NRC Publications Archive Archives des publications du CNRC

Problem solving with the TOPAS macro language: corrections and constraints in simulated annealing and Rietveld refinement

Whitfield, Pamela S.; Davidson, Isobel J.; Mitchell, Lyndon D.; Wilson, Siobhan A.; Mills, Stuart J.

This publication could be one of several versions: author's original, accepted manuscript or the publisher's version. / La version de cette publication peut être l'une des suivantes : la version prépublication de l'auteur, la version acceptée du manuscrit ou la version de l'éditeur.

For the publisher's version, please access the DOI link below. / Pour consulter la version de l'éditeur, utilisez le lien DOI ci-dessous.

Publisher's version / Version de l'éditeur:

<https://doi.org/10.4028/www.scientific.net/MSF.651.11>

Extending the Reach of Powder Diffraction Modelling : Special topic volume with invited peer reviewed papers only, pp. 11-25, 2010-05-01

NRC Publications Record / Notice d'Archives des publications de CNRC:

<https://nrc-publications.canada.ca/eng/view/object/?id=dcfc6a70-756a-4a42-a1f5-470ce77f906f>

<https://publications-cnrc.canada.ca/fra/voir/objet/?id=dcfc6a70-756a-4a42-a1f5-470ce77f906f>

Access and use of this website and the material on it are subject to the Terms and Conditions set forth at

<https://nrc-publications.canada.ca/eng/copyright>

READ THESE TERMS AND CONDITIONS CAREFULLY BEFORE USING THIS WEBSITE.

L'accès à ce site Web et l'utilisation de son contenu sont assujettis aux conditions présentées dans le site

<https://publications-cnrc.canada.ca/fra/droits>

LISEZ CES CONDITIONS ATTENTIVEMENT AVANT D'UTILISER CE SITE WEB.

Questions? Contact the NRC Publications Archive team at

PublicationsArchive-ArchivesPublications@nrc-cnrc.gc.ca. If you wish to email the authors directly, please see the first page of the publication for their contact information.

Vous avez des questions? Nous pouvons vous aider. Pour communiquer directement avec un auteur, consultez la première page de la revue dans laquelle son article a été publié afin de trouver ses coordonnées. Si vous n'arrivez pas à les repérer, communiquez avec nous à PublicationsArchive-ArchivesPublications@nrc-cnrc.gc.ca.

<http://www.nrc-cnrc.gc.ca/irc>

Problem solving with the TOPAS macro language: corrections and constraints in simulated annealing and Rietveld refinement

NRCC-53313

Whitfield, P.S.; Davidson, I.J.; Mitchell, L.D.;
Wilson, S.A.; Mills, S.J.

May 2010

A version of this document is published in / Une version de ce document se trouve dans:
Materials Science Forum, 651, pp. 11-25, May 01, 2010, DOI:
[10.4028/www.scientific.net/MSF.651.11](http://dx.doi.org/10.4028/www.scientific.net/MSF.651.11)

The material in this document is covered by the provisions of the Copyright Act, by Canadian laws, policies, regulations and international agreements. Such provisions serve to identify the information source and, in specific instances, to prohibit reproduction of materials without written permission. For more information visit <http://laws.justice.gc.ca/en/showtdm/cs/C-42>

Les renseignements dans ce document sont protégés par la Loi sur le droit d'auteur, par les lois, les politiques et les règlements du Canada et des accords internationaux. Ces dispositions permettent d'identifier la source de l'information et, dans certains cas, d'interdire la copie de documents sans permission écrite. Pour obtenir de plus amples renseignements : <http://lois.justice.gc.ca/fr/showtdm/cs/C-42>

National Research
Council Canada

Conseil national
de recherches Canada

Canada

Problem Solving with the TOPAS Macro Language: Corrections and Constraints in Simulated Annealing and Rietveld Refinement

Pamela S. Whitfield^{1,a}, Isobel J. Davidson^{1,b}, Lyndon D. Mitchell^{2,c},
Siobhan A. Wilson^{3,d,*} and Stuart J. Mills^{3,e}

¹Institute of Chemical Process and Environmental Technology, National Research Council Canada, 1200 Montreal Road, Ottawa, ON, K1A 0R6, CANADA

²Institute for Research in Construction, National Research Council Canada, 1200 Montreal Road, Ottawa, ON, K1A 0R6, CANADA

³Mineral Deposit Research Unit, The University of British Columbia, Vancouver, BC, V6T 1Z4, CANADA

^apamela.whitfield@nrc.gc.ca, ^bisobel.davidson@nrc.gc.ca, ^clyndon.mitchell@nrc.gc.ca,
^dsiowilso@indiana.edu, ^esmills@eos.ubc.ca

*current address: Department of Geological Sciences, Indiana University, Bloomington, IN 47405-1405, USA

Keywords: Powder diffraction, structure solution, simulated annealing, Rietveld refinement

Abstract. The TOPAS macro language can be a powerful tool for increasing the capabilities of X-ray powder diffraction analysis. New corrections and constraints can be implemented without altering the program's code, allowing for experimentation with new ideas and approaches. Examples are given, exposing the power and flexibility of the macro language to help solving problems with a few lines of code. The use of simulated annealing for structure solution of an organic material from data exhibiting preferential orientation is one example. Another one is about extraction of useful structural information in Rietveld refinement of natural hydrotalcite-group minerals, a problematic case that would normally be regarded as over-parameterized for the data available.

Introduction

Advances in the analysis of powder diffraction data have largely involved extracting ever increasing amounts of information (be it the crystal structure, microstructure, etc) from what is after all, poor quality data in comparison with the 3D information from single crystal diffraction.

Many of these advances have required the application of different corrections, constraints/restraints or the use of prior knowledge about the sample in order to squeeze out that extra bit of useful information. The extra capabilities are often implemented in the compiled code, usually a major operation performed by the author of the code. The real power of the TOPAS macro language [1,2] is to allow users to implement almost any correction or constraint they can think of without recompilation provided it can be coded using the extensive range of available keywords and mathematical relationships. The learning curve for advanced use of the language can be steep, but the results that can be obtained make it well worth the effort. Recent achievements utilizing the TOPAS macro language include parametric refinements where many datasets are refined at once [3], and robust refinements where the fitting of a phase is not adversely affected by artefacts from a poorly fitted impurity [4].

Preferential orientation and simulated annealing

One of the key and basic concepts of structure solution methods from powder diffraction data is that the relative intensities of the Bragg reflections have to be close to those expected from a true random powder. Two of the most common causes of deviations from this requirement are poor particle statistics and preferential orientation. Poor particle statistics can be improved by intensity averaging along the Debye rings collected with 2D detectors. Unfortunately, little can be done to correct this experimental problem by data analysis.

Some progress has been made in the use of data exhibiting preferential orientation during simulated annealing. Two types of corrections for preferential orientation are commonly implemented in software: the first is the March-Dollase correction (MD) [5], and the second is a correction based on spherical harmonics [6]. The March-Dollase (MD) correction uses a single variable but the orientation plane has to be supplied by the analyst. The application of spherical harmonics (SH) require no orientation information but can require a large number of variables - the number depending on crystal symmetry and the order of the spherical harmonics function. Obviously the lack of assumptions makes the spherical harmonics approach more tempting with unknown materials, but the probable chaotic behaviour of the variables during simulated annealing (SA) is a well known drawback. The probability of success using spherical harmonics with simulated annealing has been regarded as so low that they have not been implemented at all in some structure solution programs, e.g. FOX [7].

The March-Dollase correction has been used successfully in FOX to solve crystal structures with simulated annealing/parallel tempering [8,9]. In the case of an orthorhombic structure [8,9] the issue of an orientation direction was tackled by attempting separate solutions with (100), (010) and (001). Had none of these directions been correct, then the possibilities would have been daunting.

As it happens the elements for solving the problem of instability of the spherical harmonic variables during simulated annealing were present in the TOPAS macro language [2] and have been easily implemented. The key to maintaining stability through the temperature ramping of the simulated annealing is to remove any prior orientation at the start of a cycle. Variables can then find a new minimum that is unbiased by results from the previous cycle. In practical terms this requires resetting the refineable spherical harmonics variables to zero before a new cycle. The TOPAS keyword *val_on_continue* is used within the program for other routines, but it may be used to perform exactly the task we want here. Appending the command '*val_on_continue=0;*' after each SH variable declaration is all that is required. An example of this in TOPAS code is:

```
prm test 0 val_on_continue=0; (1)
```

Although the variable '*test*' is allowed to refine here without limits, the '*val_on_continue=0;*' will set it back to 0 at the beginning of each cycle. As mentioned previously, the number of variables required for a spherical harmonic correction depends on the order and symmetry. The technique was first applied to succinonitrile [10] which is monoclinic. In that case, second order (the lowest possible) of spherical harmonics was sufficient, which leads to only 3 additional variables in the simulated annealing.

The combination of triclinic symmetry with higher order spherical harmonics is significantly more challenging. An analysis of orientated wollastonite (CaSiO_3) was undertaken [11] as a proof of concept. Wollastonite is an inorganic oxide lacking the inherent level of known connectivity of most molecular systems. The use of polyhedral rigid bodies in this case also requires the merging of corner-sharing oxygens to remove the excess scattering from the initial setup. Wollastonite tends to occur as ribbon-shape crystallites which adds a very significant complication, in that it tends to orientate in two directions at once [12].

Despite the massively more complex system, the combination of simulated annealing and spherical harmonics correction was successful [11] in finding the correct structure for wollastonite [13]. The trends in R_{wp} residuals with the different spherical harmonic orders are shown in Fig 1. Simulated annealing with the conventional single-direction March-Dollase correction was unable to solve the structure with [100], [010] or [001] directions. TOPAS is able to implement a 2-direction March-Dollase correction, which was successful in solving the wollastonite structure only when the both [100] and [010] directions were supplied simultaneously. This example shows the power of the spherical harmonics approach where unknown and complex orientation behaviour may occur.

Figure 1. Values of R_{wp} during simulated annealing runs on wollastonite data using different orders of spherical harmonics [11].

One application that becomes much more tractable with such a correction is the structure solution using capillary powder diffraction data from frozen solvents. Some solvents used in the electrolytes of lithium-ion batteries as well as some of the potential additives used in electrolytes are of particular interest. The low-temperature performance of lithium-ion batteries is greatly affected by the choice of liquid electrolytes, some of which start to freeze not far below 0 °C. Very little diffraction work has been carried out on these solvent systems and their low-temperature crystal structures remain unsolved. The rest of this section will cover the structure solution of an additive called 4-fluoroethylene carbonate (FEC), the molecular structure of which is shown in Fig 2.

Figure 2. Molecular structure of 4-fluoroethylene carbonate (FEC)

The experiment was carried out using a custom designed liquid nitrogen cryoflow system (Fig 3) which allows variable temperature data to be collected from capillary samples on a powder diffractometer. Combined with focussing mirror optics, this setup allowed complex ramp-soak experiments to be carried out relatively quickly as well as more conventional fixed temperature datasets. The possible effects of poor particle statistics on diffraction data have to be considered even in capillary geometry. As large crystallites tend to form upon slow cooling of the liquid, quenching was attempted in order to produce small crystallites. The sample was chilled from room temperature to 80 K in a matter of a few seconds so very rapid crystallization occurred along the capillary. Although the crystallites were small, the directional nature of the crystallization along the capillary made preferential orientation very likely.

Figure 3. Orientation of the cryo-nozzle parallel to the capillary. The goniometer head is protected from icing by a goniometer heat shield.

The diffraction data from FEC at 170 K are shown in Fig 4. The data were collected using a Bruker D8 with a $\text{CuK}\alpha$ focussing mirror and a Vântec-1 position sensitive detector (PSD). A variable count and step procedure was used to improve the counting statistics at high angles. Structure solution is performed on low angle data, with higher angle data becoming more important during refinement.

Figure 4. Powder diffraction data of 4-fluoroethylene carbonate at 170 K.

In a molecular system such as FEC it is very common to use a rigid body to describe the known molecular connectivity during the simulated annealing. The appropriate use of such a rigid body greatly increases the likelihood of success and/or speed of the structure solution process. In this case the molecule was described using a z-matrix in the TOPAS input file. The code describing the z-matrix is shown below:

```

prm !cc 1.52
prm !co1 1.15
prm !co2 1.33
prm !co3 1.4
prm !ch 1.06
prm !cf 1.35
prm tw 20 min -20 max 20
rigid
  z_matrix C1
  z_matrix O1 C1 =co1;
  z_matrix O2 C1 =co2; O1 124.5
  z_matrix O3 C1 =co2; O1 -124.5 O2 0
  z_matrix C3 O2 =co3; C1 -109 O1 0
  z_matrix C5 O3 =co3; C1 -109 O1 0
  z_matrix H31 C3 =ch; O2 109 C5 120
  z_matrix H32 C3 =ch; O2 109 C5 240
  z_matrix H51 C5 =ch; O3 109 C3 120
  z_matrix F52 C5 =cf; O3 109 C3 240
  Rotate_about_points(@ 20 min -20 max 20,O2,O3,"C3 C5 H51 F52 H31 H32")
  Rotate_about_points(=tw;: 20,O2,C5,"C3 H31 H32")
  Rotate_about_points(=tw;: 20,O3,C3,"C5 H51 F52")

```

The top five lines define the different bond lengths which are fixed in the first instance by the use of a '!' before the variable name. The lines starting with *z_matrix* build up the molecule atom by atom in terms of relative distance, bond angles and torsion angles. Normally, hydrogen atoms are not

added until the refinement process but they are included here. The matrix-creation code shown above produces the molecule in Fig 5a. The *Rotate_about_points* macro simplifies the task of distorting molecules as a unit by allowing geometric changes to the input conformation without describing the change for each atom individually. The first *Rotate_about_points* macro as described above allows the molecule to bend in the middle along a line joining atoms O2 and O3. The min/max statements tell TOPAS that the bend can be no greater than 20 ° in either direction. Fig 5b shows the effect of this macro when the value of *Rotate_about_points* is 20. The second and third macros allow for a twisting of the C3 and C5 carbon atoms out of the plane, as shown in Fig 5c with values of 20 for each. The values of the variables in the 2nd and 3rd macro are constrained to be the same by the use of a variable name, 'tw' as opposed to '@' for a freely refined variable. The construction of z-matrices is simplified by the use of the 'rigid body editor' in TOPAS [1] which also allows distortions such as changing torsion angles and *Rotate_about_points* to be visualized before trying them in an actual input file.

The data for FEC were indexed quite easily to a monoclinic cell with space group $P2_1/n$. Using the density of the room temperature liquid as a guide it was deduced that the unit cell contained four molecular units. Given the general site multiplicity of four in $P2_1/n$, this leads to a single molecule in the asymmetric unit cell ($Z'=1$).

Figure 5a. Planar molecule created by the FEC z-matrix description in the TOPAS rigid body editor

Figure 5b. Effect of *Rotate_about_points*(20,O2,O3,"C3 C5 H51 F52 H31 H32") on the FEC molecule

Figure 5c. Combined twisting effect of *Rotate_about_points*(20,O2,C5,"C3 H31 H32") and *Rotate_about_points*(20,O3,C3,"C5 H51 F52") on the FEC molecule

The spherical harmonics preferential orientation can be added to the input file using the macro *PO_Spherical_Harmonics*(sh, 4) for a 4th order correction. However, there are advantages to coding the correction using a more generic expression. The equivalent long-hand expression is:

```
spherical_harmonics_hkl sh
    sh_order 4
scale_pks = sh; (3)
```

The major advantage of the above long-hand definition is that a limit may be added to prevent negative intensities by adding *scale_pks = Max(sh, 0)*;. This isn't necessarily a good approach during structure solution, but can be useful in refinements. However, given the ease of adding and removing a comment it is easier to code it long-hand rather than rewriting it part way through. After running TOPAS for a single cycle to generate the spherical harmonics variables, the *val_on_continue* statements are added. This yields the final code in the input file:

```
spherical_harmonics_hkl sh
    sh_order 4 load sh_Cij_prm {
        y00 !sh_c00 1.00000
        y20 sh_c20 0.19033 val_on_continue=0;
        y22p sh_c22p -0.13502 val_on_continue=0;
        y22m sh_c22m -0.48058 val_on_continue=0;
        y40 sh_c40 0.00910 val_on_continue=0;
        y42p sh_c42p 0.70956 val_on_continue=0;
        y42m sh_c42m -0.37823 val_on_continue=0;
        y44p sh_c44p -0.58750 val_on_continue=0;
        y44m sh_c44m 0.88124 val_on_continue=0;
    }
    scale_pks = sh;
    ' scale_pks = Max(sh, 0); 'no neg peaks version commented out for possible use later (4)
```

In this simple case of FEC, the correct basic structure can be found without the preferential orientation correction due to the limited degrees of freedom. This is not always the case however, as was shown with succinonitrile and wollastonite [10,11]. Even with FEC, the fit and residuals from the simulated annealing are much improved as seen in figures 6 and 7. The result with the spherical

harmonics reflects more closely the degree of twisting expected in many of these 5-membered cyclic carbonates [14]. The 'peak decomposition' was turned off in these examples to better demonstrate the fits. Scattering from the capillary was modelled using a single broad peak, the position of which is visible as the vertical line in figures 6 and 7.

During the final refinement of the structure it is highly desirable to add a correction for capillary absorption. With the focussing configuration used here, peak shifts due to absorption are not observable, so the Sabine correction is used to separate out the peak shift effect. The use of the Sabine absorption correction [15] in TOPAS is straightforward, but it can be informative to add some extra lines of code in the μR calculation to add some clarity to the input parameters:

```
prm !packing_density 1 min 0.1 max 1.0
prm !capdia 1 'capillary diameter in mm
prm !linab = Get(mixture_MAC) Get(mixture_density_g_on_cm3)::16.55779
'in cm-1
prm muR = (capdia/20)*linab*packing_density;
Cylindrical_I_Correction(muR)
```

(5)

Figure 6. Result of the simulated annealing of the FEC without a preferential orientation correction ($R_{wp} = 21\%$)

Figure 7. Result of the simulated annealing of the FEC with a 4th order spherical harmonics preferential orientation correction ($R_{wp} = 8\%$)

In most circumstances the packing density of a capillary is between 0.2 and 0.5 but with a solidified liquid a value of 1 is appropriate. Rather than inputting a fixed, previously calculated value for the linear absorption coefficient (LAC), an expression can be used which automatically calculates the LAC for the 'mixture'. The *Mixture_LAC_1_on_cm* macro cannot be used directly in this case as it produces a recursion error. The 'mixture' LAC has the advantage that it is easily accessible from the scan 'scope' (see the TOPAS Technical Reference for explanation of scope within an input file). In a multi-phase situation the mixture LAC is actually the correct one to use, but for the more common single phase refinement it is equivalent to the phase LAC so the expression is appropriate for either case. It is worth remembering though that a fixed LAC may be preferable to improve stability if the phase density is likely to change significantly, e.g. through merging of heavy atoms.

For accurate work using Debye-Scherrer geometry (i.e. fixed incident angle) it is possible to implement a peak-shift correction to account for displacement of the capillary sample from the centre of the goniometer [16,17]. The effect will be minor for a well-aligned system but the fit can be improved slightly with data covering a very wide angular range. Such a correction is not pre-coded in TOPAS but it can be added as a macro, either locally in the input file or the 'local.inc' file. The correction can be written as:

$$\text{macro DS_Capillary_SD}(x_offset, x_val, y_offset, y_val) \quad \{ \quad (6)$$

$$\quad th2_offset = ((Rad \ x_offset * Sin(2 \ Th)) - (Rad \ y_offset * Cos(2 \ Th))) / Rs; \quad \}$$

The 'Rad' statement is used in the calculation to tell TOPAS that the expression should be calculated in radians as opposed to degrees. 'Deg' is the corresponding statement to specify angles in degrees. 'x_offset' is the capillary displacement parallel to the incident beam direction and 'y_offset' is the displacement perpendicular to the incident beam. Rs is the goniometer radius taken from the value specified in the input file. The macro can be called in the input file by

$$DS_Capillary_SD(!x_offset, 0, !y_offset, 0) \quad (7)$$

Occupational and charge balance constraints in Rietveld refinement

Structures too complicated to be properly analyzed using a single dataset are a common problem encountered in Rietveld refinement. These are often materials with multiple atoms on a single site and/or partial occupancies. The ideal approach to these materials is to use multiple datasets (e.g. neutron diffraction data and resonant diffraction data from synchrotrons) in simultaneous refinements. Examples in the literature include complex alloys [18] and complex multi-element lithium battery cathode materials [19,20].

Gathering data from so many techniques for the same material can be quite an undertaking so the analyst must squeeze as much information as possible from a single laboratory dataset without exceeding the complexity of what the data can provide. This often requires the use of constraints using compositional and other information, to keep the refinement in the realms of physical possibility. Knowing the chemical composition helps significantly but applying the principles of charge balance within the structure can provide a powerful tool, both to stabilize the refinement and potentially check the validity of the structure being refined.

The example used here is stichtite - a natural hydrotalcite-group mineral with the nominal formula $\text{Mg}_6\text{Cr}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}$ [21,22]. In common with the parent hydrotalcite, stichtite can be indexed to an elongated trigonal unit cell in $R\text{-}3m$. The high symmetry would often suggest quite a simple problem, but the hydrotalcite structure contains mixed and partially occupied anion sites, making an unconstrained refinement using a single dataset theoretically impossible as it leads to a singular least-squares matrix. The traditional description of hydrotalcite compositions doesn't follow neatly from the multiplicities in the $R\text{-}3m$ unit cell. A factor of 8/3 must be applied to all the calculations of occupancies, explained by the placing of nominally 8 cations (6 x Mg plus 2 x Cr) on a site with 3-fold multiplicity. The proposed structural model involves placement of the atoms on the following sites:

3a	(0,0,0)	$\text{Mg}^{2+}, \text{Cr}^{3+}$
6c	(0,0,z)	O, H (hydroxide)
6c	(1/3,2/3,1/2)	C (carbonate)
18h	(x,y,1/2)	O (water + carbonate)

Assuming that the cation and hydroxide sites are fully occupied makes the application of compositional constraints on the anion occupancies feasible. The chromium content is refined on the cation site using the assumption that $Mg + Cr = 1$. That leaves the additional scattering from the water oxygens the only freely refined occupancy variable. The cation charge assuming Mg^{2+} and Cr^{3+} can be expressed simply in terms of the magnesium occupancy as:

$$prm\ cat = 9 - 3*mg; \quad (8)$$

The only anions in the system are carbonate and hydroxide ions. The occupancy of the carbonate carbon on the 6c site can be calculated from charge balance as follows where oh is the hydroxide occupancy:

$$prm\ co3 = (9 - 3*mg - 6*oh)/(6*2); \quad (9)$$

The carbonate oxygen site is 18h, so the site multiplicity naturally takes care of the 1:3 carbon:oxygen ratio for the carbonate. The remaining scattering from the 18h site must be from the oxygen atom of the water molecule, so the 18h site occupancy can be described in the 'site' as:

$$occ\ O-2 = h2o + co3; \quad (10)$$

where $h2o$ is a refinable variable.

An added complication in the analysis of data from stichtite is the presence of some anisotropic peak broadening which becomes apparent during a Le Bail unit cell refinement. This is problematic in Rietveld refinement as ignoring it would introduce errors into the fitted peak intensities. This can be dealt with using a multi-variable spherical harmonics-based correction or some other broadening relationship to accurately fit all of the peaks. Similar anisotropic broadening in layered *R-3m* materials has been addressed previously in deintercalated lithium battery cathode materials [23]. In this case a reciprocal-space based relationship can perform the correction with a single variable. The spherical harmonic-based correction can be coded as:

```
prm p1 0.08055 min 0.0001
spherical_harmonics_hkl sh
sh_order 6
lor_fwhm = sh p1;
```

(11)

This yields a correction with 6 variables. In this particular case in *R-3m*, an alternative is an expression in reciprocal space using a single variable. *TOPAS* makes accessing such corrections quite simple as a^* , b^* and c^* may be expressed in the macro language using *A_star*, *B_star* and *C_star* respectively. The expression we'd like to code is the following where $h-k \neq 3n$ the broadening is;

$$q \times L \times c^* \times \cos(c^* \wedge R^*)$$
(12)

where q is a constant, L is the l Miller index, c^* is the reciprocal space vector along c , and R^* is the total reciprocal space vector. The code to perform this in *TOPAS* using the 'Mod' modulus [2] keyword for the $h-k \neq 3n$ selection rule is:

```
prm const 0.68509`0.00703
lor_fwhm = If(Mod(Abs(H-K),3) == 0, 0,
              const * L * C_star *
              Cos(C_star^Sqrt((A_star^2)+(B_star^2)+(C_star^2)))
            );
```

(13)

In this case the single variable reciprocal space expression achieves a very similar fit to the spherical harmonics, but with the advantage of exposing the physical base for the correction.

On the experimental front, the stichtite data were obtained in a 0.5mm quartz capillary using the same focusing mirror $\text{CuK}\alpha$ Bruker D8 diffractometer as for the fluoroethylene carbonate, although the cryoflow system and Debye slit were not used. Data were collected from 9 up to $140^\circ 2\theta$ using a variable counting methodology. The sample was not entirely phase pure and some of the 2H_1 polymorph (barbertonite) and lizardite were visible, and added to the refinement. The first two stichtite reflections completely dominate the pattern, even when using a square root intensity scale as shown below. This is somewhat unfortunate as they will completely dominate the least squares fitting process, even with properly scaled variable count data. In order to better access the copious information at the higher angles, the intensity data below $30^\circ 2\theta$ were weighted to 10% of their original contribution to the least-squares.

$$\text{weighting} = \text{If}(X < 30, 0.10, 1) / (Y_{\text{obs}} + 1);$$
(14)

The effect is that misfits in that region will no longer dominate the refinement. One side-effect of this weighting is that the R_{wp} residual will be slightly worse than it would be otherwise. The difference plot obtained from the refinement of stichtite using the constraints without an anisotropic broadening correction is shown in figure 8. The effect of adding the reciprocal space anisotropic

broadening correction is shown in figure 9. The refined crystal structure of stichtite is shown in figure 10.

Figure 8. Difference plot from the Rietveld refinement of the stichtite data without an anisotropic broadening correction ($R_{wp} = 4.0\%$). The intensity is plotted on a square root scale to emphasize the fit at higher angles.

Figure 9. Difference plot from the Rietveld refinement of the stichtite data with the reciprocal space anisotropic broadening correction ($R_{wp} = 2.3\%$).

Figure 10. Refined crystal structure of stichtite $[\text{Mg}_6\text{Cr}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}]$.

In terms of extracting the compositional information from the input file it can be useful to add some parameter calculations, especially where fractional factors such as $8/3$ are required. Such calculations provide a useful cross-check of the arithmetic as well as making it easy to monitor the refinement results. The lines of code required in this case are:

```
'nominal stoichiometry Mg6Cr2(OH)16CO3 4H2O                                     (15)
' Mg6 Cr2 O23 H24 C
prm mg_stoich = mg1*3*8/3;:6.12351
prm cr_stoich = (1-mg1)*3*8/3;: 1.87649
prm o_stoich = (oh*6*8/3) + (h2o*18*8/3) + (co3*3*6*8/3);: 23.73319
prm h_stoic = (oh*6*8/3) + (h2o*2*18*8/3);: 25.83691
prm c_stoich = (co3*6*8/3);: 0.93825
prm oh_stoich = oh*6*8/3;:16.00000
prm co3_stoich = co3*6*8/3;: 0.93825
prm h2o_stoich = h2o*18*8/3;:4.91845
```

The final refined composition for the stichtite is $\text{Mg}_{6.1}\text{Cr}_{1.9}(\text{OH})_{16}(\text{CO}_3)_{0.9} \cdot 4.9\text{H}_2\text{O}$. Although the water content is a little higher than anticipated, this result is very respectable for a natural mineral sample where the water content can often vary and other ions such as Al^{3+} could readily substitute onto the cation site. The effect of significant variability in actual composition versus the nominal composition has been seen in a related mineral, woodallite $[\text{Mg}_6\text{Cr}_2(\text{OH})_{16}\text{Cl}_2 \cdot 4\text{H}_2\text{O}]$. In that case, the presence of significant residual carbonate prevented similar structural analysis without the results of microprobe analysis.

Conclusions

The appropriate use of constraints and corrections can be valuable in all forms of analysis using the *TOPAS* software. During structure solution of molecular solids using simulated annealing, *z*-matrices are a fundamental tool to improve the probability of success by reducing the number of variables in the problem. One additional advantage of simulated annealing as a real-space method is the ability to correct for unknown preferential orientation effects using spherical harmonics. The use of a single *TOPAS* keyword in conjunction with the spherical harmonics variables is the key to success in this case.

The use of constraints to reduce the complexity of a refinement to reflect the available data is a valuable tool where a structure may be too complex to refine all structural variables using a single dataset. Given the natural predominance of analyses using a single laboratory-based dataset, problems may easily be over-parameterized for the amount of information available. The use of additional information such as chemical composition or chemical principles such as charge balance can help greatly in reducing the complexity to a more reasonable level. The inorganic mineral example in the text shows how the simple use of charge-balance principles may maximize the information that can be extracted from a single dataset.

TOPAS offers the flexibility to write code and macros for user-defined corrections and convolutions, giving the user almost unlimited freedom to experiment. In the examples shown in the text, code was written to clarify the use of the Sabine capillary absorption correction, apply a Debye-Scherrer capillary displacement correction, and fit anisotropic peak broadening using both spherical harmonics and reciprocal space-based corrections. All this crucial coding could be performed with macros in the lab and required no modification to the compiled *TOPAS* code.

Acknowledgement

The authors would like to thank Yvon Le Page (NRC-ICPET) for reviewing this manuscript and for his helpful suggestions.

References

- [1] Bruker-AXS, DIFFRACPlus TOPAS: TOPAS 4.2 User Manual, Bruker-AXS GmbH, Karlsruhe, Germany (2008)
- [2] Bruker-AXS, DIFFRACPlus TOPAS: TOPAS 4.2 Technical Reference, Bruker-AXS GmbH, Karlsruhe, Germany (2008)
- [3] G.W. Stinton and J.S.O. Evans: *J. Appl. Crystallogr.* Vol. 40 (2007), p. 87-95
- [4] K.H. Stone, S.H. Lapidus and P.W. Stephens: *J. Appl. Crystallogr.* Vol. 42 (2009), p. 385-391
- [5] W.A. Dollase: *J. Appl. Crystallogr.* Vol. 19 (1986), p. 267-272
- [6] M. Järvinen: *J. Appl. Crystallogr.* Vol. 26 (1993), p. 525-531
- [7] V. Favre-Nicolin and R. Cerný: *J. Appl. Crystallogr.* Vol. 35 (2002), p. 734-743
- [8] Y. Filinchuk, A.V. Talyzin, D. Chernyshov and V. Dmitriev: *Phys. Rev. B* Vol. 76 (2007), p. 092104-1-092104-4
- [9] M. Husak, A. Jegorov, J. Brus, W. van Beek, P. Pattison, M. Christensen, V. Favre-Nicolin and J. Maixner: *Structural Chemistry* Vol. 19 (2008), p. 517-525
- [10] P.S. Whitfield, Y. Le Page, A. Abouimrane and I.J. Davidson: *Powder Diffr.* Vol. 23 (2008), p. 292-299
- [11] P.S. Whitfield: *J. Appl. Crystallogr.* Vol. 42 (2009), p. 134-136
- [12] P.Y. Zavalij and M.S. Whittingham: *Rigaku Journal* Vol. 21 (2004), p. 2-14
- [13] Y. Ohashi: *Physics and Chemistry of Minerals* Vol. 10 (1984), p. 217-229
- [14] C.J. Brown: *Acta Cryst.* Vol. 7 (1954), p. 92-96
- [15] T.M. Sabine, B.A. Hunter, W.R. Sabine and C.J. Ball: *J. Appl. Crystallogr.* Vol. 31 (1998), p. 47-51
- [16] H.P. Klug and L.E. Alexander: *X-ray diffraction procedures for polycrystalline and amorphous materials*, (Wiley, New York 1974).

- [17] L.B. McCusker, R.B. Von Dreele, D.E. Cox, D. Louer and P. Scardi: J. Appl. Crystallogr. Vol. 32 (1999), p. 36-50
- [18] J.-M. Joubert, R. Cerný, M. Latroche, A. Percheron-Guégan and K. Yvon: J. Appl. Crystallogr. Vol. 31 (1998), p. 327-332
- [19] P.S. Whitfield, I.J. Davidson, L.M.D. Cranswick, I.P. Swainson and P.W. Stephens: Solid State Ionics Vol. 176 (2005), p. 463-471
- [20] P.S. Whitfield, I.J. Davidson, P.W. Stephens, L.M.D. Cranswick and I.P. Swainson: Zeitschrift für Kristallographie Supplement Vol. 26 (2007), p. 483-488
- [21] L.D. Ashwal and B. Cairncross: Contributions to Mineralogy and Petrology Vol. 127 (1997), p. 75-86
- [22] S.J. Mills, P.S. Whitfield, S.A. Wilson, J.A. Woodhouse, G.M. Dipple, M. Raudsepp and C.A. Francis, submitted to American Mineralogist
- [23] P.S. Whitfield, S. Niketic, Y. Le Page and I.J. Davidson: Advances in X-Ray Analysis Vol. 49 (2005), p. 149-155