peaks", displaying a light-orange rectangle in the background of experimental peaks with a certain minimum intensity that have not been assigned to identified phases yet.	View/Pattern/Uncorrelated peaks
<b>Ctrl+V</b>	Paste (add) text data in clipboard as a new experimental diffraction pattern	Edit/Paste diffraction pattern
<b>Ctrl+W</b>	Finish Match!, i.e. run the finishing actions defined on the "Automatic" page of the Options dialog	File/Finish
<b>Ctrl+X</b>	Toggle the displaying of a vertical line at the mouse cursor position inside the diffraction pattern (e.g. for peak position comparison)	View/Pattern/Cursor position
<b>Ctrl+Shift+X</b>	Toggle the displaying of a "spectrum" of X-ray line positions as vertical line at the mouse cursor position inside the diffraction pattern.  This can be handy for the investigation of peaks resulting e.g. from alpha2 or beta radiation contributions.	View/Pattern/X-ray spectral lines
<b>Ctrl+Y</b>	Redo last undo operation	Edit/Redo
<b>Ctrl+Z</b>	Undo last operation/command	Edit/Undo
<b>Ctrl+'-'</b>	Decrease vertical distance between experimental patterns in diffraction pane (only available if two or more patterns are present/stacked)	View/Pattern/Reduce pattern distance
<b>Ctrl+'+'</b>	Increase vertical distance between experimental patterns in diffraction pane (only available if two or more patterns are stacked and the vertical distance has been reduced before)	View/Pattern/Increase pattern distance
<b>Ctrl+'&lt;'</b>	Switch back to the previously used zoom (pattern area)	View/Previous zoom
<b>Del</b>	Delete the currently marked item(s), e.g. peaks or candidate list entries	Edit/Delete
<b>F1</b>	Open help window	Help/Index
<b>F2</b>	Increase peak search sensitivity	Pattern/Peak searching/ Increase sensitivity
<b>Ctrl+F2</b>	Increase flexibility of automatically determined background curve, to follow the structures of the pattern more closely.	Pattern/Background/Increase flexibility

<i>Button(s)</i>	<i>Effect</i>	<i>Menu command</i>
<b>Ctrl+Shift+F2</b>	Raise the whole background a little bit (relative intensities +0.5)	Pattern / Background / Raise background intensity
<b>F3</b>	Decrease peak search sensitivity	Pattern/Peak searching/ Reduce sensitivity
<b>Ctrl+F3</b>	Decrease flexibility of automatically determined background curve, to attribute more intensity of the peak foots to the peaks (and maybe reveal small peaks).	Pattern/Background/Decrease flexibility
<b>Ctrl+Shift+F3</b>	Lower the whole background a little bit (relative intensities -0.5)	Pattern / Background / Lower background intensity
<b>F4</b>	Optimize peak searching sensitivity, to obtain the best overlap between experimental and calculated pattern	Pattern/Peak searching/ Optimize sensitivity
<b>Ctrl+F4</b>	Smooth raw data. This may sometimes be helpful when determining the peaks if the noise is rather large.	Pattern / Smooth raw data
<b>F5</b>	Perform profile fitting	Pattern / Profile fitting / Profile fit
<b>F6</b>	Enable/disable fitting of 2theta values during profile fitting	Pattern / Profile fitting / Fit 2theta
<b>F7</b>	Enable/disable fitting of intensity values during profile fitting	Pattern / Profile fitting / Fit intensity
<b>F8</b>	Enable/disable fitting of FWHM values during profile fitting	Pattern / Profile fitting / Fit FWHM
<b>Ctrl+Alt+A</b>	Open dialog in which the individual automatic raw data processing steps can be configured	Pattern / Automatic / Configure...
<b>Ctrl+Alt+G</b>	Open dialog in which the options for the diffraction pattern graphics can be adjusted	Options / Diffraction pattern options...
<b>Cursor up/down</b>	Move the line mark in the candidate list up/ down (if it has the input focus)	-
<b>Space</b>	Select current entry in candidate list (if it has the input focus) as "matching" (i.e. move it to the match list)	Entries / Select as matching
<b>Alt+Space</b>	Select the entry that is currently marked in the candidate list as "matching", by creating a "working copy" of its data into a new manual entry (p. 130) in the match list. The manual entry can then be modified in order to adapt it to your requirements, by double-clicking on it in the match list.	Entries / Select/add copy as manual "matching" entry
<b>Shift</b>	If you have zoomed into the pattern previously, you can now move the visible diffraction pattern section around (tracking) simply by moving the mouse	-

<i>Button(s)</i>	<i>Effect</i>	<i>Menu command</i>
<i>Shift+Del</i>	Delete all peaks in the current experimental pattern	Peaks / Delete all peaks

## Support

In case of trouble when using Match!, please pay attention to the following hints:

- If you do not know how to operate in a dialog window, carefully read all information in the window. Make sure that you understand the meaning of the buttons, input fields, lists, etc. Look at the way several functions are grouped into frames and read the frame titles, too.
- Press the F1 key (<Cmd+?> on the Mac) in order to open the online help, and examine the context sensitive help text. Especially read the items mentioned under Note: and See also: Check the help jumps, too, which are underlined like links in a web browser.
- Look for appropriate keywords in the Help Index, and use the free-text search facility of the online help.
- If you do not find a command, use the Help Index (Index tab on the Match! Application Help window) to get an alphabetic list of search items.
- Visit the Match! web page at:

<https://www.crystalimpact.de/match/update.htm>

This page offers the latest versions of online help files, sample files, and software patches for the executables.

- If this page does not give you an answer, or if the trouble is caused by an error in the software (a "bug"), send an e-mail to [putz@crystalimpact.de](mailto:putz@crystalimpact.de)

Or – if you are not connected to the internet – send a fax to: ++49-228-9813644

or write to:

Crystal Impact GbR  
Kreuzherrenstr. 102  
D-53227 Bonn  
Germany

Please describe how the bug can be reproduced as detailed as possible, and attach possibly required files (e.g. diffraction data)!



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