

First FullProf School 2025:

Diffraction data analysis of energy materials



Mathematical Modelling of Powder Diffraction Patterns

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Outline

1. Mathematical modeling of powder diffraction patterns
2. The Voigt approach to peak shapes
3. Live: Individual Peak fitting in WinPLOTR-2006
4. Live: Le Bail fit of powder diffraction patterns using FullProf

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The calculated profile of powder diffraction patterns

$$y_{ci} = \sum_{\{h\}} I_h \Omega(T_i - T_h) + b_i$$

$I_h = I_h(\beta_I)$ Contains structural information:
atom positions, magnetic moments, etc

$\Omega = \Omega(x_{hi}, \beta_P)$ Contains micro-structural information:
instr. resolution, defects, crystallite size...

$b_i = b_i(\beta_B)$ Background: noise, incoherent scattering
diffuse scattering, ...

The model to calculate a powder diffraction pattern is:

$$y_{ci} = \sum_{\mathbf{h}} I_{\mathbf{h}} \Omega(T_i - T_{\mathbf{h}}) + b_i$$

$$\int_{-\infty}^{+\infty} \Omega(x) dx = 1$$

Profile function characterized by its
full width at half maximum (FWHM= H)
and *shape* parameters (η , m , ...)

$$\Omega(x) = g(x) \otimes f(x) = \text{instrumental} \otimes \text{intrinsic profile}$$

$$h(x) = g(x) \otimes f(x) \quad \text{usual notation in literature}$$

The calculated profile of powder diffraction patterns

$$y_{ci} = \sum_{\{h\}} I_h \Omega(T_i - T_h) + b_i$$

The symbol $\{h\}$ means that the sum is extended only to those reflections contributing to the channel “ i ” .

This should be taken into account (resolution function of the diffractometer and sample broadening) before doing the actual calculation of the profile intensity.

This is the reason why some Rietveld programs are run in two steps

Several phases ($\phi = 1, n_\phi$) contributing
to the diffraction pattern

$$y_{ci} = \sum_{\phi} s_{\phi} \sum_{\{\phi\mathbf{h}\}} I_{\phi,\mathbf{h}} \Omega(T_i - T_{\phi,\mathbf{h}}) + b_i$$

Several phases ($\phi = 1, \dots, n_\phi$) contributing
to several ($p=1, \dots, n_p$) diffraction patterns

$$y_{ci}^p = \sum_{\phi} s_{\phi}^p \sum_{\{\phi\mathbf{h}\}} I_{\phi,\mathbf{h}}^p \Omega^p(T_i - T_{\phi,\mathbf{h}}) + b_i^p$$

$$y_{ci} = \sum_{\{h\}} I_h \Omega(T_i - T_h) + b_i$$

$$I_h = S \left\{ L p O A C F^2 \right\}_h$$

Integrated intensities are proportional to the square of the structure factor F . The factors are:
 Scale Factor (S), Lorentz-polarization (Lp), preferred orientation (O), absorption (A), other “corrections” (C)

Crystallographic R-factors used in Rietveld Refinement

$$'I_{obs,k}' = I_{calc,k} \sum_i \left\{ \frac{\Omega(T_i - T_k)(y_{obs,i} - B_i)}{(y_{calc,i} - B_i)} \right\}$$

Provides 'observed' integrates intensities for calculating Bragg R-factor

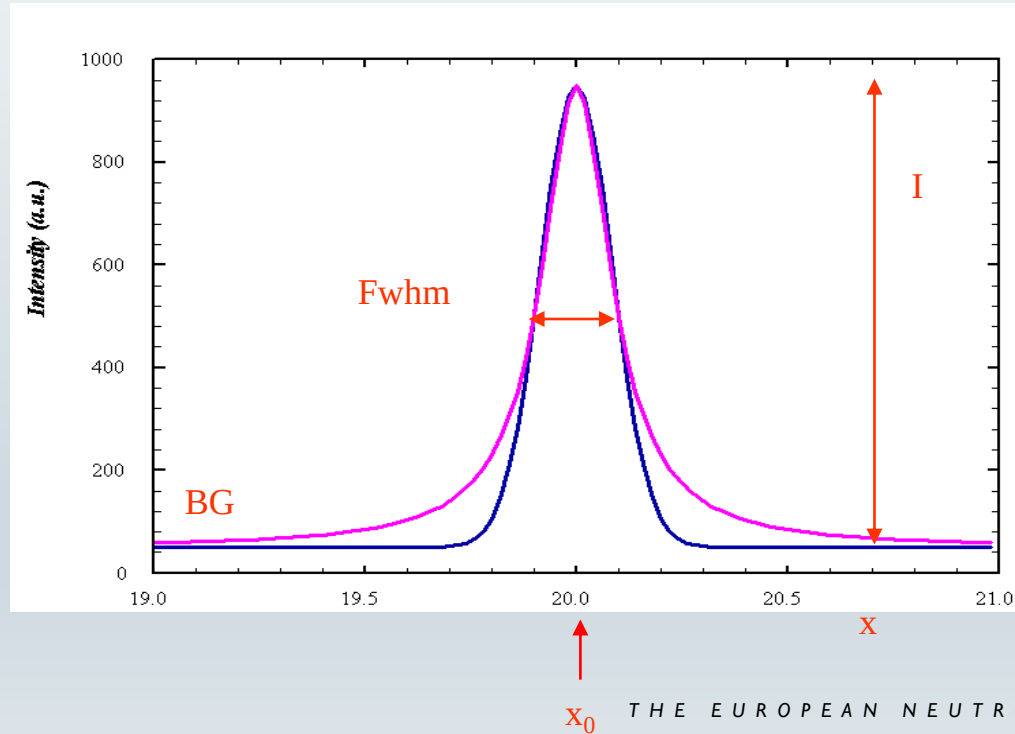
$$'F_{obs,k}' = \sqrt{\frac{'I_{obs,k}'}{jLp}}$$

In some programs the crystallographic R_F -factor is calculated using just the square root of ' $I_{obs,k}$ '

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Comparison of **Gaussian** and **Lorentzian** peak shapes of the same peak height “**I**” and same width “**Fwhm**”



Convolution properties of Gaussian and Lorentzian functions

$$L(x, H_1) \otimes L(x, H_2) = L(x, H_1 + H_2)$$

$$G(x, H_1) \otimes G(x, H_2) = G(x, \sqrt{H_1^2 + H_2^2})$$

$$L(x, H_L) \otimes G(x, H_G) = V(x, H_L, H_G)$$

The Voigt function

$$V(x) = L(x) \otimes G(x) = \int_{-\infty}^{+\infty} L(x-u)G(u)du$$

$$V(x) = V(x, H_L, H_G) = V(x, \beta_L, \beta_G)$$

The pseudo-Voigt function

$$pV(x) = \eta L'(x) + (1-\eta)G'(x)$$

$$pV(x) = pV(x, \eta, H)$$

Properties of the Voigt function

$$V(x) = V_1(x) \otimes V_2(x)$$

The Voigt function has proven to be a very good experimental approximation in many cases

$$\beta_L = \beta_{1L} + \beta_{2L}$$

→ Lorentzian breadths simply have to be summed

$$\beta_G^2 = \beta_{1G}^2 + \beta_{2G}^2$$

→ Gaussian breadths have to be summed quadratically

$$\beta_{fL} = \beta_{hL} - \beta_{gL}$$

$$\beta_{fG}^2 = \beta_{hG}^2 - \beta_{gG}^2$$

← Correction for instrumental broadening

Instrument and sample contribution to broadening

$$H_{hG}^2 = \boxed{U_f \tan^2 \theta + \frac{I_{fG}}{\cos^2 \theta}} + \boxed{H_{gG}^2}$$
$$H_{hL} = \boxed{X_f \tan \theta + \frac{Y_f}{\cos \theta}} + \boxed{H_{gL}}$$

Sample

Instrument

The Gaussian and Lorentzian contributions of the instrument must be determined experimentally with a size/strain-free sample

Modeling the Gaussian and Lorentzian components for the general anisotropic case in FullProf

Instrument resolution function characterized by: $(U, V, W, X, Y)_g$

$$H_{hG}^2 = (U_g + U_f + (1 - \xi_f)^2 D_{fST}^2(\alpha_D)) \tan^2 \theta + V_g \tan \theta + W_g + \frac{I_{fG}}{\cos^2 \theta}$$

$$H_{hL} = (X_g + X_f + \xi_f D_{fST}(\alpha_D)) \tan \theta + \frac{[Y_g + Y_f + F_f(\alpha_S)]}{\cos \theta}$$

$$D_{fST}^2(\alpha_D) = 10^{-8} \cdot 8 \ln 2 \left(\frac{180}{\pi} \right)^2 \frac{\sigma^2(M_{hkl})}{M_{hkl}^2}$$

THE EUROPEAN NEUTRON SOURCE

Example: General 2θ dependence of the instrumental broadening (determined by a standard sample)

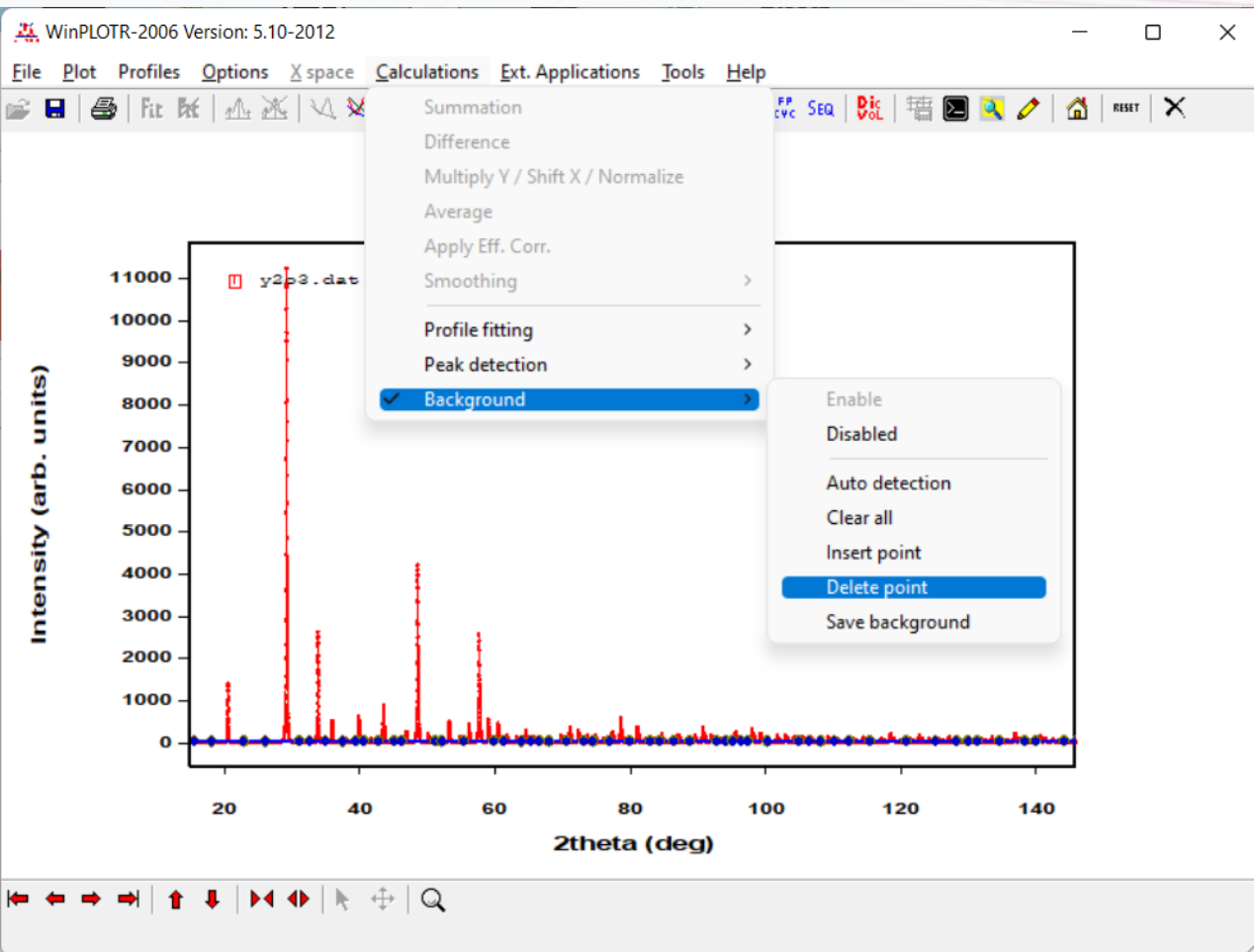
$$H_{hG}^2 = (U_f + (1 - \xi_f)^2 D_{fST}^2(\alpha_D)) \tan^2 \theta + \frac{I_{fG}}{\cos^2 \theta} + H_{gG}^2$$
$$H_{hL} = (X_f + \xi_f D_{fST}(\alpha_D)) \tan \theta + \frac{[Y_f + F_f(\alpha_S)]}{\cos \theta} + H_{gL}$$

The Gaussian and Lorentzian components of the instrumental Voigt function are interpolated between empirically determined values.

If needed, axial divergence is convoluted numerically with the resulting profile.

Outline

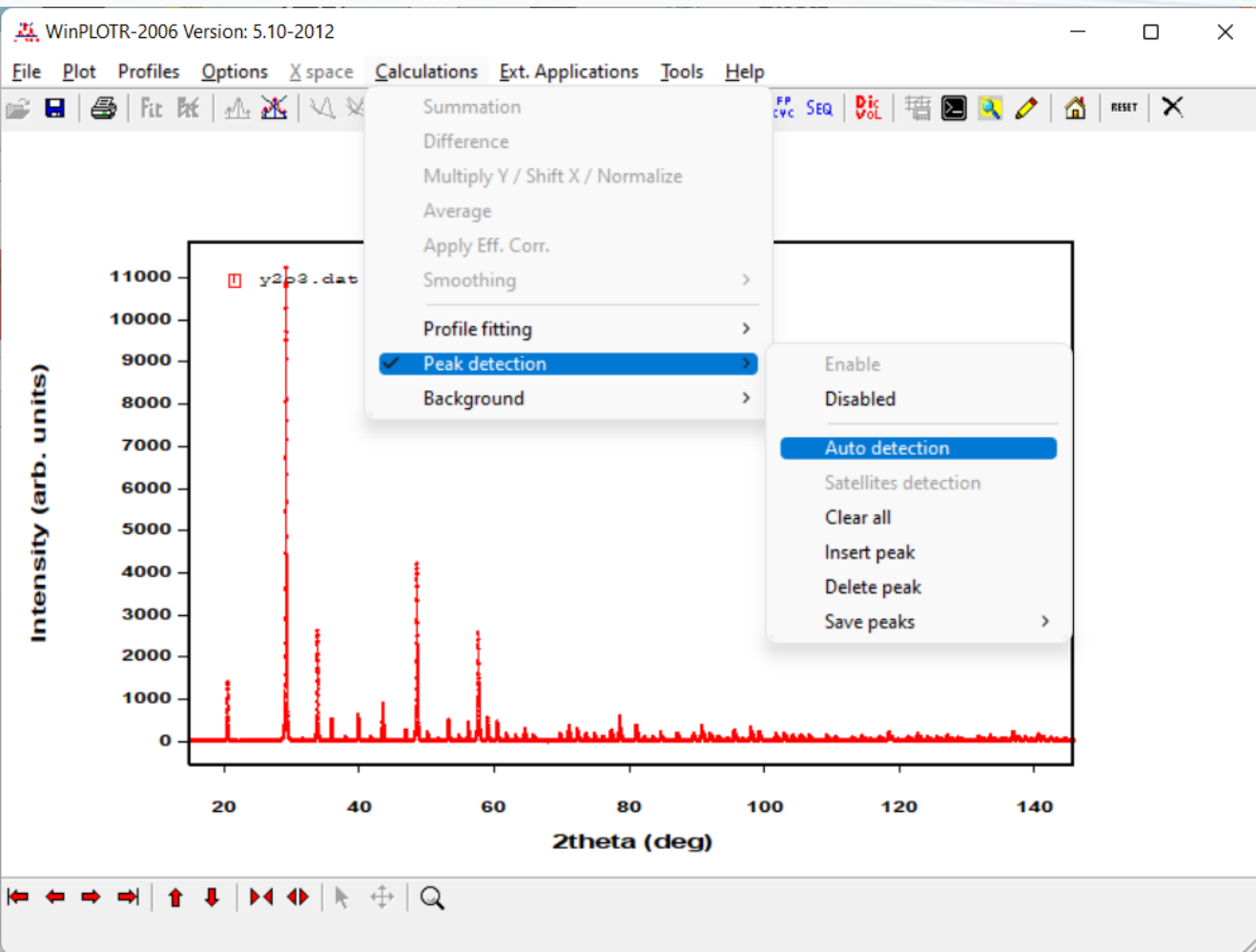
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After opening the diffraction pattern in WinPLOT-2006, go to the **Calculations** menu, select Background > Auto detection

Delete excessive background points, mostly those too close to the tails of the peaks. Insert points if needed

When finished, select **Disabled**
The points remain in memory



Peaks detection condition

0.0080 : peak_threshold
2.0000 : shoulder_threshold
0.0050 : bkg_threshold
1 : iterations

Peak type

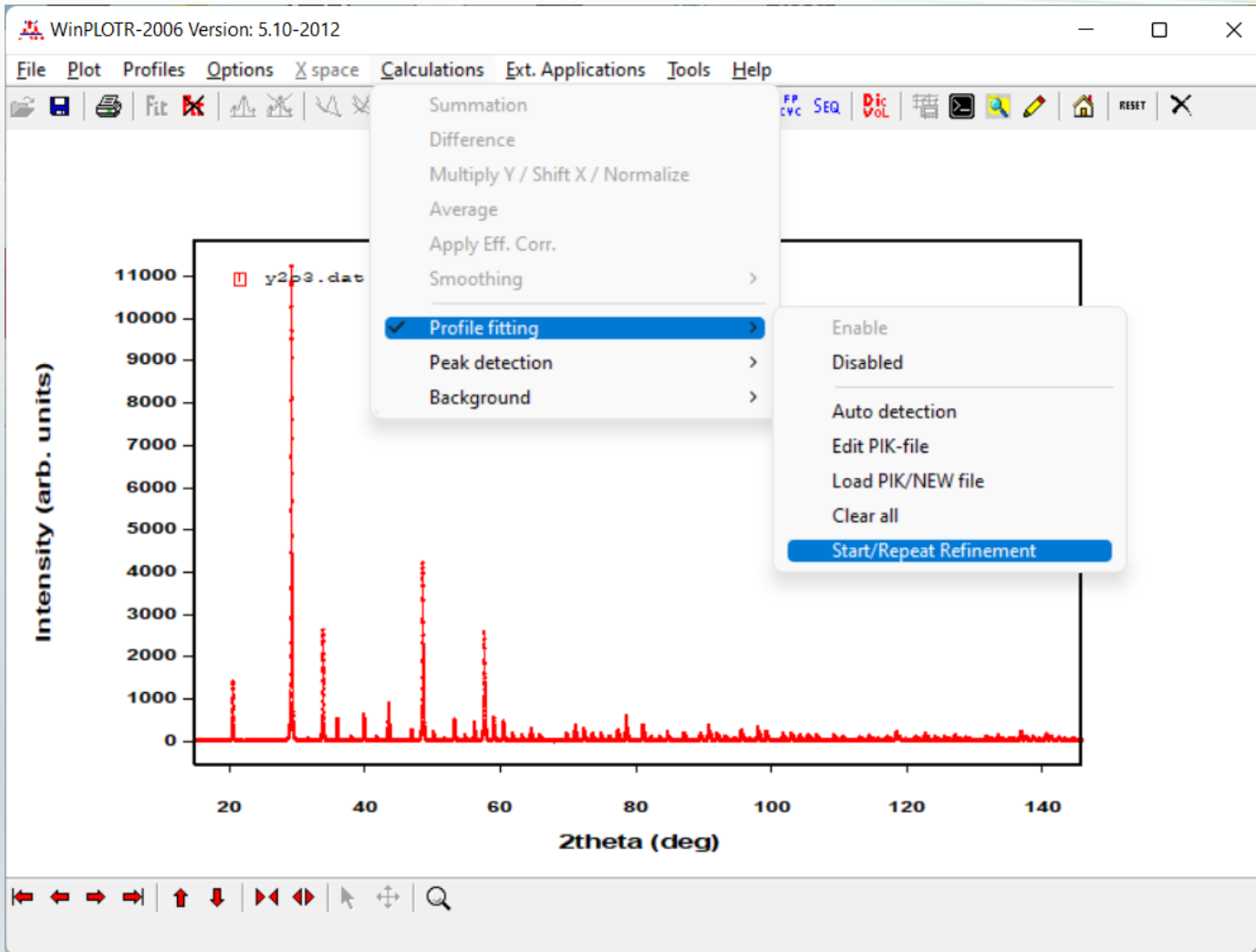
☐ Single peaks
☒ doublets: (Cu-Ka)
☐ doublets: (Mo-Ka)
☐ doublets: (Co-Ka)

OK Cancel

The figure shows a 'Peaks detection condition' dialog box. It contains four input fields for peak_threshold (0.0080), shoulder_threshold (2.0000), bkg_threshold (0.0050), and iterations (1). Below these fields is a 'Peak type' section with four radio button options: Single peaks, doublets: (Cu-Ka) (which is selected), doublets: (Mo-Ka), and doublets: (Co-Ka). At the bottom are 'OK' and 'Cancel' buttons.



Then, the diffraction pattern appears alone in the screen. Then select **Profile fitting** > **Enable**



After enabling, the Profile fitting menu, select **Start/Repeat Refinement**

Then a dialog appears with all the background points, and peaks, etc.



Number of Cycles:

30

IRF / IPC File

☒ None☐ Create .IRF File☐ Create .IPC File

Background Information

	Position	Intensity	
1	15.48000	17.00	☐
2	18.03000	16.00	☐
3	22.78000	14.67	☐
4	26.00000	15.00	☐
5	31.03000	20.00	☐
6	32.55000	19.33	☐

Wavelength

Lambda1	Lambda2	I (Ka2/Ka1)	
1.540599	1.544390	0.500000	☐

Nullify all Shifts

Fix all Shifts

Vary all backg. points

Fix all backg. points

Vary all 2Theta_Positions

Fix all 2Theta_Positions

Vary all Shift-FWHM

Fix all Shift-FWHM

Vary all Shift-ETA

Fix all Shift-ETA

General Profile Parameters

U		V		W		Z		Eta		X	
0.00000	☐	0.00000	☐	0.00000	☐	0.00000	☐	0.00000	☐	0.00000	☐

Asymmetry Parameters

S_L		D_L	
0.00000	☐	0.00000	☐

IRF File

Load IRF file

Peaks Parameters

		2Theta-Position		Intensity		Shift FWHM		Shift ETA	
1	☒	20.5044	☒	294.393	☒	0.12978	☒	0.00000	☐
2	☒	29.1584	☒	2509.591	☒	0.13934	☒	0.00000	☐
3	☒	31.5612	☒	10.959	☒	0.10229	☒	0.00000	☐
4	☒	33.7915	☒	629.597	☒	0.14897	☒	0.00000	☐
5	☒	35.9097	☒	106.856	☒	0.12544	☒	0.00000	☐
6	☒	37.9452	☒	27.761	☒	0.17103	☒	0.00000	☐
7	☒	39.8479	☒	122.995	☒	0.12544	☒	0.00000	☐
8	☒	41.7045	☒	5.642	☒	0.04628	☒	0.00000	☐

☐ Plot Individual Peaks☐ Save Calculated Pattern

OK/Start Refinement

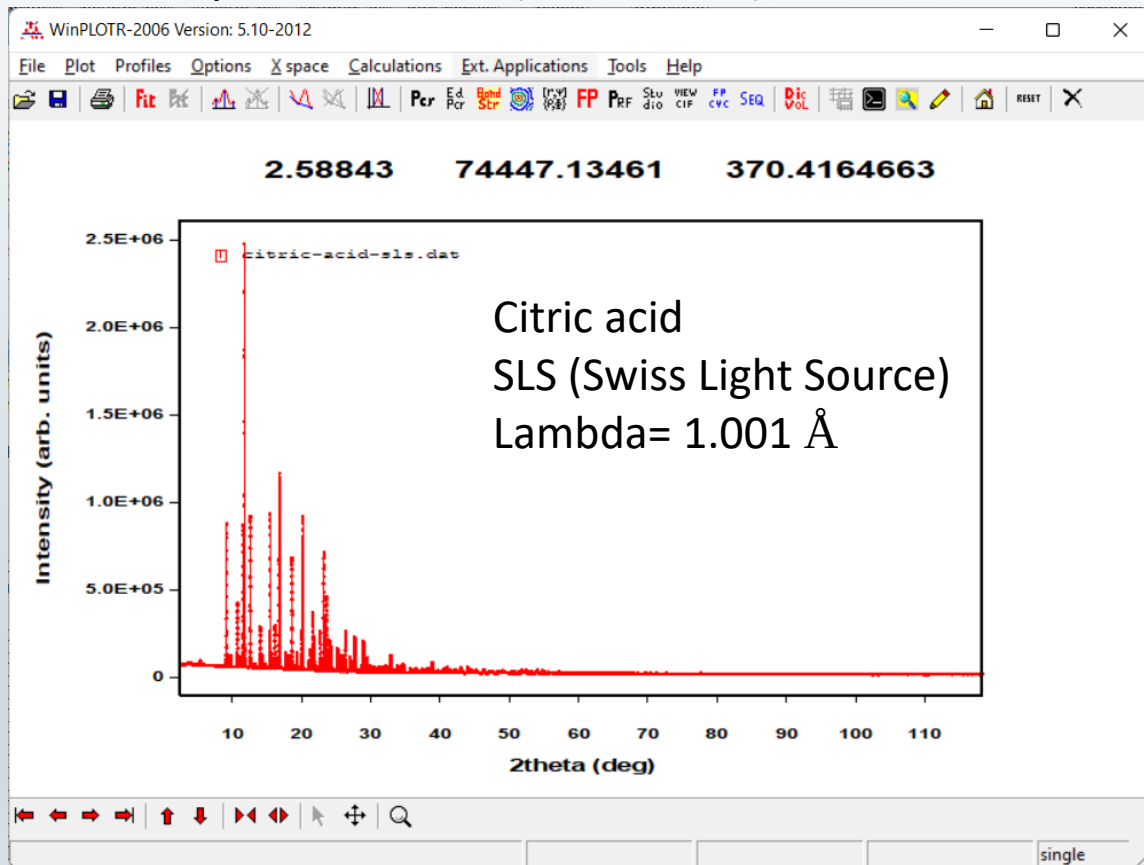
Cancel

The dialog contains instructions for refinement. Each peak is independent and its position, FWHM and intensity can be refined.

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Let us start by indexing a powder diffraction pattern coming from the synchrotron SLS (Switzerland)

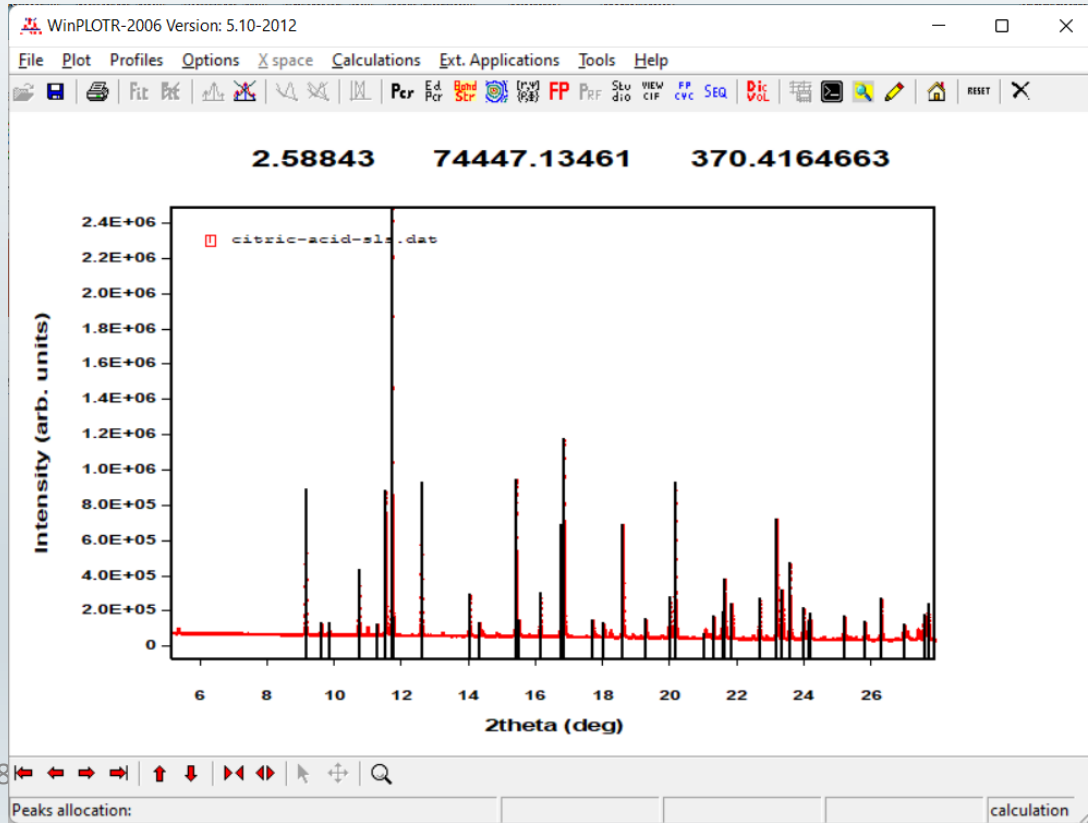


For indexing a PDP it is important to select the low-angle peaks, otherwise the overlap may hinder the solution.

Also it is important, in the first approximation, to discard small intensity peaks.

Within WinPLOR-2006

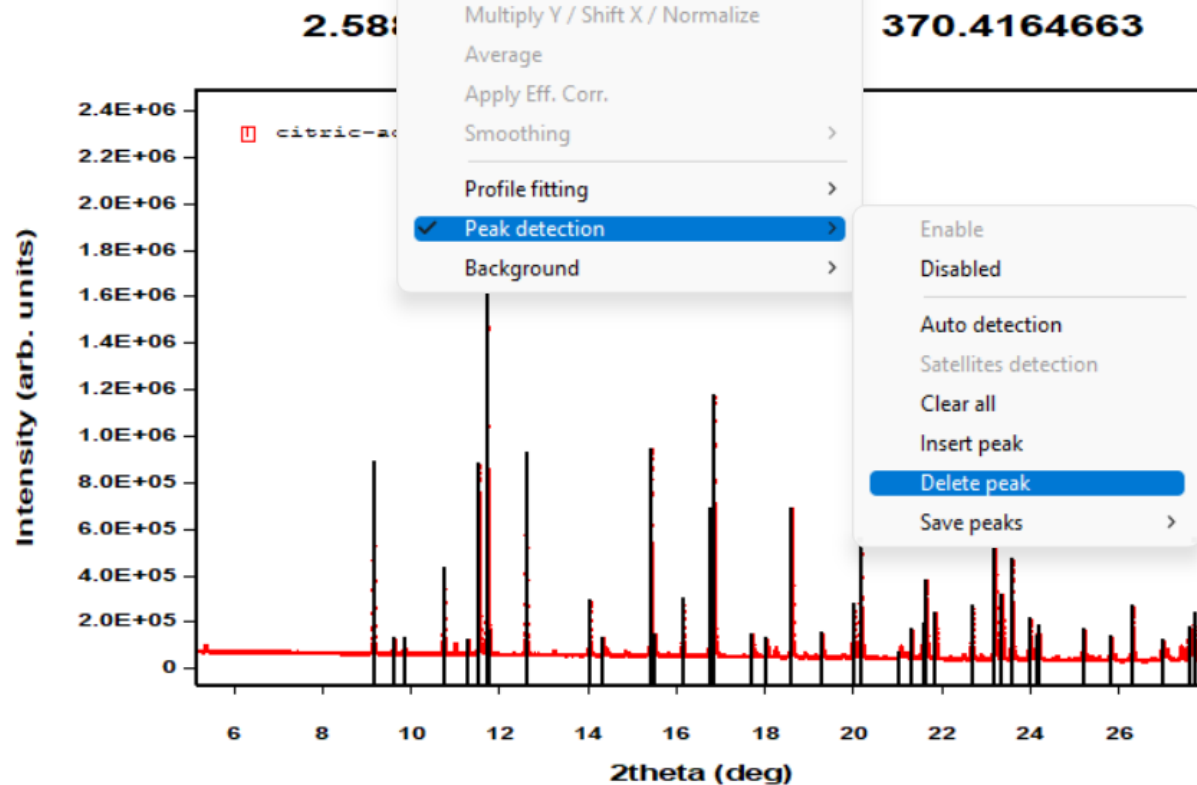
1. Select the low angle region containing at least 20 visible peaks
2. In the Calculations menu select Peak Detection > Enable
3. Select Autodetection



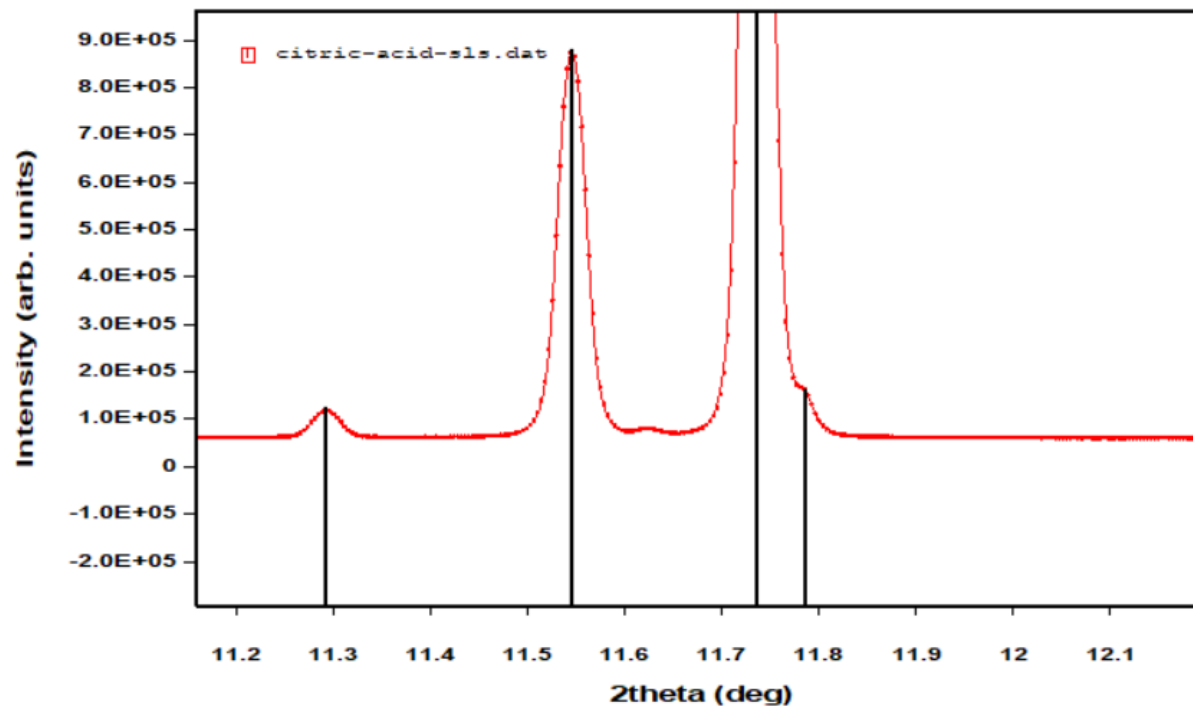
- Eliminate some of the smallest intensity peaks and peaks on shoulders
- Insert high intensity peaks if they have not been detected



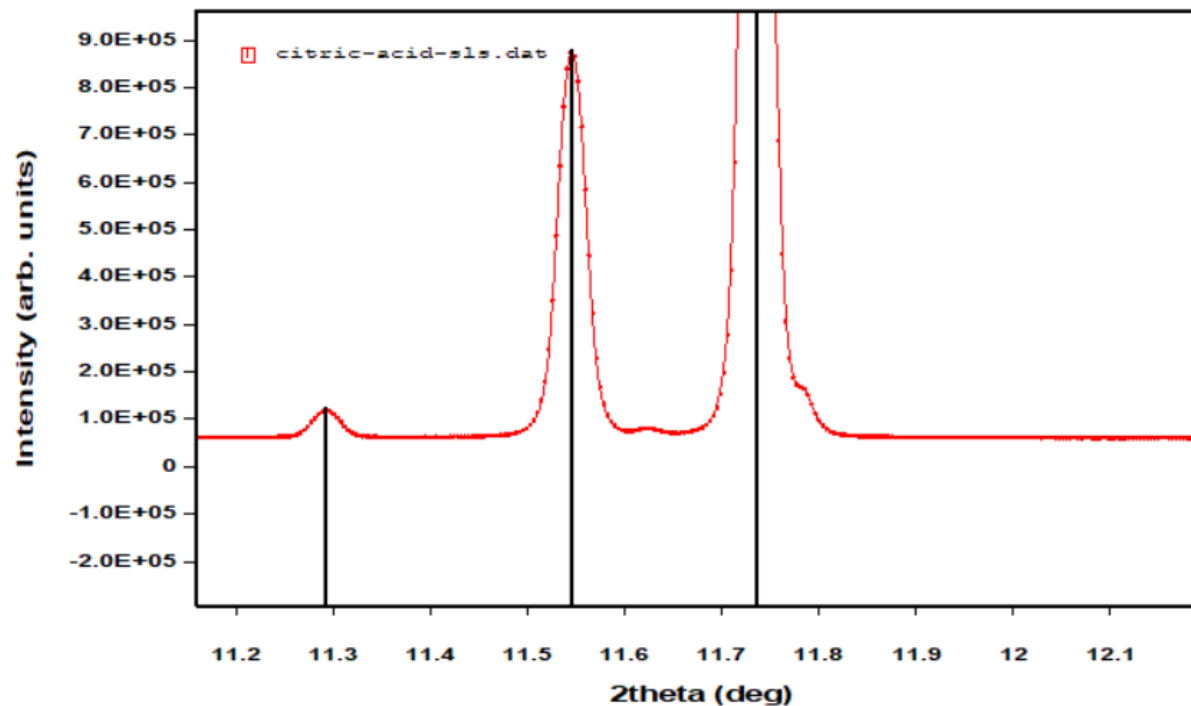
- Summation
- Difference
- Multiply Y / Shift X / Normalize
- Average
- Apply Eff. Corr.
- Smoothing
- Profile fitting
- ☒ Peak detection
- Background



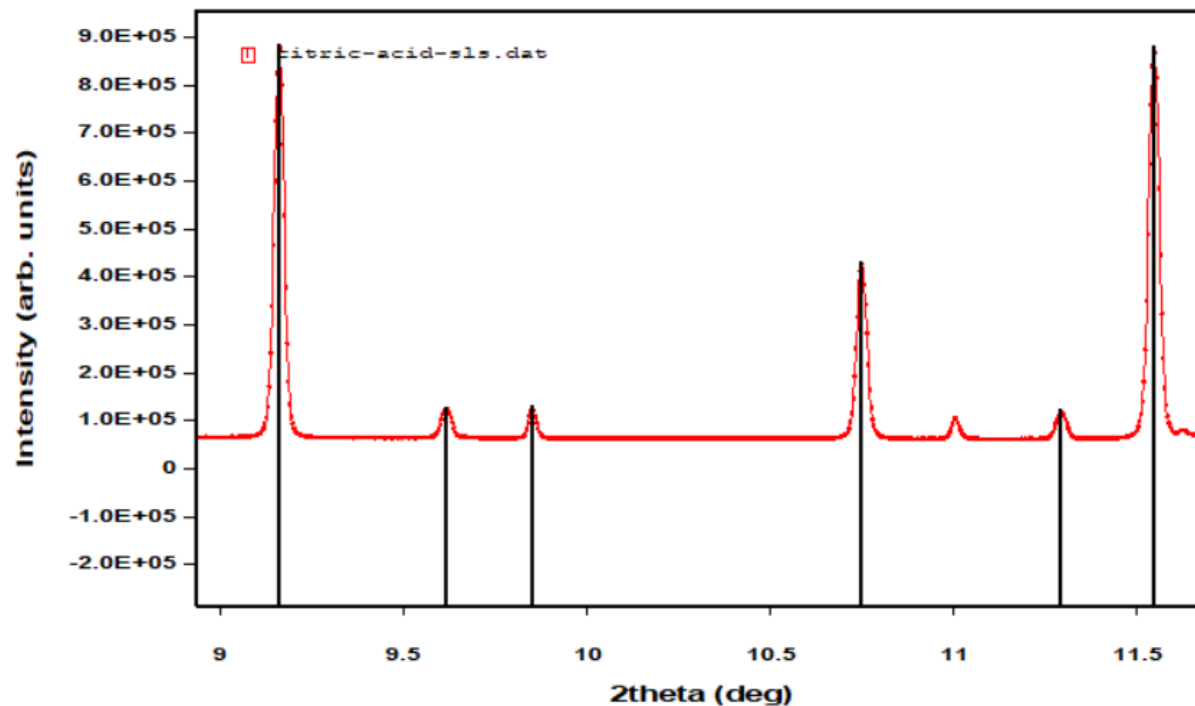
2.58843 74447.13461 370.4164663



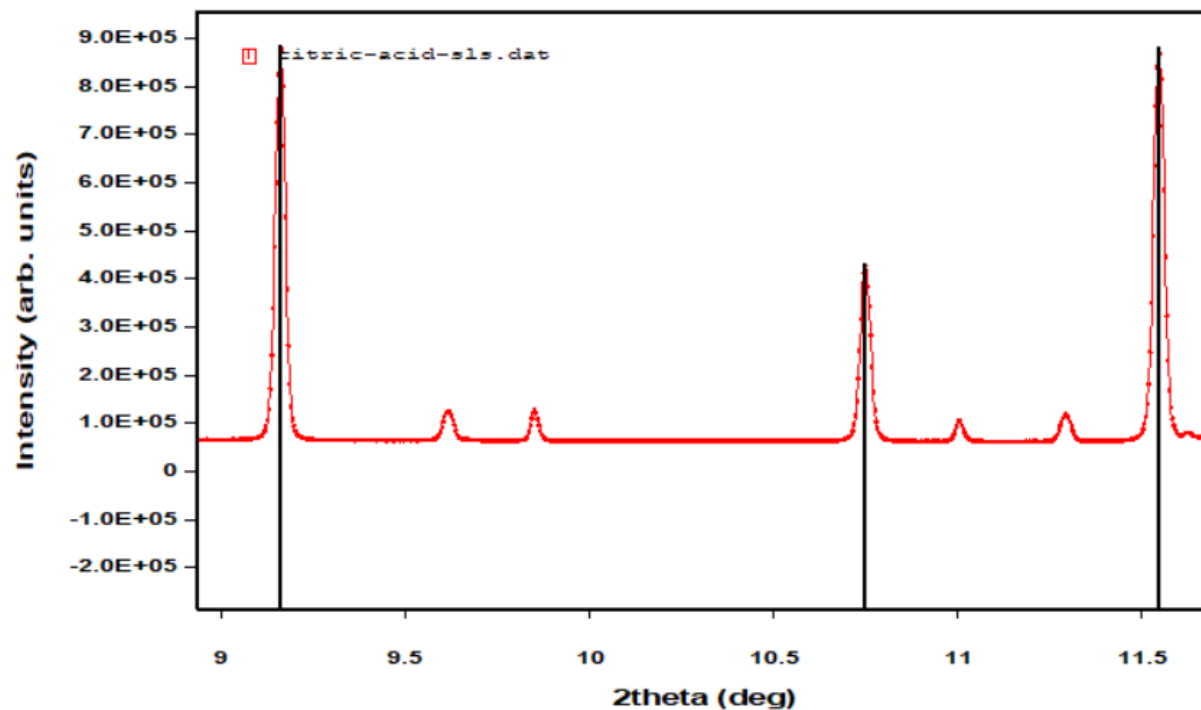
2.58843 74447.13461 370.4164663

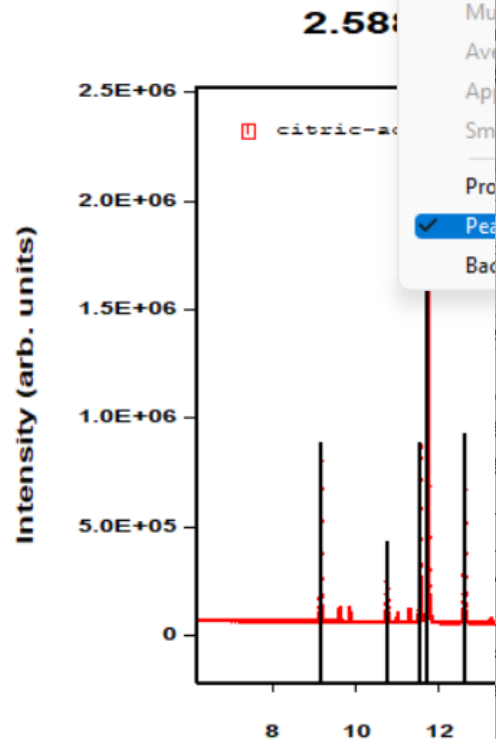


2.58843 74447.13461 370.4164663



2.58843 74447.13461 370.4164663





Input parameters for DICVOL

Title: 2.58843 74447.13461 370.4164663

of lines used: 39

Spacing Data:

- ☐ Theta Bragg
- ☒ 2theta angle
- ☐ d-spacing
- ☐ Q specified

Tested Crystal Symmetry:

- ☒ Cubic
- ☒ Tetragonal
- ☒ Hexagonal
- ☒ Orthorhombic
- ☒ Monoclinic
- ☐ Triclinic

Unit Cell Limits

25.000	: Amax (A)
25.000	: Bmax (A)
25.000	: Cmax (A)
90.000	: BEmin (o)
125.00	: BEmax (o)
0.0000	: VOLmin (A3)
2500.0	: VOLmax (A3)

Experimental parameters

1.0010	: Wavelength (A)
0.0000	: Mol. weight (g)
0.0000	: Density (g/cm3)
0.0000	: Density error

DicVol 04 parameters

0.0300	: Data absolute error (EPS)
10.000	: Lower figure of merit (FOM)
0	: # Max. impurity lines (eg. 3 or 4)

☐ A priori search of zero shift

☒ Zero shift refinement

☐ DicVOL06 option

OK Cancel

Free Format

Dicvol Format

Ito Format

K_Search Format

Treor Format

VOLUME DOMAIN BEING SCANNED :

=====

LOWER BOUND = 400.00 A**3 HIGHER BOUND =

ANGLE RANGE SCANNED : BETA MIN= 90.000 Deg. BETA MAX= 95.000
 ANGLE RANGE SCANNED : BETA MIN= 95.000 Deg. BETA MAX=100.000
 ANGLE RANGE SCANNED : BETA MIN=100.000 Deg. BETA MAX=105.000
 ANGLE RANGE SCANNED : BETA MIN=105.000 Deg. BETA MAX=110.000
 ANGLE RANGE SCANNED : BETA MIN=110.000 Deg. BETA MAX=115.000
 =====> CELL VOLUME = 770.3 A**3 M(39)= 22.8 F(39)= 88.
 ANGLE RANGE SCANNED : BETA MIN=115.000 Deg. BETA MAX=120.000
 ANGLE RANGE SCANNED : BETA MIN=120.000 Deg. BETA MAX=125.000

ITERATION NUMBER AT EACH DICHOTOMY LEVEL:

4544	3053	183	15	28	83	351
------	------	-----	----	----	----	-----

--- T O T A L CALCULATION TIME : 1.340 SEC

>>>> PLEASE READ THE DICVOL OUTPUT FILE: citric-acid-s

D I C V O L 0 4 S O L U T I O N (S)

a(A)	b(A)	c(A)	alfa	beta	gama	symmetry	Volum
12.8168	5.6231	11.4681	90.000	111.253	90.000	Monocl.	7

==> citric-acid-sls-c_1.cry file has been created (CELREF format)

==> citric-acid-sls-c_dicvol_cell.sum file has been created (Crys

Select your diffractometer:

X-Rays diffractometer:

- ☐ conventionnal powder diffractometer
☒ **synchrotron radiation**
☐ my X-Ray diffractometer

Neutron diffractometer:

- ☐ G42 (LLB) I=2.343A
☐ G41 (LLB) I=2.42A
☐ 3T2 (LLB) I=1.225A
☐ D2B (ILL) I=1.59A
☐ my neutron diffractometer
☐ Read IRF file

OK

Cancel

The program DICVOL generates a PCR file for doing a Le Bail fit and extract the Integrated intensities. The PCR file is limited to the region selected for the peaks and has other limitations.

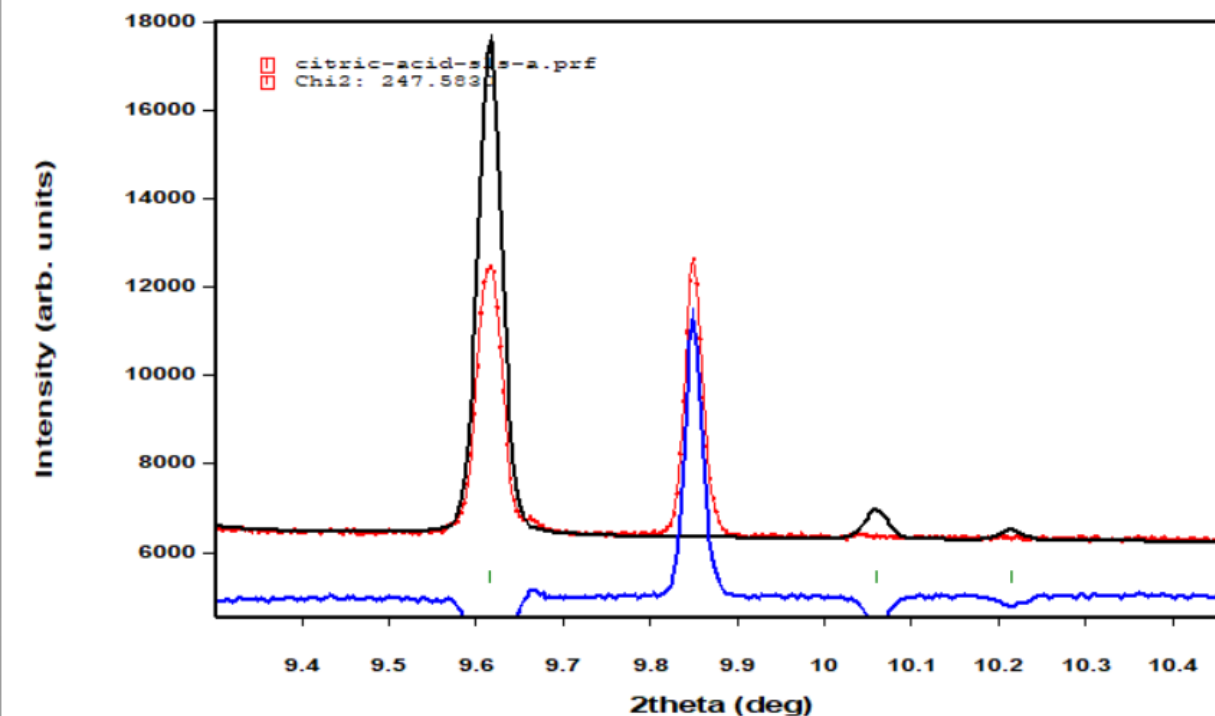
```

COMM WDICVOL04 solution (Automatic generated PCR file)
!Job Npr Nph Nba Nex Nsc Nor Dum Iwg Ilo Ias Res Ste Nre Cry Uni Cor Opt Aut
   0  7  1 39  2  0  1  1  0  0  1  0  0  0  0  0  0  0  0  1
!
!Ipr Ppl Ioc Mat Pcr Ls1 Ls2 Ls3 Syo Prf Ins Rpa Sym Hkl Fou Sho Ana
   0  0  1  0  1  0  0  0  0  3  10  0  0  0  0  0  0
! >>> WARNING: Please check CTHM value <<<
! lambda1 Lambda2      Ratio      Bkpos      Wdt      Cthm      muR      AsyLim      Rpolarz
1.001000 1.001000  1.0000 40.0000  7.0000  0.0000  0.0000 30.0000  0.0000
!
!NCY  Eps R_at R_an R_pr R_gl      Thmin      Step      Thmax      PSD      Sent0
   10 0.30 1.00 1.00 1.00 1.00
!! >>> WARNING: Select manually background points to improve the quality of the background <<<
!  2Theta/TOF      Background
      9.160      65300.945
      10.749      62927.422
      . . . . .

```

```
! >>> WARNING: Extend the angular range to the whole measured pattern <<<
! Excluded regions (LowT  HighT)
      0.00      7.13
     31.55     180.00
!
      0          !Number of refined parameters
!
! Zero   Code   Sycos   Code   Sysin   Code   Lambda   Code
0.0027   0.0000   0.0000   0.0000   0.0000   0.0000
!
phase 1:
!
!Nat Dis Mom Pr1 Pr2 Pr3 Jbt Irf Isy Str Furth      ATZ   Nvk Npr More
      0   0   0 0.0 0.0 0.0   2   0   0   0   0      0.00   0   7   0
! >>> WARNING: The following space group corresponds to the Lauë group      <<<
! >>> in the crystal system that has been found by WDICVOL06. Please check <<<
! >>> carefully possible extinctions and Bravais lattice to find the      <<<
! >>> correct space group.      <<<
P 2/m                                     <--Space group symbol
! Scale      Shap1      Bov      Str1      Str2      Str3      Strain-Model
.10000E-03    0.00      0.0000   0.0000   0.0000   0.0000      0
      0.00000   0.00      0.00      0.00      0.00      0.00
!
      U      V      W      X      Y      GauSiz   LorSiz   Size-Model
0.0000  0.0000  0.0008  0.0600  0.0000  0.00000   0.00000   0
      0.00      0.00      0.00      0.00      0.00      0.00      0.00
!
      a      b      c      alpha      beta      gamma
12.816800   5.623100  11.468100  90.000000  111.252998  90.00000
```

WDICVOL04 solution (Automatic generated PCR file)



Impurity peaks influence the intensity of adjacent peaks, because the Le Bail fit is an iterative procedure aiming to fit the integrated intensities and not the profile.

In order to obtain better intensities of the phase to be solved it is better to exclude impurity peaks

! Excluded regions (LowT HighT) for Pattern# 1

0.00	7.12
9.74	10.10
10.90	11.10
14.41	14.50
14.90	15.00
18.80	19.09
19.60	19.86
60.50	180.00

Impurity peaks have to be excluded

The range of the calculation has been extended up to 60.5 degrees

!-----
! Data for PHASE number: 1 ==> Current R_Bragg for Pattern# 1: 0.0675
!-----

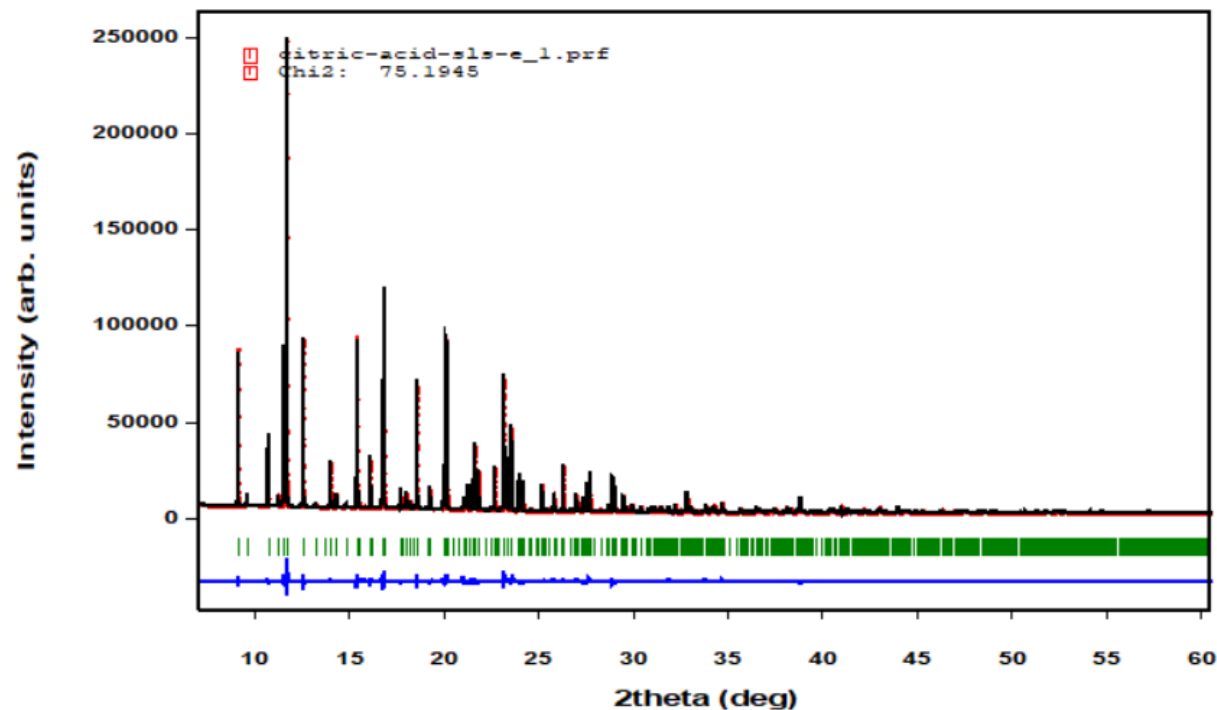
Phase 1:
!
!Nat Dis Ang Pr1 Pr2 Pr3 Jbt Irf Isy Str Furth ATZ Nvk Npr More
0 0 0 0.0 0.0 1.0 2 2 0 0 0 0.000 0 7 1
!
!Jvi Jdi Hel Sol Mom Ter Brind RMua RMub RMuc Jtyp Nsp_Rel Ph_Shift N_Domains
11 0 0 0 0 0 1.0000 0.0000 0.0000 0.0000 0 0 0 0

Generate a file with integrated intensity clusters to be used in Simulated Annealing job

P 21/a <--Space group symbol
!-----> Profile Parameters for Pattern # 1 ----> Phase # 1
! Scale Shapel Bov Str1 Str2 Str3 Strain-Model
0.1000000E-03 0.00000 0.00000 0.00000 0.00000 0.00000 0
0.00000 0.000 0.000 0.000 0.000 0.000
!
! U V W X Y GauSiz LorSiz Size-Model
0.000000 0.000000 0.000789 0.069406 0.000000 0.000000 0.000000 0
0.00 0.00 31.00 71.00 0.00 0.00 0.00
!
! a b c alpha beta gamma #Cell Info
12.811221 5.621978 11.464072 90.000000 111.227379 90.000000
11.00000 41.00000 51.00000 0.00000 61.00000 0.00000
!
! Pref1 Pref2 Asy1 Asy2 Asy3 Asy4 S_L D_L
0.000000 0.00000 0.00000 0.00000 0.00000 0.00000 0.00000 0.00000
0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00

28/03/2025

WDICVOL06/14 solution (Automatic generated PCR file)



Final LeBail
refinement in
which some
impurity peaks
have been
excluded and the
range of the
calculation has
been extended
up to 61 degrees

! Phase No.: 1 Phase 1: Overlapped reflections re-grouped -> Obs = j LP F^2

(3i4,2f16.5,i4,3f14.4)

1.00100	0	2	0.0000						
0.0000		0.0000							
0	0	1	908.34271	15.12186	1	0.0000			
-2	0	1	28712.10938	16.53712	1	0.0000			
2	0	0	2445.29346	7.17257	1	0.0000			
0	0	2	14002.19238	13.42684	1	0.0000			
1	1	0	2280.65063	5.23953	1	0.0000			
-2	0	2	-1.00000	4.89305	1	0.0000			
0	1	1	31372.63477	8.87230	1	0.0000	0.0000	11.5465	
-1	1	1	91564.67188	21.19823	1	0.0000	0.0000	11.7368	
2	0	1	33548.95703	18.23029	1	0.0000	0.0000	12.6108	
1	1	1	912.97614	11.04930	1	0.0000	0.0000	13.2432	
.	.	.							
-9	2	8	1397.27820	2.27191	1	0.0000		54.8340	
4	3	6	-1.00000	0.08982	1	0.0000		54.9027	
-9	1	9	-1.00000	0.58520	1	0.0000		54.9351	
4	4	4	-1.00000	0.57493	1	0.0000		54.9357	
10	0	2	-1.00000	0.68488	1	0.0000		54.9500	
7	4	0	306.99512	1.29702	1	0.0000		54.9531	
9	3	0	-1.00000	0.26166	1	0.0000		55.0553	
-7	1	10	-1.00000	1.32122	1	0.0000	0.0000	55.0897	
3	5	0	-1.00000	1.01764	1	0.0000	0.0000	55.1026	
4	0	8	-1.00000	1.06261	1	0.0000	0.0000	55.1073	
2	5	2	743.89368	2.04895	1	0.0000	0.0000	55.1369	
.	.	.							

File containing the integrated **intensity clusters** that is directly usable by simulated annealing

Cluster of reflections contributing to a single observation