QUESTIONNAIRE FOR the
STRUCTURE DETERMINATION BY POWDER DIFFRACTOMETRY ROUND ROBIN - 3

Questionnaire completed for sample 1 by Esther C. Schilder and Jaap N. Louwen, Albemarle Catalysts Amsterdam.

O.0 Precise date of
- data download : ex : Fri, 14 Feb 2008 17:28
- results submission : Tuesday 5 Mar 2008

0.1 Is the first sample structure solvable with this quality of data ? Yes [X] No [ ]

1. Preliminary work

1.1 Did you obtain additional information ?
(for instance from CSD or ICSD or ICDD databases)

Based on the most probable space group P-1 (because based on volume there must be 2 units of Ca tartrate tetrahydrate in the unit cell and P-1 is a much more frequent space group than P1) we concluded that the sample was either the ld (racemic) form (in fact, on wikipedia racemic calcium tartrate is listed as crystallizing in a triclinic lattice) or the meso (R,S) tartrate form. We found that a crystal structure for the meso form has been determined by the late prof. Kroon. According to Mastai et al (Chem. Eur. J. , 2002, 8, 2430-2437) the structure of the racemic form has been determined but not published, so we started with the working hypothesis that we were looking for the structure of the racemic compound. With this hypothesis in mind we did some model building to see if the special positions in the P-1 unit cell were likely to be the loci of Ca ions. Based on the results of that, we believed it unlikely that these positions would play a role. We were therefore confident that we could apply the direct space method to a whole Ca tratrate unit in the unit cell.

1.2 Did you obtain additional information from the powder pattern ? If yes, how and what information ? Yes [ ] No [X]
(for instance using the JCPDS-ICDD database)

1.3 Did you extract the structure factors ? Yes [ ] No [X]

1.3.1 If yes, which program(s) did you use ?
1.3.2 Give the angular range:
1.3.3 Give the number of extracted structure factors:
1.3.4 Give the Rp and Rwp (conventional Rietveld, background subtracted):
1.3.5 Give the Rp and Rwp (background not subtracted):
1.3.6 If not, did you use the whole pattern ? Yes [X] No []
1.3.7 Or a partial pattern (if yes, give the angular range):
1.3.8 If you use the whole or a partial pattern, did you keep fixed the profile parameters, and if yes, how did you obtained them ?

Using program TOPAS3 we did an “hkl phase” fit to the whole profile using a Pearson VII type profile function. The profile/zero shift/background parameters thus derived were kept fixed in the subsequent direct space minimization (see below).

2- Structure solution

2.1 Did you use direct methods ? Yes [ ] No [X]

2.1.1 If yes, was it on the whole dataset ?
2.1.2 Or on a partial dataset ?
2.1.3 Give the number of reflections:
2.1.4 Which program(s) did you use ?
2.1.5 Did you modified intensities of closely neighbouring reflections ? If yes, explain how.

2.2 Did you use Patterson methods ? Yes [ ] No [X]

2.2.1 If yes, was it on the whole dataset ?
2.2.2 Or on a partial dataset ?
2.2.3 Give the number of reflections:
2.2.4 Which program(s) did you use ?
2.2.5 Did you modified intensities of closely neighbouring reflections ? If yes, explain how.

2.3 Did you use another method ? Yes [X] No [ ]
2.3.1 If yes, which method(s) (give details : molecule location by direct space - genetic algorithm, Monte Carlo, Simulated annealing, scratch, charge flipping, other) ?

We used a direct space method, the simulated annealing method programmed in TOPAS3.

2.3.2 Which program(s) did you use (name and reference) ?

TOPAS3 obtained from Bruker AXS.

2.3.3 If you used direct space methods, how many independent molecules did you use (give details on these molecules)? How many degrees of freedom (total) ? How many torsion angles ?

A CaC4O6H2 unit was taken from one of the single crystal structures (Boese and Heinemann) supplied. Its placement in the unit cell yields six degrees of freedom (location, angles). The torsional angle around the tartrate central C-C bond was treated as an additional degree of freedom. Four O atoms (scattering as O-2) were also placed in the unit cell as independent entities, giving 12 additional degrees of freedom: a total of 19. We applied P-1 symmetry, so the Ca S,S-tartrate unit as well as four additional water molecules were automatically taken into account.
When we were confident we had found the solution with lowest R value, we also released all other torsional angles as well as a bond length and a bond angle that defined the position of Ca with respect to the tartrate moiety.
This led to the following unrefined coordinates:

Ca1 0.6806243 0.7681486 0.334758
O2 0.5268448 0.837689 0.617118
C3 0.3749606 0.7472149 0.5843096
C4 0.3550029 0.6134307 0.3912883
O5 0.4810985 0.5932163 0.3167423
H6 0.5377471 0.908819 0.6929947
O7 0.2070396 0.5433271 0.2937395
H8 0.2653507 0.7915551 0.5426196
C9 0.3809792 0.7188205 0.8119019
C10 0.3414528 0.8340079 0.9898726
H11 0.3054539 0.63864 0.7791865
O12 0.5293018 0.6610329 0.8990094
O13 0.4688656 0.8958067 0.1759368

H14 0.5167272 0.5868544 0.8393467
O15 0.2058141 0.8796793 0.9260415
Ow1 0.1890154 0.1183684 0.8855014
Ow2 0.8432469 0.5976134 0.1702842
Ow3 0.1332594 0.2832322 0.3095161
Ow4 0 0.1996324 0.989495 0.3946887

2.4 Did you first locate the whole structure ? Yes [X] No [ ]

2.4.1 If not, how many atoms did you locate ?
2.4.2 Give their name and initial atomic coordinates

Atom x y z
.....
.....
.....

2.4.3 Were the initial atomic coordinates taken from a known structure ? Yes [X] No [ ]

Boese and Heinemann, Z. Kristallogr., 1995, 205, 348.

3- Structure completion

3.1 Did you performed Fourier difference syntheses before refining the structure by the Rietveld method ? Yes [ ] No [X]
3.2 If yes, with what program ?
3.3 If yes, how many additional atoms did you obtained from Fourier difference syntheses ?
3.4 Give their name and atomic coordinates as they were obtained

Atom x y z
.....
.....
.....

3.5 Did you made first Rietveld refinements without preliminary Fourier difference syntheses ? Yes [X] No [ ]
3.5.1 If yes, with what program ?

The GSAS program used through the EXPGUI interface.

3.5.2 What were the Rp and Rwp (background subtracted AND not subtracted) and RB and RF that you obtained at the first Rietveld application ?

See output from final refinement cycle:

```
Y:\08XRD012_SDPD_RR-3\Sample1\GSAS_JNL>set SYMOP=d:\gsas\data\symop.dat

Y:\08XRD012_SDPD_RR-3\Sample1\GSAS_JNL>d:\gsas\exe\genles.exe REFAT

 Restraint data statistics:
 No restraints used

 Powder data statistics                Fitted         -Bknd              Average
            Bank Ndata Sum(w*d**2)  wRp     Rp     wRp     Rp     DWd  Integral

 Hstgm  1 PXC   1  4865 1.19584E+05 0.0993 0.0700 0.1470 0.0899   0.277   0.958
 Powder totals     4865 1.19584E+05 0.0993 0.0700 0.1470 0.0899   0.277
 Cycle 425 There were   4865 observations.
 Total before-cycle CHI**2 (offset/sig) = 1.1958E+05 ( 1.1776E+03)

 Reduced CHI**2 =  25.15     for   111 variables
 Histogram  1  Type PXC   Nobs = 1570 R(F**2) =  0.1470

 CPU times for matrix build     2.44 sec; matrix inversion     0.00 sec
 Final variable sum((shift/esd)**2) for cycle 425:       0.00 Time:    2.44 sec
STOP GENLES terminated successfully statement executed

Y:\08XRD012_SDPD_RR-3\Sample1\GSAS_JNL>pause
Press any key to continue . . .
```

3.5.3 Did you get the structure factors from this result and performed a Fourier difference synthesis ? Yes [ ] No [X]

3.5.4 Did you locate additional atoms at this stage ? Yes [ ] No [X]

3.5.5 And which one ?

Atom x y z
.....
.....
.....

3.5.6 If you repeated Rietveld refinements and Fourier synthesis several times before to complete the model, give the number of times and which atoms you locate and the Rp, Rwp RB, RF at each times.

Atom x y z
.....
.....
.....

4- Final refinement

- Give the final atomic coordinates, thermal parameters,

Final refinement with GSAS. A spherical harmonics correction (order 8) was applied to address preferred orientation effects.
H atoms of the tartrate unit were not refined. Water H atoms were not located.
Uiso values were contrained to have the same value for all tartrate atoms as well as the same value for all water oxygen atoms.
Lattice and space group:

_cell_length_a	8.22547(23)
_cell_length_b	10.43543(28)
_cell_length_c	6.24960(22)
_cell_angle_alpha	105.9625(21)
_cell_angle_beta	107.5287(24)
_cell_angle_gamma	94.9311(25)
_cell_volume	483.403(25)
_symmetry_cell_setting	triclinic
_symmetry_space_group_name_H-M	P-1

No special positions are occupied so all atoms have a multiplicity of 2.

Atom	x	Y	z	Uiso
Ca1	0.6843(5)	0.7714(4)	0.3428(7)	0.0384(11)
O2	0.5199(12)	0.8357(9)	0.6282(18)	0.0362(12)
C3	0.3648(18)	0.7475(13)	0.5785(26)	0.0362(12)
C4	0.3545(15)	0.6093(12)	0.4005(27)	0.0362(12)
O5	0.4571(13)	0.5880(9)	0.2982(18)	0.0362(12)
H6	0.53775	0.90882	0.693	0.0362(12)
O7	0.2046(11)	0.5389(10)	0.2934(17)	0.0362(12)
H8	0.26535	0.79155	0.54262	0.0362(12)
C9	0.3809(17)	0.7201(14)	0.8153(26)	0.0362(12)
C10	0.3547(18)	0.8407(14)	1.0025(27)	0.0362(12)
H11	0.30545	0.63864	0.77919	0.0362(12)
O12	0.5301(12)	0.6707(9)	0.9013(19)	0.0362(12)
O13	0.4760(13)	0.9032(9)	0.1736(18)	0.0362(12)
H14	0.51673	0.58685	0.83935	0.0362(12)
O15	0.2029(11)	0.8588(10)	0.9142(18)	0.0362(12)
Ow1	0.1615(10)	0.1095(8)	0.8610(15)	0.0385(15)
Ow2	0.8463(9)	0.5969(8)	0.1811(15)	0.0385(15)
Ow3	0.1266(9)	0.2793(9)	0.2925(16)	0.0385(15)
Ow4	0.1881(9)	0.9880(8)	0.3928(15)	0.0385(15)

5- Feel free to add any intermediate results (list of extracted structure factors, software decisive input and output data...) or comments you might consider as essential (details on hardware, time for solving the structure, number of moves by Monte Carlo or molecule position trial, any picture...).