First FullProf School 2026:

Diffraction data analysis of energy materials

NEUTRONS FOR SOCIETY

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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1. **Mathematical modeling of powder diffraction patterns**
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The calculated profile of powder diffraction patterns

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

$I_{\mathbf{h}} = I_{\mathbf{h}}(\boldsymbol{\beta}_{\mathbf{I}})$ **Contains structural information: atom positions, magnetic moments, etc**

$\Omega = \Omega(x_{\mathbf{h}i}, \boldsymbol{\beta}_{\mathbf{P}})$ **Contains micro-structural information: instr. resolution, defects, crystallite size…**

$b_i = b_i(\boldsymbol{\beta}_{\mathbf{B}})$ **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, …)

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

$$h(x) = g(x) \otimes f(x)$$

usual notation in literature

The calculated profile of powder diffraction patterns

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

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 (ϕ = 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 (ϕ = 1 ,… n$_\phi$) contributing to several (p=1 ,… n$_p$) diffraction patterns

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

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

$$I_{\mathbf{h}} = S\left\{ L\, p\, O\, A\, C\, F^2 \right\}_{\mathbf{h}}$$

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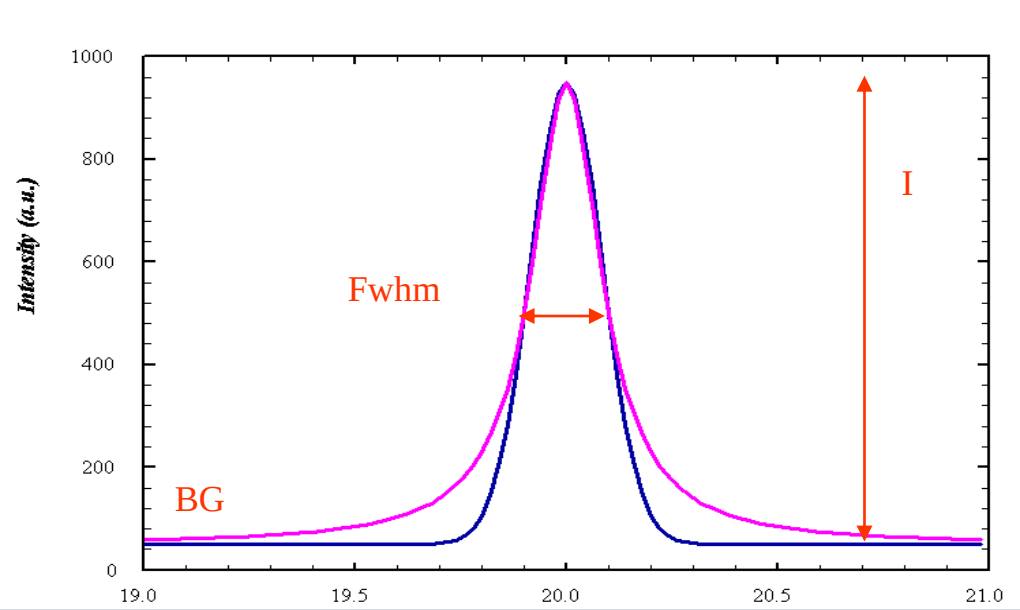
Comparison of **Gaussian** and **Lorentzian** peak shapes of the same peak height "I" and same width "Fwhm"



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

$$H_{hG}^2 = U_f \tan^2\theta + \frac{I_{fG}}{\cos^2\theta} + H_{gG}^2$$

$$H_{hL} = X_f \tan\theta + \frac{Y_f}{\cos\theta} + H_{gL}$$

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: $(U, V, W, X, Y)_g$

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

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

$$D_{fST}^2(\boldsymbol{\alpha}_D) = 10^{-8}\ 8\mathrm{Ln}2 \left(\frac{180}{\pi}\right)^2 \frac{\sigma^2(M_{hkl})}{M_{hkl}^2}$$

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

$$H_{hG}^2 = (U_f + (1-\xi_f)^2 D_{fST}^2(\boldsymbol{\alpha}_D))\tan^2\theta + \frac{I_{fG}}{\cos^2\theta} + H_{gG}^2$$

$$H_{hL} = (X_f + \xi_f D_{fST}(\boldsymbol{\alpha}_D))\tan\theta + \frac{[Y_f + F_f(\boldsymbol{\alpha}_S)]}{\cos\theta} + H_{gL}$$

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.

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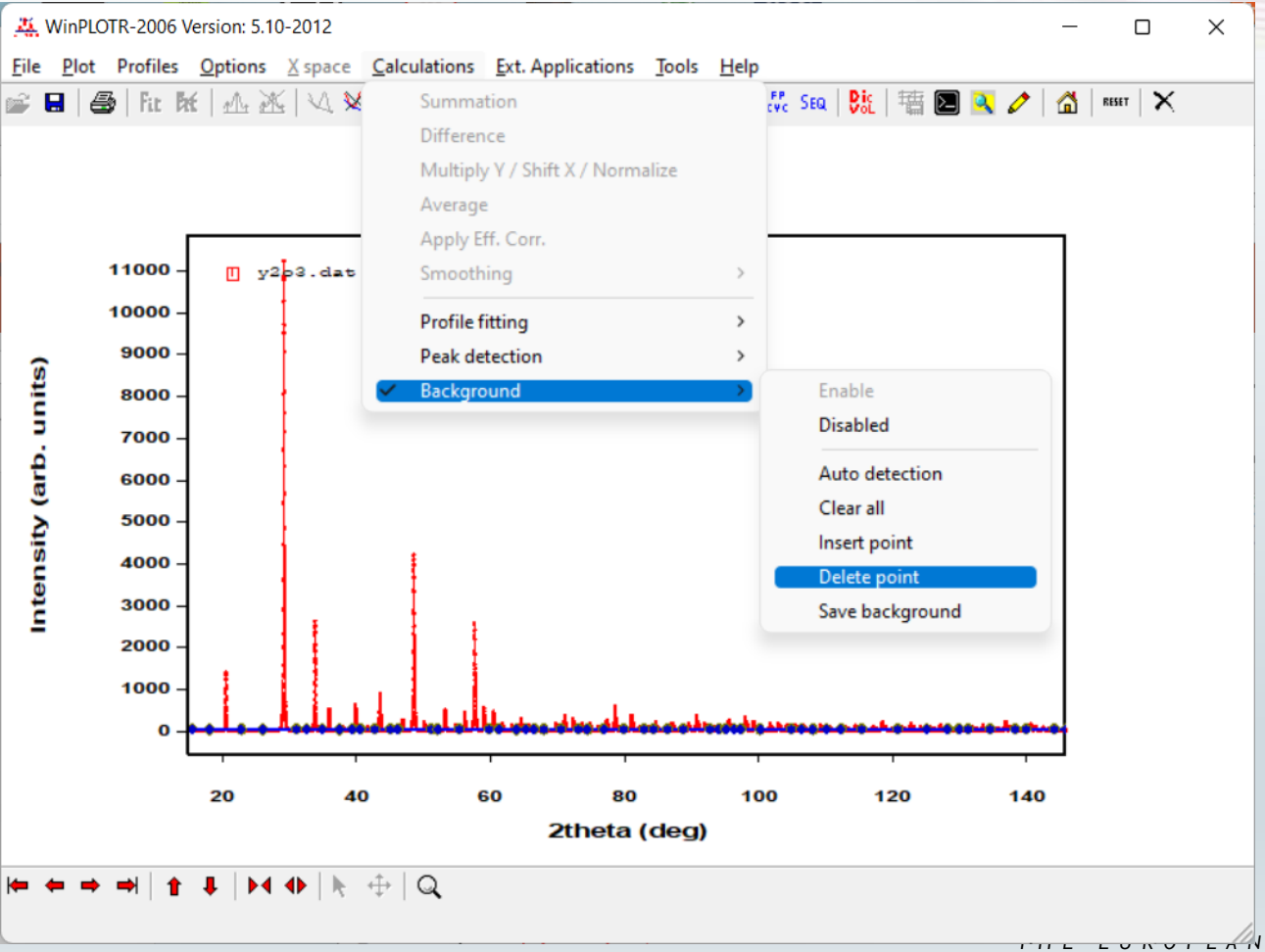
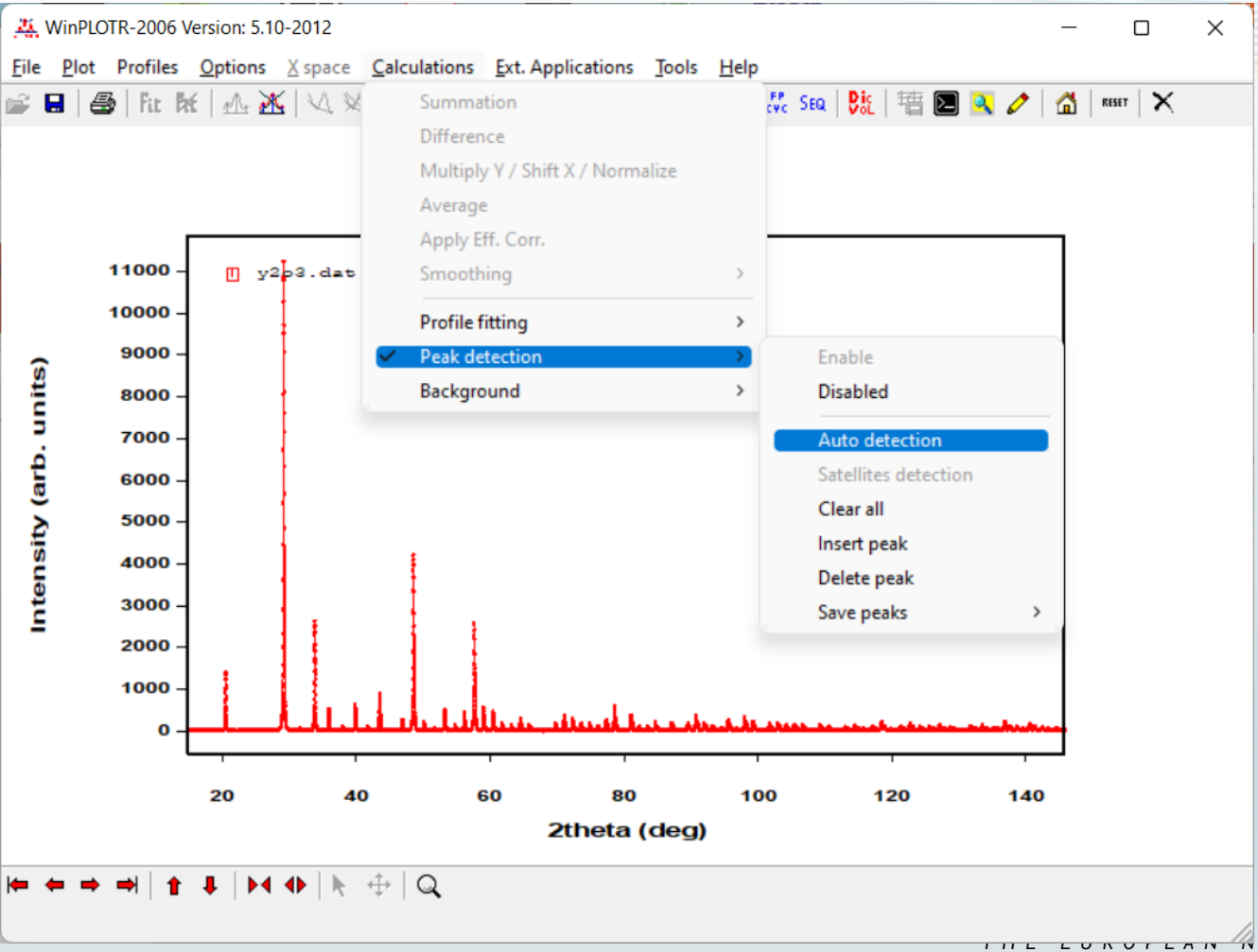
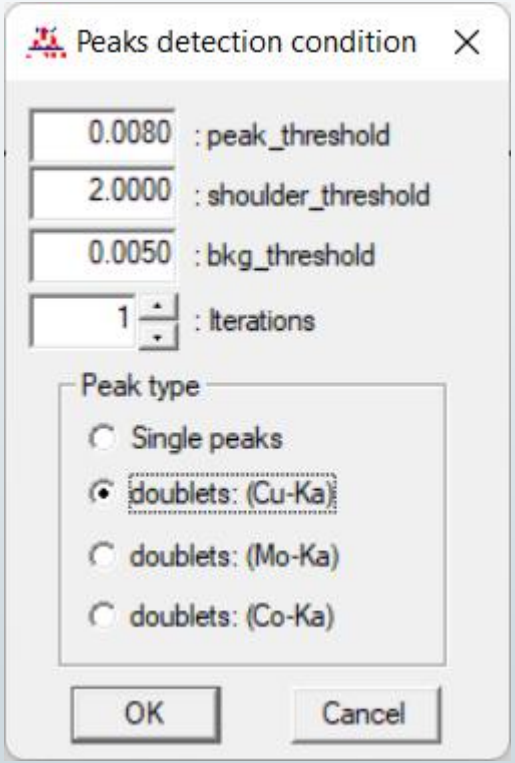


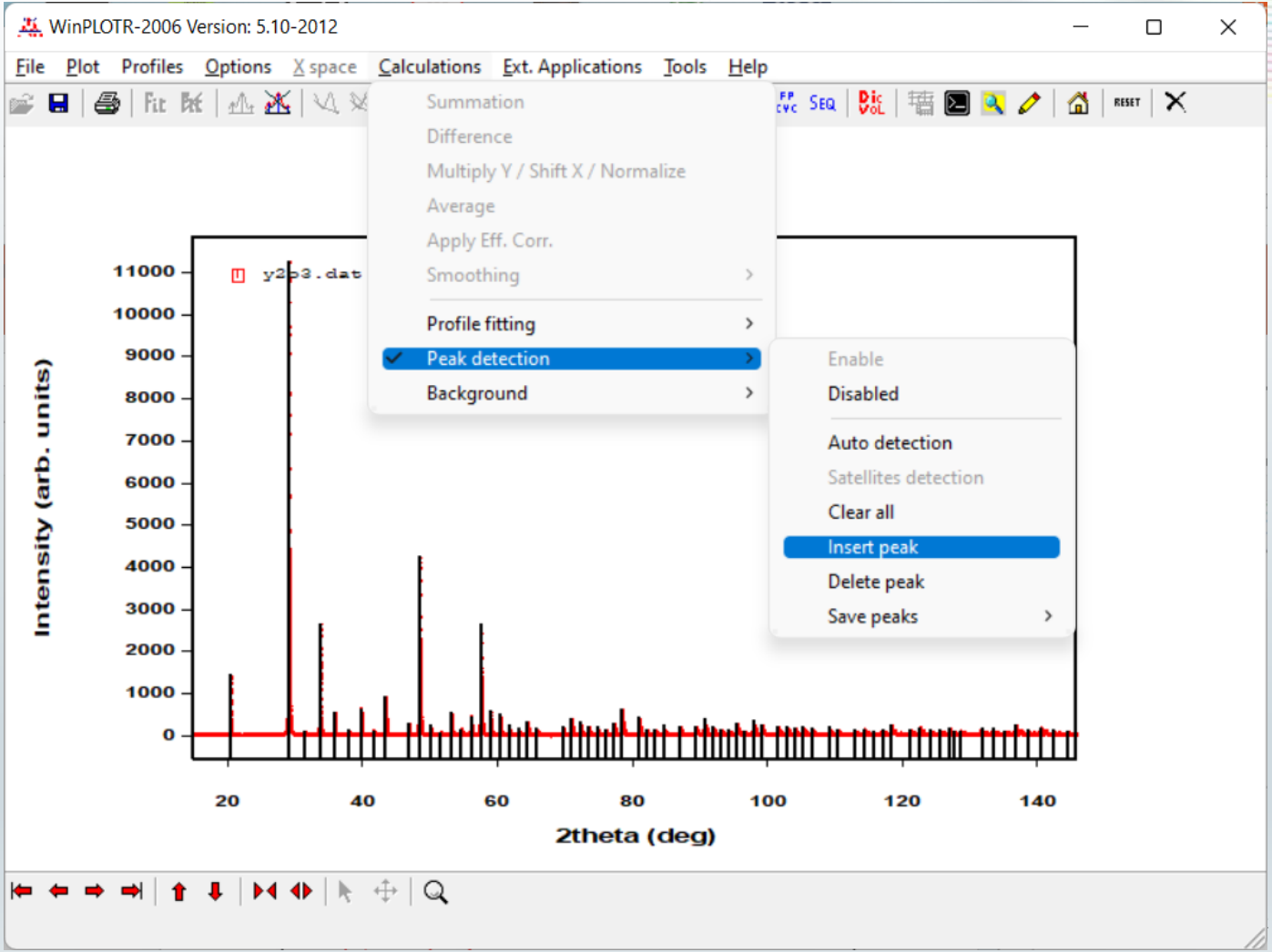
After opening the diffraction pattern in WinPLOTR-2006, go to the **Calculations** menu, select Background > Auto detection

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

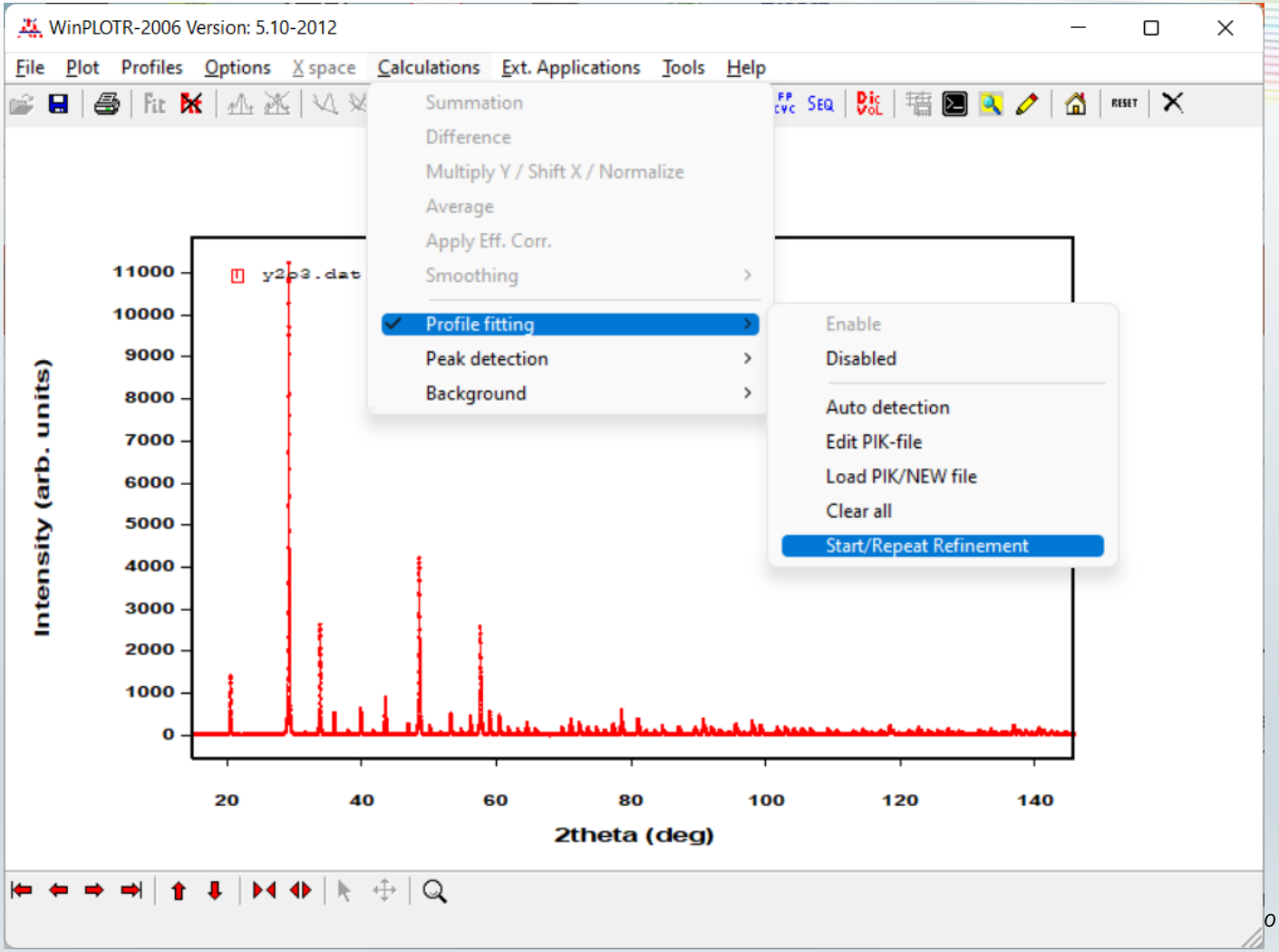

WinPLOTR-2006 Version: 5.10-2012
File Plot Profiles Options X space Calculations Ext. Applications Tools Help
Summation
Difference
Multiply Y / Shift X / Normalize
Average
Apply Eff. Corr.
Smoothing
Profile fitting
Peak detection
Background
Enable
Disabled
Auto detection
Satellites detection
Clear all
Insert peak
Delete peak
Save peaks
Intensity (arb. units)
2theta (deg)


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



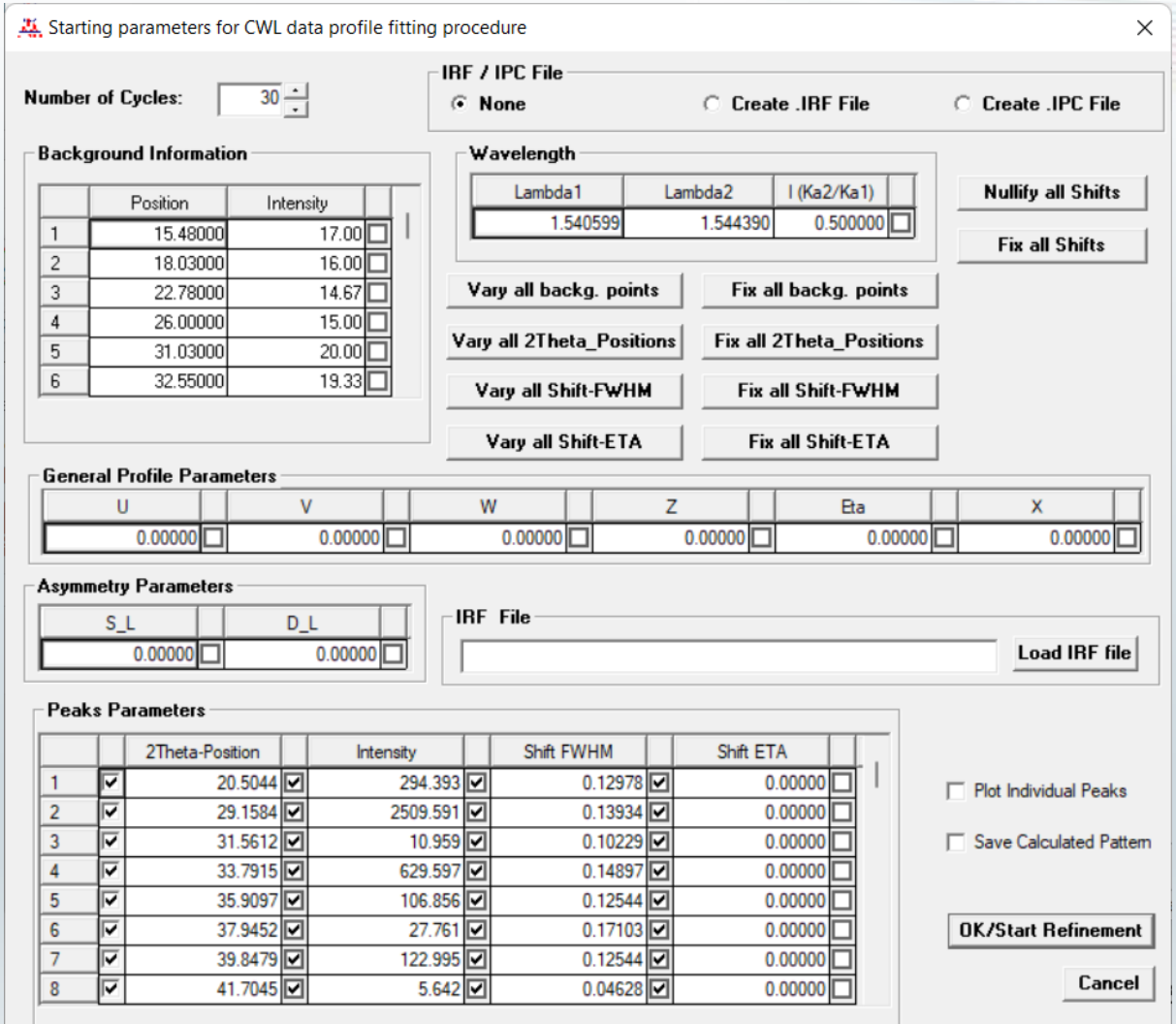
After selecting, deleting and inserting the appropriate peaks. Select **Disable** in order to keep the selected peaks in memory

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.



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

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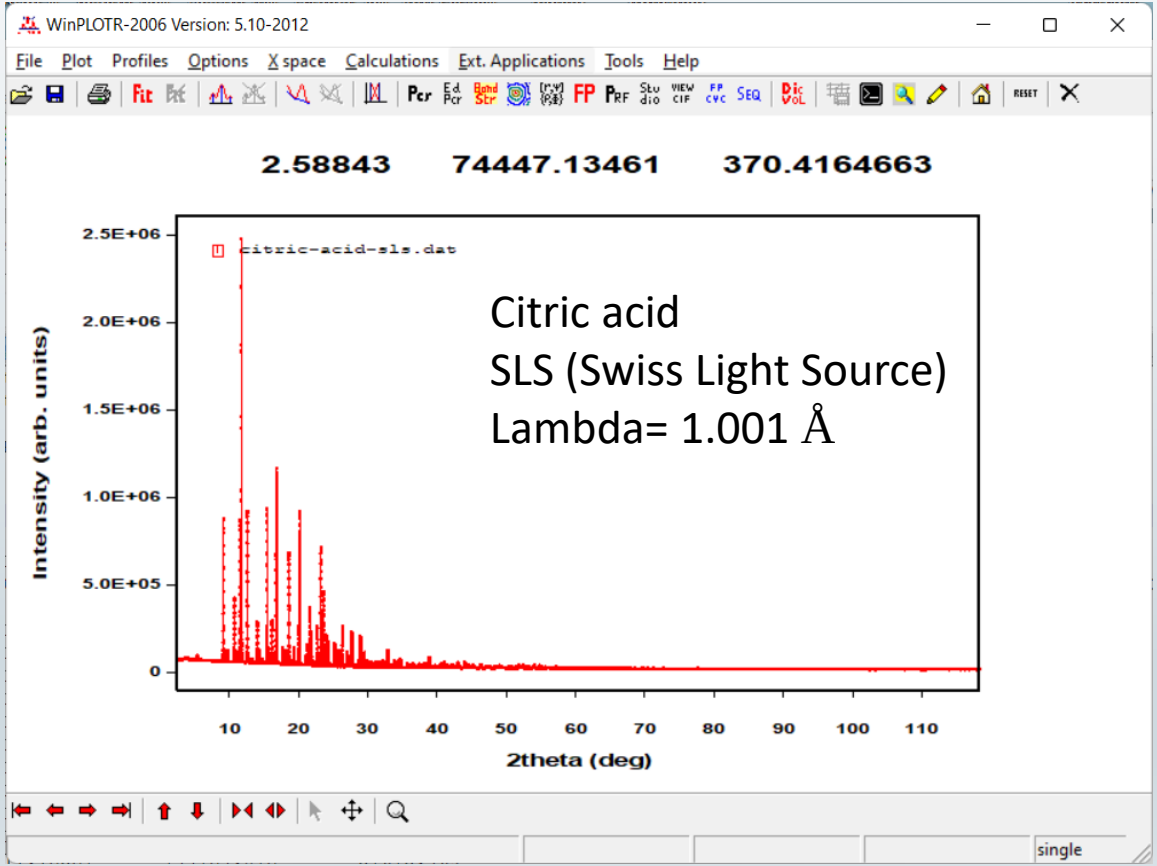
Let us start by indexing a powder diffraction pattern coming from the synchrotron SLS (Switzerland)

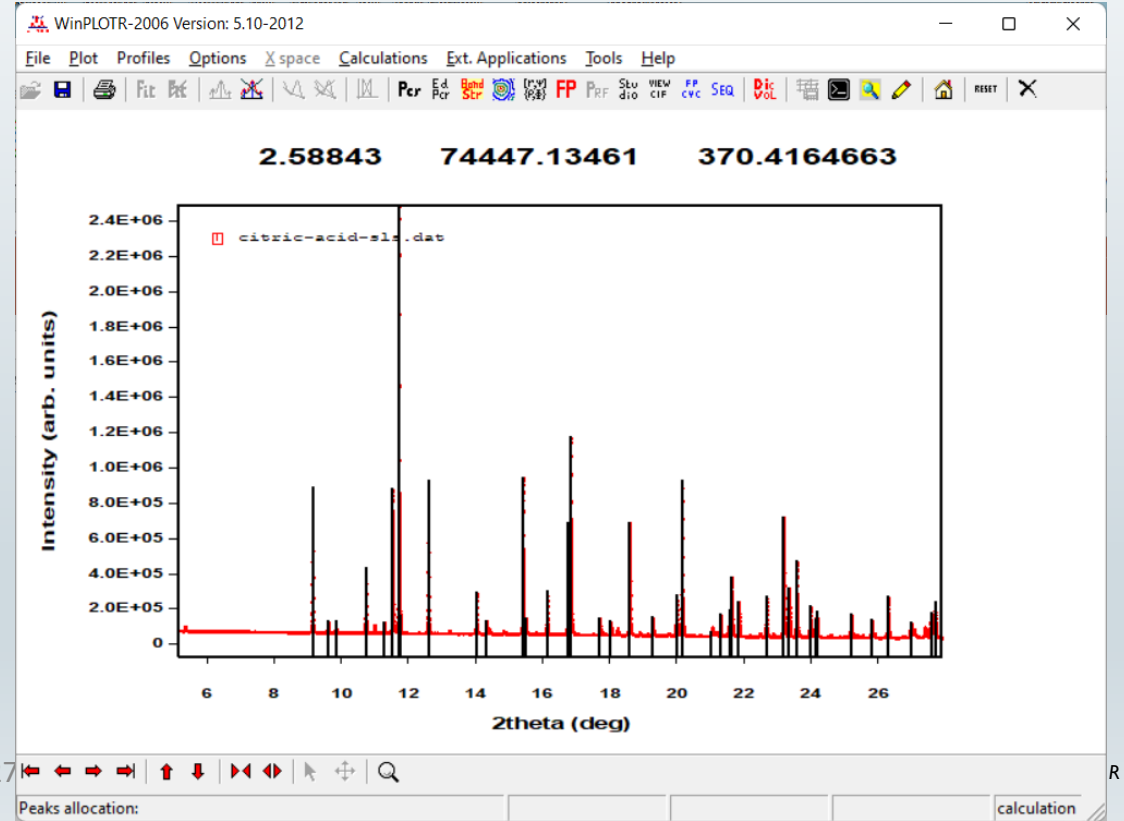


For indexing a PDP it is important to select the low-angle peaks, otherwise the overlap may hinder the solution.

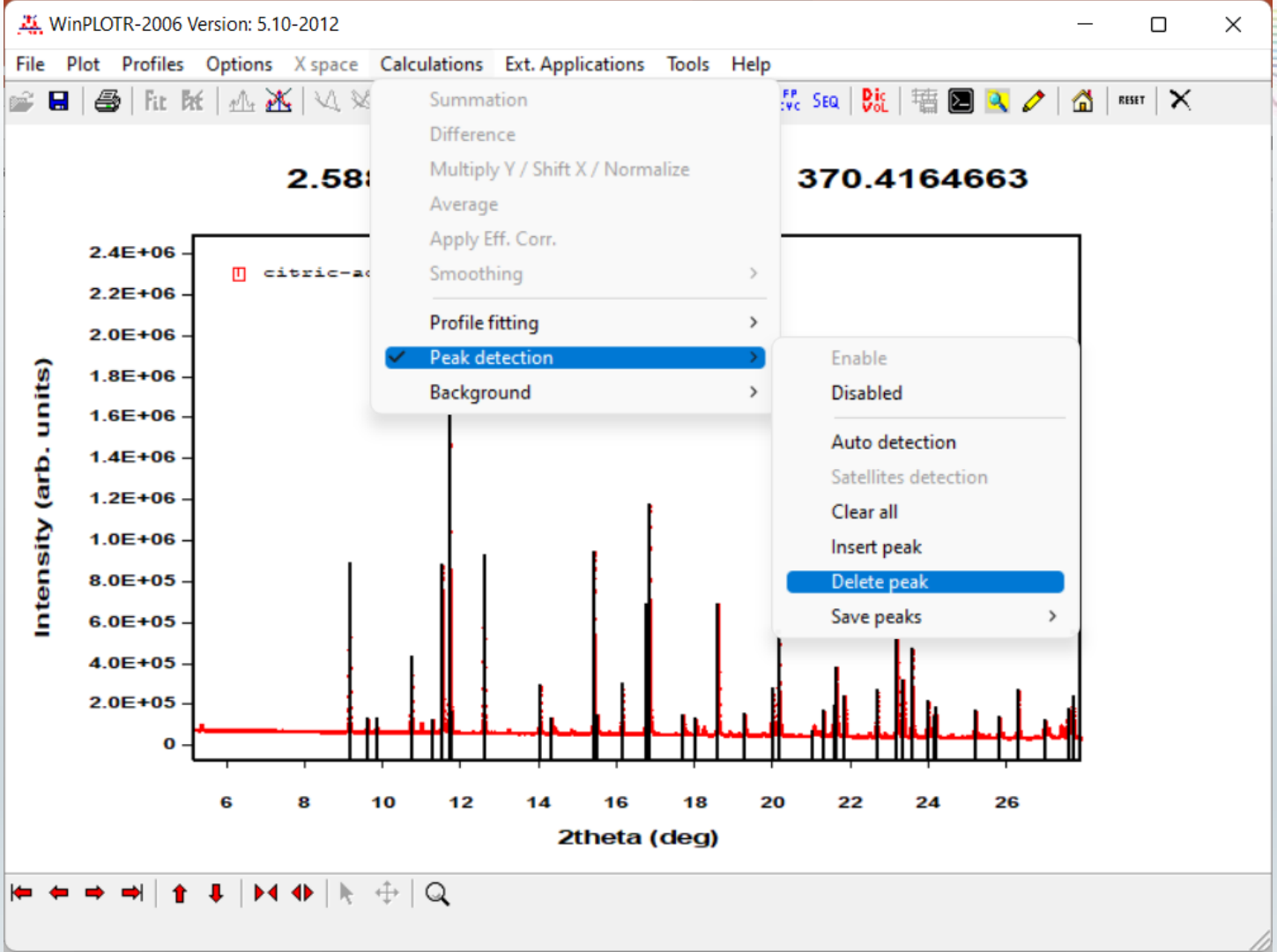
Also it is important, in the first approximation, to discard small intensity peaks.

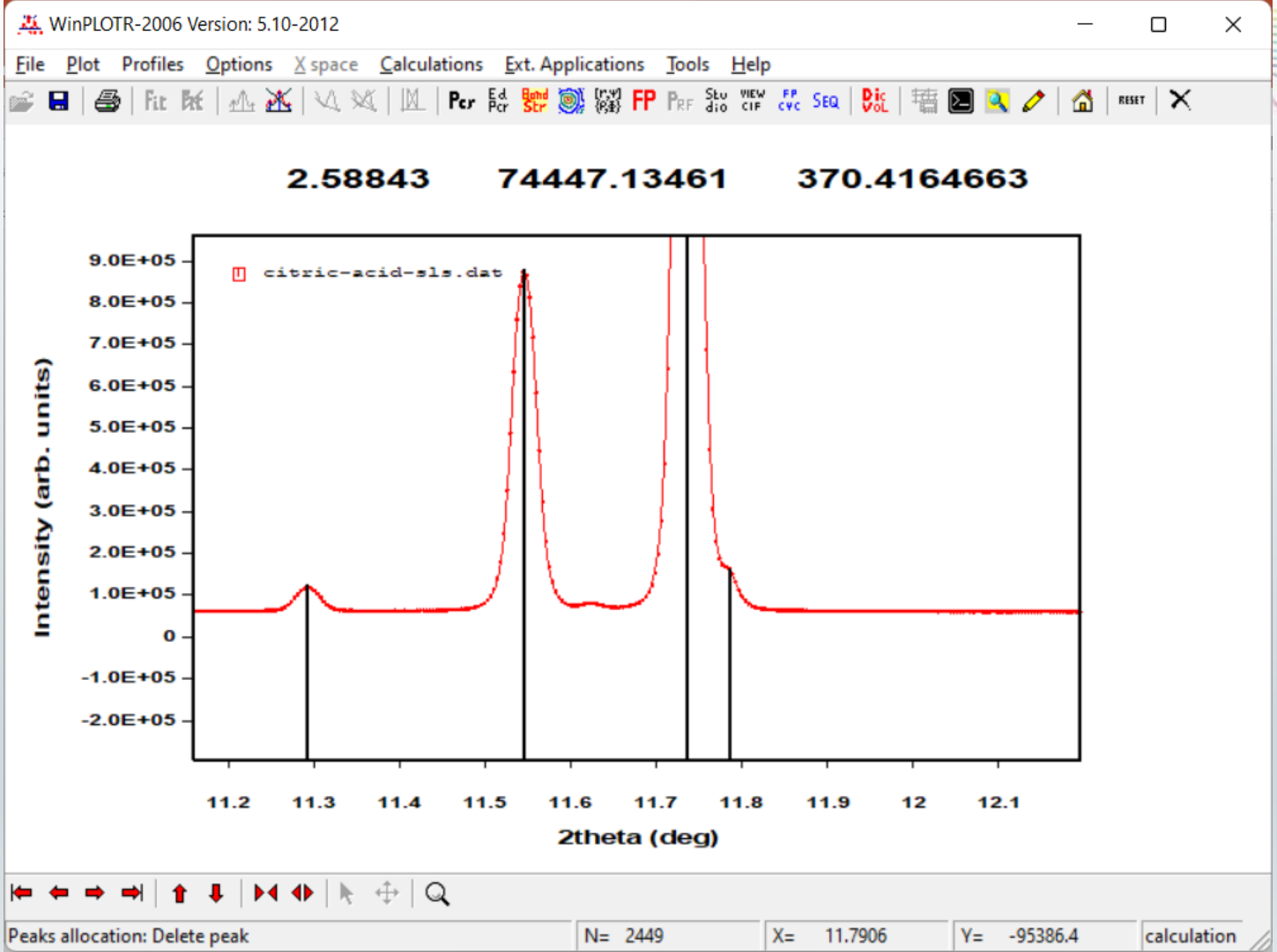
Within WinPLOR-2006

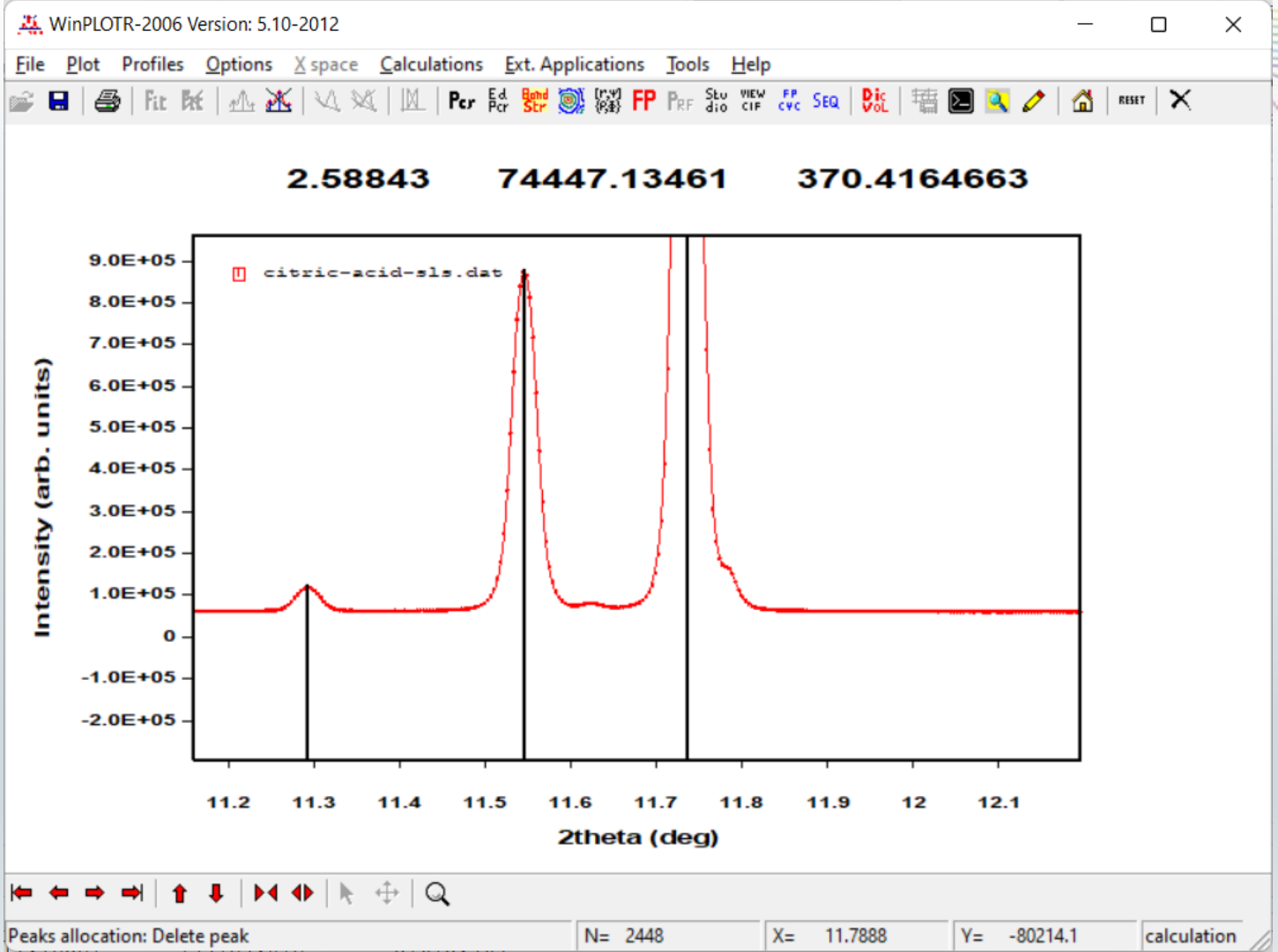
1. Select the low angle region containing at least 20 visible peaks
2. In the Calculations menu select Peak Detection > Enable
3. Select Autodetection

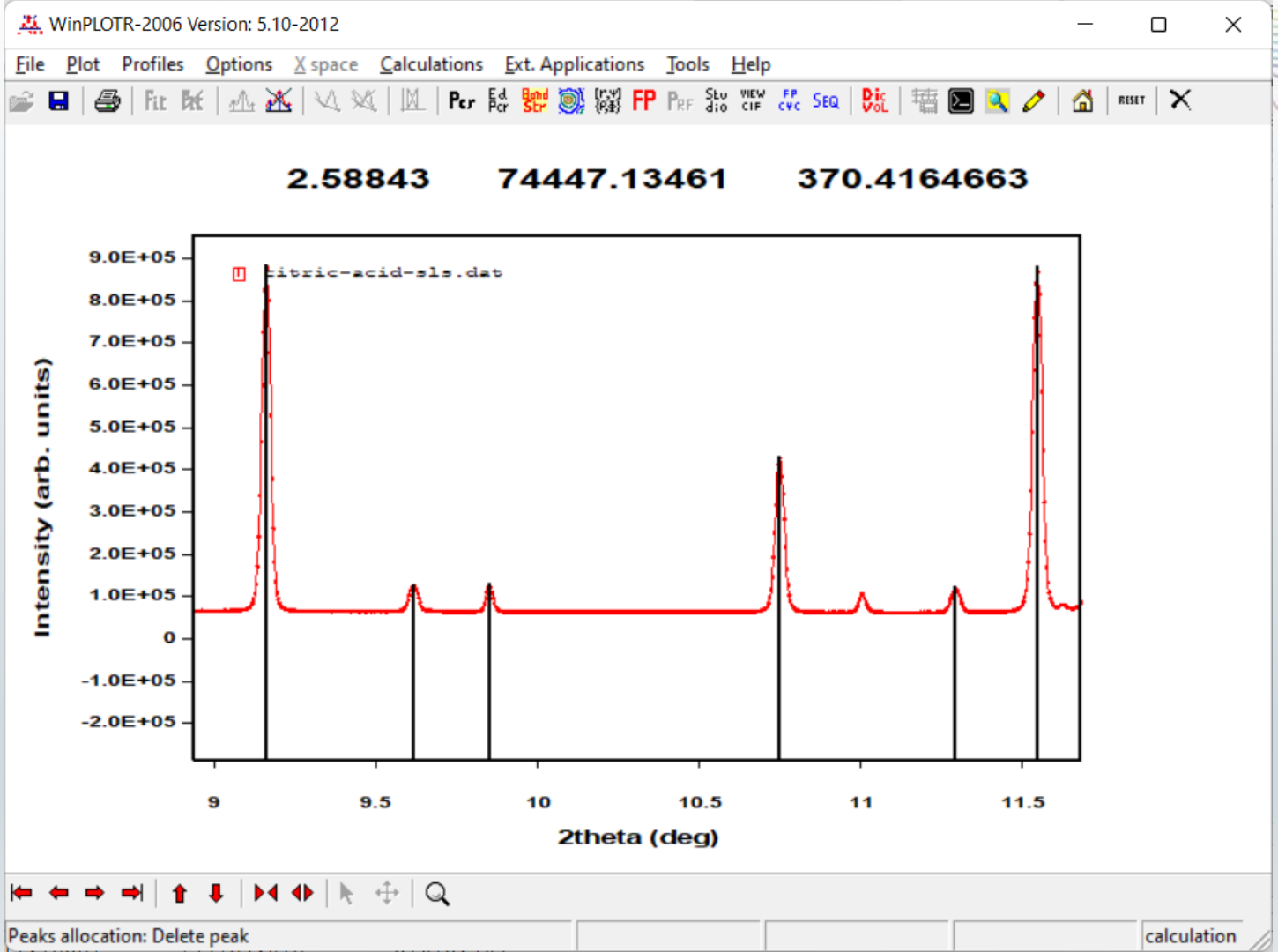


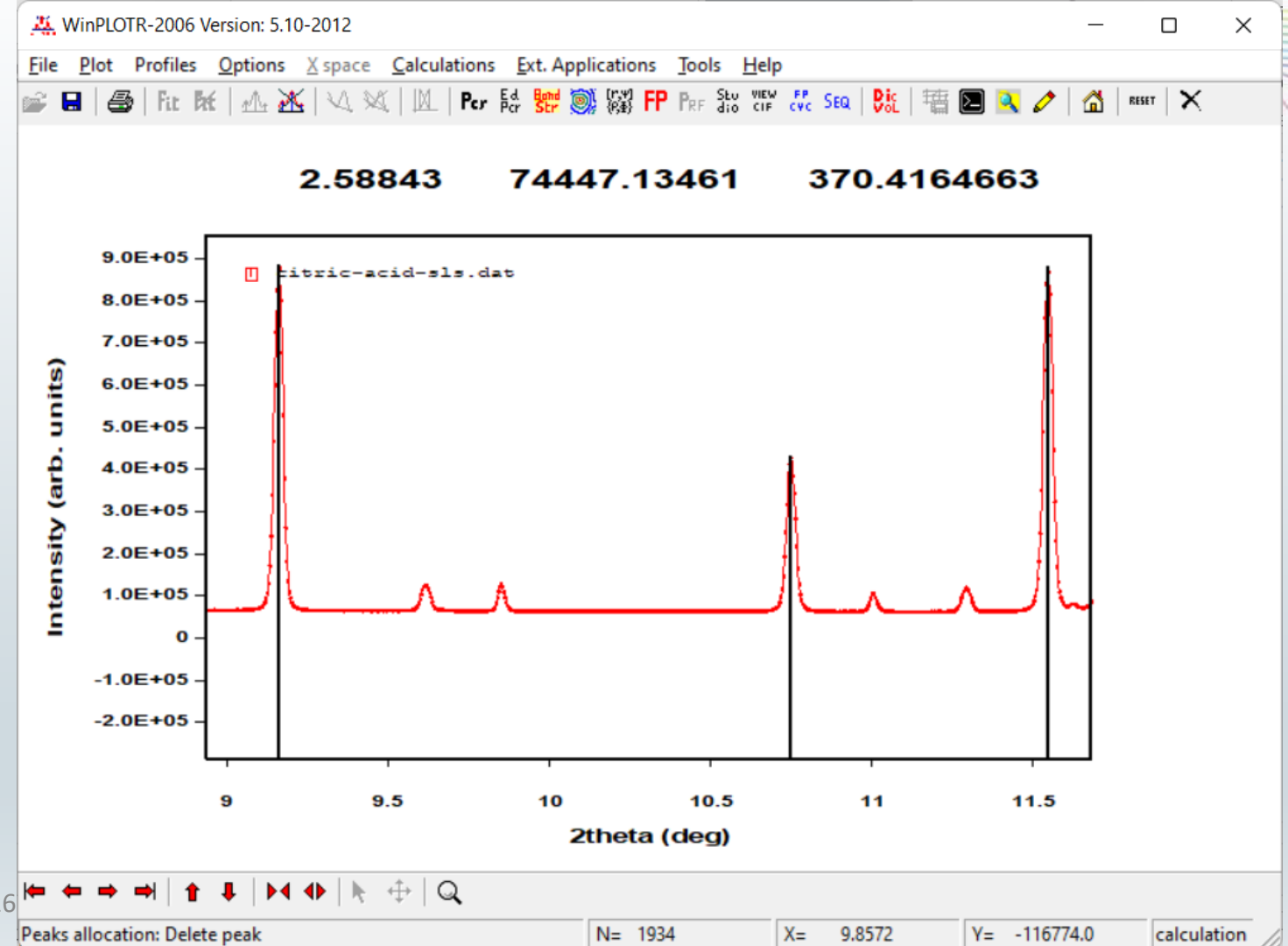
- Eliminate some of the smallest intensity peaks and peaks on shoulders
- Insert high intensity peaks if they have not been detected

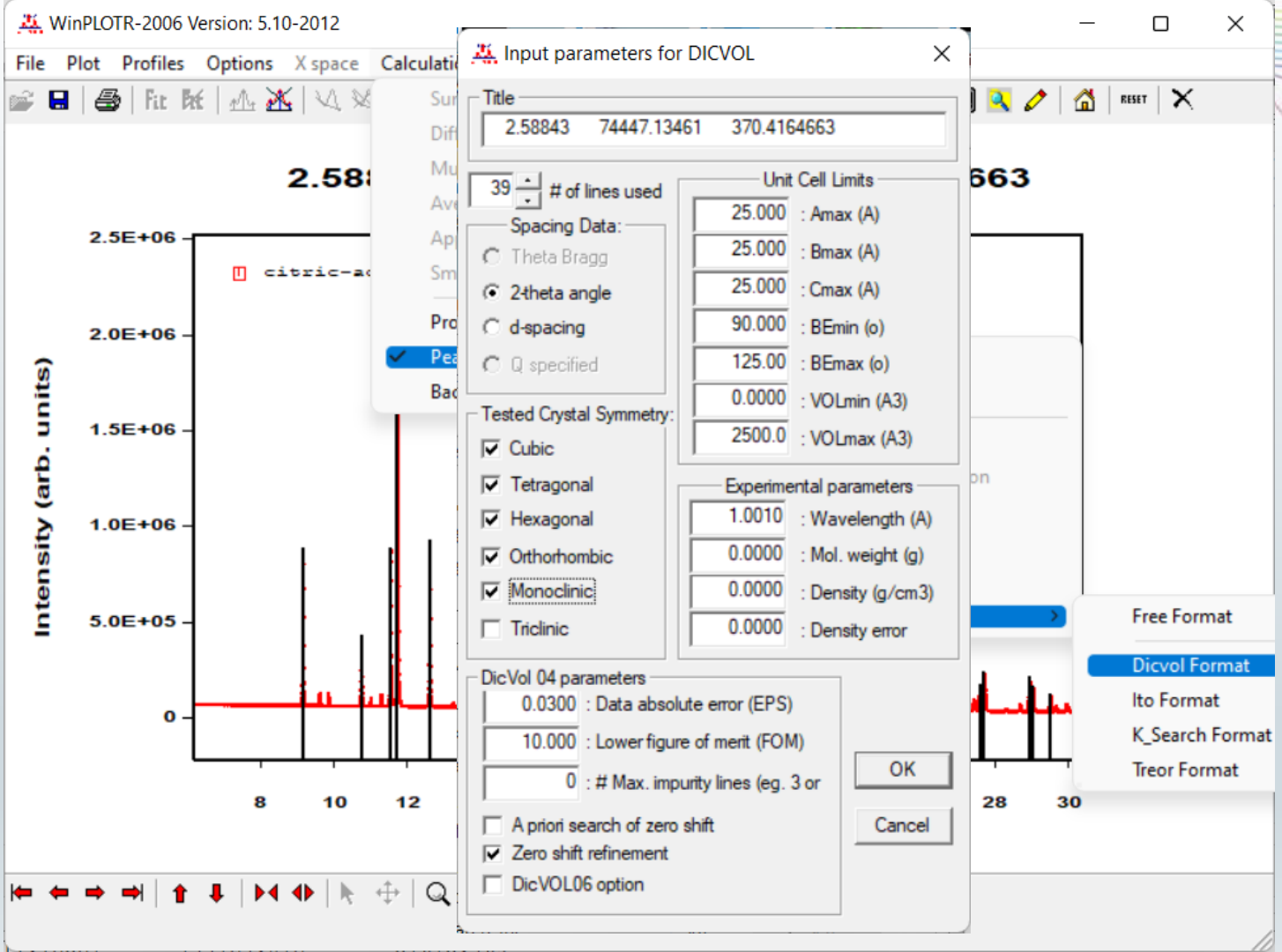

WinPLOTR-2006 Version: 5.10-2012
File
Plot
Profiles
Options
X space
Calculations
Ext. Applications
Tools
Help
Summation
Difference
Multiply Y / Shift X / Normalize
Average
Apply Eff. Corr.
Smoothing
Profile fitting
Peak detection
Background
Enable
Disabled
Auto detection
Satellites detection
Clear all
Insert peak
Delete peak
Save peaks
370.4164663
Intensity (arb. units)
2theta (deg)

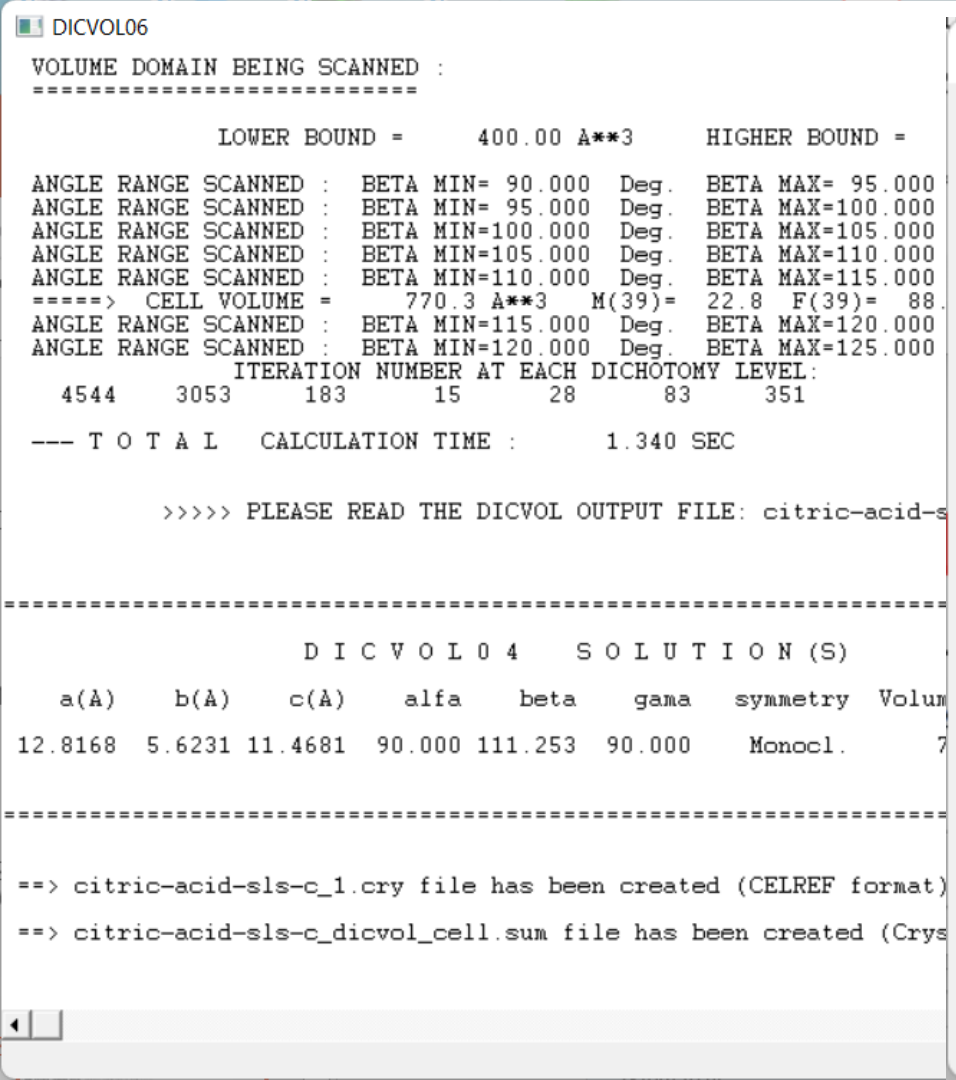


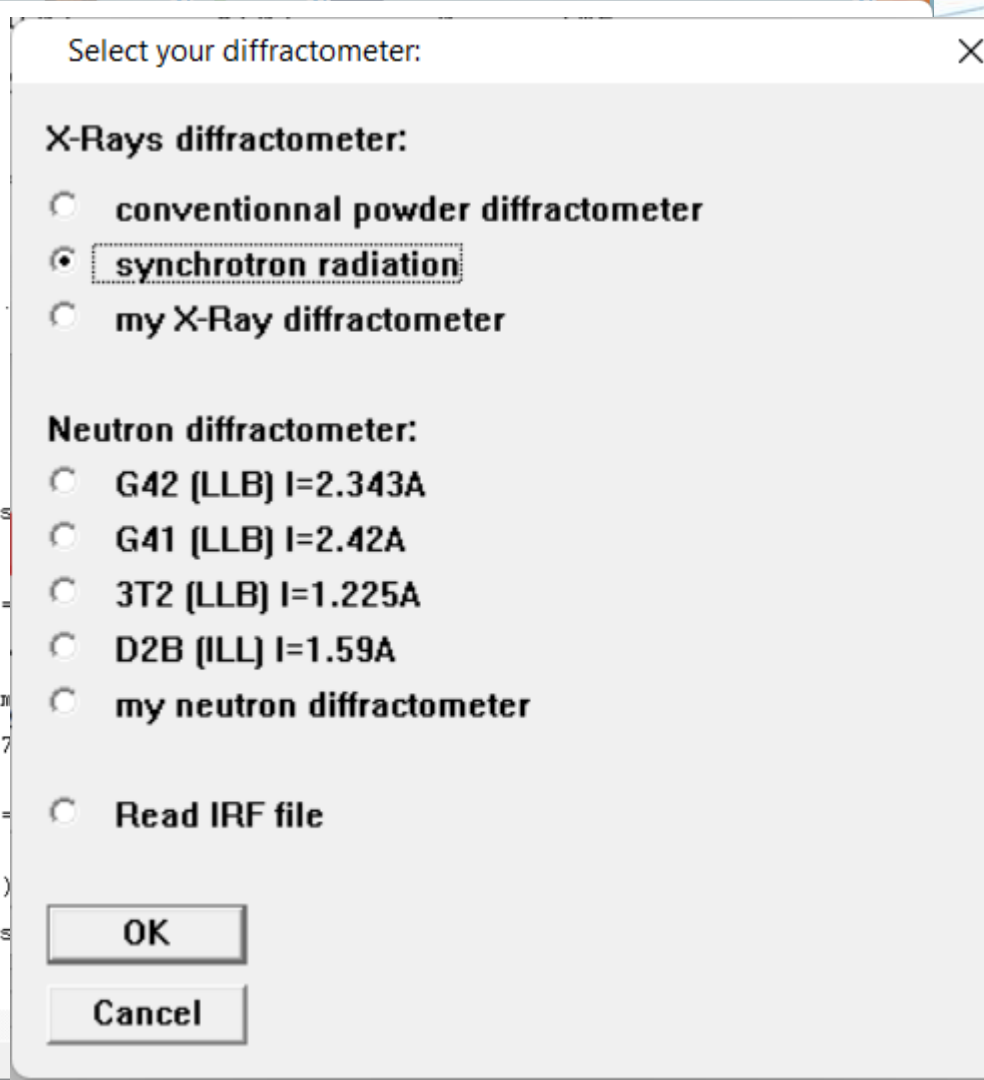

WinPLOTR-2006 Version: 5.10-2012
File Plot Profiles Options X space Calculations Ext. Applications Tools Help
2.58843 74447.13461 370.4164663
citric-acid-sls.dat
Intensity (arb. units)
9.0E+05
8.0E+05
7.0E+05
6.0E+05
5.0E+05
4.0E+05
3.0E+05
2.0E+05
1.0E+05
0
-1.0E+05
-2.0E+05
11.2 11.3 11.4 11.5 11.6 11.7 11.8 11.9 12 12.1
2theta (deg)
Peaks allocation: Delete peak
N= 2448
X= 11.7888
Y= -80214.1
calculation


WinPLOTR-2006 Version: 5.10-2012
File Plot Profiles Options X space Calculations Ext. Applications Tools Help
2.58843 74447.13461 370.4164663
citric-acid-sls.dat
Intensity (arb. units)
9.0E+05
8.0E+05
7.0E+05
6.0E+05
5.0E+05
4.0E+05
3.0E+05
2.0E+05
1.0E+05
0
-1.0E+05
-2.0E+05
9
9.5
10
10.5
11
11.5
2theta (deg)
Peaks allocation: Delete peak
calculation


WinPLOTR-2006 Version: 5.10-2012
File Plot Profiles Options X space Calculations Ext. Applications Tools Help
2.58843 74447.13461 370.4164663
citric-acid-sls.dat
Intensity (arb. units)
9.0E+05
8.0E+05
7.0E+05
6.0E+05
5.0E+05
4.0E+05
3.0E+05
2.0E+05
1.0E+05
0
-1.0E+05
-2.0E+05
9
9.5
10
10.5
11
11.5
2theta (deg)
Peaks allocation: Delete peak
N= 1934
X= 9.8572
Y= -116774.0
calculation


WinPLOTR-2006 Version: 5.10-2012
File
Plot
Profiles
Options
X space
Input parameters for DICVOL
Title
2.58843 74447.13461 370.4164663
39 # of lines used
Spacing Data:
Theta Bragg
2-theta 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
A priori search of zero shift
Zero shift refinement
DicVOL06 option
OK
Cancel
Free Format
Dicvol Format
Ito Format
K_Search Format
Treor Format
Intensity (arb. units)
2.5E+06
2.0E+06
1.5E+06
1.0E+06
5.0E+05
0
8
10
12
28
30

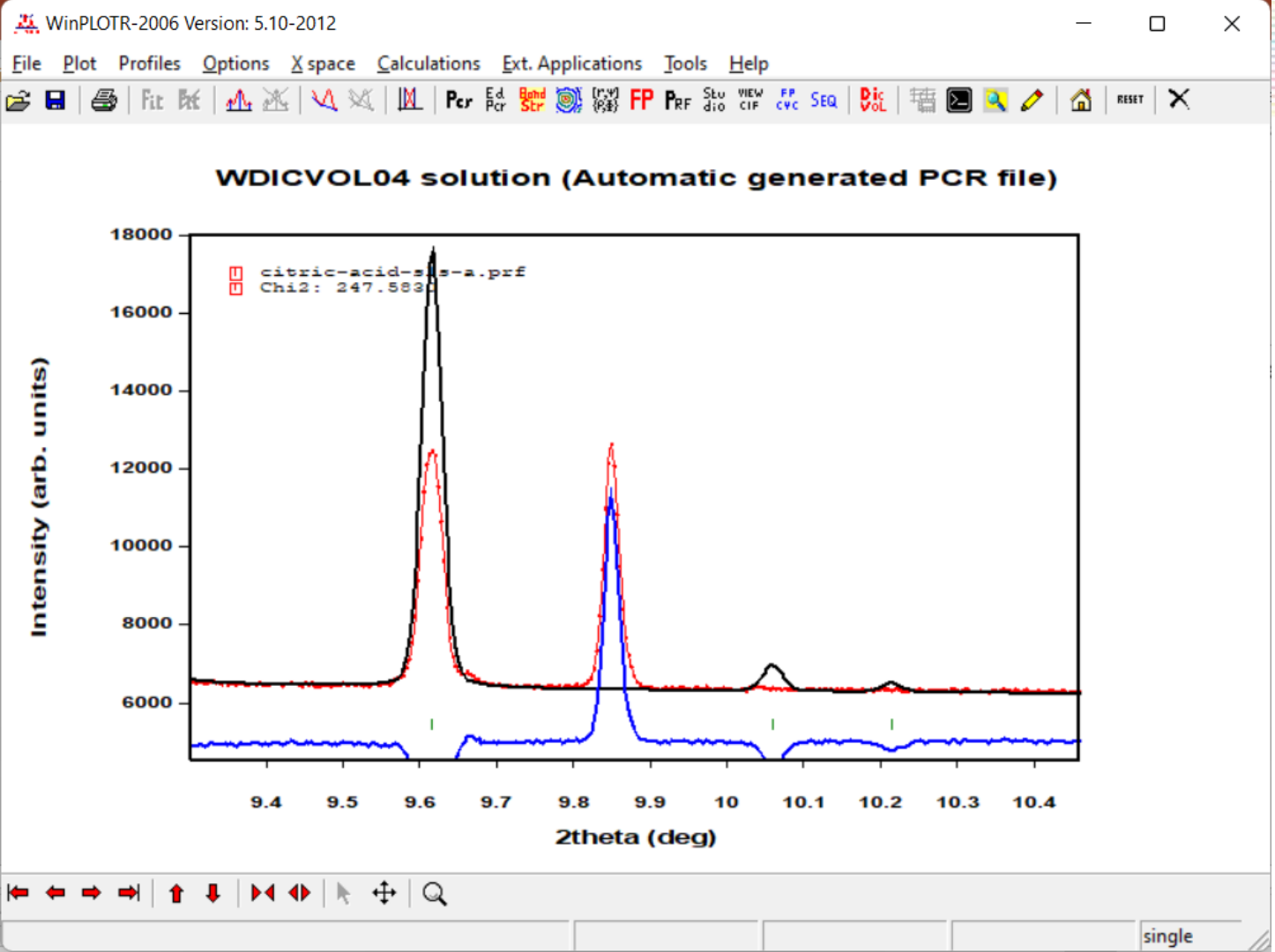

DICVOL06
VOLUME DOMAIN BEING SCANNED :
LOWER BOUND = 400.00 A**3 HIGHER BOUND =
ANGLE RANGE SCANNED : BETA MIN= 90.000 Deg. BETA MAX= 95.000
ANGLE RANGE SCANNED : BETA MIN= 95.000 Deg. BETA MAX=100.000
ANGLE RANGE SCANNED : BETA MIN=100.000 Deg. BETA MAX=105.000
ANGLE RANGE SCANNED : BETA MIN=105.000 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) l=2.343A
G41 (LLB) l=2.42A
3T2 (LLB) l=1.225A
D2B (ILL) l=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   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        Shape1       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
```



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.

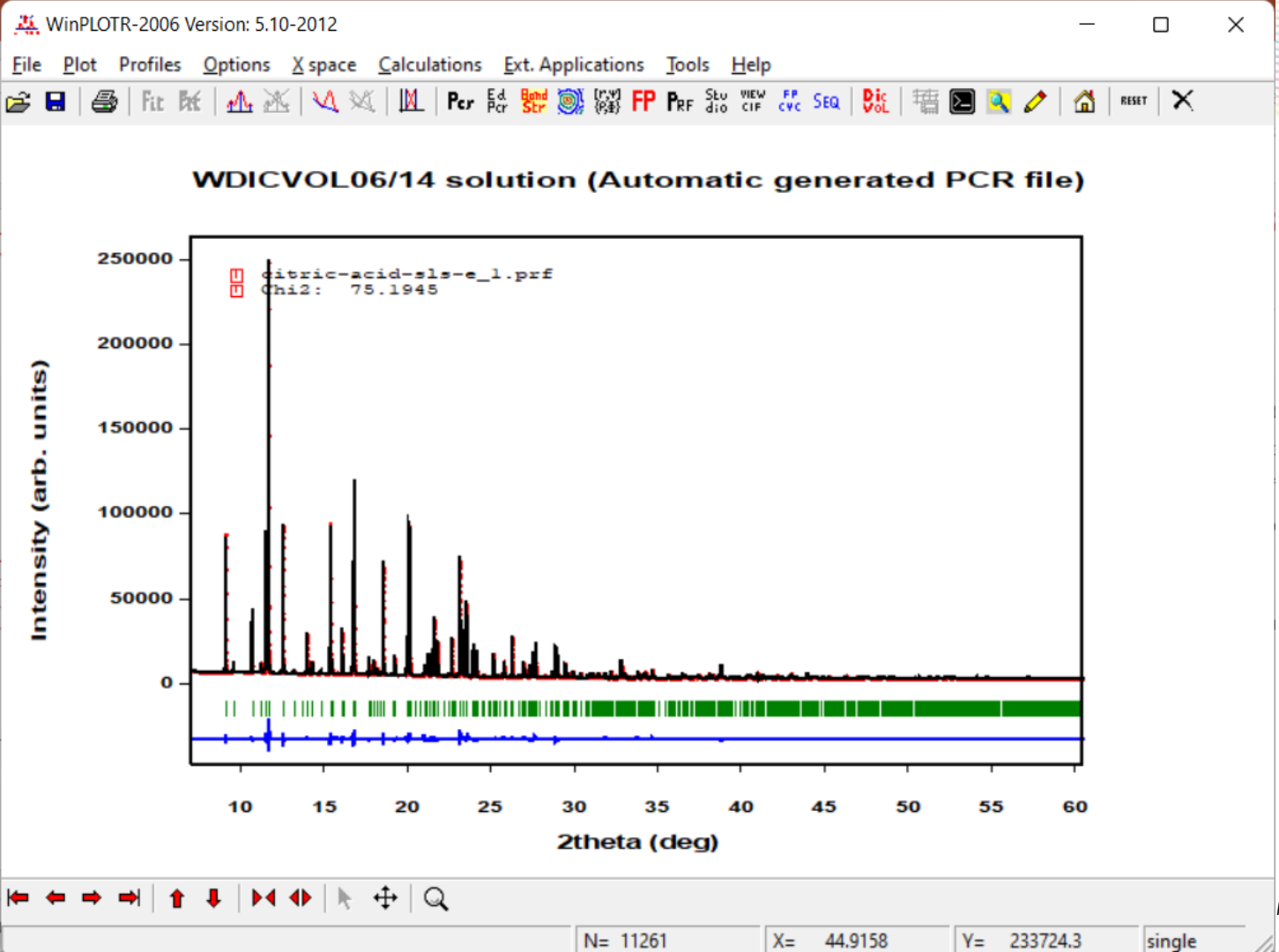
In order to obtain better intensities of the phase to be solved it is better to exclude impurity peaks

```
! 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
. . .
!-------------------------------------------------------------------------------
!  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_Ref Ph_Shift N_Domains
  11   0   0   0   0   0  1.0000  0.0000   0.0000   0.0000     0       0       0       0
!
!
P 21/a                    <--Space group symbol
!-------> Profile Parameters for Pattern #   1  ----> Phase #   1
!  Scale          Shape1       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
   1.00000  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
```

Impurity peaks have to be excluded

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

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



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
  -1    1    1       91564.67188         21.19823    1          0.0000
   2    0    1       33548.95703         18.23029    1          0.0000
   1    1    1         912.97614         11.04930    1          0.0000
. . .
  -9    2    8        1397.27820          2.27191    1          0.0000
   4    3    6          -1.00000          0.08982    1          0.0000
  -9    1    9          -1.00000          0.58520    1          0.0000
   4    4    4          -1.00000          0.57493    1          0.0000
  10    0    2          -1.00000          0.68488    1          0.0000
   7    4    0         306.99512          1.29702    1          0.0000
   9    3    0          -1.00000          0.26166    1          0.0000
  -7    1   10          -1.00000          1.32122    1          0.0000
   3    5    0          -1.00000          1.01764    1          0.0000
   4    0    8          -1.00000          1.06261    1          0.0000
  -3    5    2         743.89368          2.04895    1          0.0000
. . .
```

0.0000 11.5465
0.0000 11.7368
0.0000 12.6108
0.0000 13.2432
0.0000 54.8340
0.0000 54.9027
0.0000 54.9351
0.0000 54.9357
0.0000 54.9500
0.0000 54.9531
0.0000 55.0553
0.0000 55.0897
0.0000 55.1026
0.0000 55.1073
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