

A guided training exercise of quantitative phase analysis using EXPGUI

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INTRODUCTION

In the last decade, quantitative phase analysis (QPA) using the Rietveld method (Rietveld, 1969; Bish & Howard, 1988; Bish & Post, 1993; Hill, 1991) has been applied to systems of gradually increasing complexity (in the number of phases, their structure complexity and even their degree of structure order). In the QPA using the Rietveld method, the weight fraction w_i of each i^{th} crystalline component in the mixture is calculated from the corresponding refined scale parameter S_i , according to the equation

$$w_i = \frac{S_i M_i V_i}{\sum_j S_j M_j V_j}$$

with M_i and V_i , the unit cell mass and volume, respectively. This algorithm is based on the normalisation condition $\sum w_i = 1.0$. The scattering contribution of any amorphous component possibly existing in the sample is a part of the background and the above normalisation equation does not include it. The specific problem is usually solved using an internal standard, suitably chosen, which is added in a known amount to the investigated mixture and treated as a mixture component itself. At the end of the Rietveld process, the refined phase fractions are converted into weight fractions and rescaled to the values of the original mixture by the ratio between the refined ($X_{s,c}$) and the known (X_s) amount of added standard. Whenever an amorphous phase exists in the system, the values of the weight fractions are overestimated to satisfy the normalisation condition. The percentage of the amorphous phase X_a in the original mixture can be calculated directly from the weight of the internal standard according to the equation

$$X_a = \frac{100}{(100 - X_s)} \left(1 - \frac{X_s}{X_{s,c}} \right)$$

One of the ultimate challenges of QPA is to achieve accurate weights in complex systems containing crystalline and amorphous phases as shown by the number of papers recently published in the specific literature (see for example Artioli et al., 2002; De La Torre et al., 2000, 2002; Feret & Roy, 2002; Gualtieri, 2000; Guirado et al., 2000; Orhac et al., 2000 using an internal standard and Riello et al., 1998a,b using empirical functions to fit the contribution of the amorphous phase). The interest in this area is predicted to increase if one considers that the appealing nano-science world describes crystal-size dependent properties of systems that cover a broad range between the crystalline and the amorphous state. These analyses can be performed using the existing freeware software GSAS and EXPGUI.

The aim of this contribution is to give a guided training exercise designed for beginners of QPA of a ternary mixture containing an amorphous phase using EXPGUI.

THE GSAS AND EXPGUI PACKAGES

This short paragraph is to help the reader to find information and download software for GSAS and EXPGUI. GSAS (General Structure Analysis System) is a comprehensive system for the refinement of structural models to both x-ray and neutron diffraction data. GSAS has been created by Allen C. Larson and Robert B. Von Dreele of Los Alamos National Laboratory. Executable versions of GSAS are distributed more-or-less freely but the source code is not distributed. The principal GSAS site is <ftp://ftp.lanl.gov/public/gsas/>. Here are some GSAS mirror sites:

<http://www.ccp14.ac.uk/ccp/ccp14/ftp-mirror/gsas/public/gsas/>

<ftp://ftp.ccp14.dl.ac.uk/ccp14/ftp-mirror/gsas/public/gsas/>

<http://ccp14.sims.nrc.ca/ccp/ccp14/ftp-mirror/gsas/public/gsas/>

The manual can also be found on-line: <ftp://ftp.lanl.gov/public/gsas/manual/GSASManual.pdf>. The manual is what you should cite when publishing a structure refined with GSAS [and of course you will cite it: A.C. Larson and R.B. Von Dreele, "General Structure Analysis System (GSAS)", Los Alamos National Laboratory Report LAUR 86-748 (2000). Mirror sites for the manual are

<http://www.ccp14.ac.uk/ccp/ccp14/ftp-mirror/gsas/public/gsas/manual/GSASManual.pdf>

<http://ccp14.sims.nrc.ca/ccp/ccp14/ftp-mirror/gsas/public/gsas/manual/GSASManual.pdf>

Much of the same is true for EXPGUI: B. H. Toby, *EXPGUI*, a graphical user interface for *GSAS*, *J. Appl. Cryst.* **34**, 210-213 (2001). EXPGUI is a graphical user interface (GUI) editor for GSAS experiment (.EXP) files and shell which allows all the other GSAS programs to be executed with a GUI. EXPGUI is not a replacement for the GSAS program EXPEDT. EXPGUI is written in the Tcl/Tk scripting language, so it is largely platform independent. Documentation is found at B. H. Toby, *EXPGUI*, a graphical user interface for *GSAS*, *J. Appl. Cryst.* (2001). **34**, 210-213). You can also find EXPGUI documentation at:

<http://www.ncnr.nist.gov/xtal/software/expgui/expgui.html>

If you are new to GSAS & EXPGUI, it is recommended to start with this:

<http://www.ncnr.nist.gov/xtal/software/expgui/tutorial3>

as the data and web pages were intended to be "user-friendly." There are also three tutorials in the GSAS manual as well as several on the CCP14 site. Two of the tutorials from the GSAS manual are repeated as examples for EXPGUI: <http://www.ncnr.nist.gov/xtal/software/expgui/tutorial1> and <http://www.ncnr.nist.gov/xtal/software/expgui/tutorial2>. These tutorials are intended to be read in parallel with the GSAS manual. A web page covers problems related to GSAS & EXPGUI: NCNR GSAS FAQ page. Send your contributions (preferably in HTML) for inclusion on this page to crystal@NIST.gov. Software bugs should be reported for GSAS to Bob Von Dreele (vondreele@lanl.gov) and for EXPGUI to Brian Toby (brian.toby@NIST.gov).

A REAL CASE AS A TRAINING EXERCISE OF QPA

It is reported here a guided training exercise designed for the user who has never used GSAS and EXPGUI for the QPA of a ternary mixture containing corundum, hydroxyapatite and an amorphous phase using EXPGUI. The refinement is described in detail step by step. A special attention is devoted to the refinement strategy which is of paramount importance to achieve a sound result. Practical advices and suggestions are also given together with literature citations. Although this is addressed to the beginner, it is strongly encouraged to time some time to read the milestones papers by McCusker et al. (1999), Madsen et al. (2001) and of course the GSAS manual before the start of the QPA Rietveld refinement.

Sample selection and preparation

The example reported here is a full description of a Rietveld refinement using EXPGUI for the determination of the phase weights in a polyphasic mixture containing an amorphous phase. The glass (amorphous) fraction must be determined indirectly with the aid of an internal standard (Gualtieri, 2000). The mixture is composed of 45 wt% glass, 10 wt% corundum NIST 676 (the internal standard) and 45 wt% hydroxyapatite NIST 2910. The glass has composition (wt%): SiO₂ = 20.72; BaO = 8.09; PbO = 71.13; Al₂O₃ = 0.02; CaO = 0.02; K₂O = 0.02. The powder was obtained by carefully weighing the crystalline and the amorphous phases using an analytical balance and homogenize the powder by hand grinding in agate mortar. One of the problems in the quantification of the amorphous phase using the internal standard methods is that the standard may not be fully crystalline. Corundum NIST 676 was annealed to increase the crystallinity to 100 wt%. The value of amorphous phase in the treated standard was reasonably assumed to be about 0 wt% by checking the peak ratio of the peak intensities before and after the treatment with the intensities of an internal standard (fluorite 311 and 422) although it is not possible to exclude that a minor quantity of amorphous alumina may still be present in the standard. Similarly, hydroxyapatite NIST 2910 was annealed for 1 d at 250 °C to eliminate the certified amorphous fraction of 7.5(4.1).

Data collection

Prior to the quantitative phase analysis one is generally supposed to have a preliminary qualitative phase analysis in order to determine:

- (i) the number and phases in the mixture – remember that you need the structure model of each phase! In the example, the phases are known a priori but that was just a test case! It should be remarked that if the structure model of a phase does not exist, EXPGUI cannot be used. There are other codes (e.g. QUANTO) capable of handling mixtures which contain phases with an unknown structure model assuming that a powder pattern of the pure phases with unknown structure is provided (Giannini et al., 2002);
- (ii) the angular range needed for the QPA data collection. In the example the first peak of hydroxyapatite is found at about 10.9 °2θ so it is useless to just collect background at 2θ < 10°;
- (iii) whether the mixture already contains the phase you want to use as an internal standard.

For a Rietveld refinement, it is essential that the powder data is properly collected. Factors to consider prior to data collection are the geometry of the diffractometer (for Bragg-Brentano geometries it is important that the incident beam is kept on the sample at all angles to ensure a constant-volume condition. Often the divergence slits used are too wide and the beam hits the sample holder at low angles so the intensities measured at these angles are too low), the quality of the alignment and calibration, the used radiation and wavelength, appropriate sample preparation, slit sizes, and step (there should be at least 5 steps across the top of each peak, that is step size = FWHM/5) and sufficient counting times (McCusker et al., 1999).

For this sample, the powder (with average particle size lower than 5 μm to get an ideal particle size for powder diffraction experiments) was side loaded to minimize preferred orientation (remember that the elimination of the problem experimentally is better than the empirical corrections!). The holder was a 2 mm thick flat Al holder and the data collection was performed using a Philips PW 1710 instrument with a conventional Bragg-Brentano (BB) parafocusing geometry equipped with a copper tube and a secondary beam pyrolytic graphite crystal monochromator. The data for the QPA refinements were collected in the angular range 10-100 $^{\circ}2\theta$ with steps of 0.02 $^{\circ}$ and 10 s/step, a divergence slit of 1 $^{\circ}$ and a receiving slit of 0.2 mm.

Structure models

The starting structure models were corundum from Ishizawa et al. (1980) and hydroxyapatite from Sudarsanan & Young (1969). Structure models can be taken from crystal structure databases such as ICSD (see <http://barns.ill.fr/dif/icsd/>) or The Cambridge Structural Database System (see www.ccdc.cam.ac.uk). There is a nice *on line* structure database for minerals on the Mineralogical Society of America web site: http://www.minsocam.org/MSA/Crystal_Database.html. A number of structure models were also provided by Ian Madsen within the IUCr Round Robin on Quantitative Phase Analysis (<http://www.iucr.ac.uk/iucr-top/comm/cpd/QARR/data-kit.htm>).

Data reduction

The raw data should be converted into a GSAS file for EXPGUI. The conversion can be achieved using one of the many freeware available programs. I personally use ConvX (www.ceramics.irl.cri.nz/Convert.htm) but a number of equivalent programs can be downloaded at CCP14 web site (www.ccp14.ac.uk). If ConvX is used, select the input format (in this example, Philips PC RD) and the output format = GSAS, then click Do Convert!

Rietveld refinement

The data set was refined using EXPGUI. To get the refinement started you need three files:

- 1) the data file, an ascii GSAS format file described above.
- 2) the instrumental file (generally called INST.PRM or INST.DAT), an ascii file which contains the wavelength of the experiment and other information such as polarization factor. The Lorentz-Polarization correction used in the refinements with both programs was $[P_h + (1 - P_h)\cos^2 2\theta] / [2\sin^2 \theta \cos \theta]$ with an independently refined P_h value of 0.55 (POLA) using the GSAS IPOLA = 0. The independently refined KRATIO was 0.44. These informations can also be added later in the Histogram menu of EXPGUI.
- 3) the experiment file (file.EXP).

In the following sections, all the operations to start and run a refinement with EXPGUI are fully described in order to let the reader be able to reproduce the result for the specific example. Please note that the data file (QPA.GSA) and the instrumental file (INST.DAT) are available upon request from the author.

Creation of the experiment file

Click on the EXPGUI icon on the desktop and put a name in the white field for the EXP file in the directory you want to use. Click READ. Let's say that the file name is QPA. EXPGUI says that the file QPA.EXP does not exist. OK to create? Create! Put a title to this experiment file (say: ternary mixture QPA and SET. Now the EXPGUI interface appears.

Click on the LS Controls menu and put a number of cycles for the refinement (I suggest 999). Flag the Extract Fobs flag for the reflection intensity extraction.

Click on Phase menu, followed by the "Add phase": add the two phases corundum and hydroxyapatite one by one. Do the following for corundum and repeat later for hydroxyapatite: insert a phase name (e.g. corundum), space group ($R\bar{3}c$) and cell constants [$a=b=4.7592$ and $c=12.992$ (\AA)] then Add and Continue. Click on Add New Atoms and fill the white spaces with Atom type = Al, Name = Al1, $x = 0.0$, $y = 0.0$, $z = 0.35228$. Change the U_{iso} to the correct value from the input single crystal model = 0.0041 (Remember to transform the thermal parameters to U_{iso} if you have a B_{iso} or B_{eq} value!). Finally click Add atoms. Repeat the same for the oxygen atom O at 0.3064, 0.0, 0.25 and $U_{\text{iso}}=0.004 \text{\AA}^3$. It is possible to add phases from other existing EXP files by selecting the option "Import phase from (GSAS.EXP file)" in the Add phase submenu.

Click on the Histogram menu, select (Add new histogram) the data file name (ex QPA.gsa), select the Instrument parameter file (ex inst.dat) and define the usable data limit (the maximum collected 2θ) then Add. Make sure that the

white fields Ratio, Zero, POLA and IPOLA are filled with numbers (in this case: 0.44, 0.0, 0.55, 0). Flag the Refine zero option with Damping = 7. It is time now to define a background function and prepare it for the refinement. Click on Edit Background and chose the function type and number of terms. Good results even with complex structured backgrounds are obtained with Function type 1 (Shifted Chebyshev). Initially set a number of terms = 9 (fill the white empty spaces with zeros). Click Set and on the previous menu Flag the Refine background option with Damping = 7. Another possibility with the background is to estimate it by linear interpolation between selected points between peaks and then subtracted. Nonetheless, I agree with McCusker et al. (1999) that for complex patterns with a high degree of reflection overlap, the majority of the peaks are not resolved to the baseline so the estimation of the background is difficult. This means that if the subtraction is performed, the background usually has to be re-estimated and re-subtracted several times during a refinement.

Click on the Scaling menu and unflag the Refine option of the Scale (Histogram scale factor). Oppositely, flag the Refine option of both Phases 1 and 2 with Damping = 7. I suggest to set the initial values of the phase fractions to a large value (50).

Click on the Profile menu and change the type of the profile function of both phases (Change Type). Set the function to type 2 (the pseudo-Voigt function, the most widely used for X-rays) with initial standard values $GW = 25$ and $LX = 5$ and Set. If you have independently refined an Asymmetry value for the experimental setup used to collect the data, add the Asy value ($Asy = 2$ here). An advantage of the pseudo-Voigt is that it allows the Gaussian and Lorentzian components of the peak shape to be introduced in a physically intuitive way to model the overall line broadening which furnishes useful information about the microstructure of the sample (McCusker et al., 1999).

Change the initial cutoff value to 0.005 (0.5% of the maximum peak intensity) although other values are possible depending upon the peak shape (wide Lorentzian peaks need a smaller cutoff value).

We are ready for the first cycles of refinement! Remember the strategy used here is to refine first the zero shift, the background, the phase fractions with Damping = 7.

Least square minimization: the first run

To run the Least square minimization procedure click “powpref”. When done, click “genles”. Although it is useless when the histogram related parameters are not changed, I suggest to always run “powpref” before “genles” so to have an updated observed and calculated file.

Let the procedure reach convergence. If not, re-run! When the “Convergence was achieved” message appears the calculation stops (it means that a certain convergence criterion has been reached). Load the new file. Repeat every time you want to update the old result with a new one.

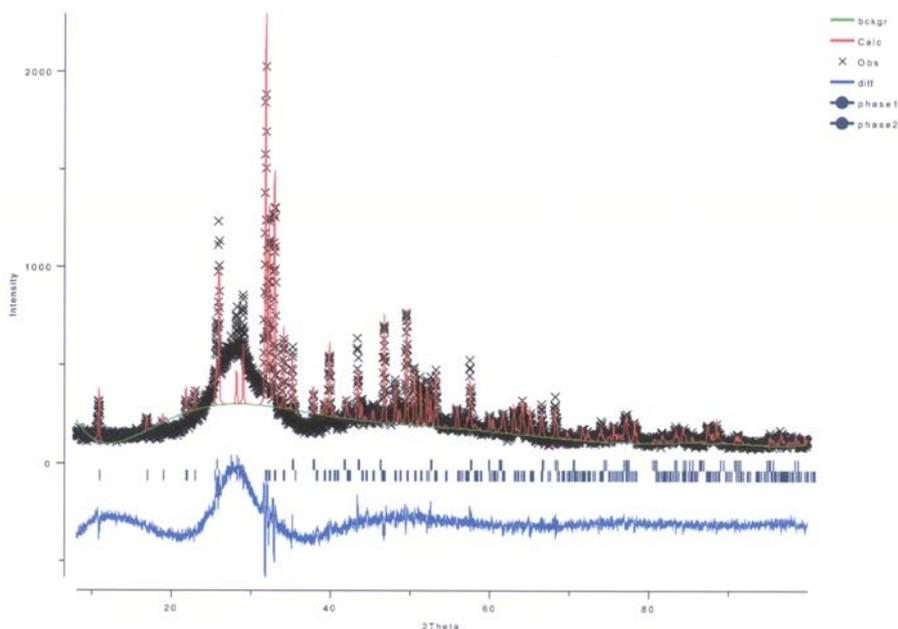


Fig. 1

Now, please check the agreement factors (wRp , Rp , CHI^{**2} , RF^{**2} – see the meaning on the GSAS manual - on the display window or click on lsviiew to see the output LST file which also contains the results of the minimization procedure with standard deviations. EXPGUI automatically goes to the last cycle of refinement and highlight the lines with the agreement factors. They are still pretty large at this point. $WRp = 0.2166$, $Rp = 0.1660$, $CHI^{**2} = 10.27$ and $R(F^{**2}) = 0.3258$. The misfit is large as you will see. To see the observed and calculated patterns, click on liveplot. From the Options menu, first select Auto locate and then Phase 1 for which you will unflag the use of dashed lines and flag the use of show reflections. Repeat the same for Phase 2. On the plot you will see the markers of the reflections of

each phase (Fig. 1). As you can see, the fit of the background is still very poor as well as the peak intensities. On the other hand, the peak positions seem fairly good that is the peaks are correctly centred for both phases. You can save a postscript file to print later. Repeat the described actions to see the plots after the next refinements cycles.

I must remark that although the use of Liveplot is described here, a much better graphic routine, Powplot, is available in EXPGUI. Powplot is more difficult to use because it retains the old dos interface but gives a much wider range of useful graphic options such as high resolution zoom or switch from 2θ to interplanar distance on the x-axis.

Least square minimization: the second run

At this point we should refine other parameters. In the Phase menu, flag the Refine cell for both phases and put a Damping = 7. In the Histogram menu, add more terms to the background function: with the Edit option put 18 and Set. From the Profile menu, flag the LX refinement for both phases with Damping = 7. Run powpref first and genles. When convergence is reached, a significant improvement of the fit is observed: $wRp = 0.1082$, $Rp = 0.0847$, $CHI^{**2} = 2.573$ and $R(F^{**2}) = 0.1689$. Someone may claim this result is ready for publication but if you give a close look at the graphic profiles, you will see that the the fit of the background is still very poor (Fig. 2).

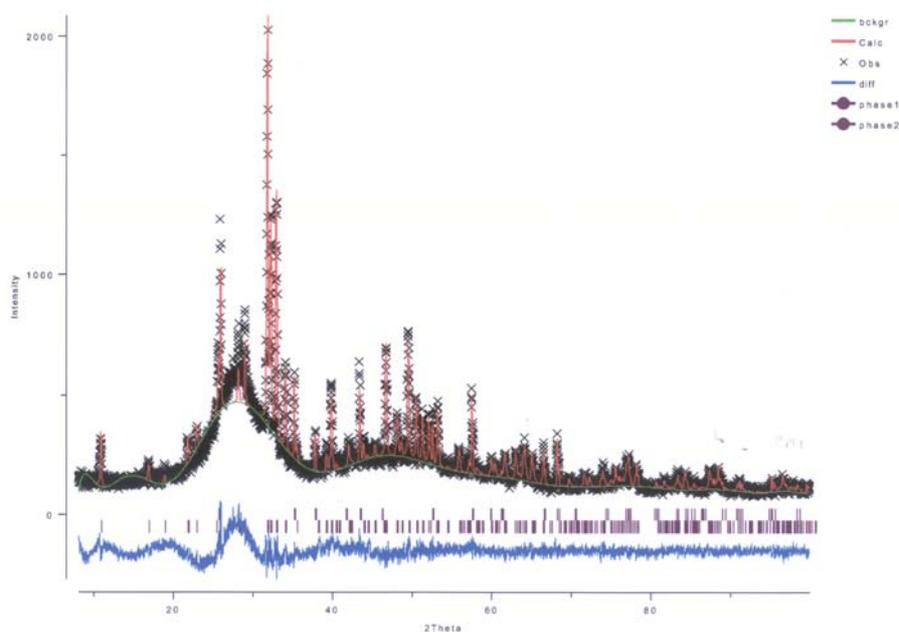


Fig. 2

Least square minimization: the third run

In the Histogram menu, add more terms to the background function (with the Edit option put 24 and Set) and unflag the refine zero. From the Profile menu, flag the GW and LY refinement for both phases with Damping = 7 and unflag the LX refinement. In the same menu, flag the “shft” parameter (the sample displacement correction: see the GSAS manual for explanation). Since this correction should be the same for both the phases in a homogeneous powder, you have to set an hard constraint so to refine the same value for both the phases. To do this, go to the Constraints menu and select Profile. Click Add Constraint, flag parameter # 8 = shft and choose phase 1. Then click continue. Click New Column and highlight phase 1 and histogram in the first column and phase 2 and histogram in the second column, and save. The constraint will be automatically set.

Run powpref first and thereafter genles. When convergence is reached, $wRp = 0.0853$, $Rp = 0.0677$, $CHI^{**2} = 1.601$ and $R(F^{**2}) = 0.1302$ indicate an improvement of the fit. Unfortunately the fit of the background is not yet acceptable.

Least square minimization: the last run

In the Histogram menu, add more terms to the background function (with the Edit option put 32 and Set). From the Profile menu, unflag the refined LY and shft parameters.

The convergence is reached with $wRp = 0.0765$, $Rp = 0.0599$, $CHI^{**2} = 1.291$ and $R(F^{**2}) = 0.0945$. Fig. 3a reports the final observed and calculated patterns plus the difference curve. A closer inspection, using the Powplot routine shows the very good fit in a selected region which contains many peaks of both phases (Fig. 3b). It is important to zoom carefully the graphic output at every region of the pattern.

In the QPA.LST file which is huge now as it contains all the results of the refinement cycles, check the final weight estimates. They will look like this:

Phase/element fractions for phase no. 1

Hist Elem: 1 1 PXC
Fraction : 5.78372
Sigmas : 0.120116
Shift/esd: 0.01
Wt. Frac.: 0.18406
Sigmas : 0.311899E-02

Phase/element fractions for phase no. 2

Hist Elem: 1 1 PXC
Fraction : 15.6128
Sigmas : 0.129599
Shift/esd: 0.00
Wt. Frac.: 0.81594
Sigmas : 0.124664E-02
Phase/element fraction sum(shift/error)**2 : 0.00

Knowing that the amount of added corundum is 0.1, to determine the amount of hydroxyapatite, calculate $(0.1/0.18406) \times 0.81594 = 0.44330$. The glass fraction is then $1 - (0.44330 + 0.1) = 0.45669$ in a very good agreement with the expected result. The final result with standard deviation is:

Corundum = 10.00(0) wt%
Hydroxyapatite = 44.3(82) wt%
Glass = 45.67(82) wt%

In this example we did not refine any preferred orientation direction. In some cases (e.g. clay minerals), it is necessary to refine preferred orientation directions. Two options are possible in EXPGUI: the March-Dollase model (MD Pref Orient menu) described in Dollase (1982) and the spherical harmonics (SH Pref Orient) described by Von Dreele (1997). To my experience, when there is just one preferred orientation direction it is better and safer to use the MD model because the SH model gives a better fit but the physical meaning can be lost if too many coefficients of the polynomial are refined.

It is important to say that the described example was rather simple but the strategy can be used even for more complex systems. One should be very careful with parameter correlations (e.g. profile parameters) especially when many phases are present in the mixture. Use large Damping factors (8 or 9).

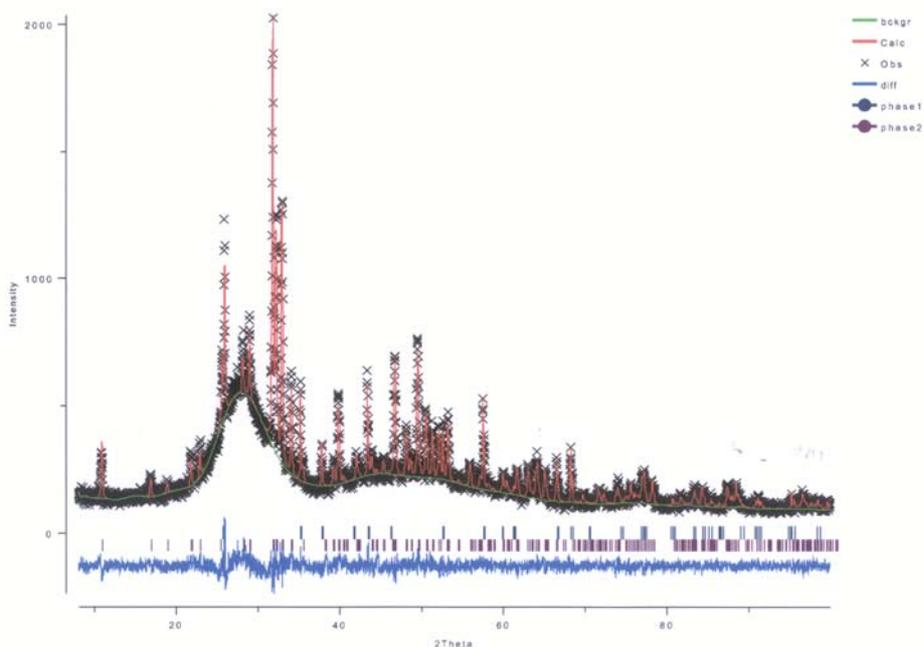


Fig. 3a

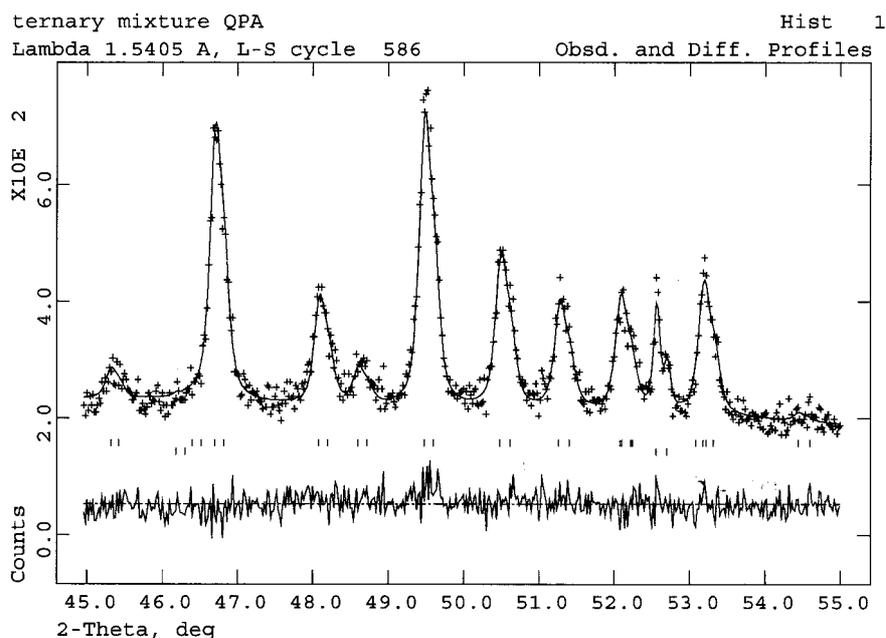


Fig. 3b

The results of the IUCr RR on QPA (Madsen et al., 2001) indicate that high levels of accuracy down to about 1 wt% are possible using laboratory equipments although the refined mixtures were as simple as the one described in the example here. More complex systems with their problems of phase identification, chemical substitutions, microabsorption, preferred orientation, excessive peak overlap can only reduce the levels of accuracy and precision that can be attained. Especially microabsorption effects are very hard to handle. There is a general feeling that the existing models for the correction of microabsorption effects should be revised as they appear to be not adequate even for simple systems containing only crystalline phases (Madsen et al., 2001). It is finally important to remember that these effects can be minimised by reducing the particle size or by using a more penetrating radiation, otherwise they should be corrected using for example the Brindley model.

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