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# MacDiff 4.1.2

## Manual

R. Petschick, June 29, 2000

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### About MacDiff

MacDiff is a programme for analysis and display of X-ray powder diffractogrammes on Apple Macintosh platforms. It is designed as a complement to the XRD applications distributed by Philips or Siemens and it is equipped with a GUI to facilitate user-friendly and interactive processing of XRD profiles. It offers conventional XRD profile-correction processes (e.g. outliers, smoothing, divergence, alpha<sub>2</sub>-stripping) and supports qualitative and quantitative phase analysis. Moreover, by its programmable peak analysis (recording of intensities, peak areas, half widths, etc.) it offers an automated analysis of entire series of diffractogrammes. By means of peak fits the contributions of coinciding lines can be calculated. The user has at his disposal the capability of continuous measurement checks and the possibility to perform corrections as well (e.g. by manual or computed background adaptations). For peak indication the user has the option to employ variable peak data sets. High resolution hardcopies of the diffractogrammes can be produced. The standard single-scan formats (Philips-ADP or some Siemens-RAW, ASCII, and others) are identified automatically. Data and plots can be exported to most of the available table-processing or vector-graphics programmes.

The applications of MacDiff range from routine analysis in sedimentology, especially clay minerals, over analysis of X-ray diffractogrammes of all types of rocks and minerals all the way to phase analysis of various crystalline substances.

**MacDiff is freeware and is available to everyone free of charge. It may be copied and distributed without restrictions for non-profit and non-commercial use. All rights reserved. Usage at your own risk.**

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MacDiff can be downloaded from the URL:

**"<http://servermac.geologie.uni-frankfurt.de/Rainer.html>"**

or alternatively:

**<http://www.geol.uni-erlangen.de/html/software/soft.html>**

As intensive user of Macdiff the author would appreciate any reports about bugs or problems and suggestions for programme improvements. He is very interested in geoscientific problems in connection with X-ray diffractometry and is available for cooperation especially in sedimentology and clay mineralogy. Within the range of his programming skills he is willing to develop filters and functions not yet implemented.

**Attention Windows-users!** MacDiff is available for Macintosh only! For Windows 3.1/95/98/NT I recommend **Winfit** (also free of charge) of Dr. Stefan Krumm, Inst. f. Geologie, Univ. Erlangen, URL: <http://www.geol.uni-erlangen.de/html/software/soft.html>. Alternatively, **DiffTool** of Olaf Filies, Universität Münster may be employed. URL: <http://pikp15.uni-muenster.de/IKPXRR/difftool/difftool.htm>

## System requirements

MacDiff runs on a PowerMacintosh with 8 MB RAM minimum. However, 16 MB with colour monitor is recommended. RAM requirements are 3.5 MB minimum. Hard disk requirements are between 2 and 8 MB memory.

All Mac OS-systems older than 8.0 require the extension 'Appearance Extension' as well as the control panel 'Appearance CDEV', which is available for downloading (name: 'Appearance Lib').

### Minimum system:

Power Macintosh or first generation PPC-PowerBook (PPC 601) with 14" colour monitor (800x600, minimum 256 colours), system 7.1.2

### Optimal system (required in particular for profile-adaptations):

Power Macintosh or latest generation PPC-PowerBook (604e or G3) with 32 MB RAM minimum, 17 to 21" colour monitor (16 mio. colors), system 8.x

Unfortunately, the MacDiff 4.x is not available as 68K-version for earlier processors (68020 to 68040), a consequence of too many cutbacks in performance and more frequent and non-reproducible as well as non-locatable compiler errors. Therefore, the last 68K-version 3.3.1 of October 1997 will remain available and supported by the author. However, an upgrade to PowerMacintosh is recommended for a sensible use of MacDiff.

The software was developed in the Visual Interactive Programming BASIC-environment of Mainstay. The code was converted to ANSI-C and compiled by CodeWarrior.

## Attention beginners

Operating skills of MacDiff can be obtained quickly. Therefore, beginners in X-ray diffractometry or in the use of computers will familiarise themselves with the programming environment quite fast. Nevertheless, knowledge about the theory of X-ray diffraction analysis as well as practical experience with analysis of X-ray powder diffractograms is a prerequisite. We refer to the appropriate literature, e.g:

- Klug & Alexander, X-Ray Diffraction Procedures, Wiley & Sons 1974 (very profound);
- Moore & Reynolds, X-Ray Diffraction and the Identification Analysis of Clay Minerals, Oxford Univ. Press 1989;
- Hardy & Tucker, X-ray powder diffraction of sediments- in: Methods in Sedimentology, 1988;
- Bish & Post (eds) Modern Powder Diffraction, Reviews in Mineralogy, 20, 1989
- Allmann, Röntgenpulverdiffraktometrie, Clausthaler Tekt. Hefte, 29, 1994.

Supported by the GUI the computed data remain transparent. However, the user is advised to check his data continuously and to take corrective measures instantly in case of emerging errors. Avoid a 'black-box' attitude.

We strongly recommend to the computer novice to familiarise himself with the Macintosh operating system and the use of files and GUIs. However, experience showed that most beginners acquire their skills in Mac OS rather quickly.

## Installation

MacDiff is available both as stand-alone programme and as a complete set of files. In case the Stuffit archive compressed version is supplied, unpack it with the Stuffit Expander.

The complete MacDiff packet contains the following files:



- '**MacDiff 4.x**' – current PowerPC version of MacDiff



- '**Testfile 1**' and  
- '**Testfile 2**' - two diffractogramme files in MacDiff-4 format for testing.



- '**Program Test**' - Demo file for an analysis programme (type TEXT)



- '**MacDiff Release Notes 4.x**' - latest informations about the current version (simple text document).

**MacDiff4\_Database\_Install:** This is an installer programme of a 2.5 MB set of mineral databases with hkl-data of over 500 minerals (with more than 22.000 peaks), which can be implemented in the folder 'Preferences:MacDiff' in the current system folder. Every part of the database consists of three files, which belong together. They must not be separated!



- Central database. Currently available are mineral data of: Complete Set, Sedimen-

tary rocks, Magmatic rocks, Metamorphic rocks, Clays, Ore minerals, Minerals (old)



- '...**Peaks**' related peak database (position, intensity and hkl-indices).



- '...**Index**' related index file for a quick-listing of all peaks.



- '**MacDiff Manual E**' - english version of this manual - i.e. this document.  
 '**MacDiff Manual D**' - german version of this manual



- testfiles for all specific data formats readable by MacDiff (Philips-RD and -UDF, Siemens-RAW, div, ASCII formats).



- **Test 2-78°\*500.RAW** - Test file (8 bit scan of a diffractogramme) for testing the Raw-scan import (section of 2 to 78° with 500 pixel per step = 5000 counts in steps of 0.04°)



- **Test 2-78°\*500.PICT** - PICT file of the same scan.



**xrd2-81.7.pict** - PICT file of a Debye-Scherrer scan for testing the **Import-Film Scan** - routine.

## Starting MacDiff

Start MacDiff by double clicking the programme icon or through the files associated with MacDiff. Also, you may drag and drop one or several file(s) readable by MacDiff onto the programme symbol.

After a short loading period the MacDiff logo will appear. Then the file '**MacDiff 4 Prefs.**' will be loaded, provided it exists in the preference folder (in the system folder). This file contains numerous settings of the previous run of MacDiff. If no preferences or faulty preferences exist MacDiff will load its own standard settings.

After a successful start the following menu will appear:

 **File Edit Profile Base Analyse Window**

**File** is used for input-output, for printing and quitting.

**Edit** controls display and editing of the diffractogramme.

**Profile** contains functions and filters to adjust the profile line.

**Base** takes care of setting and manipulation of the base line (background).

**Analyse** controls peak measurements and performs current data administration.

**Window** performs window administration.

## Running MacDiff - Basics

Diffractogramme files can be loaded and viewed with the menu command **'Open'**, via drag & drop, or by double-clicking the document symbol. You may display up to 10 diffractogrammes (= profiles) simultaneously (see Fig. 1) - each in its own window.

The display range of a diffractogramme is limited to 2-theta-angles between 0 and 180°, for intensities up to 1,000,000 counts, always starting from 0. The smallest section depictable is 0.1° 2-theta and 10 counts, respectively. The step size may vary between 0.001 and 0.2°.

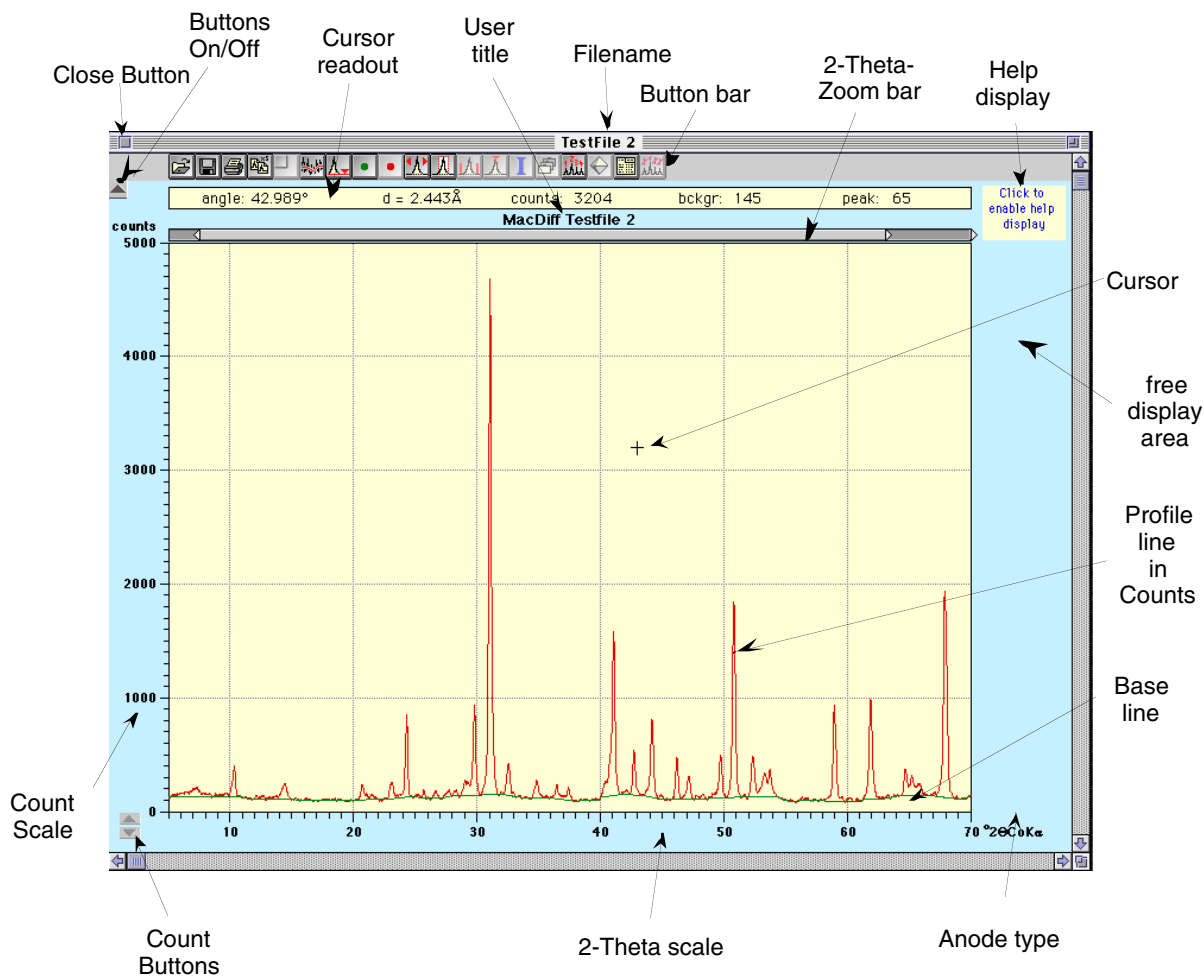


Fig. 1: MacDiff window and its control functions (17 inch resolution, reduced)

The diffractogramme is being controlled by mouse, menus, or buttons. Frequently used functions can be invoked via the keyboard as well.

Being positioned within the diagramme environment the cursor position is displayed in the **cursor readout**. The display shows the current angle (2-theta), the associated d-value (Ångstrom), the absolute cursor intensities, the background intensity and the background line intensity at cursor position (for positive values only).

Dragging while holding the mouse key effects a **zooming** of the diagram. The zoom range must not drop below 0.1° or 10 counts, respectively, as this will be interpreted as single click. The zero count basis as bottom limit is mandatory.

As long as the **control key** (CTRL) is pressed, a little magnify window appears right down of the diffractogram, showing a detailed view of the profile around of the cursor.

Mouse clicks outside the diagram environment invoke a set of different functions:

- clicking one of the triangles in the bottom left corner ('**count buttons**') invokes a 20% enlargement or 25% reduction, respectively, of the maximum count.
- clicking the user title opens a window within which the title name may be changed (equivalent to the menu function '**Edit : Rename Title**').
- Above the diagramme is a **zoom bar** flanked by two triangles. Clicking and shifting the triangles with mouse button depressed will modify the angle scaling accordingly. The current minimum and maximum angles are displayed while shifting the bar (see Fig. 2).

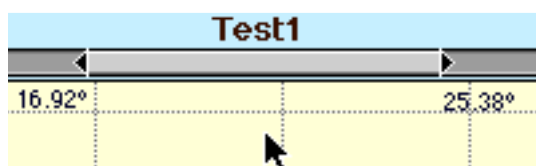



Fig. 2: Moving the zoom bar.


- clicking the fields left and right of the zoom bar will shift the zoomed diagramme by a certain amount to the left or right. Also, a direct shift of the zoom pattern via depressed mouse button may be done. A single click within the zoom pattern causes a full display of the diagramme.
- in order to effect a precision setting of the count- and angle boundaries, click within the appropriate scale. This will open a dialogue window equivalent to the menu functions '**Edit:Count Axis**' or '**Edit:Angle Axis**' (see below).


The **button bar** contains a set of buttons for frequently used functions. In case of small monitors or slower machines the button bar can be deactivated or reactivated via the '**button on/off**' (see Fig. 1). Some of the buttons are not active at all times; they are used for peak analysis only. The functions of the buttons can be queried over a **help display** in the top right corner.


## Peak analysis

**Single-clicking** within the diagramme environment initiates a peak analysis, which is started by a second click. The method employed for peak position calculation is indicated by cursor type, which can adopt four different symbols and can be switched via keyboard:

 = the peak (= reflex) is defined by maximum count - key 'M'. The definition range within which the count maximum is to be found can be set as '**Minimum Peak Range**' in the preference dialogue window (menue function '**File : Preferences...**').

 = the peak is positioned in the centre - key 'P'. The centre is the maximum point averaged over all counts of the top ten percent of peaks.

 = the peak is set precisely at the current cursor position - key 'N'.

 = the peak is fitted through a profile function - key 'F' (see following chapter).

It also may be selected in the preference dialogue window which of the four peak peak computation methods is to be activated on a standard basis.

**Double-clicking** a peak will immediately cause a peak analysis. Alternatively, the user can move from peak to peak by **ALT-click**. After a short time the following data will be shown in the peak data display in the top right corner (Fig. 3):

- the peak position (in  $^{\circ}2\Theta$  and  $d[\text{\AA}]$ ),
- the peak intensity (counts minus background,  $I[c]$ ),
- the peak area (integration of all peak counts above background,  $F[\Sigma]$ ),
- the full width at half maximum or half-height-width,  $H[\Delta]$ , equivalent to FWHM  $[\Delta^{\circ}2\Theta]$ ,
- the diffractogramme profile number in the report-table (1-255),
- the peak number of the report-table (1-32),
- an identification name (crystal name or the like) as suggestion, if available.

These data are stored automatically in the so-called **report-table**. This table can store data of a maximum of 32 peaks of up to 255 XRD spectra (profiles), and it remains in memory while the programme is active, unless the user actively erases it. The programme takes care about a structuring of the data, as far as this is possible. The table can be saved in standard text format.

Even in case of a programme crash the data remain preserved in the TEXT file '**MacDiff Report.temp**' (Excel Text file), which is placed temporarily in the system folder by the programme.

The automatic storage of the data in the report table can be suppressed by holding down the '**X**' key during peak analysis.

Moreover the data of a peak currently measured will be placed on the clipboard in order to be read instantly by a text or table processing programme. This function can be turned off in the dialogue field '**File : Preferences...**' (see below).

The **peak area** is computed by integrating = summing the counts above the background within the interval determined by **peak borderlines** (see Fig. 3).

The half width (**FWHM = Full Width at Half Maximum**) is computed doubly sided, that is, a mean value of the half widths of the inner and outer boundaries of the peak profile is calculated. These two values are different only for broad reflexes or unsmoothed profiles.

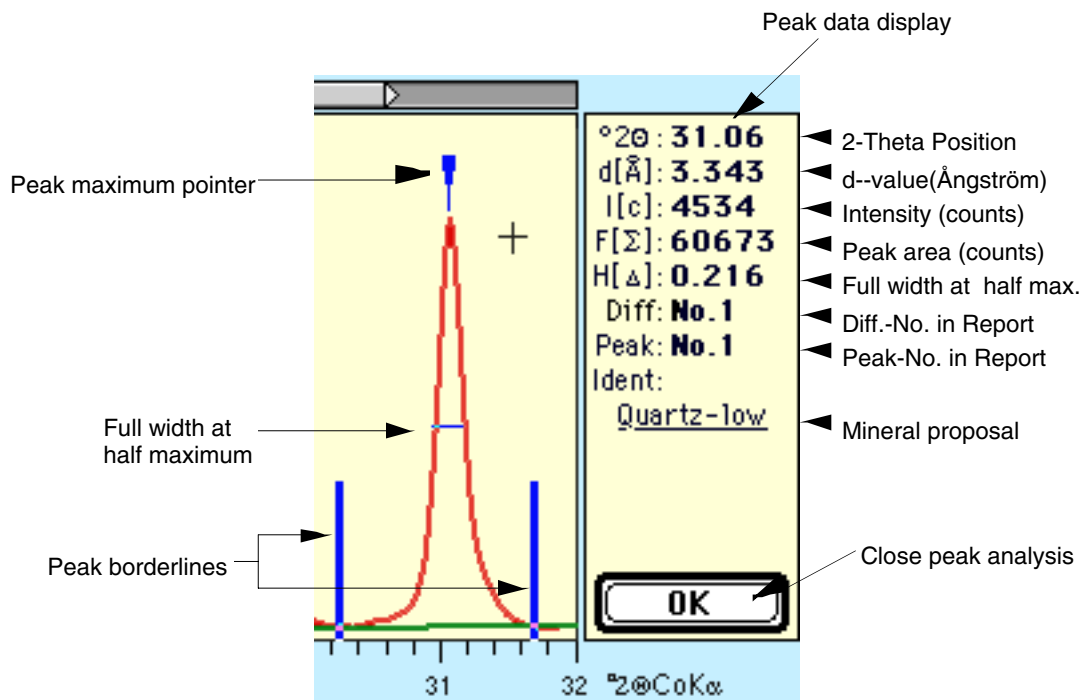








Fig. 3: Peak analysis


It is possible to deliberately alter the measuring parameters for a currently activated and measured peak. As a consequence, MacDiff will recalculate automatically. The following changes are possible:

- **Manipulate background line** (button  or menu function '**Base : Manipulate**'). The course of the background is determined by setting fix points in the diagramme through mouse clicks. The button colour is identical to the background colour.
- **Manipulate profile** (button )- enables the temporary removal of parts of the current profile (e.g., disturbing or coinciding side reflexes). Just like with background manipulation the new course of profile is determined through fix points set by mouse click. As this is data manipulation, care should be taken with this procedure. The button colour is identical to the profile line colour. Reclicking the button or terminating the peak analysis will replace the altered profile by the original one.
- **Shift the peak border lines** (button ) via mouse. Optionally, this routine can be performed after directly clicking the line (mouse arrow becomes active). A recalculation of the peak follows. The routine serves to correct errors when calculating the peak boundaries in case the measurements comprise more than one peak or if only a part of the reflex was analysed.
- **Shift the peak maximum indicator** (button ) , which can be activated by direct clicking as well (watch mouse arrow). Observe the type of the current peak maximum search being symbolised by the cursor (see above).

Three important menu functions or buttons respectively support the peak analysis:

- Invoke the report content display (button ) - also see the menu function '**Analyse : Show Report**'.
- Display additional peak data (button ) - this will open a window with additional data about the current peak (identical to '**Analyse : Peak Info...**', see below).



- Invoke the lines stored in the active peak database (button ) - this will list all available lines of the peak database in a separate window. The available lines within the angle range of the currently analysed peak will be displayed. Also see the menu function '**Analyse : Identify**' for further information.

## Peak analysis by peak fitting

Besides the peak analysis considered so far, which relates to the measured or filtered peak data, MacDiff offers the option to obtain peak data by means of profile shape functions (PSF). For this purpose a PSF must be optimally fitted to the peak shape of the current profile (best fit). This should always require the use of unsmoothed original data.

Besides a single peak analysis (single peak fit) an option exists to distinguish up to 7 superimposed reflexes by means of peak fitting in order to reveal the parameters (intensity, FWHM, a.o.) of the individual peaks. This is done by finding functions, which optimally approximate (multipeak fit) in their combination the original profile (envelope).

The following PSFs are available: Gauss, Lorentz (simple, intermediate, modified), Pearson, VII and Pseudo Voigt. For peak fitting method see Howard & Preston (in Bish & Post, 1989) or Allman (1994). The function equations are displayed in chapter 'The menu analyse : Peak Fit Settings...'. For X-ray reflexes the best fits are obtained with the Pearson VII- and Pseudo Voigt function. Each one of the PSFs can be fitted as symmetric, or splitted asymmetric peaks. These and other settings can be chosen in the 'Peak Fit Settings', see chapter 'The menu analysis'.

During a peak fit the function parameters (coefficients) intensity, FWHM (half height width), and peak position (Bragg angle) as well as potential flank parameters are being approximated until they optimally retrace the peak course of the original profile. The fit is being improved by the least-squares method (or chi-square, resp.) on the base of a robust-fit method. An independent measure for the quality of fit is the residuum, which represents the relative (in percent) aberration of all measuring points on the profile function.

Before a peak fit MacDiff independently computes initial function parameters, which give a first approximation. As a rule, the following peak improvement takes place only within the angle range defined by the peak border lines. For this purpose, each parameter of every function is being updated up to 20 times, or until the sum of squares between the original and computed profile reduces by less than 0.001, by a bisection method while all other parameters are being kept constant. The resulting new function value is now being kept constant and the next parameter is adjusted until all parameters of all functions are computed. This procedure can be repeated iteratively, as user-set, up to 100 times ('**Loop No of Refinement**'). In general, the resulting residua rarely show any further reduction after 5 to 20 iterations. Therefore, the refinement process can be terminated prematurely, if the residuum reduction drops below a certain value ('**Residuum Reduction**' in 'Peak Fit Settings'-dialogue, settings between 0.001 and 1%).

The refinement algorithm used by MacDiff has the advantage to instantly produce an optimal fit in case of carefully selected settings (robust fit). Further calculations with selected parameters being kept constant (to be set in the 'Peak Fit'-dialogue window) rarely improve the fit. Good fits may produce residua of less than 10%. The drawback of the robust fit routine consists of a substantial computation time, which is required especially for multipeak fit analysis, as the amount of operations increases exponentially to the number of peaks to be calculated.

**Procedure for one peak fit:** Zoom the diagramme appropriately on the peak(s) to be measured. (alternatively: turn on '**Zoom Peak Area**' in the menu '**Analyse**'). Select according to your needs the appropriate profile function and other parameters in the 'Profile Fit Setting'-dialogue (menu '**Analyse: Peak Fit Settings...**').

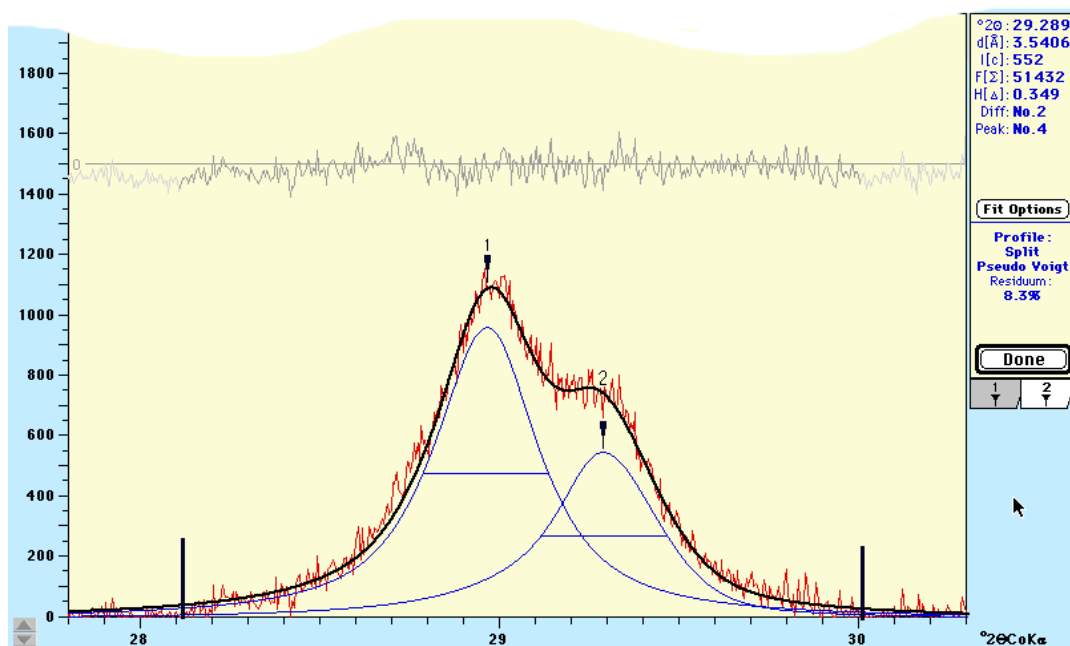



Fig. 4: Peak fit analysis of kaolinite (1) and chlorite (2) (3.58 and 3.54Å). Profile function (blue): Pseudo Voigt (splitted). Black: curve in common (envelope), grey: residuum curve, red: original data. Background removed. The peak data display shows the data of the 2nd peak (chlorite)

**Single peak fit:** Click the selected peak. The cursor must appear as -symbol. If this is not the case, press the F-key or select the 'Fitting Profile Function'-checkbox in the preference dialogue (menue '**File:Preferences...**'). Double click the peak selected for analysis. After a short computation time (depending on the settings as well as the machine) MacDiff will plot the function calculated directly into the diffractogram. It will disappear upon clicking '**Done**'. The profile fit data will be displayed in the same place and format like the original peak data in the peak data display on the top right corner. In addition, the profile function and the quality of fit (residuum in %) will be displayed (Fig. 4). The complete set of function parameters is displayed in the '**Peak info**'-window (use the '**Fit Data**'-indicator). The report list now contains the function's peak data as well (d-value, intensity, area, FWHM). Notice: All data from filtered functions are **displayed in blue!**

**Multiplex fit:** Hold down shift key and click all lines to be fitted. The cursor will show the current peak numbers from 1 to 7. Click the '**Fit now**'-button on the left-hand side to start the peak analysis. Drag the peak border lines to the angles of your choice, if necessary. Wait and observe the top right display to monitor the refinement performance (it will show the residuum, which is supposed to reduce gradually). Optionally, you can get graphics of interim results (go to the Peakfit Settings dialogue). After the calculation is completed MacDiff plots all functions together with their combining curve (envelope) and the residuum curve directly onto the diffractogram. In the top right corner the data of the peak last selected will be displayed. To display the data for the other lines, activate the indicator number below the display window (Fig. 4). The d-values, intensities, areas and half widths of all functions of the lines selected will be saved in the report. To display all these data (**in blue**) simultaneously, open the report window (menue '**Analyse : Show Report**').

## The 'File' menu

File	
Open...	⌘O
Set File Format...	
Close	⌘W
Open File Session...	
Open Next Session File	⌘N
Save	⌘S
Save As...	
Import Plot Scan...	
Import Film Scan...	
Digitize Plot...	
Export...	
Info...	⌘I
Preferences...	
Page Setup...	
Print Diffractogramme...	⌘P
Print Data...	
Quit	⌘Q

Fig. 5



- this will open the standard Mac dialogue box for file input. Files of different formats can be read. MacDiff automatically tries to identify the correct file format, unless a particular format has been selected through the menu function '**Set File Format...**' (see below). In case a file cannot be read, an error message will be displayed. The following formats can be read:

**MacDiff format** (all versions, DIFF and DIF4) - programme intrinsic, binary, very compact format with high speed input-output. Contains, if computed, the background line as well.

**Philips-APD-3.0-MS-DOS-Format** - (single scans only!) Binary format of the current APD version 3.0 of Philips.

**Philips-APD-VMS-Format** - (single scans only!) Binary format of the VMS version of Philips diffractometer software.

**Siemens-RAW2-Format** - (single scan only) Binary format of Siemens diffractometer software.

**Siemens new RAW1-Format** - binary format of the current Siemens DIFFRAC software (Attention: this format is newer than the RAW2 format!)

**Siemens old RAW** - older binary format of the Siemens DIFFRAC software, used before introducing the RAW2 format.

**Philips-ASCII-MS-DOS-Format** - (also called **UDF** format) Text format.

**Philips-ASCII-MS-DOS-Format** - also Text format of measuring values, as being saved under '**View Scan**' in the APD software.

**MacXFit-Format** (ASCII) of the same-name programme of H. Stanjek (TU Munich).

More formats (all in TEXT - ASCII format):

**Rigaku-ASCII-RAW-Format**

**Sietronic-ASCII format**

**MDI-ASCII format** (Rigaku-Software)

**OUT-ASCII format**

**Lauterjung-ASCII-format** - being used for Quax programme by H. Lauterjung

**CIF-ASCII-format**

**NewMod ASCII format** of NewMod software

**Scintag ASCII format** - Text output format coming from the current SCINTAG 2000 software.

From all these file types MacDiff reads the first and last angle, the step size, the measuring points count, the anode type, and, if available, a user title and the counting time.

**Special ASCII-Column-Formats:** they must have a simple structure without header: angle-measuring value-background value (the latter optional), separated by a special delimiter: tabulator (ASCII symbol no. 9), comma, blank or slash. A carriage return (ASC symbol no. 13 = line break, enter key) is set between the individual data sets.

*Please note, that the file type of an imported text- or binary file may be wrong, depending upon by which software the data transfer between DOS- and Mac world was performed. Although all possible files are loadable by the file selection dialog, for technical reasons MacDiff will open only the file types 'DIFF', 'TEXT', 'crlf', '????', 'BINA', and 'PCLF'. It is possible to change a file type by the freeware programme 'ResEdit' by Apple or by the shareware programmes 'Creator Changer' by C.L. Waskovich, e-mail CLW95002@UConnVM.UConn.Edu or Drop\*Attribute (SouthSide@kagi.com). Please contact me if you have input problems. If you have files with special formats and you know their data structure, please inform the author to have them integrated into MacDiff.*

Diffraction patterns with more than 16,768 individual values as well as those with multiple scans (multiscan) cannot be read. In case of appearances of intensities larger than 1,000,000 counts a dialogue will show up querying whether the values to be read shall be reduced to 10%. That is, the maximum intensity readable is 10,000,000 counts.

Up to 10 diffraction patterns can be open simultaneously. Optionally, the opening process can be performed in the finder as well (double click the document icon of MacDiff or drag & drop the file to be read onto the MacDiff icon).

### Set File Format...

is being used to identify a specific file format readable by MacDiff (Fig. 6). In case a setting different than '**Decide automatically**' is active the automatic file identification of MacDiff is suspended.

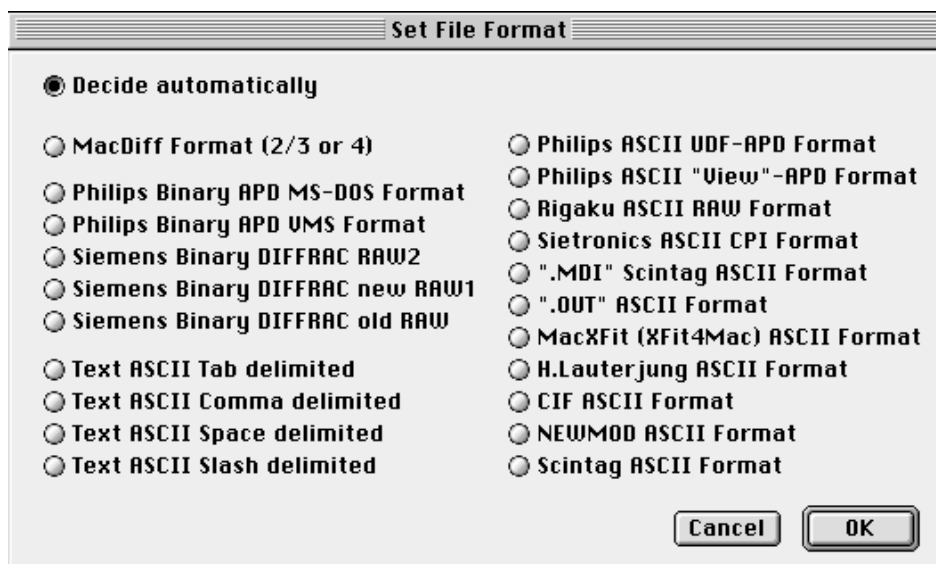


Fig. 6

**Close**

Closes the currently active window. In case changes took place it will be queried whether the data are to be saved.

**Open File Session**

An entire set of files can be processed in a so-called **File Session**. This will open a file selection dialogue where a file from a folder is selected. MacDiff opens all or a part of the files contained therein step by step and in alphabetical order. Such a file session is useful in particular for automatic and fast conversion and processing of diffractogrammes. The way of data handling is facilitated by a dialogue (Fig. 7).

- The left scroll window lists the selected files. At the beginning all files are active. Clicking individual files will exclude them from or include them into the session respectively. With clicks during shift key is depressed several consecutive files can be selected. Via the buttons '**All**' or '**None**' the entire list can be activated or deactivated respectively. '**New Folder**' helps select another folder.

- The top right 11 check buttons serve to turn on or off filter routines to be used after the session files have been read. These relate to procedures in the menus '**Profile**' and '**Base**' (see below). By means of '**Options**' the appropriate settings for these filter routines can be selected.

- Clicking '**Auto Load**' (= Batch-Operation) will consecutively load all session files ('**OK**' button turns into '**Start Job**' button). The currently loaded files can then be processed automatically as well as being displayed, printed, and finally saved (indented check buttons). Optionally, the existing files can be overwritten or placed in a new folder 'Changed Diffs'. Even an automatic peak measuring is possible in case an analysis programme is available (for further details see '**Analyse : Analysis program.**'). To export the files into another format (provided it is supported by MacDiff) turn on '**Export Files**'. After loading the first file of the session this will display the export dialogue shown in Fig.10 for selection of the desired export format.

Use '**Options...**' to calculate a mean or additive diffractogram of all loaded files of a session.

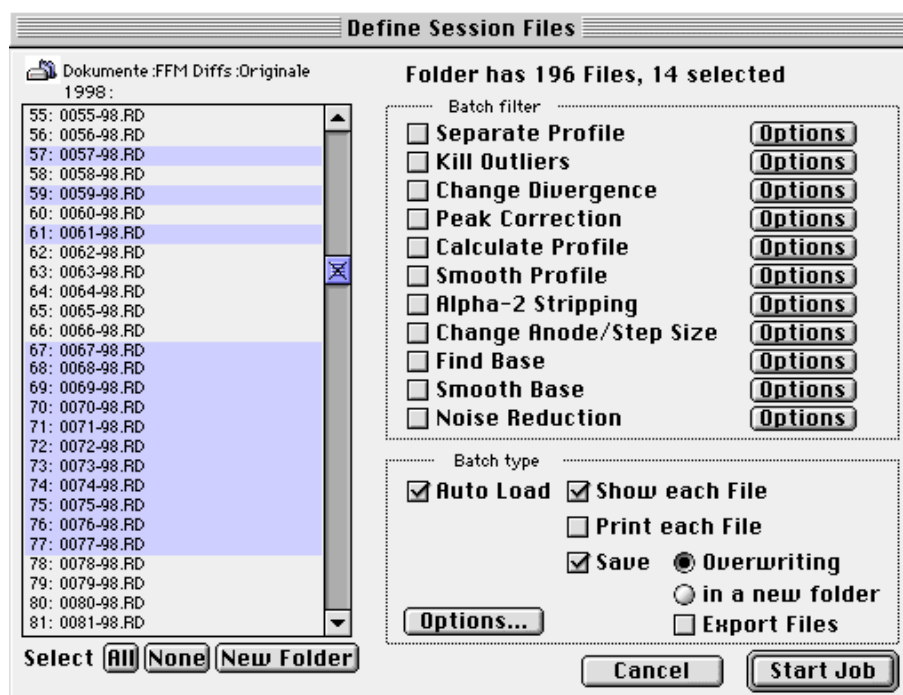


Fig. 7

## Open Next Session File

This menu function is used to individually load the files contained in session file list (the **'Auto Load'**-function in **'Open File Session'** must be deactivated for this). As opposed to **'Open'** the current window will be overwritten by the following diffractogramme.



**Save**

Save the diffractogramme in the current window in MacDiff 4 format.

**Save As...**

Save the active diffractogramme after previous query for file name.

**Import Plot Scan...** this serves to digitise grayscale pixel plots of scanned diffractogrammes. First, the file to be read, which must have the so-called RAW format, is identified (not to be mixed up with the Siemens software format!). Many image processing programmes such as Adobe Photoshop (commercial), GraphicConverter (shareware) or NIH Image/Image SMX (freeware) are capable of writing RAW files. This very simple format lists all pixels with 8 bit (256 grayscales) line by line. Therefore the size of a raw document (without resources) in Byte is just the existing pixel count of a plot. However, due to this simple structure the reading programme must be informed about the pixel count per line.

The scan must be oriented to have a horizontal (= line) count axis and a vertical (= column) axis for the angles. It must not contain margins of any type. If possible, it should only show the plotter line and no remnants of the paper plot scale (a red plotter line can be separated relatively easy form a black scale if the diffractogramme is being colour scanned with red colours intensified in comparison to other colours, and then converted to grayscale). Occasional free pixel remnants must be removed if the appear below the plotter line.

To secure a good scan quality the horizontal pixel count should be 500 or more (max. 32768), whereas the vertical pixel count should coincide as close as possible with the measuring points to be calculated (however, this is not mandatory). For instance, to scan an analogue plot from 2 to 40° 2Theta in order to digitise it with a step size of 0.02° 2Theta, at least  $1 + ((40-2)/0.02) = 1901$  pixel should be present in the vertical.

When saving the raw file the following informations should be logged:

- 1) the horizontal and vertical pixel resolution of the picture
- 2) the first and last angle of the region scanned
- 3) the maximal counts in the horizontal axis (base is 0 count)
- 4) the anode used
- 5) the count and angle orientations (ascending or descending).

These parameters are entered in the following dialogue window (Fig. 8). In '**Pixel per Step**' record the horizontal pixel count. MacDiff checks if this value divides the file size (= total pixel count) without remainder and displays the resulting vertical pixel count (= step- or measuring point count) on its right side. If the resulting value is not integer, the horizontal pixel count is evidently wrong, being signalled by the error message 'Note! Wrong file length/pixel per step!'. Starting the routine is in this case not possible. In case a smaller than anticipated count of existing measuring points should result due to the step count, MacDiff will also inform how many new measuring points have to be interpolated.

The other entries comprise title, first and last angle, step size, the scan count maximum as well as anode information. Moreover, the grayscale threshold value for a pixel to be detected can be set: the lower the value, the darker the plotter line must be. Therefore, do not choose a too low grayscale value, as this might cause the plotter line to be missed. In '**Count order**' or '**Angle order**' respectively the scan orientation is set, depending on whether the counts increase or decrease from left to right or the angles increase or decrease from top to bottom.

The accordance of the resulting diffractogramme with the original mainly depends on the care exercised when scanning and processing the plot. In ascending counts MacDiff finds the first pixel group with grayscale smaller than the set threshold value. Relevant for the count determination is the position of the last pixel still being element of the plotter line.

Because most diffractogrammes digitised by 'Trace Scan' require smoothing, plots redrawn carefully on a digitising table tend to be of better quality. Moreover, it has been experienced that manual redrawing works considerably faster than the processing of scans.

Using the file 'Test 2-78°\*500.RAW' (optionally available) you may test how the digitisation of a scan is performed. The affiliated original PICT file 'Test 2-78°\*500.PICT' serves to view the scan in any graphics programme. The correct settings are shown in Fig. 8. Be aware, that sharp reflexes might possibly require extra corrections!

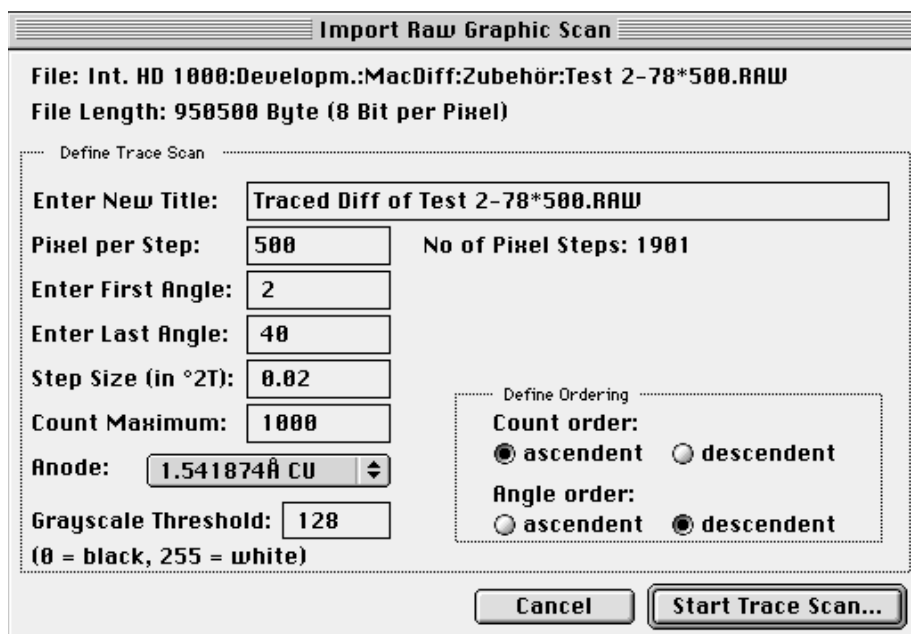


Fig. 8: Digitising dialogue of a scanned script.

**Import Film Scan...** digitises a scanned X-ray photo film of a Debye-Scherrer or Guinier camera. Before starting, a PICT file of a greyscaled scan of the exact angle interval is required, which should have sufficient pixel in lengthways direction, as the resulting measuring points to be calculate (at least the half amount). On the other hand, it is not required that the horizontal pixel number coincides with the number of the resulting measuring points. Furthermore, the colour depth of the monitor must be at least of 256 greyscales.

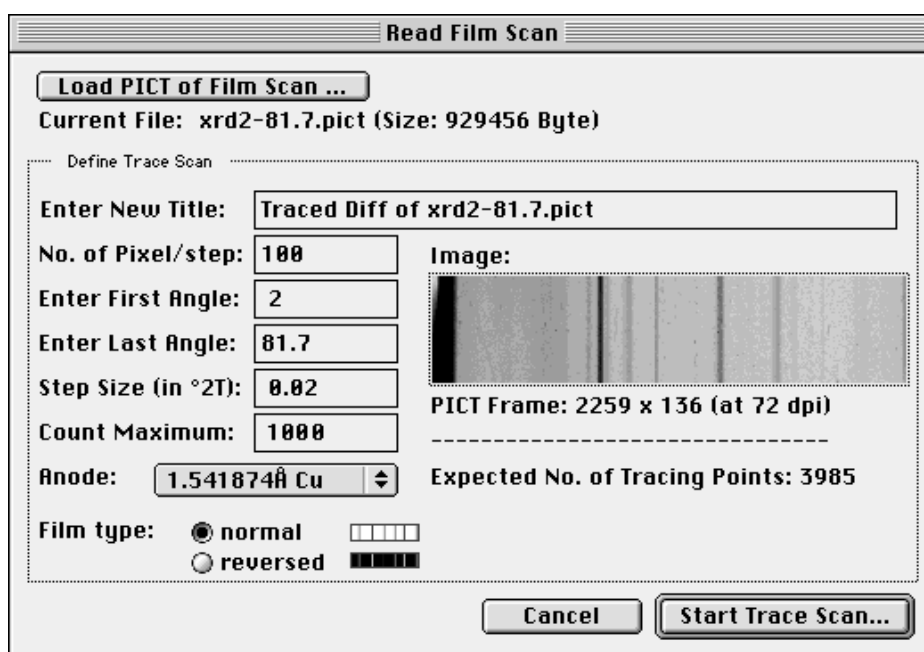


Fig. 8a: Film Scan dialogue

Open the PICT file in the dialogue window as shown in Fig. 8a. using the "**Load PICT of Film Scan**" button. Before reading the PICT file take care that MacDiff has allocated sufficient memory. Otherwise an error message appears.



Furthermore you can edit the following settings:

- a new title for the digitised profile;
- the amount of pixel to calculate a count value per step (vertically pixel number). This number must not higher than the real number of vertically pixels in the scan. The higher this pixel number, the more the resulting profile will be smoothed;
- the first angle (first pixel column on left side of the scan);
- the last angle (last pixel column on right side of the scan);
- the step size of your choice;
- the count maximum (depending from film type, in accordance to the lightest or darkest pixel of the scan);
- the type of anode material (wavelength);
- film type: either normal (darkest pixel means highest count value), or reversed (lightest pixel means highest count value).

**Digitize Plot...** is being used for digitising a script employing a graphic tablet. The tablet should be as large as possible, optimally DIN A3 or larger. Also, a monitor with supported resolution of at least 1024x768 pixel should be available to guarantee satisfactory quality, since MacDiff reads the cursor position.

In preparation for the digitisation a dialogue window is being opened (Fig. 9), in which the first and last angle of the original script is to be entered. Since many plotter scripts cannot be digitised in one step, the size of the current part in degrees must be indicated (Tile Length). MacDiff computes the number of parts required inclusive the remainder and later ensures the correct course of the digitisation. The partitioning is displayed in a preview.

Further, step size, maximal count of plot (if necessary) and the anode used is to be entered. Finally, it must be indicated if the angles increase going from left to right or if they evolve inversely (check '**Inverted Angles**').

Use „**Play Sound on Tracing**“ to play a signal while digitizing the single values.

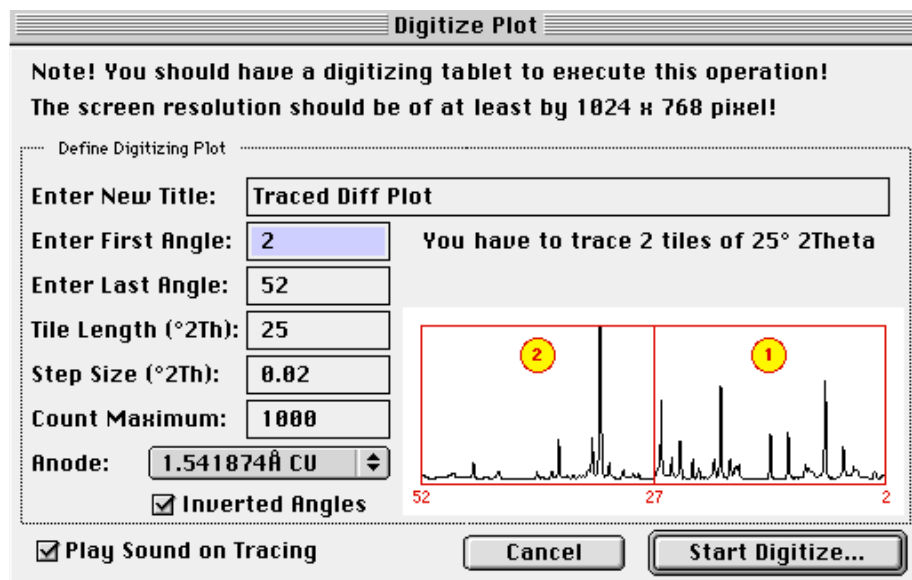


Fig. 9: dialogue window for preparation of an analogue script for digitisation via graphics tablet.

After '**Start Trace Job**' a window will open covering most of the monitor in order to create an area as large as possible. Adjust your graphics tablet so it matches this area optimally and keep some margin between your master copy and the display area on your tablet.

After activating the 'Trace tile xxx'-buttons all four plot corners must be tipped off to ensure correct scaling. Then retrace the plotter line with stylo pressed or tipped and taking your time. Pick your own starting point direction of drawing. Retracing can be done any time. All plot regions should be digitised with sufficient accuracy even if not every resulting measuring value is being copied. Striking any key will stop transfer of any partial plot. After every tile has been transferred, reassemble the digitised diffractogramme to an integral unit for further processing.

### Export...

This menu function serves to export the data of the active diffractogramme, the diffractogramme graphics, or an existing report table, into another programme. This is done by the dialogue window as displayed in Fig. 10.

The first fold-up menu helps you to decide, what is to be exported.

Use 'MacDiff 2+3' to save with the old MacDiff2/3-format, which can be read by all versions previous to MacDiff 4. Moreover, the following export formats are available: Raw Data-TEXT-format, MacXFit, Philips UDF, Scintag MDI, Sietronic CPI and Lauterjung. All these formats can save the entire angle range ('All Counts') or, in case of a zoomed diagramme, the current angle range ('Same as shown: from x to y').

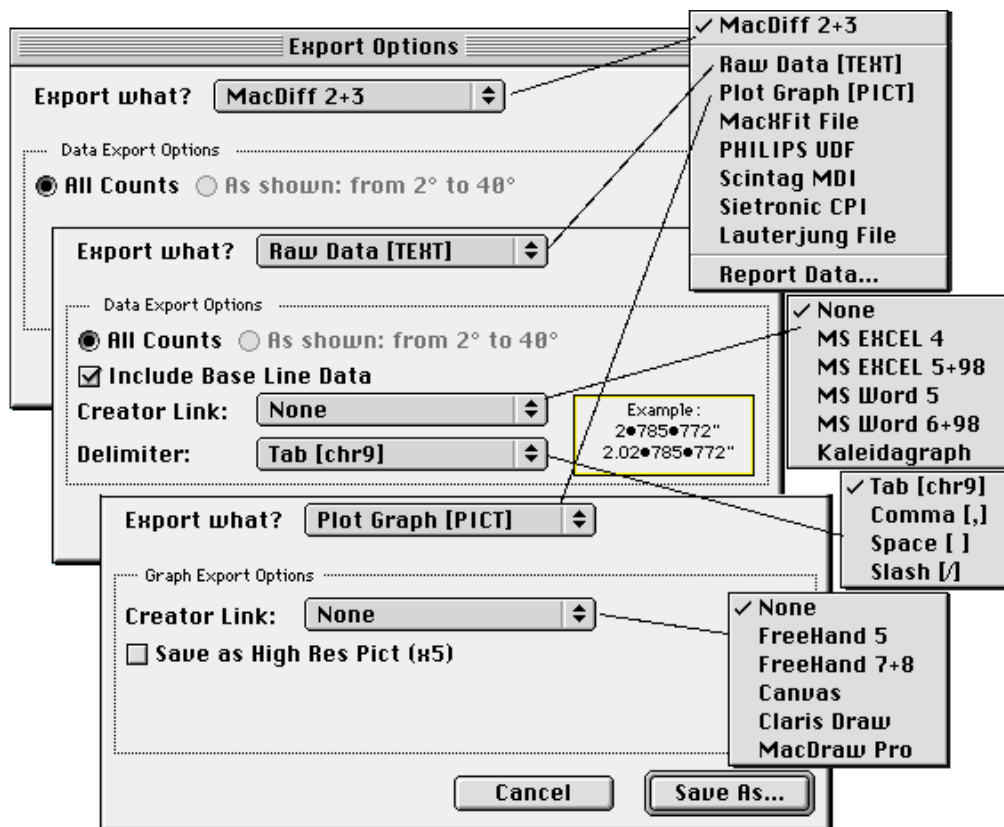


Fig. 10

With an active 'Raw Data [TEXT]' menu several settings are possible (Fig. 10). Angles, counts and, optionally, background values are being saved as ASCII-TEXT file. 'Include Base Line Data' provides setting for background values to be saved. If the data are to be linked with the programmes Excel, Word or Kaleidagraph and be represented by an associated icon, activate a popup menu. Moreover, the separator symbol between individual values can be set (tabulator, comma, blank or slash). If it is not certain, which import format is accepted by the table calculation

programme or XRD programme in use, employ the tabulator first. MacDiff reimports all TEXT formats available there.

An active '**Plot Graph [PICT]**' saves the current diagramme as vector PICT2 file with optional settings for links (Creator link) to some vector graphic programmes (Freehand, Canvas, ClarisDraw or MacDrawPro). For particular high-value large-format graphics activate '**Save as High Res Pict (x5)**'. This can be rescaled to 20% after import into the graphics programme in order to obtain excellent reproduction quality.

An active '**Report Data**' save the current report table. A dialogue appears identical to '**Analyse : Save Report**' (see below).

### Info...

provides a window with essential data of the currently active diffractogramme (see Fig. 11).

Click '**Get Comment**' to enter or read user-specific comments about the current diffractogramme. These will be saved along with the file (in MacDiff 4 format only).

Click '**Get History**' to read all changes performed since the last import of the diffractogramme into MacDiff 4.

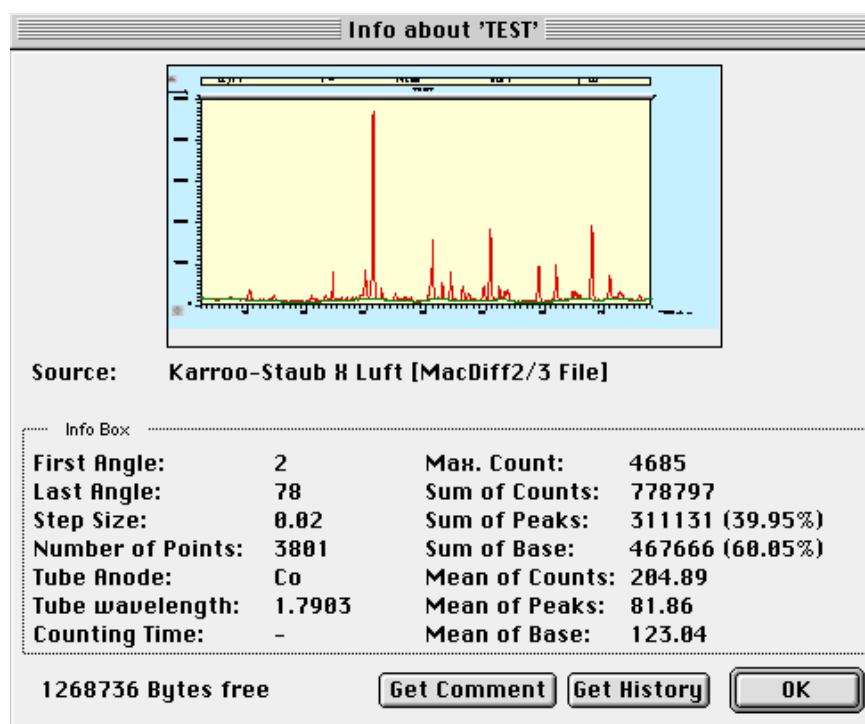


Fig. 11

**Preferences...** serves to enter some initial settings. They split into three divisions (figs. 12-14):

### Peak Measurement Preferences (Fig. 12)

**Minimum Peak Range (in 2-Theta)** sets the angle range, within which MacDiff, via double click, looks for a maximum during a peak correction or an automatic peak search. Besides, its size determines the precision of correct order of lines measured in the report table. Default is  $0.2^\circ$ , minimum is  $0.01^\circ$ , maximum is  $0.99^\circ$ .

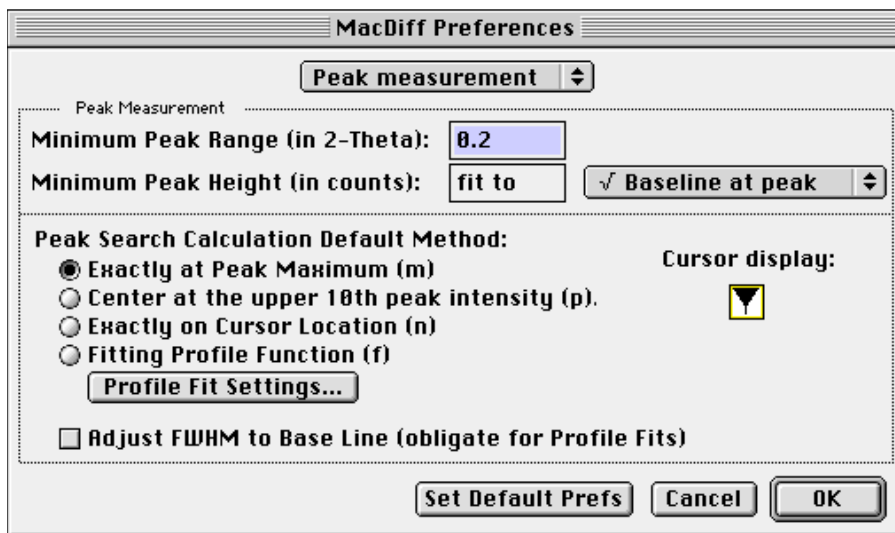
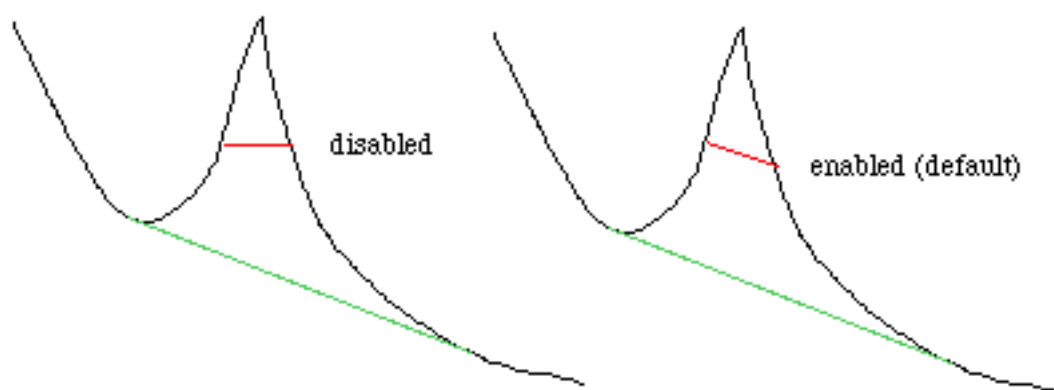


Fig. 12

**Minimum Peak Height (in counts)** is the minimum size for a peak. It is defined as constant count value or as a multiple of the background line's root ( $1$  to  $5 \cdot \sqrt{\text{Back-line}}$ ,  $1$  is default).

**Peak Search Calculation Method** selects, if the peak fixing after double clicking is to be done by default through the **Maximum**, the **Center**, **Exactly on Cursor location**, or through a profile fit. The appropriate cursor will be displayed top right. As already noted, the type of peak search can be changed during peak analysis by keyboard input as described.

**Adjust FWHM to Base Line** - this setting determines if the half width is always oriented horizontally or parallel to the background line of a peak (button active). In case you want to work in the mode of versions previous to MacDiff 4, deactivate the button.



### Print Preferences (Fig. 13):

The second part of the preference dialogue contains initial settings for diffractogram hardcopies (Fig. 13). **Print Logo** determines, if a logo of the affiliation, say, is to be placed in the top left corner. **Next Logo** selects another logo from 8 sample logos available, associated with some affiliations. In case you desire your own logo, invoke **Paste Logo**, which will attach to the existing logo list a PICT graphic from a vector graphics programme located on the clipboard. The picture should not exceed a size of about  $20 \times 5$  cm ( $\approx 8 \times 2.5$  inch); it will be reduced to 25% on DIN-A4 or letter hardcopies. It is advisable to use a logo of less than  $10 \times 2.5$  cm ( $< 4 \times 1$  inch). If desired, the author offers to intergate your logo. **Print**

**Date/Time/ Operator/File** determines, if date, time, operator, and file name are to be printed in the top right corner. The **Operator** edits his name in the appropriate window. Use **Print Header** to print a three-line header, e.g., for processing parameters, which is the default. Underneath, an extra line may be printed (**Print Data Info**), providing information about measuring points count, angle range displayed, step size and anode type. **Color Prints** should be checked for colored hardcopies.

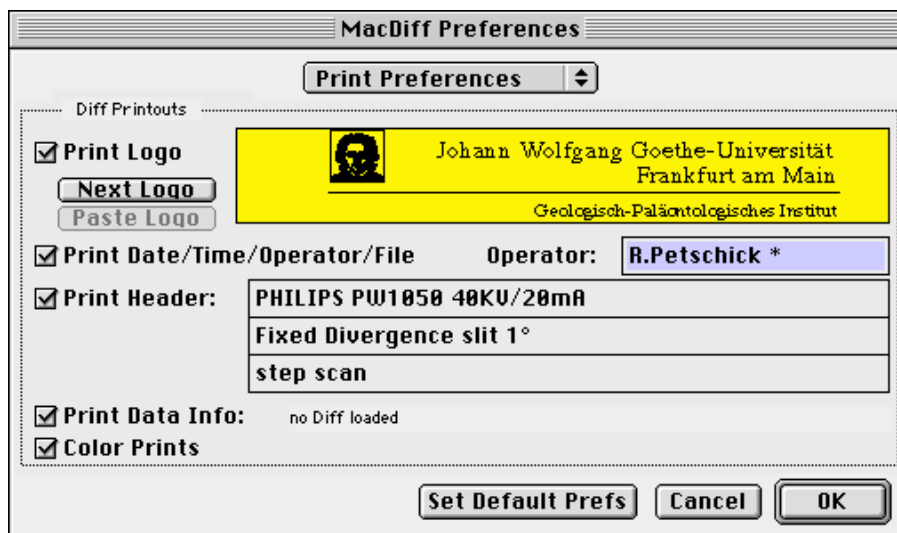


Fig. 13

#### Miscellaneous Prefs (Fig. 14):

**Default Analysis Program** determines an analysis file for MacDiff to automatically work with after start.

**Default Anode** determines via pop-up menu the default anode type in case insufficient information is supplied by the file read in (as is the case e.g. with the old MacDiff 2.4 format)

**Display/Save Data as integers** - all data saved or displayed will be rounded to the next integer.

**Precise Cursor** determines, whether for high-resolution diffractogramme details the cursor position is to be computed for each pixel (x-checked, default) or only be oriented at the angles of the measuring points (not x-checked).

**Draw Profiles as Polygons** determines, whether the diffractogramme vector graphics are to be drawn as independent lines (button off) or as connected polygons (button on). In order to administer easy processable diffractogrammes the latter is the better option for most graphics programmes. The highest possible count for a polygon is 8000.

***Attention!** Some vector graphics programmes like e.g. Freehand up to version 5.5, however, are not capable to accept polygons with more than 1000 individual elements. The programme MacDrawPro causes problems as well when printing very complex polygon lines. In this case turn off the option or split the diffractogramme to be transferred into several parts.*

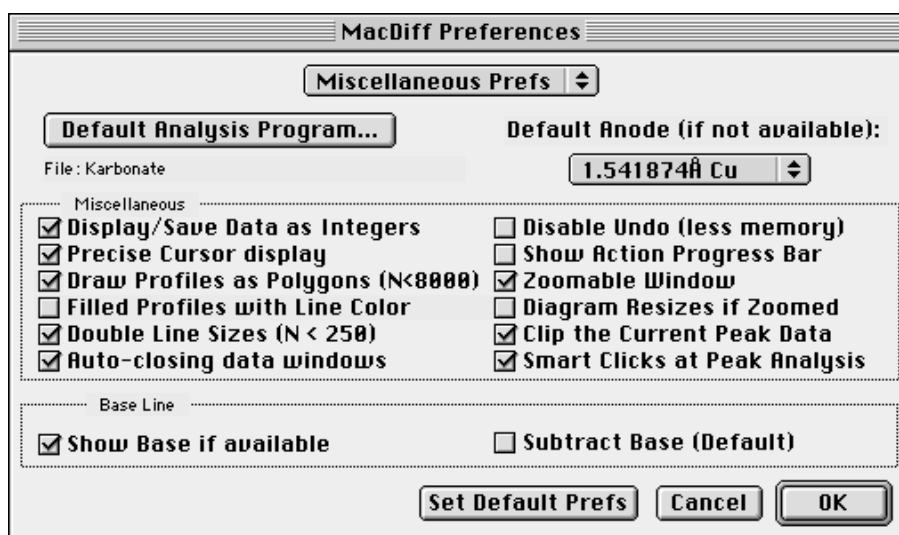


Fig. 14

**Filled profiles with Line Color** turned on will colour the area down of the profile line with the line colour. This produces optically pleasant peak distributions, however, it might be irritating during measurements. Only for polygon drawing turned on the button will be active.

Use **Double Line Size** to draw zoomed diagrams (less than 250 individual measurements) with double width line.

Turn on **Auto-closing data windows** to close Report, Peak Info, and Identify windows as automatically after activating a profile or a dialog window (increases the performance during peak analysis).

**Disable Undo (less memory)** - activate to suppress Undos - can be helpful in case of memory problems.

**Show Action Progress Bar** - turns off the running displays of many routines - particularly sensible for fast Macs.

**Zoomable Window** is used to work with scaleable and scrollable windows. Alternatively, windows of fixed size are employed.

**Diagram Resizes if Zoomed** will automatically adapt diffractograms after an enlargement/reduction of the window.

**Clip the Current Peak Data** offers option to automatically pass the current four peak data (d-value, intensity, area, FWHM) to the clipboard during peak measurements. This option may be very helpful in case of retroactively measured data, which are to be transferred into existing tables like e.g. in Excel. The data will be tab-separated.

Turn on **Smart Clicks** in order to terminate a peak analysis by single mouse click (i.e., without OK or ENTER).

**Show Base** and **Subtract Base** suppresses or pulls the background line down to zero by default, respectively. Also see the related menu functions in '**Base**'.

**Set Default Prefs** restores default parameter settings.

**Page Setup...** creates the standard Macintosh layout dialogue window. For optimal diffracto-

gramme hardcopies on US letter or DIN-A4 **set a reduction by 25% and landscape format**. Also, the option 'larger print area (less font sets)' is recommended for Postscript printers. Hold down <Alt> and click '**OK**' to adopt these settings as default. A dialogue will appear and confirm this.

**Print Diffractogramm...** 

creates a hardcopy of the current diffractogramme. First, the graphics are being created in the background; then, the print dialogue window appears. In case MacDiff realises the graphics will not fit onto a US letter or DIN-A4 page, a page setup window will open to allow for corrective settings. Depending on graphical complexity and hardware the printing process may take between 1 and 5 minutes. Hardcopy quality will be about 3 to 6 times above that of the monitor image (depending on size). Independent of the setting in '**Optimized Drawing**' in the '**Edit**' menu all count values of the current diagramme will be printed as a rule.



**Print Data...** automatically creates a list of all count values of a diffractogramme, which may be printed thereafter.

**Quit** exits MacDiff. In case changed diffractogrammes or report tables have not been saved yet, appropriate dialogue windows and queries will appear.

## The 'Edit' menu



Fig. 15

- Undo...** will reverse the latest change on the current diffractogramme.
- Cut** without function. Implemented for reasons of compatibility.
- Copy** transfers the current diffractogramme onto the clipboard in 72 dpi-PICT format. All available values within the displayed angle range are considered irrespective of the setting in the menue '**Edit : Optimized Drawing**'.
- Copy x5**  transfers a 5-fold enlarged PICT image of the current diffractogramme into the clipboard. A suitable vector graphics programme will rescale the plot (20% reduction) to regain the resolution of common laser- or inkjet printers (360 dpi).
- Attention!** Vectorially transformed diffractogrammes are generally rather complex, because of the resulting large amount of objects (several thousand lines) or very large polygons. In case several diffractogrammes have to be combined, e.g., for a poster or paper the capacity of the machine might be exceeded. Try to simplify the graphics to be exported by using e.g. sections only or by enlarging the step size (via '**Profile : Change Anode/Step Size**').*
- Copy Data** copies the data (counts only) of the currently visible diffractogramme onto the clipboard.
- Paste** without function. Implemented for reasons of compatibility.
- Show All**  shows the entire current diffractogramme with count axis optimally fitted.
- Count Axis...** (or click count scale) opens a dialogue window (Fig. 16) where the count size (vertical axis) to be displayed may be entered. Also, the count display can be converted to **logarithmic** or **square root scale** and/or the count axis inverted. Click '**Set as Default**' to make this setting permanent.



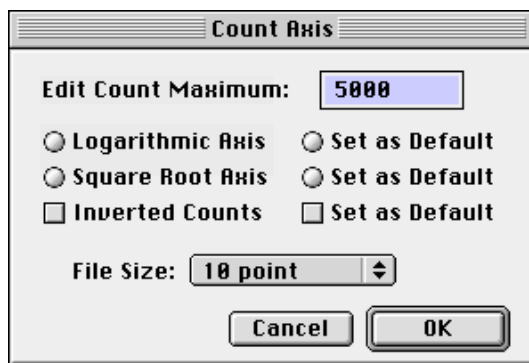


Fig. 16

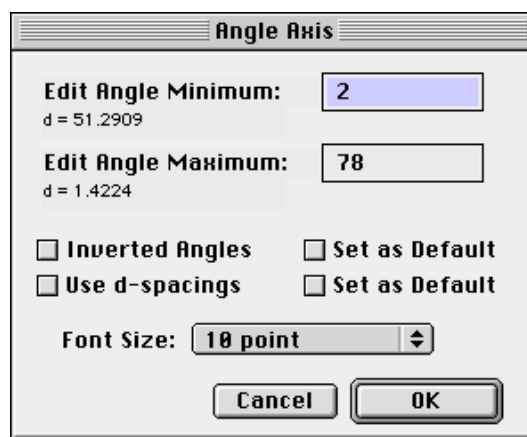


Fig. 17

**Angle Axis...** (or click angle scale) opens the appropriate dialogue window for the horizontal angle axis (Fig. 17). Enter your valid initial and final angle here. For an inversely oriented diagramme, i.e., going from right to left (relevant for users familiar with analogue scripts), click '**Inverted Angles**'. '**Use d-spacings**' switches to an alternative d-value display (in Angstrom). Click '**Set as Default**' for a permanent setting.

**Rename Title...** opens a dialogue window for editing the diffractogramme title. A maximum of 255 characters can be entered.

**Show Grid** applies a grid to the diffractogramme. This will give your hardcopies a professional appearance.

**Show Big Cursor** will mark your mouse position by a hair line cross spanning the entire diffractogramme.

**Show Film Image** activates the option for the display of a Debye-Scherrer-like film strip below the plot. It applies a grayscale of 256 shades, using white for maximum deflection and black for background as reference. A square root scale is applied to intensity.

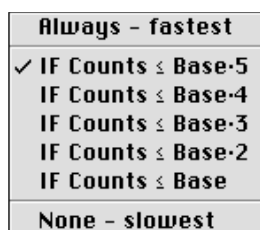


Fig. 18

## Optimized Drawing

is the first of three settings for monitor acceleration for full screen view. Depending on the setting in the submenu shown (Fig. 18) only parts of the counts available in the displayed angle range are redrawn on the monitor, the graphics being simplified this way and the speed for image buildup increased by a factor of 2 to 6. The number of values processed depends on the horizontal pixel count available, that is, for small windows the increase of speed is higher than for large ones. The fastest setting for image buildup (**Always - fastest**) causes for full screen views the unpleasant effect of high and sharp reflexes showing smaller intensities as actually present. This effect can be suppressed in the settings '**If Counts ≤ Base-x**'. The lower the intensity at which MacDiff shall draw optimised lines, the slower will be the buildup speed. '**None - slowest**' will not optimise at all - with the according result. Note this option will not affect print- or clipboard quality.

### **Buffered Drawing**

is used for invisible buffering of the graphics generation in order to draw them very much faster afterwards. Thereby, the absolute speed of graphics generation increases by about 40%. Drawback: we cannot see the graphics buildup. Disabling this setting is worth while for older Macs.

### **Disable Interrupt**

will prevent an interruption in the graphics buildup due to mouse clicks or menu selection. The graphics will be processed considerably faster, drawback being the operator cannot stop the process. Disabling this option is only worth while for very slow older Macs if the diffractogramme buildup takes more than 5 sec. '**Buffered Drawing**' should be turned of as well in this case. After every 100 measuring values an internal check for mouse clicks by the user takes place. With many background programmes running (e.g. hardcopy generation or network activities) the graphics generation happens more or less convulsed.

### **Clipboard...**

shows the clipboard contents. Both data and graphics are indicated. Also shown is the graphics size in pixel and the scaling factor.

## The 'Profile' menu

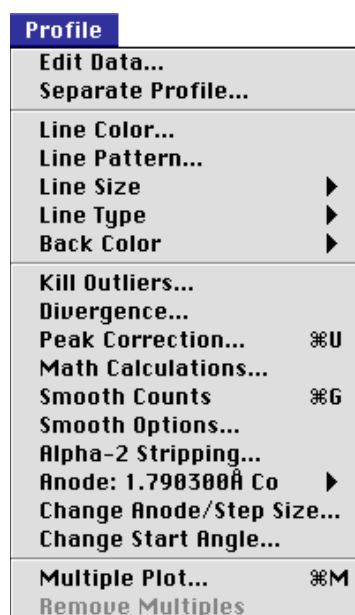


Fig. 19

**Edit Data...** opens a dialogue window where each count and the conjugate background values of the current diffractogramme can be edited (Fig. 20). This way, individual angle ranges can be manipulated in case this is not possible through another function. Navigate using the scroll bar.

Edit Data								
Angle	Counts	Base	Angle	Counts	Base	Angle	Counts	Base
2	215	189	2.2	164	189	2.4	176	173
2.02	215	189	2.22	178	187	2.42	174	171
2.04	215	189	2.24	172	185	2.44	170	169
2.06	215	189	2.26	171	184	2.46	172	168
2.08	215	189	2.28	174	182	2.48	172	166
2.1	215	189	2.3	173	181	2.5	168	165
2.12	215	189	2.32	183	179	2.52	170	163
2.14	215	189	2.34	183	177	2.54	165	161
2.16	168	189	2.36	181	176	2.56	157	160
2.18	161	189	2.38	179	174	2.58	155	158

Fig. 20: The Edit Data window

**Separate...** offers the possibility to reserve a section as basis for a new diffractogramme, optionally in a new window (cmp. Fig. 21)

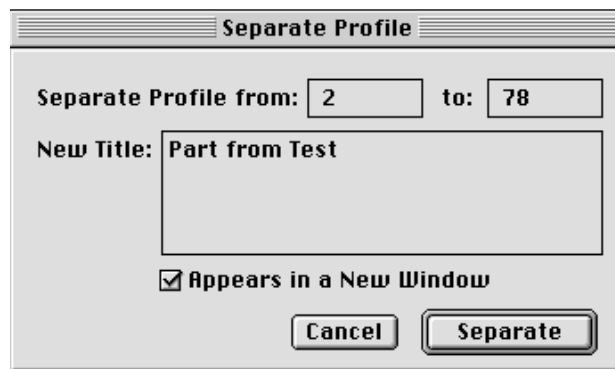


Fig. 21

- Line Color...** this will open a window where the profile line colour may be changed. The upper line is reserved for for the eight system colours or the selection of a deliberate colour (Apple icon). The following lines offer choice between 256 preset colours.
- Line Pattern...** will change the line pattern of the diffractogramme offering from a table of 38 system patterns.
- Line Size** enables a setting of the profile line width between 1 and 5 points. Generally values between 1 and 2 make sense. For small sections (< 400 individual values) the line width will be doubled by default. This option may be turned off in the preference dialogue.
- Line Type** determines by a hierachial menue the way the profile line is to be reproduced.  
 'Only Line' reproduces the profile line only.  
 'Line + Black Dots' reproduces the profile line as well as black measuring dots.  
 'Line + White Dots' reproduces the profile line as well as white measuring dots.  
 'Only Dots' reproduces the measuring points in black only.
- Back Color...** determines the interior and exterior colour of the diffractogramme (**Inside...** - and **Outside...** -submenu), offering the eight standard colours, one custom colour (Apple), alternatively no colour, and 256 further colours.
- Kill Outliers...** is a routine for removal of individual stray values which, for instance, may be caused by short-term power fluctuations. A dialogue window (Fig. 22) will open where a minimum value (in counts) is to be set. Optionally, use 'Use  $\sqrt{\text{Baseline}}$ ' (square root of background). In case this measuring point value will be exceeded by his immediate neighbours it will be handled as stray value and be replaced by the mean of the two neighbours. In version 3.1 and later stray values situated in a peak flank will be removed as well.



Fig. 22

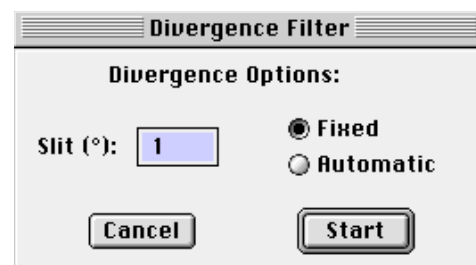


Fig. 23

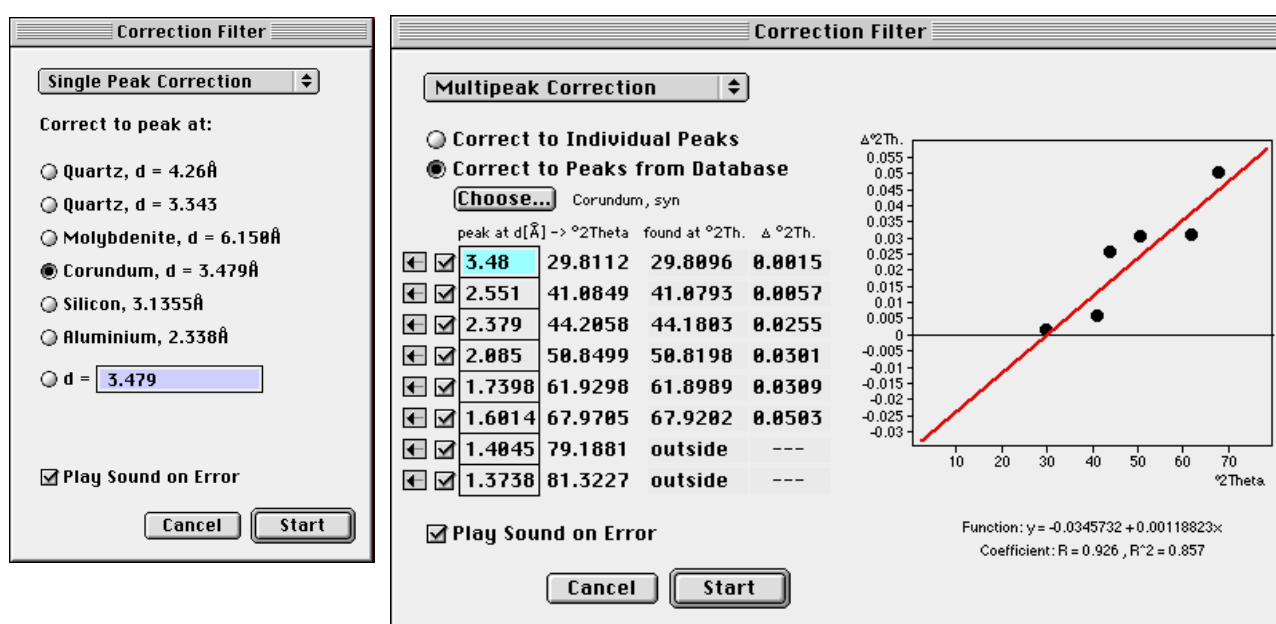
- Divergence...** transforms the individual value counts either to an automated or fixed divergence slit. The procedure (whether '**Fixed**' or '**Automatic**') as well as the slit angle used is set via a dialogue window (Fig. 23). This function may serve to adapt diffractogrammes of differently equipped diffractometres. The appropriate formula is:

$$C_F = S * 0.20268 * C_A / \sin(11.16 + (79 * S / 90)) - 0.19355$$

$C_F$  is the fixed aperture count value,  $C_A$  is the value for automated aperture.  $S$  is the divergence slit angle. The inverse function serves for transformation to automated aperture.

### Peak Correction...

will open either a dialogue box holding settings for correction the diagram using one defined peak (Single Peak Correction, Fig. 24a), or a larger dialogue box for the correction by a regression line, calculated from deviations of the position of several peaks (Multipeak Correction, Fig. 24b). Use the popup menu on top to switch.



Figs. 24 a + b

### Single Peak Correction

changes the initial angle of the diffractogramme, which is being determined by linear adaptation by means of the d-value of a known peak position of a crystalline substance. The dialogue window supplies d-values of some given minerals (Fig. 24a). In case another d-value is required for adaptation it can be entered below. In case the programme finds a peak in the given d-range (if not, an optional warning signal will be sounded, as activated with "Play Sound on Error"), the diffractogramme will be corrected and set onto the exact d-value in the peak maximum.

### Multipeak Correction

Up to eight peak positions (as d-values) can be entered. MacDiff automatically proves, whether these maxima exist in the current diffractogramme and calculates the differences ( $\Delta^{\circ}2\text{Theta}$ ) between their given and their real positions. For calculation of their accurate angle positions the centre method is used (The centre is the maximum point averaged over all counts of the top ten percent of peaks. See chapter Peak analysis). If at least two peaks exist in the diagram, a linear regression equation of type  $y = a + b*x$  will be calculated from deviations. It is possible to remove single peaks out of the regression calculation by unchecking the boxes on left side. Click on the icon and hold down the mouse button to look at a larger

view of each peak maximum and its correct position (signed as blue line) in the diagram.

There are two ways to determine the peaks of your choice for correction. First, you can manually edit d-values of well-known peak maxima by keyboard (**Correct to Individual Peaks**). The other way is to read the highest peaks of a phase from the current peak database (**Correct to Peaks from Database**). For selection, click on **Choose** to open a list of all the phases in the database. Theanafter, the eight highest peaks of the phase will be appear in each of the edit fields, respectively.

### Math Calculations...

produces a dialogue window (Fig. 25) where a formula at choice (for syntax see the separate window '**About Syntax**') or one of the four basic arithmetic operations can be selected to be applied on the measuring values (Simple Math Calculation). In the latter case a separately entered constant links the counts with the operators. Moreover, the profiles can be transformed to a scale of 100, 1,000, or 10,000, or inverted, respectively. Example: to reduce your entire diffractogramme by 100 counts, select the minus sign ('-') and the constant 100.

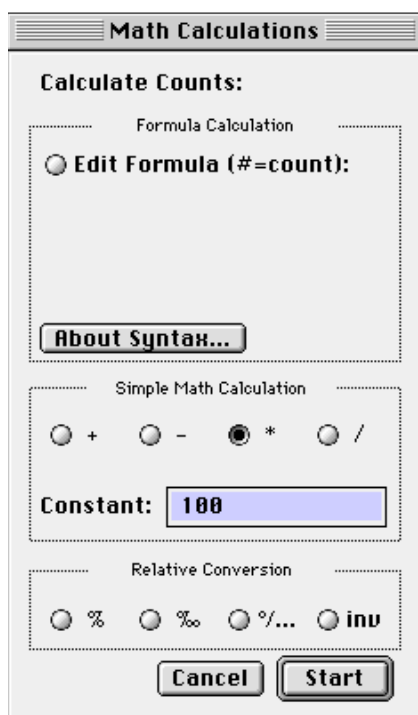


Fig. 25

Calculations via formula generator are particularly CPU intensive, because the formula must be interpreted individually for each operation. When determining your operation, please make sure each resulting count is placed in the range between 0 and 1,000,000.

### Smooth Counts



This will smooth the profile curve according to the filter selected in '**Smooth Options...**'. Reinvoking the function enables further smoothing or return the unsmoothed profile curve.

**Smooth Options...** will open the dialogue shown in Fig. 26. This gives the option between three types of smoothing algorithms. First, there is the 17-term filter based on weighted means available in all previous versions of MacDiff. This algorithm multiplies 8 values before and after each measuring point with a Gauss constant (see factors) and adds them up. This smoothing routine will not shift the diffractogramme, but will cause a slight increase in FWHM.

The second algorithm, smoothing by polynomial fitting, goes back to Savitsky & Golay, 1964. You have choice between a 5-, 7-, 9-, 11-, 15-, and 21-term filter. The higher the number of terms, the stronger will be the resulting smoothing effect. Note the factors being used for each term.

Thirdly, you may smooth by moving averages ('Simple Moving Average') (published in Davis, 1973). There is a choice between 10 filters, based on 3 to 21 terms.

If the counts of the first and last angle of the diagramme are to be smoothed in dependence of the number of selected terms, activate '**Smooth Margins**'. Then, the values are being simply replaced by their common mean.

Confirm '**Smooth Now**' to immediately start smoothing.

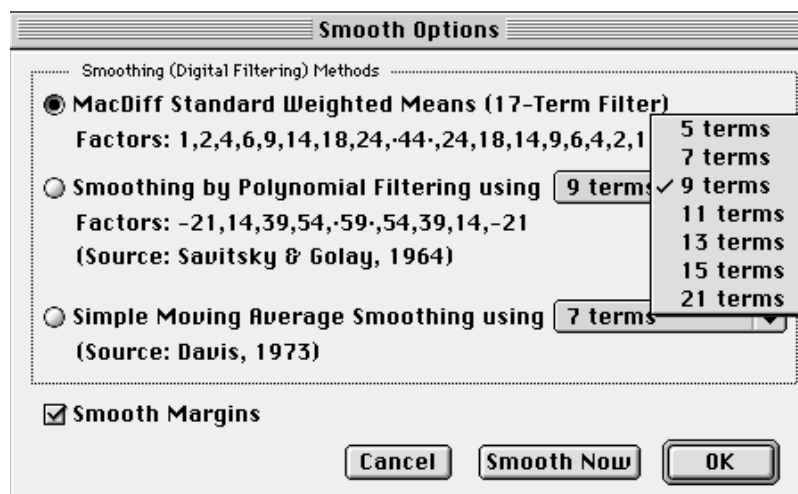


Fig. 26. Smooth Options dialog

### Alpha-2 Stripping

Removes the alpha-2 contribution from the alpha-1 component. This makes sense especially for diffractogrammes in the high angle range (e.g., for Cu-radiation  $> 40^\circ 2\theta$ ). Afterwards, the background has to be recalculated or redrawn. The original algorithm was adopted from a work of Allmann 1994 (after Rachinger). Through a dialogue (Fig. 27) the original alpha-2/alpha-1 intensity ratio (standard 0.5) as well as the wave lengths for alpha-1 and alpha-2 can be entered.

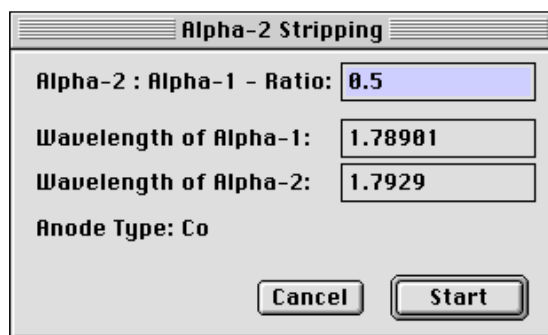


Fig. 27

**Anode:**

Selects the currently used anode material to be activated in the appropriate submenu from 9 anodes offered (Fig. 28). Their wavelength control all peak data to be calculated. Optionally, you may select between alpha-1, alpha-2, or a list resulting from one of the two wavelengths. MacDiff will not check the validity of this association. In case this association repeatedly turns out to be wrong after loading the diffractogramme, change the standard anode in the preference dialogue (see above).

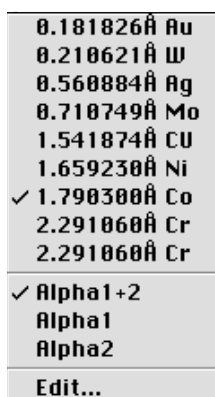


Fig. 28

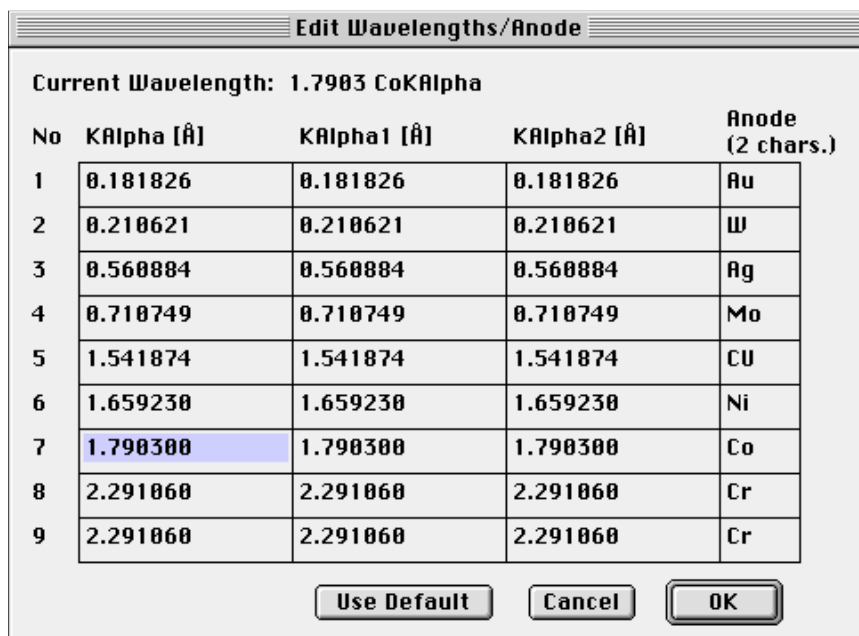


Fig. 29

Use 'Edit...' to enter your own values (Fig. 29) if the available wavelengths are not applicable.

**Change Anode/Step Size...**

This function transforms the angles associated with the measuring values in the diffractogramme onto another anode wavelength or step size, respectively. This is necessary if diffractogrammes of different anodes are to be compared. A dialogue window will appear (Fig. 30) offering on its left-hand side the anodes or wavelengths to be changed and on its right-hand side the desired step sizes to be set by popup menu. A short info line tells about the new angle range as well as the resulting new number of individual values. In case there are more than 16,768 individual values or the permitted angle range of 0 -180° is exceeded, a computation is not possible. The programme transfers the values as accurately as possible and will determine intermediate values if necessary. However, an adaptation of counts to the current anode tube characteristic will not be performed.



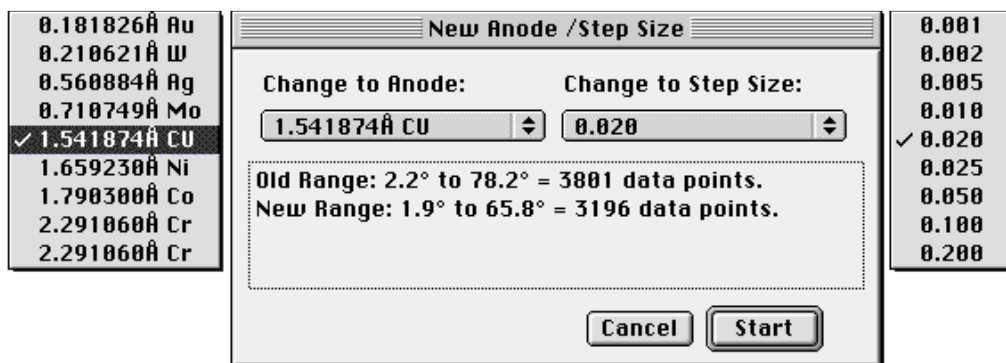


Fig. 30

### Change Start Angle...

This function will change directly the initial angle of the diffractogramme. It is useful if measurement profiles are based on wrong theta angles due to faulty adjustment or incorrect settings of your diffractometer control unit.

### Multiple Diagram...

This function facilitates a superposition of the current diffractogramme (= 'Main Profile') with up to seven further 'multiple' profiles in order to reveal differences or common features. A dialogue window (Fig. 31) will list all files in the current folder in a scroll window on the right hand side, similar to the selection of the session file list. Click up to 7 files from this list in order to select or deselect 'multiple' diagrammes.

By means of 'Get New Folder...' a different folder containing diffractogramme files can be picked via open-selection dialogue.

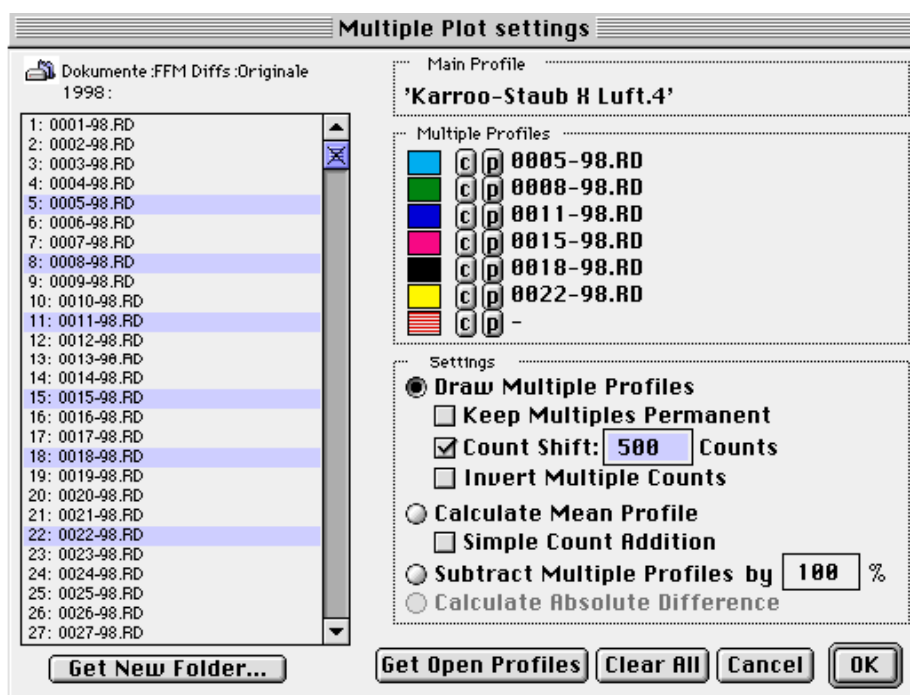


Fig. 31

Clicking the ‘**c**’-icon will open a selection of 8 colours; clicking the ‘**p**’-icon will open the pattern selection window.

‘**Draw multiple profile**’ will draw up the diffractogrammes together (Fig. 32). All actions like mouse cursor values, peak analysis, etc. still relate to the basis diffractogramme. The multiple diagrammes remain intact, until the menue ‘**Remove Multiples**’ is activated.

‘**Keep Multiples Permanent**’ will keep the multiple files preserved even after closing of the window and reloading further files.

The ‘**Count Shift**’ option determines, by how many counts every secondary diffractogramme is to be displayed ‘stacked’ as compared to the one loaded previously.

An active ‘**Invert Multiple Counts**’ will issue secondary count diagrammes inverted.

‘**Calculate Mean Profile**’ will add and average the counts of all diagrammes inclusive the base diagramme. The user has to make sure all profiles cover the same angle range, otherwise parts of the profile will not be averaged correctly.

‘**Subtract Multiple Profiles by ... %**’ will use the profiles of the secondary diffractogrammes to subtract reflexes with identical angle position in the main diagramme by a given percentage (1-100). This computation is done always in relation to the highest peak of the current multiple diagramme. It may serve to make the individual reflexes visible by filtering.

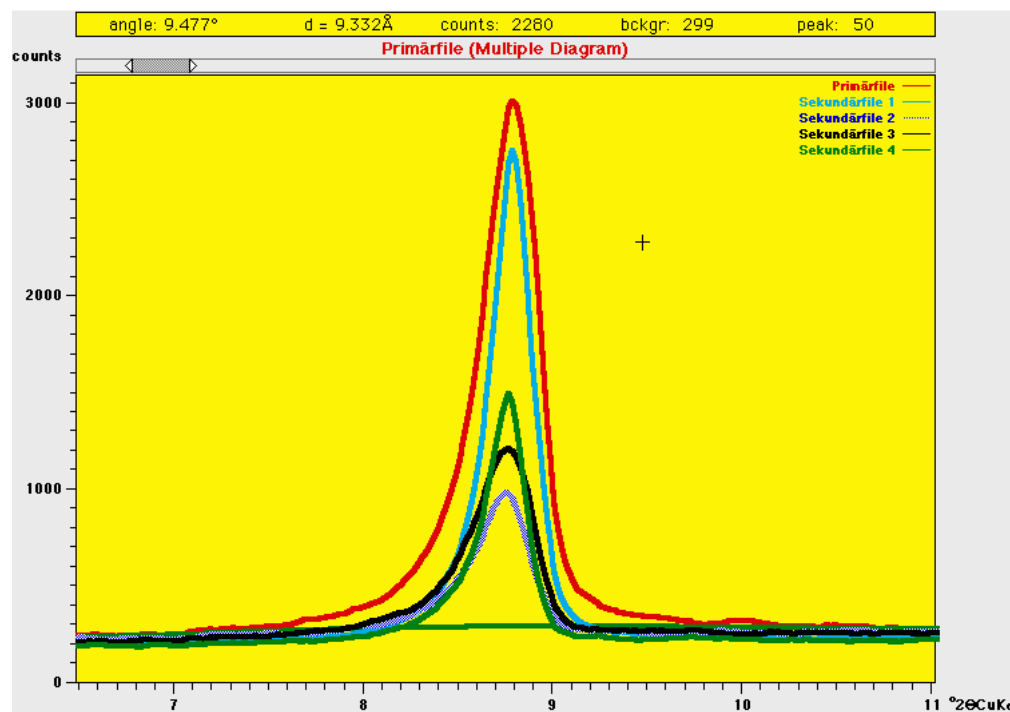


Fig. 32: Multiple diffractogram of a single peak

‘**Calculate Absolute Difference**’ will calculate the absolute count difference between two diffractogrammes.

Click "**Get Open Profiles**" to take up to 7 currently opened diffractogrammes as multiple profiles, if available. This function starts immediately using the current settings.

Use '**Clear All**' to erase the current multiple files from the list.

**Remove Multiples** This menu function is only active if multiple files are active. The function serves to remove them.

## The 'Base' menu



Fig. 33

### Show Base Line

is a toggle function to render the background line visible or invisible respectively. Determine within the preference dialogue, which settings are to be used as default if a diffractogramme file is to be read.

### Subtract Base Line


With this function switched on the background line will be suppressed graphically onto the base (Null counts). This switch can be set per default in the preference dialogue as well.

**Base Line Color...** creates a submenu for the setting of colours in the background menu.

**Base Line Pattern...** serves to set the background line pattern.

**Base Line Size** is used to set the base line width (between 1 and 5 points).

**Base Line Type** determines the base line type (line only, line with black measurement points, line with white measurement points, measurement points only).

**Find Base**  will start up the automatic background search routine with the settings put down in 'Find Base Options...'. It is based on a very simple adaptation (modified after Sonneveld and Visser, J. Appl. Cryst., vol.8,1975 and Allmann, Clausthaler Tekt. Hefte, 29, 1994). First, every n-th angle of the diffractogramme will be averaged (the value for n can be set). Then each resulting term will be compared repeatedly with its neighbours and reduced to the mean of these values, in case this value is higher. The size of n and the number of iterations determines the quality of background adaptation. In general a value of n = 10 to 30 makes sense and 20-30 repetitions are sufficient for the generation of satisfactory results for diffractogrammes with sharp reflexes.


**Find Base Options...** opens a dialogue window (Fig. 34) for the settings of the automatic background search routine. Set an even value for n in the top line, i.e., for 10 every tenth value will be employed for computation. The higher the value, the straighter the adaptation. Moreover, the number of the iterations explained above can be given for the entire 2-theta range. Default is 30. It is also possible to perform additional iterations in 3 angle ranges of choice in order to obtain better adaptations, e.g., for broad reflexes, e.g., in the clay mineral line range, i.e., between 2 and 15° (= default).

'Find Now' will perform the background adaptation directly.

Fig. 34

Fig. 35

### Manipulate Base

or alternatively, click the  -button to start the manual setting of the background. This is facilitated by means of 'clicking in' up to 200 fix points via mouse at the selected spots of the diffractogramme. If the cursor displays the  $\times$  -symbol, the fix point will be inserted at the spot the click took place. If the cursor displays the  $\sphericalangle$  -symbol the fix point will be placed on the height of the counts at the angle position. Switch between the two modi by hitting the keys 'L' (line) or 'N' (normal). The order of entry positions is deliberate. 'OK' will cause a recalculation of the background line between the support points of the smallest and largest angle according to the points available in between.


**Smooth Base** causes a smoothing of the background line the same way as this can be applied to the profile lines ("Profile : Smooth Counts").

**Noise Reduction...** serves for background reduction. Within the dialogue window (Fig. 35), set a percentage on how far the background is to be suppressed. Values between 10 and 100% are admissible. All counts below the background line will be reduced by the percentage set. Counts above the background will be raised proportionally. This routine will not change the peak proportions.

## The 'Analyse' menu

Analyse	
Start Analysis	⌘Y
Analysis Program...	
Zoom Peak Area	
Peak Info...	⌘T
Show Report...	⌘R
Save Report...	
Remove Report	
Peak Search...	⌘E
Identify...	⌘J
Peak Database...	⌘B
Marker Lines...	
Comment Peak...	
FWHM Calibration...	
Peak Fit Settings...	

Fig. 36

**Start Analysis**  Once this menu function is active the analysis programme is in memory (see the menu 'Analysis Program...') and ready to be started. Then the lines of the diffractogram placed in the foreground and predetermined in the analysis programme will be looked for and, if existing, be measured. The peak analysis window on the right hand side (Fig. 37) is, for an active programme, extended by a 'Stop'-button for cancelling the analysis, by a 'Remove' button for removing the data from report list, and by two '<<<<' and '>>>>' -buttons (forward/backward) setting the direction in which the analysis programme is to work. Moreover, the phase substance name set in the analysis programme will be shown ('Ident:...') providing it is identified in the programme list.

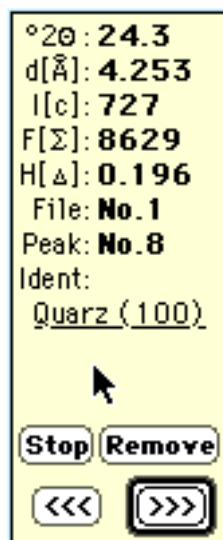


Fig. 37: Peak data display as shown by use of an analysis program

The peak analysis performs an exact division of data in the report table, according to the ordering of the analysis programme. However, this can only take place if no report table was set up before the first start of the analysis programme! Avoid double clicking on reflexes or delete existing entries via 'Analyse : Remove Report' before starting a larger analysis project.

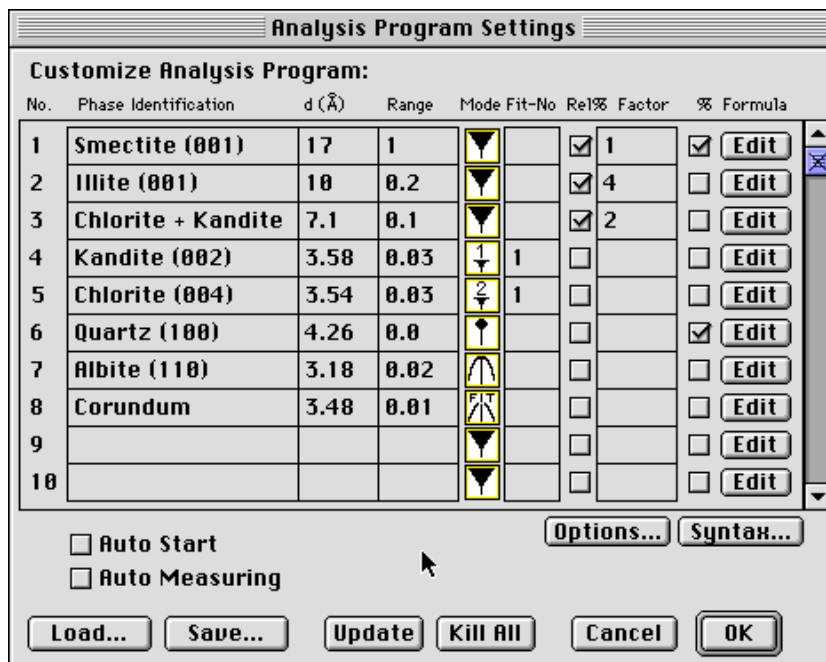


Fig. 38: Analysis program dialogue box

### Analysis Program...

This menu function opens a dialogue window for the setting and administration of analysis programmes (Fig. 38). Up to 32 crystalline substances can be entered (name, d-value and range). The table is scrollable.

*Attention! It is advisable not to enter all 32 substances, as experience shows some lines not identified here will be measured manually during analysis, and which would have no space left.*

The further column entries are optional. 'Mode' will change the destination mode of the peaks via click, i.e., ▼ (peak maximum), ∩ (peak centre), ▲ (exactly at d-value), and ∩<sup>fit</sup> (peak fitting), see section 'Peak Analysis'. The next 'Fit-No' column determines peaks to be fitted together (multifit) by entering a common peak number.

The column 'Rel%' determines relative contributions (in percent) between deliberate peaks to be saved in the report file. 'Options...' determines, if these relative contributions relate to intensities or areas. Moreover, 'Factor' accepts a multiplier to be included in the calculations of the relative contributions (e.g., Biscaye factors for clay mineral assemblages).

The last column accepts a formula to be computed automatically during peak analysis. A peak value may be integrated by hash symbols '#' into the formula, such that:

#peak number : peak data type#

with peak data type 0 = peak position (Angstrom), 1 = intensity (counts), 2 = area, and 3 = FWHM. Omit peak number to make current peak number valid.

Examples:

#1:2# - area under peak no. 1  
 #5:0# - peak position of peak under no. 5  
 #1# - intensity of current peak  
 #2#, ## oder # - area of current peak

See 'Syntax...' for more formula entry matters.

'Auto Start' will automatically start the analysis programme after loading a diffractogramme.



'Auto Measuring' automatically measures all lines without means of user interaction. *Use this function only when sure the analysis will proceed faultlessly.*


'Load' will read an existing analysis programme and 'Save' will store it.

*The latest saved programme will be default read by MacDiff when starting. Note you can set any existing analysis programme as default through 'File : Preferences'.*

"Update" removes empty rows in the table.

'Kill All' clears the analysis programme window.

**Zoom Peak Area**  or  is an on-off switch for full view of a peak during peak analysis. With menu function switched on the diffractogramme will be zoomed onto the peak range. This option should always be turned on if you are not sure your measurement proceeds faultlessly.

**Peak Info...**  displays a list of some additional data about the peak during peak analysis (Fig. 39), such as e.g. left and right half of peak, asymmetry index, various peak widths, as peak base width, integral width, and background height, valley/peak ratio (e.g. for smectites), etc.

The peak info window is auto-updating and therefore it needs not be closed since it can operate in the background. 'Print...' or 'Save...' will print or save the list. If certain data are to be saved permanently in the report table click the appropriate line; in this case the grey buttons () will turn to colour (). Reclinking will remove the value from the list. These additional data will be attached to the report table unsorted; therefore the user should check their ordering. An alphanumeric identification is entered in the first column and the actual value goes into the second column.

If the analysis was performed by means of peak fit the peak info window will contain a second page displaying the parameter values of the profile function as well as the residuum and chi-square (Fig. 40). Clicking the 'Profile function' line will save these data.

*Avoid excessive cluttering of the report table with extra peak data as this will aggravate an interpretation. About 30 additional peak data can be saved for every profile.*



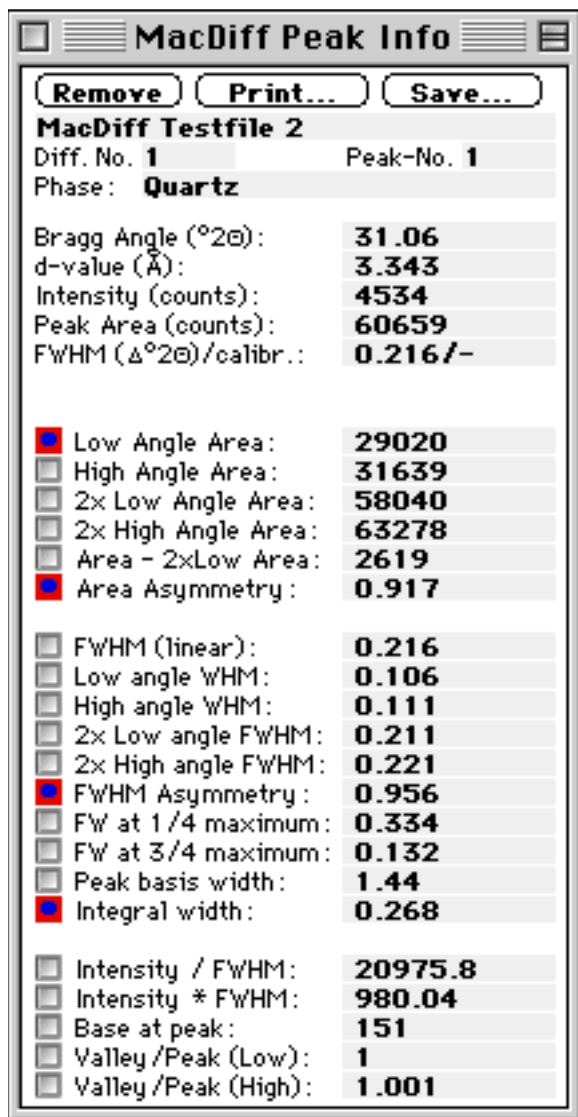


Fig. 39

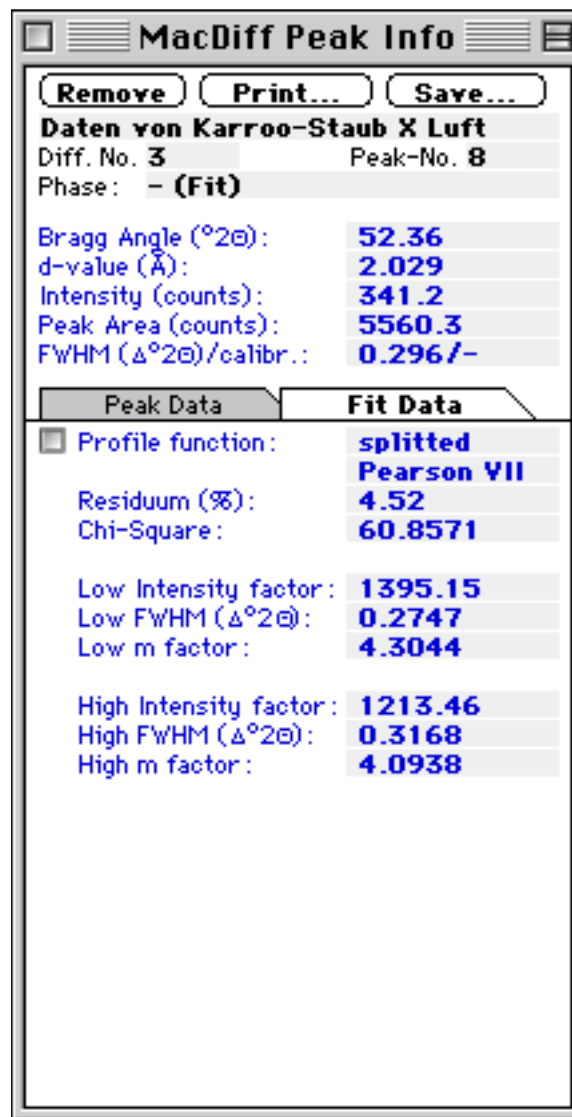


Fig. 40

**Show Report...**



will open a window which administers the data of the report table (Fig. 41). It is partitioned into pages showing the data of the individual profile. This window is self-adjusting too and can operate in the background.

Two arrow buttons navigate through all available data sheets of the individual diffractogrammes already measured. Additional peak data saved via 'Peak Info' window can be viewed by clicking the **I** button. 'Kill' will erase individual active peak entries. The program will move up the values following below (not the data from the analysis programme started initially) if no other peak of the same affiliation exists in the entire line. Moreover, there are buttons for erasing, printing or copying every individual data list ('Kill All', 'Print', 'Copy').

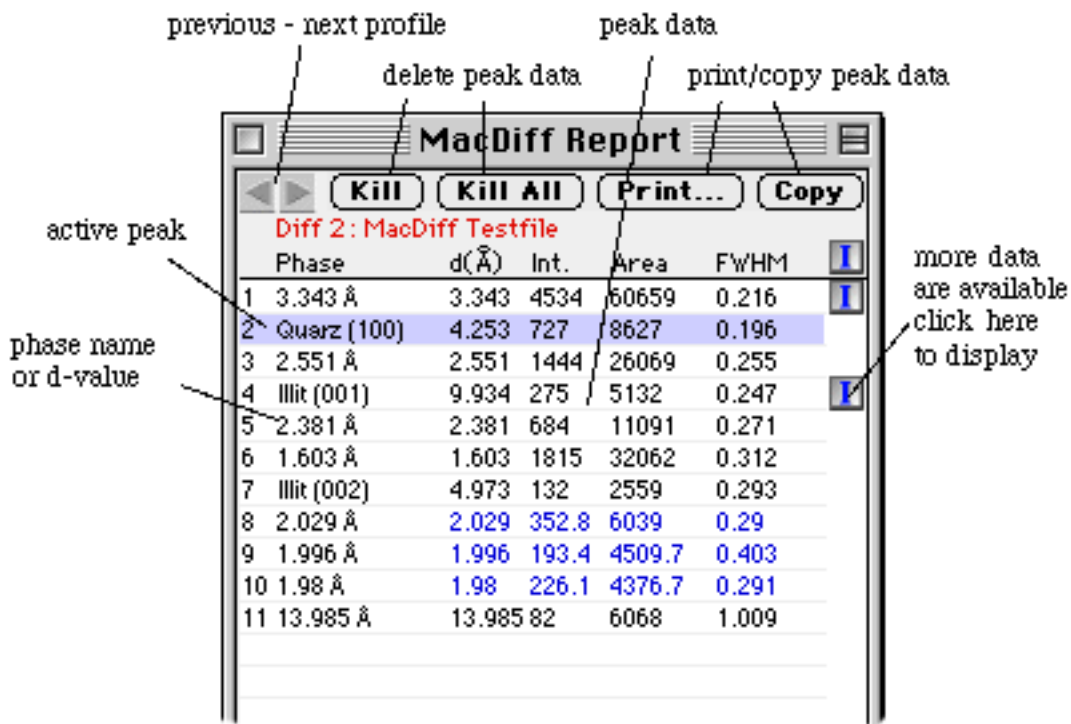


Fig. 41: The report-table

### Save Report...

opens a dialogue window accepting presettings for saving the report-table (Fig. 42). These settings relate to all diffractogrammes measured. 'Include Header' on the left-hand side determines, if column headers (substance names, d-values, data type) are to be saved. 'Append on existing File' determines, if the data are to be appended onto an existing report file (which is to be selected via 'Save As...'). Further, the 'Decimal Separator' - comma or dot (period) - may be selected, as some programmes are sensitive in this matter. Moreover it can be set which spreadsheet programme (different versions of EXCEL, Word or Kaleidagraph) is to be linked with the file, to be started by double clicking in the Finder. 'Save" 2-Thetas instead of Å' will save 2-theta angles instead of d-values.

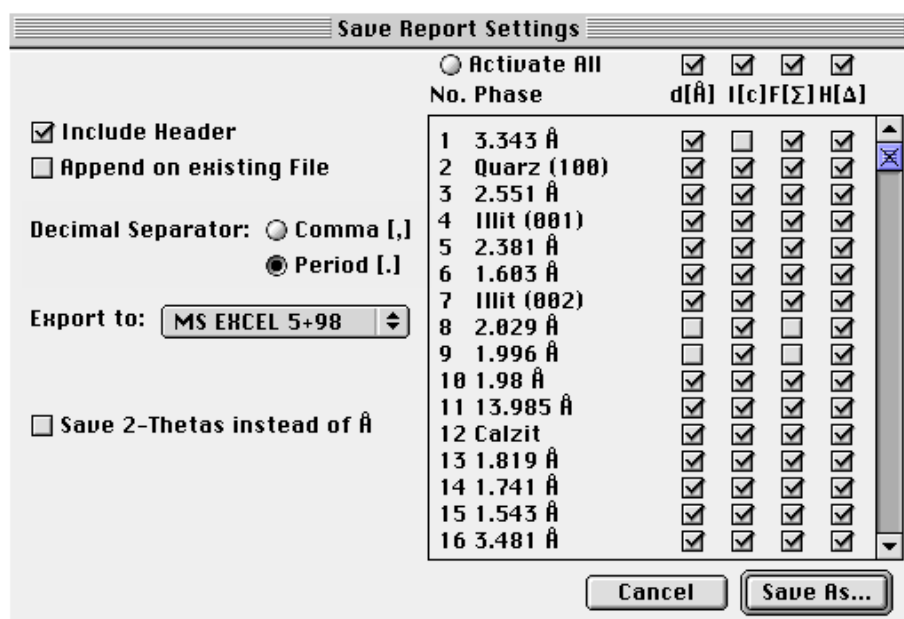


Fig. 42: Saving the report-table.

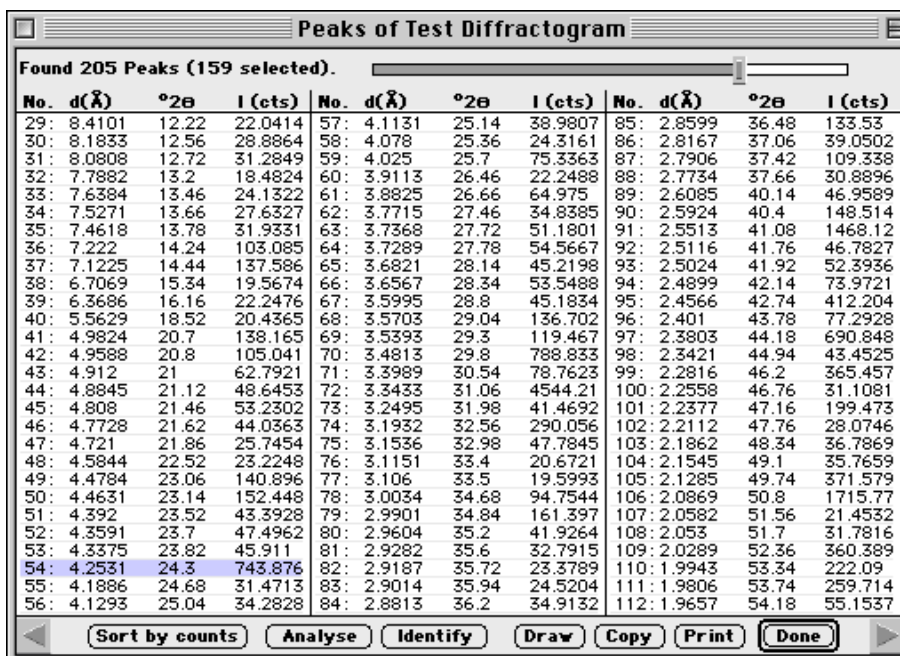
The right hand side facilitates a columnwise selection which of the four peak data ( $d[\text{Å}] = d$  value,  $I[\text{c}] =$  intensity,  $F[\Sigma] =$  area,  $H[\Delta] =$  half height width) contained in the report-table are to be saved. Often, only part of the data is required later, so the table can be reduced significantly. Clicking the buttons placed above will include or exclude entire groups of same peak elements (e.g. all half widths) in or from the list.

**Remove Report** will delete the entire report-table.

**Peak Search...** 

starts a routine calculating all reflexes of the current diffractogram using the given settings (minimal peak range and -height, see '**Preferences...**') by executing the second derivate method. These data are listed in a table (d-value, 2-theta angle and intensity, cts=counts, Fig. 43). Use the mouse to activate one of the maximal 300 reflexes. Use the arrow keys in order to navigate through a list with more than 84 entries.


You can select/deselect peaks of lower intensities by dragging the small control button.



No.	d(Å)	°2θ	I (cts)	No.	d(Å)	°2θ	I (cts)	No.	d(Å)	°2θ	I (cts)
29:	8.4101	12.22	22.0414	57:	4.1131	25.14	38.9807	85:	2.8599	36.48	133.53
30:	8.1833	12.56	28.8864	58:	4.078	25.36	24.3161	86:	2.8167	37.06	39.0502
31:	8.0808	12.72	31.2849	59:	4.025	25.7	75.3363	87:	2.7906	37.42	109.338
32:	7.7882	13.2	18.4824	60:	3.9113	26.46	22.2488	88:	2.7734	37.66	30.8896
33:	7.6384	13.46	24.1322	61:	3.8825	26.66	64.975	89:	2.6085	40.14	46.9589
34:	7.5271	13.66	27.6327	62:	3.7715	27.46	34.8385	90:	2.5924	40.4	148.514
35:	7.4618	13.78	31.9331	63:	3.7368	27.72	51.1801	91:	2.5513	41.08	1468.12
36:	7.222	14.24	103.085	64:	3.7289	27.78	54.5667	92:	2.5116	41.76	46.7827
37:	7.1225	14.44	137.586	65:	3.6821	28.14	45.2198	93:	2.5024	41.92	52.3936
38:	6.7069	15.34	19.5674	66:	3.6567	28.34	53.5488	94:	2.4899	42.14	73.9721
39:	6.3686	16.16	22.2476	67:	3.5995	28.8	45.1834	95:	2.4566	42.74	412.204
40:	5.5629	18.52	20.4365	68:	3.5703	29.04	136.702	96:	2.401	43.78	77.2928
41:	4.9824	20.7	138.165	69:	3.5393	29.3	119.467	97:	2.3803	44.18	690.848
42:	4.9588	20.8	105.041	70:	3.4813	29.8	788.833	98:	2.3421	44.94	43.4525
43:	4.912	21	62.7921	71:	3.3989	30.54	78.7623	99:	2.2816	46.2	365.457
44:	4.8845	21.12	48.6453	72:	3.3433	31.06	4544.21	100:	2.2558	46.76	31.1081
45:	4.808	21.46	53.2302	73:	3.2495	31.98	41.4692	101:	2.2377	47.16	199.473
46:	4.7728	21.62	44.0363	74:	3.1932	32.56	290.056	102:	2.2112	47.76	28.0746
47:	4.721	21.86	25.7454	75:	3.1536	32.98	47.7845	103:	2.1862	48.34	36.7869
48:	4.5844	22.52	23.2248	76:	3.1151	33.4	20.6721	104:	2.1545	49.1	35.7659
49:	4.4784	23.06	140.896	77:	3.106	33.5	19.5993	105:	2.1285	49.74	371.579
50:	4.4631	23.14	152.448	78:	3.0034	34.68	94.7544	106:	2.0869	50.8	1715.77
51:	4.392	23.52	43.3928	79:	2.9901	34.84	161.397	107:	2.0582	51.56	21.4532
52:	4.3591	23.7	47.4962	80:	2.9604	35.2	41.9264	108:	2.053	51.7	31.7816
53:	4.3375	23.82	45.911	81:	2.9282	35.6	32.7915	109:	2.0289	52.36	360.389
54:	4.2531	24.3	743.876	82:	2.9187	35.72	23.3789	110:	1.9943	53.34	222.09
55:	4.1886	24.68	31.4713	83:	2.9014	35.94	24.5204	111:	1.9806	53.74	259.714
56:	4.1293	25.04	34.2828	84:	2.8813	36.2	34.9132	112:	1.9657	54.18	55.1537

Fig. 43: Peak search result window.

- '**Sort by Counts**' switches to the list as shows the peaks sorted after their intensities.
- '**Analyse**' will analyse the active peak as would be done by direct clicking within the diagramme. The analysis will take place exactly at the angle listed here.
- '**Identify**' will also start the analysis of the active peak, however, the same-name routine of the next menu function will proceed subsequently.
- Clicking '**Draw**' will mark the computed lines in the diagramme by blue lines and the associated numbers.
- The table is printable ('**Print**') or can be placed in the clipboard ('**Copy**').

**Identify...** 

is a routine for explorative peak identification, supporting an identification of the reflex currently being analysed. A window will open with a list of peaks appearing in the neighboring range of the analysed reflex (Peak Identify, Fig. 45) and ordered by descending d-values. Basis for this list is the peak database currently

linked with MacDiff (see menu function **'Analyse : Peak database...'**). In case no database is invoked yet, MacDiff finds the one used last and automatically loads it. In case this is not possible, pick a database (Fig. 44). This one should be installed in the folder 'MacDiff' of the preference folder of the current system. In case of problems a manual activation of the database from any deliberate place can be done (**'Search in Another Folder'**).

*Please note: Peak databases always consist of three files which must not be separated!*

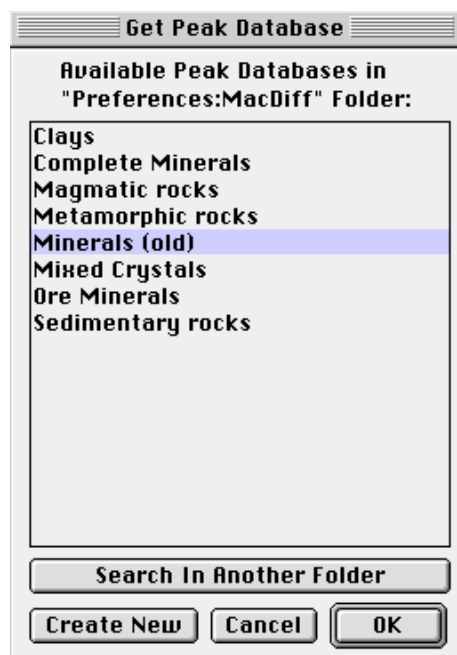


Fig. 44

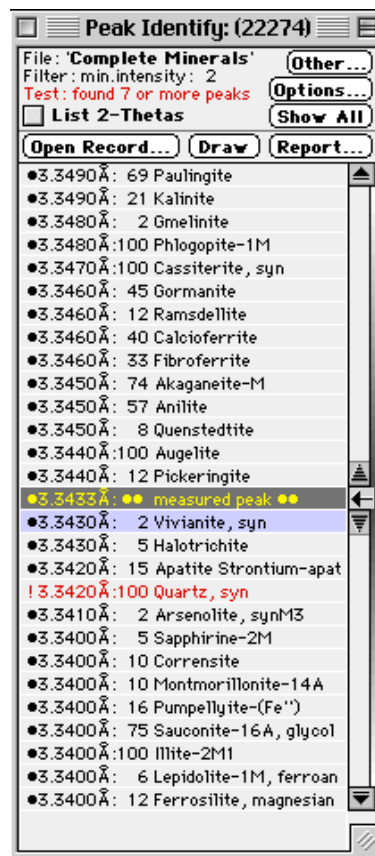



Fig. 45: Peak Identify window

The peak identify list is displayed on a self-updating window adjustable in size, which can operate in the background as well. The list is partitioned into two independent parts. The first value represents the d-value and the second one the relative intensity. Finally, there is the phase identification. On top all high d-value reflexes are listed, on the bottom those with low d-values, separated by the current 'measured peak'. Navigate through the two lists via scroll bars. Click the -icon to retrieve the list display as first viewed.

Values marked by '•' or displayed in black are in the minimum d-value range of the peak measured, therefore they are the most likely ones for identification. The other entries placed outside are in dark grey.

If a peak is activated by mouse click **'Open Record...'** will give access to the data set containing the peak (see **'Peak Database'**). Click **'Draw'** to display the spectrum of this associated data set by lines in the current diagramme (Fig. 51). **'Record'** will adopt the name of the identified peak into the report list.

## Options...

this function opens a dialogue window for the option, whether only reflexes of a minimum intensity are to be displayed ('**List peaks with relative intensities ...**') or the number of the currently highest reflexes in a data set ("**List the ... strongest peak set in record.**"). Therefore, filtered lists contain only higher and more significant reflexes, enabling a substantially easier peak identification. In certain circumstances this will cause a somewhat longer scan time. An active '**Use filter in Drawings**' will only display the filtered reflexes in the diffractogramme as lines.

There is one further filter option. '**Test in Profile with the strongest ... peaks**' permits to set the count of the currently strongest lines in the database in the current phase. When listing the neighbouring phases of the measured line the selected peak number in the diagramme will be checked for presence. The peak positions in the profile are found by the the same 2nd derivate method as used in the **Peak Search** routine. In case of presence of all the choosed number of strongest peaks the phase will be marked **in red**.

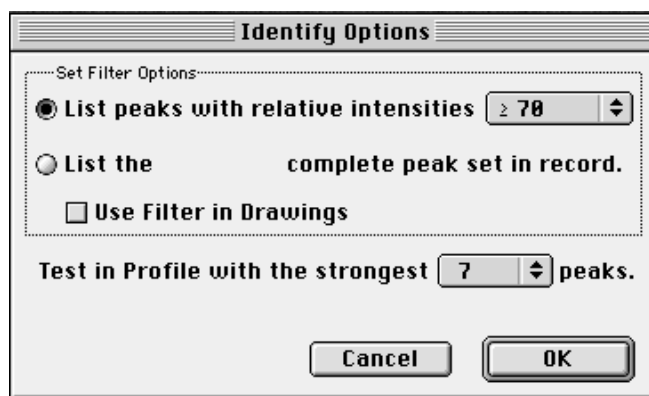


Fig. 46

'**Show All**' will turn off the filtermaking all lines listed in the database reappear.

Click '**List 2-thetas**' to display the 2-theta values instead of the corresponding d-values.

'**Other...**' opens another peak database (Fig. 44).

## Peak Database...

opens a dialogue window which administers the data sets (records) of the current peak database (Fig. 47). In case no database has been invoked yet a selection window, as depicted in Fig. 44, will show up, scanning the available databases in the folder 'MacDiff' of the preference folder in the current system. In case no database name is listed here the database may be activated by '**Search in Another Folder**' from any deliberate place. Also, '**Create New**' will create a new database.

**Note, a peak database consists of three files:** The first carries the name of the database and administers the individual data sets. The second file with the suffix 'peaks' is closely linked to the first one and contains in compressed form the entries for the saved reflexes. The third file with the suffix 'index' contains all reflexes in the ordering of their d-values and is used for the 'Identify' routine. It can be updated by the 'Update' function in case of changes in the database. All files must be placed in the same folder, usually the folder 'MacDiff' in the preference

folder of the current system. **Never separate the three linked database files as they are useless individually!**


A peak database may contain up to 2048 data sets with entries of maximally 32,766 peaks. An individual data set may consist of a maximum of 254 reflexes. 24 peaks may be displayed simultaneously. Use the scroll bars to navigate through the entire database.

The record layout is similar to that of a JCPDS/PDF card. Below the record no. is an entry field for the crystal name of the data set (max. 32 characters). Underneath a reference number may be entered (16 characters) as e.g. the JCPDS card number. 'Comment' accepts any deliberate entry of a length of 64 characters, e.g. identifying the material. The crystal system of the material may be set as well. Finally, there is space for the chemical formula of the crystal as well (64 characters).

**Peak Database: Complete Minerals**

Record No. 397 of 532      l o c k e d !      File: Complete Minerals

Quartz, syn      Sample from the Glass Section at NBS, Gaithersburg,      **Get Other Database...**

#Ref.No: JCPDS 33-1161      Comment:      **Hexagonal** 

Formula: SiO2

No.	d Å	I/100	hkl	No.	d Å	I/100	hkl	No.	d Å	I/100	hkl
1	4.257	22	100	9	1.8021	1	003	17	1.3752	7	203
2	3.342	100	101	10	1.6719	4	202	18	1.3718	8	301
3	2.457	8	110	11	1.6591	2	103	19	1.288	2	104
4	2.282	8	102	12	1.6082	1	210	20	1.2558	2	302
5	2.237	4	111	13	1.5418	9	211	21	1.2285	1	220
6	2.127	6	200	14	1.4536	1	113	22	1.1999	2	213
7	1.9792	4	201	15	1.4189	1	300	23	1.1978	1	221
8	1.8179	14	112	16	1.382	6	212	24	1.1843	3	114

Kill on Update
  Lock this Record
  Show 2°Thetas
  Auto Update

Fig. 47: Peak database dialogue (shown here: Alpha Quartz)

Note that all numbers entered here will be displayed in later lists and graphics subscripted and reduced, except there is an asterisk '\*' behind the number, as e.g. '4\*H<sub>2</sub>O'. The '+' or '-' sign stands for valences and is always superscripted, e.g. Fe<sup>++</sup> (do not use 'Fe2+').

As with the JCPDS cards each reflex is identified by its position (d in Angstrom), by its intensity (I/100) and by its lattice indices (hkl). For the d-values maximally 6 characters may be entered. The intensity field accepts only the numbers from 1 to 100, that is, no further symbols such as '<'. The field for the lattice indices may contain up to 16 characters. A minus sign in preceding a number will cause an overbar to appear above this number in all later lines and graphics, as is common with hkl indices.

An asterisk '\*' in the indices field allows to set a d-value range of variation, which will be depicted as rectangle in the diffractogramme. This variation range begins with the d-value of the line marked by '\*' and ends with the following d-value. This makes sense in case of mixed crystals and their variable d-values.

'Get other Database...' will load or generate a new peak database (Fig. 44), see

above.

Click **'Create New Record'** to enter new data sets.

**'Append...'** will combine two peak databases to a common one.

**'Kill on Update'** is used to delete a data set. The next update will remove the set from the database (see below).

**'Lock this Record'** will protect the current data set from accidental erasure. This goes for all databases offered by MacDiff.

**'Show 2°Thetas'** displays angles instead of d-values, based on the current anode characteristic.

**'Auto Update'** will invoke an automatic update upon closure of the database (see below).

**'Print Card...'** will print the current data set with all (even currently not visible) peak data. **'Copy Card'** will place it as an ASCII table in the clipboard.

**'Generate'** will create artificial (synthetic) diffractogrammes from the current data set. A dialogue window will appear (Fig. 48) containing several settings such as profile function, maximal counts, background height, half width, step size, anode type, etc. Clicking 'Generate' will cause a new synthetic diffractogramme with the lines of the current data set to be calculated.

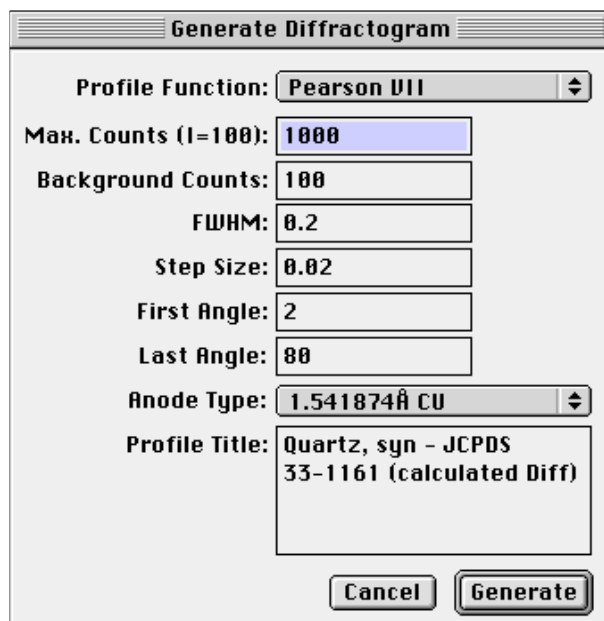


Fig. 48

**'Search...'** causes a skip to a desired data set containing a character string to be entered. This function is case-sensitive. A similar purpose serves **'Record List...'**: Behind this function is a selection list of all records present in the database in ascending order (Fig. 49).

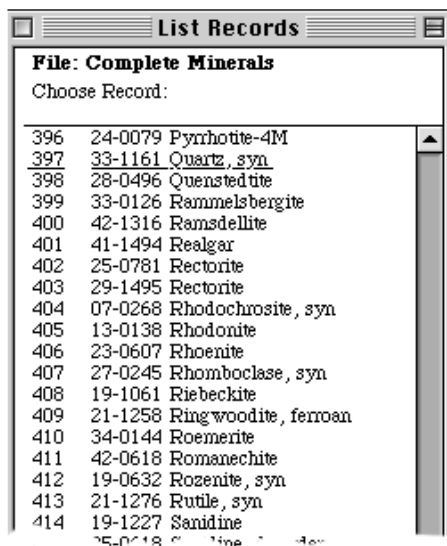


Fig. 49

'Import...' is used to import new datasets into the current peak database coming from the PDF (powder diffraction file) database. Go to PDF database retrieval software and enter all combined cards into a file of NBS\*AIDS83 format. Then click 'Import...' in the database window of MacDiff. A dialogue will appear (Fig. 50) offering several options for filtering the PDF data (read all data, read only hkls of a certain minimum intensity, read only hkls in a certain d-value range, read only a certain number of hkls per card). Then click 'Import...' again and select and read the PDF-NBS file. After that the database should be updated in order to be used for the peak identify routine.

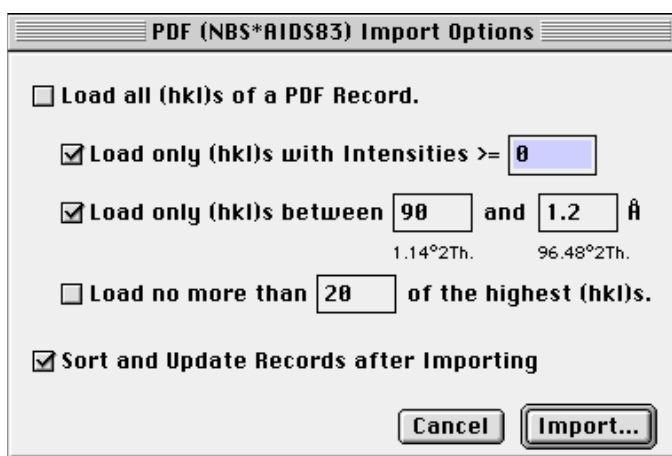


Fig. 50

'Update' will perform several tasks:

- 1) removal of all data sets marked as deleted;
- 2) alphabetic ordering of the list by phase identificatins;
- 3) rebuilding the index file containing a sorted list of all peaks.

An update of a larger database (> 200 records) may take several seconds.



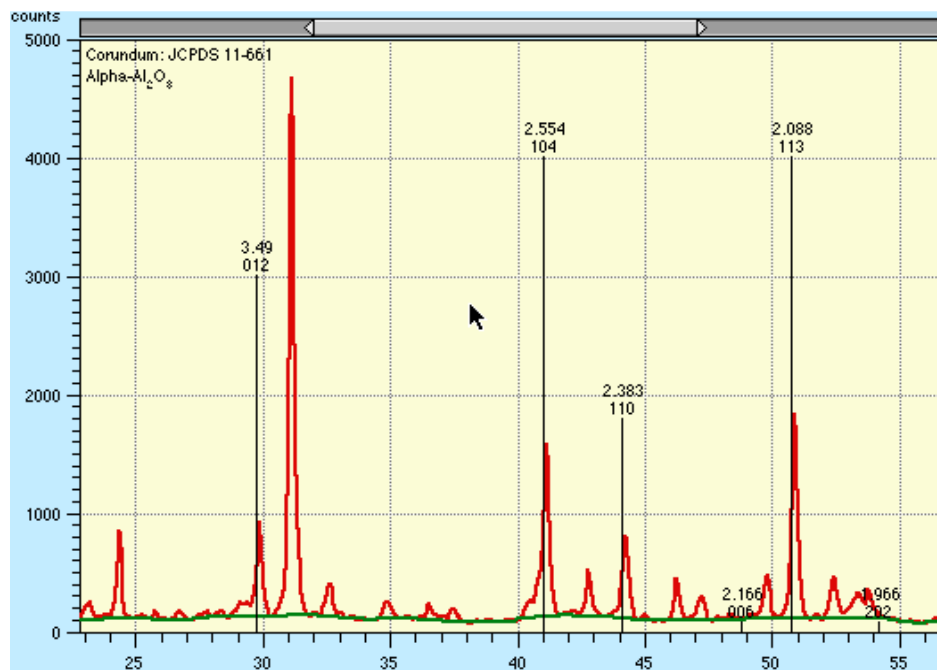


Fig. 51: Comparison of measured profile with given line reflexes from a peak database after plotting via **'Draw'**. Here: detection of corundum.

**'Draw'** will plot a line spectrum of the current data set onto the diffractogram displayed on top (see Fig. 51). Depending on the settings in the menu function **'Marker Lines...'** existing lines can be completed or replaced. Comparison with the given reflexes facilitates a very fast identification of the measured peaks. The line height is determined by the relative intensity and the maximal count size in the measurement profile. Every line is marked by the d-value (or 2-theta value) and its hkl-indices (may be deactivated in **'Marker Lines...'** dialogue).

If you click on a line of a phase in the legend list on the left side, it will be cancelled.

## Marker Lines



Invoking this routine will facilitate the administration of line markers present in the current diffractogram. They can be removed individually or as a whole. It is possible to display up to 255 lines of 7 different phases in a diffractogram. Further, their colour and pattern can be fixed (see Fig. 52). Moreover, the option, if a new line spectrum to be drawn should replace one already present, is offered (**'No multiple Marker Sets'**). It can further be set, if the lines are to be labeled with hkl and/or d-values (**'Show d-value'**, **'Show hkl'**). Furthermore, it can be set if the line marker height is to be fitted according to the highest peak of the profile or by percent to the maximal counts of the entire or current window (possibly zoomed). Finally, enable **"Keep Peak Markers ..."** to preserve the current used markers for new loaded diffractograms.

If you want to remove peak search lines or peak comments (see next chapter), click off the appropriate boxes.

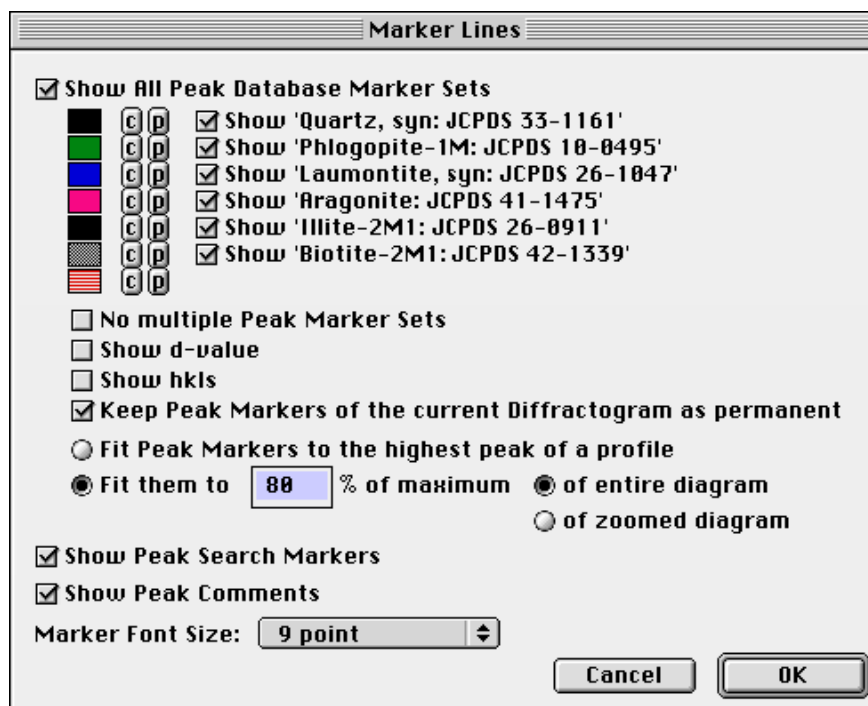


Fig. 52

### Peak Comment...



This menu function is used for commenting an analysed peak (Fig. 53). Such a comment will appear at the top of the measured peak in all diffractogramme issues. Turn on '**Keep comments permanent**' to make sure the comments are preserved even after reading in new diffractogrammes. To remove the comments, open the '**Marker Lines**' dialogue and turn off '**Show Peak Comments**'.

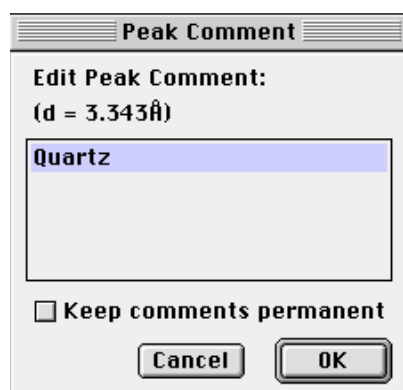



Fig. 53

### FWHM Calibration...

With this routine the FWHM (Full Width at Half Maximum) of different labs and diffractometers may be automatically calibrated. A window opens (Fig. 54) accepting entry of up to 15 value pairs of FWHM of the same samples. The first value originates from the instrumentation (**Lab**), the second one is a measurement from a reference lab or a reference device, respectively (**Standard**). Present value pairs are automatically transformed into a graphic. Further, the regression line and the correlation coefficient are computed. For testing purposes deliberate correction values may be computed under '**Test Lab FWHM**'. With '**Peak (Å)**' the reflex under question is set. The number-labeled radio buttons enable to identify further (five in total) reflexes for calibration. If a peak with this d-value within the tolerance range of the minimum peak width is found during peak analysis, the measured FWHM is

transformed automatically using the regression function and displayed as extra measurement. The peak data display on the monitor identifies this value by '\*cal'. In the report list calibrated values will appear as well (click on the -symbol). In saved report-tables an extra column is reserved for calibrated half widths.

'Options' will integrate into the table three internationally used standard series of illite and chlorite (Fig. 55).

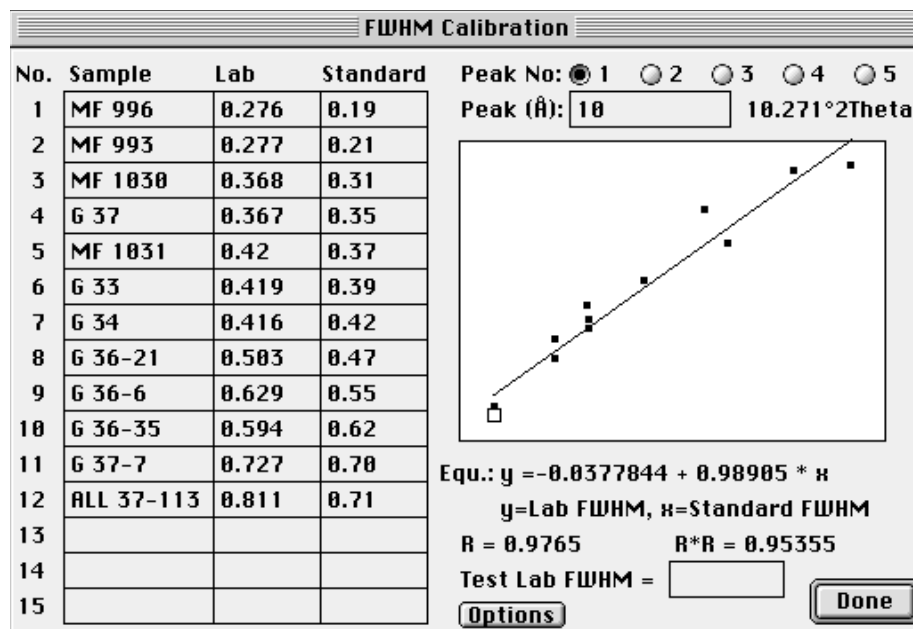


Fig. 54: Calibration of FWHM values (example Illite, 10Å)



Fig. 55

### Peak Fit Settings...

is used for administration of the peak fit routine (Fig. 56). If you have not worked yet with the peak fit analysis in MacDiff, please read the chapter 'Peak analysis by peak fitting' for introduction!

**Peak Fit Settings**

Peak Refinement settings

**Least Residuum Reduction**  \* Only used for Pearson VII (m factor) or Pseudo Voigt (Gauss/Lor.)

**Largest Loop No. of Refinement**

Split Profile (allow Asymmetry)

Include/Exclude Profile Parameter

Peak	<input checked="" type="radio"/> Bragg°	<input checked="" type="radio"/> Intensity	<input checked="" type="radio"/> FWHM	<input checked="" type="radio"/> m factor * Gauss/Lor.*	Profile Function	Split Profile (allow Asymmetry)
1	<input checked="" type="checkbox"/> 52.36	<input checked="" type="checkbox"/> 351.247	<input checked="" type="checkbox"/> 0.3069	<input type="checkbox"/>	Gauss	<input type="radio"/> All
2	<input checked="" type="checkbox"/> 53.2352	<input checked="" type="checkbox"/> 183.793	<input checked="" type="checkbox"/> 0.4675 <input checked="" type="checkbox"/> 0.3987	<input checked="" type="checkbox"/> 1.3078 <input checked="" type="checkbox"/> 146.641	Split Pearson VII	<input checked="" type="radio"/>
3	<input checked="" type="checkbox"/> 53.7416	<input checked="" type="checkbox"/> 218.54	<input checked="" type="checkbox"/> 0.4473	<input checked="" type="checkbox"/> 0.7266	Pseudo Voigt	<input type="radio"/>
4	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	Split Pseudo Voigt	<input checked="" type="radio"/>
5	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	Lorentz intermed.	<input type="radio"/>
6	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	Pearson VII	<input type="radio"/>
7	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	Split Lorentz mod.	<input checked="" type="radio"/>

Include/Exclude All     Lock Bragg Angles permanently

User-defined Boundaries     Draw Multipeak Envelope

Faster (less accurate)     Draw Residuum

Sort peak Intensities     Draw Interim Results

Play Sound if Finished     all in one

Fig. 56

**"Least Residuum Reduction"** - If the residuum decreases between profile refinement iterations by an amount smaller than the one selected, the refinement process will be terminated. Select from the values 1, 0.5, 0.1, 0.01, 0.005, 0.001%.

**"Largest Loop No. of Refinement"** - is used to set a limit on the number of refinement iterations. Select from none (no refinement) and 1, 2, 3, 5, 10, 15, 20, 40, 60, 100.

Within the Include/Exclude Profile Parameter field every profile function parameter for profile refinement can be in- or excluded. By means of the radio buttons entire series or columns may be turned on or off. All parameters are turned on by default at the start of a profile fit. The Bragg angle parameter may be excluded at any rate as the only exception if the check box **'Lock Bragg Angles permanently'** is turned on. Furthermore, select your profile function for each peak, where Gauss, Lorentz, Lorentz intermediate, Lorentz modified, Pearson VII and Pseudo Voigt are the functions available (see below). For peak asymmetry, activate the radio buttons in the Split Profile column. Alternatively, if you want to use a **'Global Function'** and/or a global split setting (**'Split All'**), select the the buttons on top.

**"User-defined Boundary"** facilitates a shift of the peak limiting angles. When turned off, the initially fixed peak limits will be fitted to the shape of the computed profile function. Default setting is on.

**"Faster (less accurate)"**. If turned on, only each third data point of the profile data available will be used for peak fitting. Furthermore, only three bisection iterations are used for fitting each parameter. This will reveal 2.5 to 3 times faster computing times but a residuum increase of about 10-30 percent. This modus is recommended for fast predictions.

**"Sort peak intensities"**. Use this option for internal sorting the peaks in descend-

ing order of their intensities before a multipeakfit routine starts.

"**Play Sound if Finished**" - plays a short beep after finishing a fit.

"**Draw Multipeak Envelope**". When turned on, the common curve (envelope) of two or more profile functions will be displayed in the diffractogram after peak fit analysis.

"**Draw Residuum**" - When turned on, the residuum curve will be displayed in the diffractogram after peak fit analysis.

"**Draw Interim Results**". If turned on, after each iteration the intermediate results will be shown graphically. If "**All in one**" is enabled, the intermediate results are shown in multiple graphics without removing older results.

### Functions used for peak fit:

#### Gauss

$$\text{Int}_p = \text{Int}_f \cdot \text{FWHM} \cdot \frac{2 \cdot \sqrt{\ln 2}}{\sqrt{\pi}} \cdot e^{(-\ln 2 \cdot \delta_{i, \max}^2)}$$

#### Lorentz

$$\text{Int}_p = \text{Int}_f \cdot \text{FWHM} \cdot \frac{2}{\pi} \cdot (1 + \delta_{i, \max}^2)^{-1}$$

#### Lorentz, intermediate

$$\text{Int}_p = \text{Int}_f \cdot \text{FWHM} \cdot \frac{2}{\pi} \sqrt{(2^{2/3} - 1)} \cdot (1 + (2^{2/3} - 1) \cdot \delta_{i, \max}^2)^{-1.5}$$

#### Lorentz, modified

$$\text{Int}_p = \text{Int}_f \cdot \text{FWHM} \cdot \frac{4 \sqrt{\sqrt{2} - 1}}{\pi} (1 + (\sqrt{2} - 1) \cdot \delta_{i, \max}^2)^{-2}$$

#### Pearson VII

$$\text{Int}_p = \text{Int}_f \cdot \text{FWHM} \cdot \frac{2 \sqrt{(2^{1/m} - 1)}}{\sqrt{\pi}} \cdot \frac{\Gamma(m)}{\Gamma(m - 0.5)} \cdot (1 + (2^{1/m} - 1) \cdot \delta_{i, \max}^2)^{-m}$$

## Pseudo Voigt

$$\text{Int}_p = \omega \cdot \text{Int}_p (\text{Lorentz}) + (1-\omega) \cdot \text{Int}_p (\text{Gauss})$$

$$\delta_{i, \max} = (\Theta_i - \Theta_{\max}) \cdot \frac{2}{\text{FWHM}}$$

$\text{Int}_p$  = Intensity at a given  $\Theta_i$  [counts]

$\text{Int}_f$  = Intensity standartization factor

FWHM = Full width at half maximum [ $\Delta^\circ 2\Theta$ ]

$\Theta_i$  = 2 Theta of a given point [ $^\circ 2\Theta$ ]

$\Theta_{\max}$  = 2 Theta of peak maximum [ $^\circ 2\Theta$ ]

$m$  = peak flank parameter (0.5 -  $\infty$ ) (only Pearson VII)

$\omega$  = weighted factor (only Pseudo Voigt)

$\Gamma$  = gamma function (only Pearson VII)

## The 'Window' menu

**Diagram Size** opens a submenu for changing the current window size, e.g. to a different monitor format. Individual sizes between 400 x 330 to 10,000 x 10,000 pixel can be set here permanently through a dialogue window as well, select '**Custom**'.

### Report, Peak Info, Identify

will activate the appropriate windows, provided they have been opened already.

The remaining menus are being used for selecting the present diffractogramme windows. The current diagramme is marked.

## If case of errors...

In case MacDiff users detect programme errors, the author would appreciate an immediate report via e-mail; please provide information about computer model and equipment as well as system configuration (system version, memory, inits, etc.). Please send the file which could not be processed by MacDiff as well.

Please report the MacDiff version you are using. You may download the latest debugged and improved version free of charge.

Current information about possible bugs and problems and their elimination can be downloaded from MacDiffs Internet Trouble Page. The URL is:

[http://servermac.geologie.uni-frankfurt.de/MacDiff trouble page.html](http://servermac.geologie.uni-frankfurt.de/MacDiff%20trouble%20page.html)

## For people in hurry:

### Fast, step-by-step standard processing of diffractogramme series

**Step 1:** Load the raw files to be processed from the measuring device of the diffractometer into an empty folder on the harddisk of your Mac (via diskette or net). Do not exceed 255. Always store raw data separately!

**Step 2:** Start MacDiff. Menu function: '**Files:Open File Session...**'. Open your folder and select a file to be processed.

**Step 3:** Select your processing options according to your needs, however at any rate '**Peak correction**', '**Smooth Counts**' (if the raw data were recorded by step scan or if they have not been smoothed already) and '**Find Base**'. Check for correct settings in '**Options**'! Turn on '**Auto Load**' and '**Overwriting (MacDiff)**', other buttons according to need only. Click '**Start**'.

**Step 4:** Have a cup of coffee (or a glass of beer) and an occasional look at your Mac to check its progress! Wait for dialogue window 'End of Session'.

**Step 5:** Set up an analysis programme or load an existing one - at '**Analyse:Analysis Program...**'. Enter the lines to be measured. Set option '**Auto Start**' (automatic startup of the analysis programme) possibly to on. Better keep '**Auto Measuring**' off if the diffractogrammes are still unknown.

**Step 6:** Repeat step 2.

**Step 7:** Do not turn on processing functions this time, deactivate **'Auto Load'** as well. Click **'OK'**.

**Step 8:** **'Open Next Session File'** (⌘-N). If no **'Auto Start'** is active, improve background adaptation manually (⌘-D), only then **'Start Analysis...'** (⌘-Y).

**Step 9:** Record each peak with care, check for correct background, shift peak limiting lines if necessary, according to choice display or save specific peak data of individual lines via **'Peak Info...'**. Remove reflex superpositions graphically or better by using peak fitting. Remove values from the report-table which may not make any sense (in **'Show Report...'**).

**Step 10:** Repeat step 8 and 9 until all files have been processed. Interruption is permissible - process the other files in their own folder later.

**Step 11:** Open **'Analyse:Save Report...'**. Deselect data types which will not be saved. Check for correct comma position and creator programme (e.g. EXCEL). If desired, append data to report files of previous sessions (**'Append on Existing File'**).

**Step 12:** Open generated files with a table processing programme. Adapt data according to choice, sort and line up. Perform further computations (e.g. ratios, calibration curve adaptations or contributions in percent). Transfer faulty or missing data individually using MacDiff via clipboard (activate option **'Send Peak data to clipboard'** in **'File:Preferences'**).

## FAQ

### 1) The diffractogramme appears to be destroyed and is just a tangle of lines.

*There is a bug in memory handling or a faultily read file. For safety, save all your reports (if existing), delete all open windows and reopen the diagramme to be processed. If the problem reappears, quit the programme and restart it with the file. If the problem is still not eliminated, do not reuse the file and report to the author. If the problem is observed repeatedly, check the **'Disable Undo (less memory)'** entry of the Preference dialogue.*

### 2) The diffractogramme hardcopies are far too large and are distributed over several pages.

*Open the **'Page Setup'** dialogue (menue **'File'**) and set the size to 25%, landscape format and possibly maybe via **'Options'** **'Larger Print Area'**. You can make this permanent by holding down the **'Alt'** key and clicking **'OK'**.*

### 3) During peak analysis the peak bordering lines shift too far into the peak, making continuous manual corrections necessary in order to obtain correct values for the peak area.

*There are inadequate settings for peak range and peak height. Increase their values in the **'Preferences'** dialogue. This is necessary in particular, if unsmoothed or barely smoothed profiles or very broad reflexes are being measured.*

### 4) The settings MacDiff is working with are faulty (e.g. wrong colours, dialogues show strange gaps or wrong entries).

*Probably the file **'MacDiff Prefs 4'** in the Preference folder in the system folder is faulty, without being so detected by MacDiff. Save your data, exit MacDiff, delete your preference file, restart the programme. Now, the default settings will be used.*

### 5) The programme FreeHand (versions previous to 7.0) will not load your dia-



**gramme or accept it from the clipboard, as it contains too complicated objects with more than 1000 support points.**

*Either you simplify your graphics, e.g., by partitioning into certain angle ranges, or you turn off the option 'Draw Polygon Lines' in the 'Preferences' dialogue. The problem has been eliminated in the update to version 7.0.*

**6) The setting of the lines measured within the report-table is faulty due to aberrating line position or some lines are overwritten by others in close proximity.**

*Use an peak analysis programme. Start this programme for the first time always while your report-table is still empty. Then, the partitioning of the substances still coincides with the programme settings.*

**7) The table processing programme (e.g. EXCEL) cannot read correctly the report table, because the decimal symbol is a period (or comma).**

*Enable the period as used for decimal point in the "Save Report" dialogue.*

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