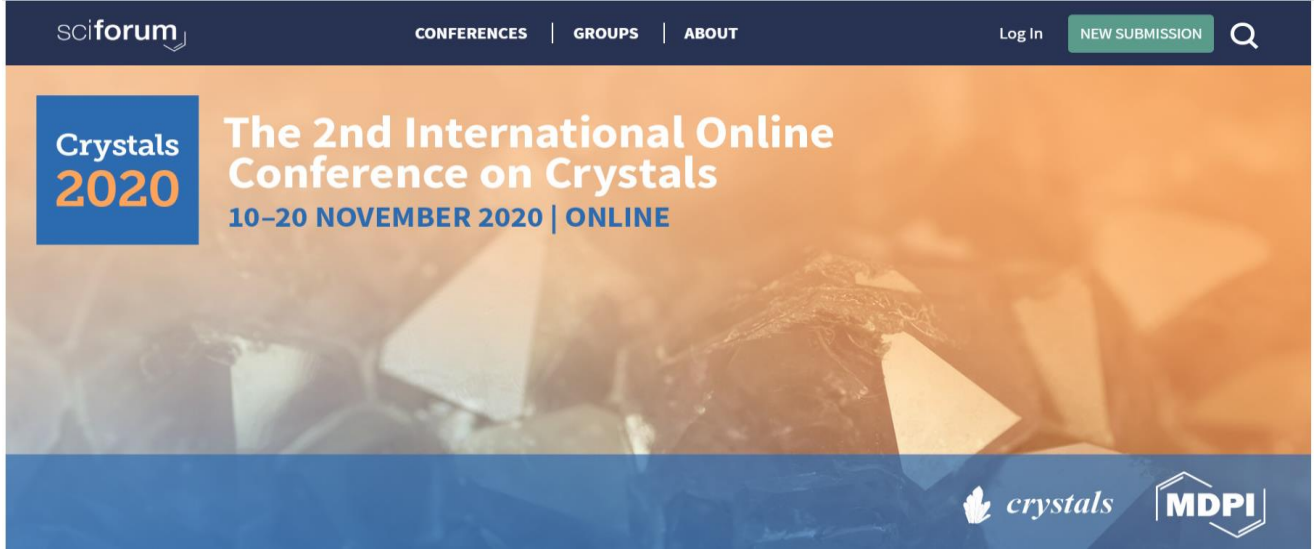

Polycrystalline Materials: Crystal Structure Solution in the Reciprocal Space or/and Direct Space?

Angela Altomare

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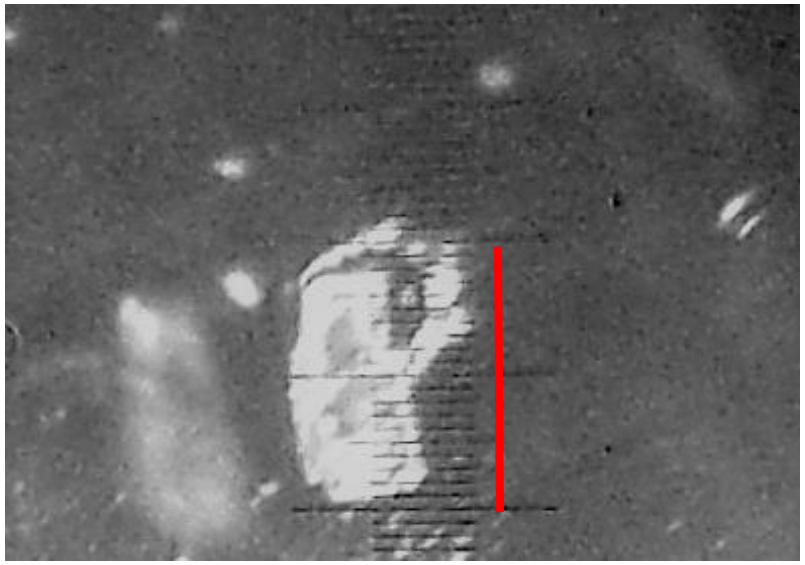
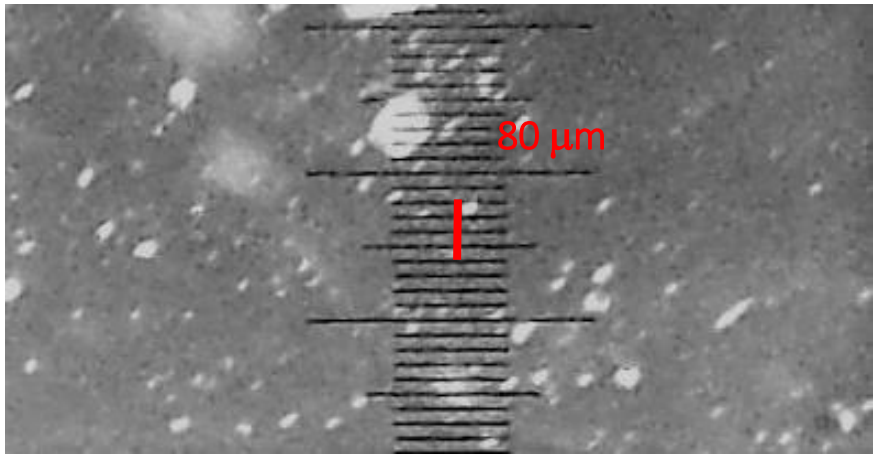
Polycrystalline materials



good quality single crystal
(tenths of a millimetre)



bad dimension single crystal

powder
(tens of microns)

X-ray Powder Diffraction (XPD) is an effective analytical method for identifying and characterizing materials available in the form of microcrystalline powder, of different nature and scientific and technological interest (chemical, pharmaceutical, biological, mineralogical, for cultural heritage, ..).

International Tables for Crystallography, Volume H, Powder Diffraction; C.J. Gilmore, J.A. Kaduk, H. Schenk Eds., Wiley: New York, 2019, pp. 270-281.

The challenge of structure solution by powder diffraction

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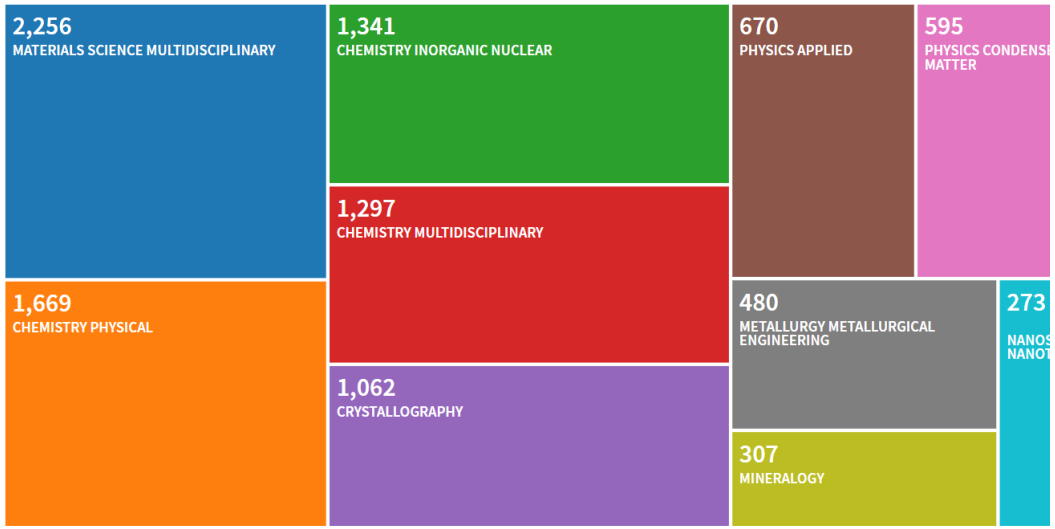
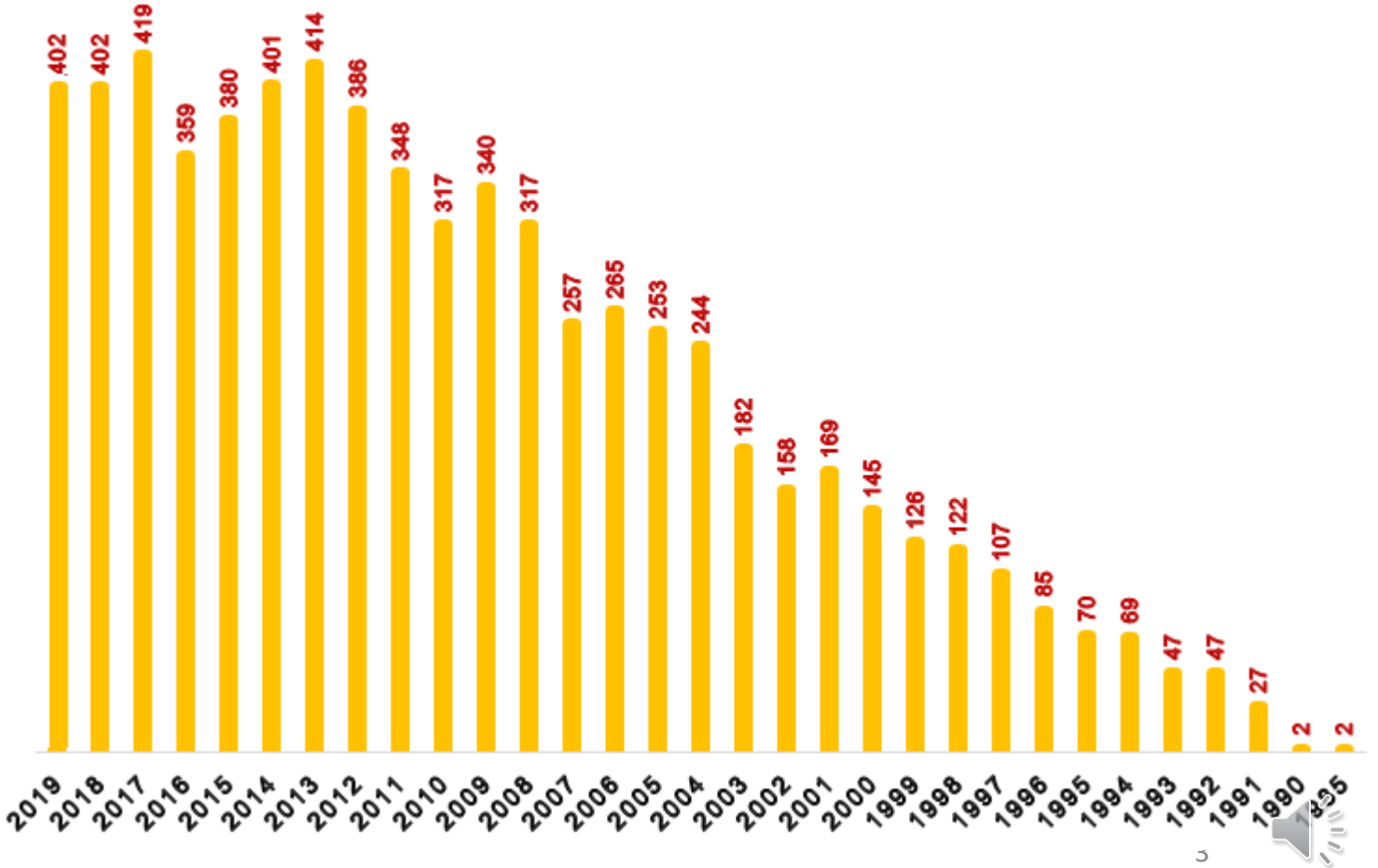
Web of Science powder diffraction crystal structure solution — Clarivate Analytics

Tools | Searches and alerts | Search History | Marked List

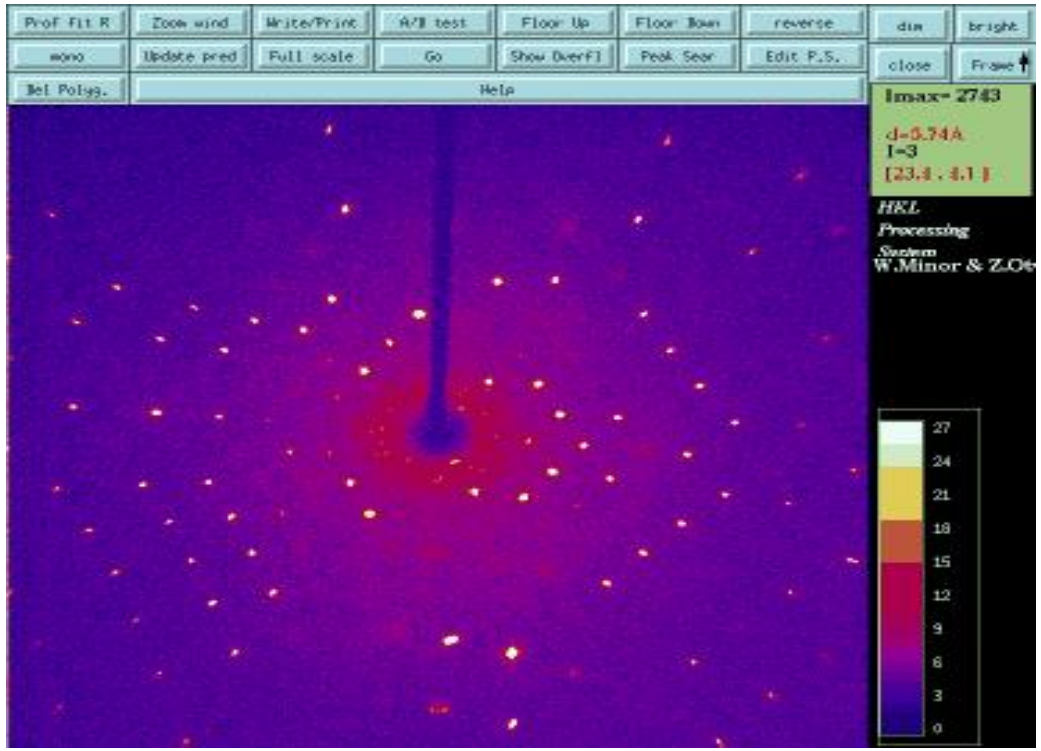
> 6800 papers



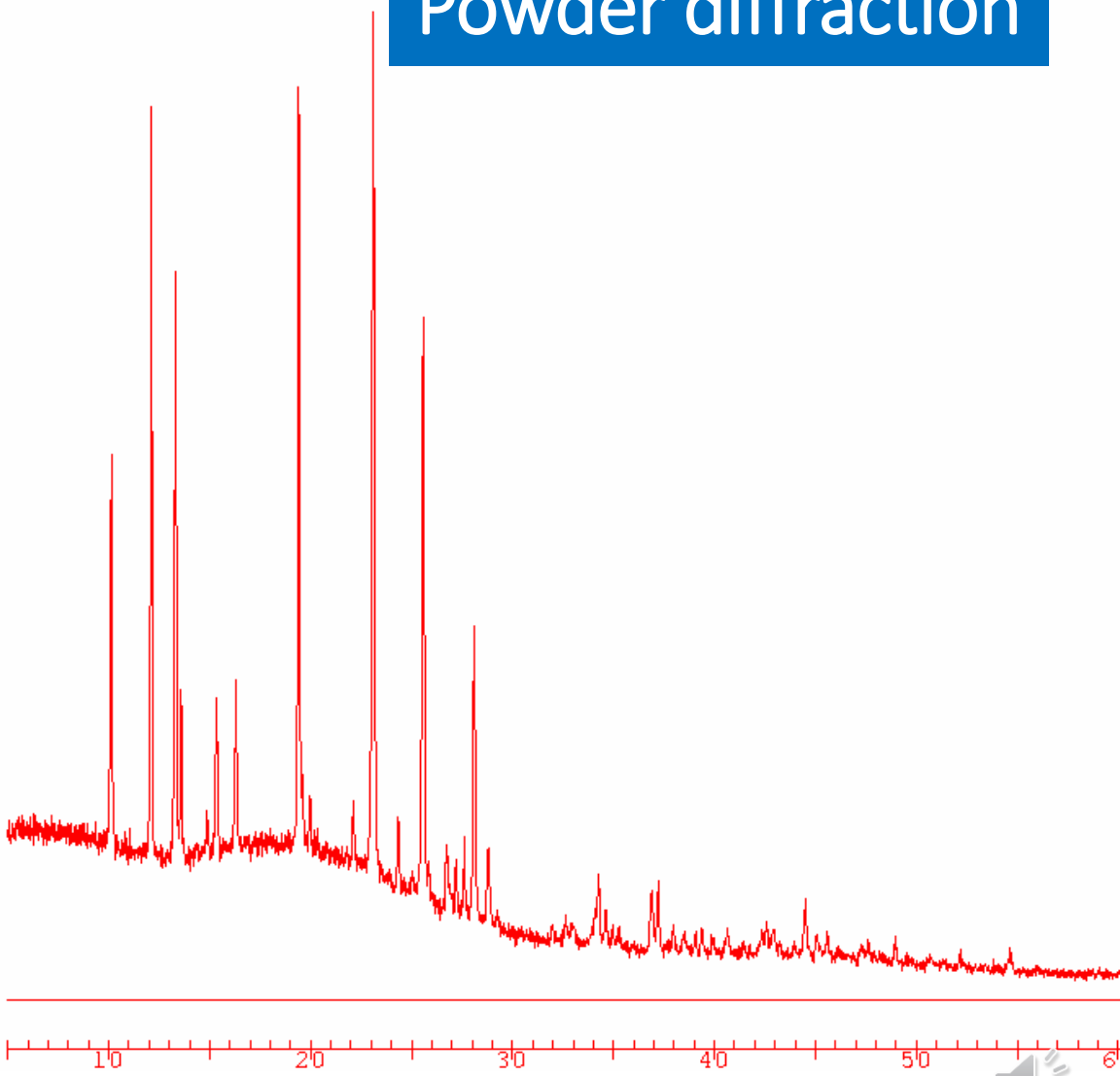


The challenge of structure solution by powder diffraction

Single crystal diffraction



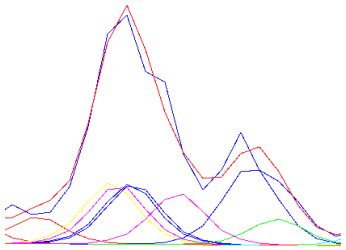
Powder diffraction



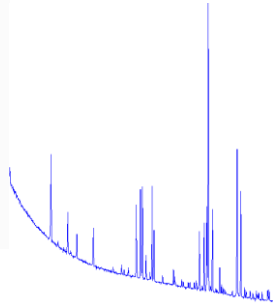
The challenge of structure solution by powder diffraction

The mono-dimensionality of the powder diffraction pattern is the greatest difficulty.

Diffraction **peak overlap** prevents from reliably estimating of experimental information derived from the powder pattern.



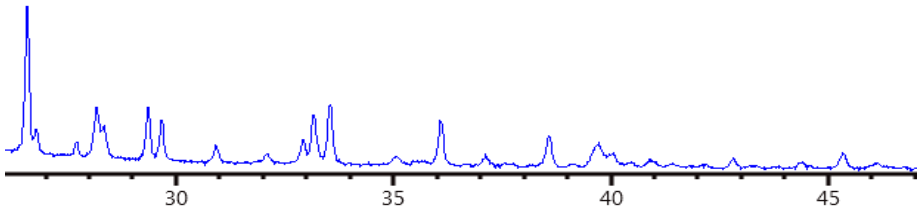
Not always **background** can be described by a simple analytical function.



If crystallites accidentally align along **preferred orientation(s)** diffraction intensities are altered.

If the scattering power is weak (light atoms), the **experimental resolution** is very far from being atomic.

$$d_{min}=\lambda/(2\sin\theta_{max})$$



The solution process by powder diffraction

- Cell parameters determination
- Space group identification

  - Full pattern decomposition and extraction of the structure factor moduli
  - Solution in the reciprocal space
  - Structure model optimization

  - Solution in the direct space

- Rietveld refinement

Structure solution by powder diffraction

Structure solution in the reciprocal space (Direct Methods, Patterson Methods)

Altomare, A.; Cuocci, C.; Moliterni, A.; Rizzi, R. Solving crystal structures using reciprocal-space methods. In International Tables for Crystallography, Volume H, Powder Diffraction; C.J. Gilmore, J.A. Kaduk, H. Schenk Eds., Wiley: New York, **2019**, pp. 395-413

- Only chemical formula and experimental profile (**easy**)
- Possibly atomic resolution (**hard**)
- Few execution time (**easy**)
- The extraction of the integrated intensity from the powder pattern for deriving the experimental structure factor moduli (**hard**)

Structure solution in the direct space (Simulated Annealing, Genetic Algorithm, ..)

David, W.I.F. Real-space methods for structure solution from powder-diffraction data: application to molecular structures. In International Tables for Crystallography, Volume H, Powder Diffraction; C.J. Gilmore, J.A. Kaduk, H. Schenk Eds., Wiley: New York, **2019**, pp. 414-432

- Not only chemical formula and experimental profile but also the knowledge of the expected molecular geometry (**easy for organic, usually hard for inorganic structures**)
- About 2-2.5 Å resolution (**easy**)
- Usually long execution time (**hard**)
- No extraction of the experimental structure factor moduli (**easy**)

The most widely used software

EXPO
Altomare, A.; Cuocci, C.; Giacovazzo, C.; Moliterni, A.; Rizzi, R.; Corriero, N; Falcicchio, A. EXPO2013: a kit of tools for phasing crystal structures from powder data. J. Appl. Cryst. 2013, 46, 1231-1235.

EXPO (Altomare *et al.*, J. Appl. Cryst. 2013, 46, 1231-1235).

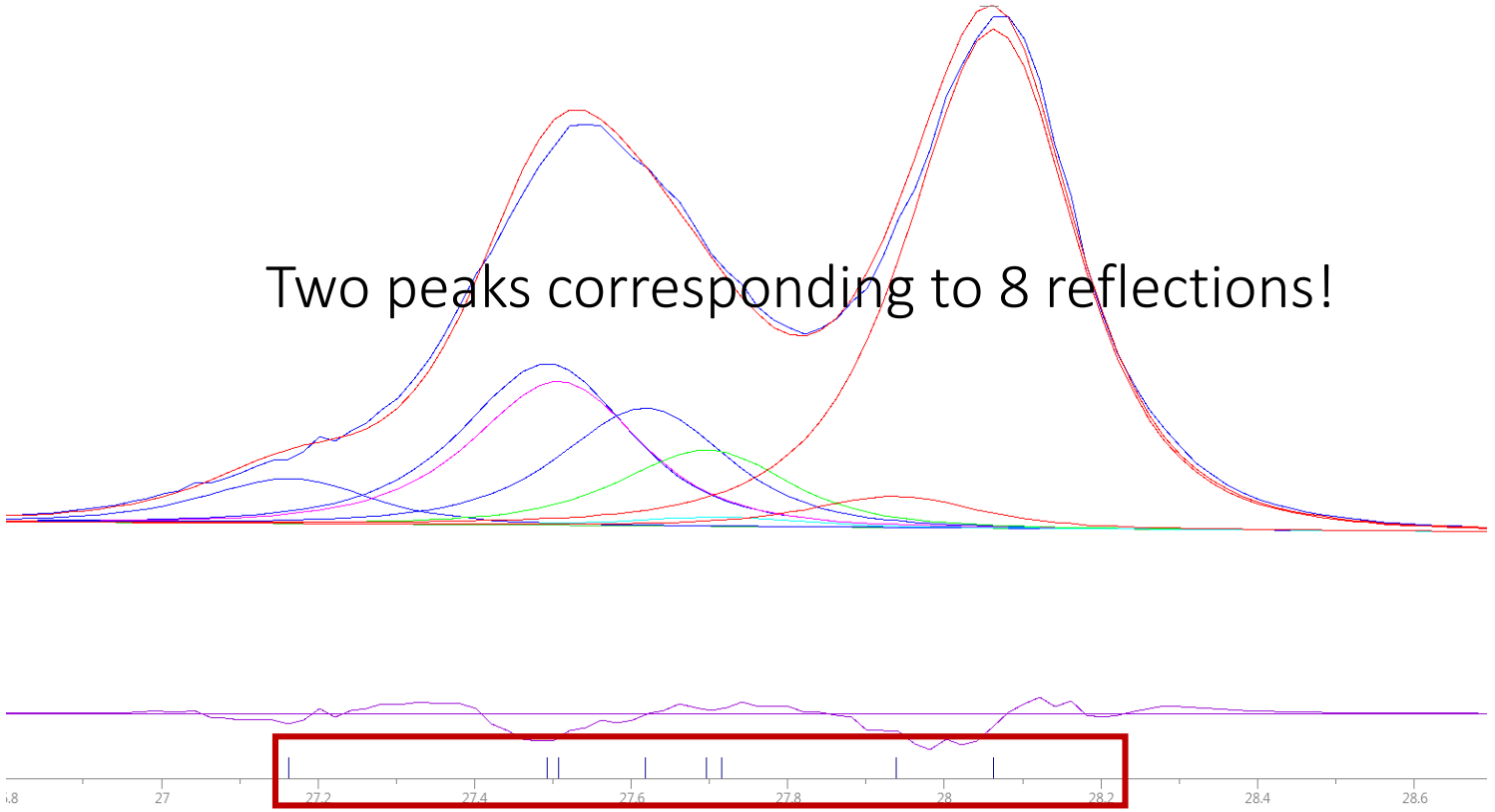
FOX (Favre-Nicolin & Černỳ. J. Appl. Cryst. 2002, 35, 734-743)
DASH (David et al., J. Appl. Cryst. 2006, 39, 910-915)

Structure solution in the reciprocal space

$$I_h \propto |F_h|^2$$

Extraction of the structure factor moduli

Two peaks corresponding to 8 reflections!



HKL List

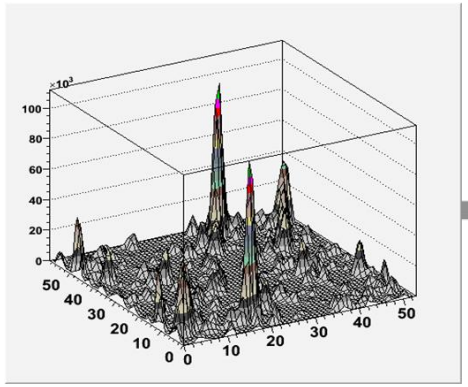
F

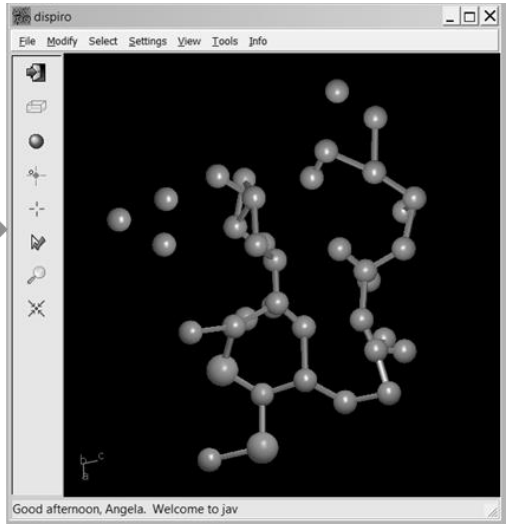
n.	h	k	l	2 theta	d	Fo
1	1	1	0	5.88268	9.26106	0.24484
2	2	0	0	6.20582	8.77927	1.45248
3	2	1	0	7.97082	6.83743	0.19459
4	0	2	0	10.00408	5.45029	0.97772
5	1	2	0	10.47625	5.20529	0.87378
6	3	1	0	10.57554	5.15656	0.20504
7	2	2	0	11.78094	4.63053	0.40476
8	1	0	-1	11.94103	4.56867	0.57880
9	1	0	1	12.24104	4.45711	1.89032
10	4	0	0	12.42994	4.38964	0.78028
11	0	1	1	12.71512	4.29158	0.28611
12	1	1	-1	12.95156	4.21355	0.29540
13	1	1	1	13.22902	4.12556	0.47659
14	4	1	0	13.40423	4.07188	0.57551
15	3	2	0	13.68518	3.98867	1.41544
16	2	1	-1	13.90076	3.92711	0.34602
17	2	1	1	14.41461	3.78781	0.32428
18	3	0	-1	14.59349	3.74163	0.49282
19	3	0	1	15.32386	3.56429	0.44224
20	1	3	0	15.35048	3.55814	0.72391
21	0	2	1	15.40483	3.54566	0.21224
22	3	1	-1	15.43421	3.53895	0.59779
23	1	2	-1	15.60131	3.50128	0.77257

Export Close

Structure solution in the reciprocal space: Direct Methods

$$\rho(\mathbf{r}) = V^{-1} \sum_{\mathbf{h}} |F_{\mathbf{h}}| \exp(i\varphi_{\mathbf{h}}) \exp(-2\pi i \bar{\mathbf{h}} \cdot \mathbf{r})$$





What do we know? $|F_{\mathbf{h}}|$

collected by the X-ray diffraction experiment. The measured integrated intensities are proportional to the structure factor amplitudes ($I_{\mathbf{h}} \propto |F_{\mathbf{h}}|^2$).

What do we still need? $\varphi_{\mathbf{h}}$

not collected by the diffraction experiment. The phase problem

Direct Methods, based on sophisticated statistical and probabilistical calculations on the experimental structure factor moduli, are able to estimate the missing phases.

Structure solution in the reciprocal space: Direct Methods

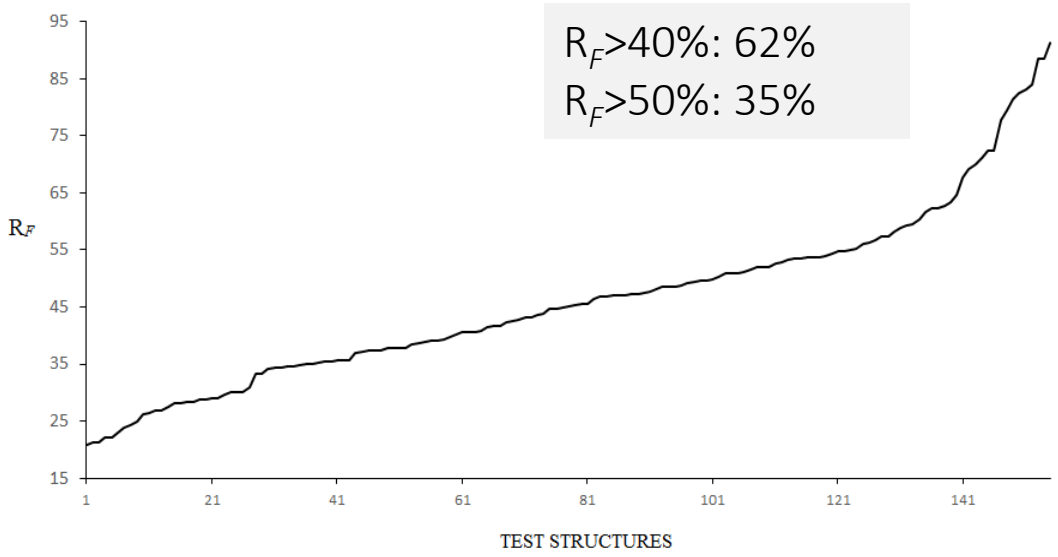
The quality of the electron density map calculated by Direct Methods depends on:

- **the experimental resolution $d_{min}=\lambda/(2\sin\theta_{max})$**
  Atomic resolution is the best condition.
- **the reliability of the integrated intensities extracted from the experimental pattern and used for phasing**
- **the structure complexity** (number of non-H atoms in the asymmetric unit)

The structure model derived by Direct Methods is often so approximate and far from the true one that it needs to be optimized before being refined by the Rietveld method.

Structure solution in the reciprocal space

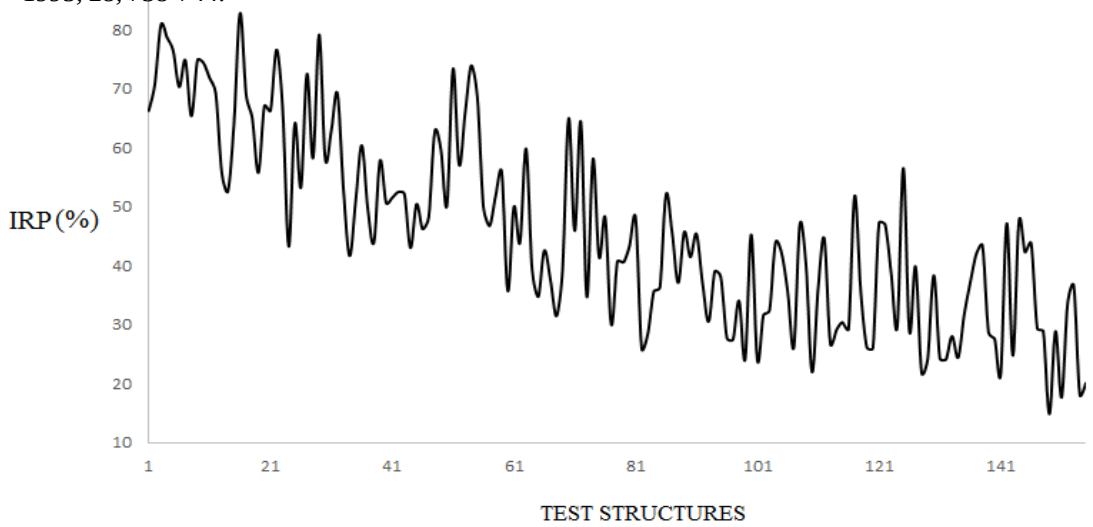
Peak overlap: uncertainties on the experimental structure factor moduli extracted from the diffraction pattern



The R_F value corresponding to each of the 155 test structures ranked by the increasing value of R_F.

Peak overlap extent in a powder diffraction pattern: percentage of independent reflections*

*Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Moliterni, A.G.G., Burla, M.C., Polidori, G. On the Number of Statistically Independent Observations in a Powder Diffraction Pattern. J. Appl. Cryst. 1995, 28, 738-744.



The percentage of independent reflections (IRP) value corresponding to each of the 155 test structures.

$<R_F>_{laboratory\ X\text{-}ray}$= 47%; $<IRP>_{laboratory\ X\text{-}ray}$ =44%; $<R_F>_{synchrothron\ X\text{-}ray}$= 42%; $<IRP>_{synchrothron\ X\text{-}ray}$ =52%;

*High success rate by Direct Methods	Low success rate by Direct Methods
IRP > 60% and RES < 1.2Å and NA-noH < 30 and IR/NA-noH > 15	IRP < 50% and RES > 1.5Å and NA-noH > 35 and IR/NA-noH < 9

RES: Experimental resolution
NA-noH: Number of non-hydrogen atom in the asymmetric unit
IR: Number of independent reflections

*Altomare, A.;Corriero, N.; Cuocci, C.; Falcicchio, A.; Rizzi, R. Solving a Structure in the Reciprocal Space, Real Space and Both by Using the EXPO Software Crystals. 2020, 10, 16.

Structure solution in the reciprocal space

5-(5-nitro furan-2-ylmethylen), 3-N-(2-methoxy phenyl), 2-N'-(2-methoxyphenyl) imino thiazolidin-4-one

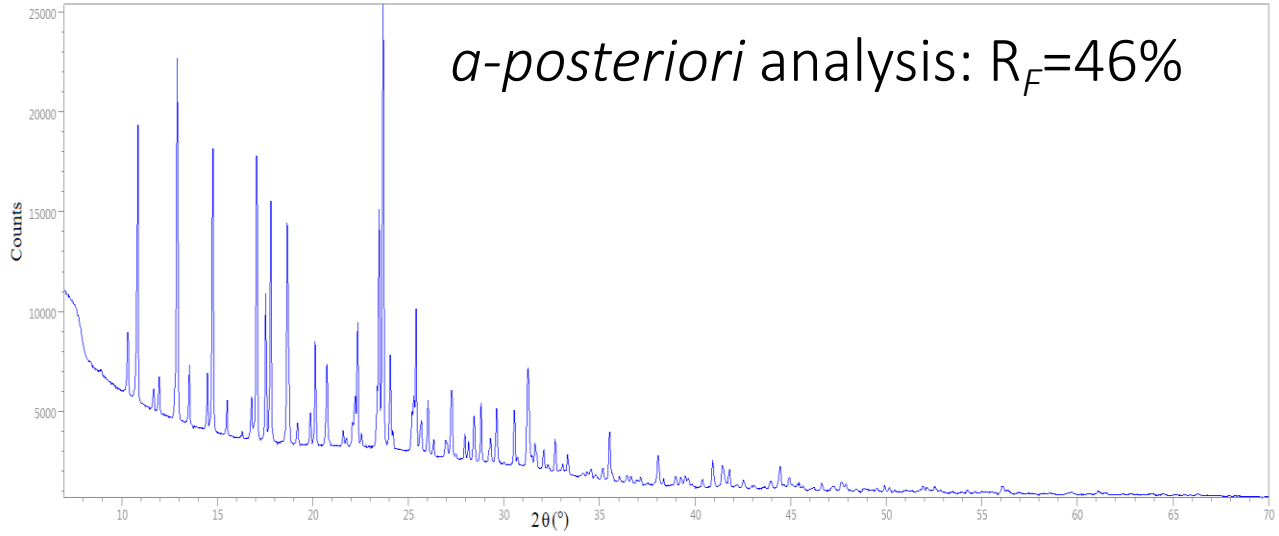
$C_{22}H_{17}O_6N_3S$

X-ray laboratory data

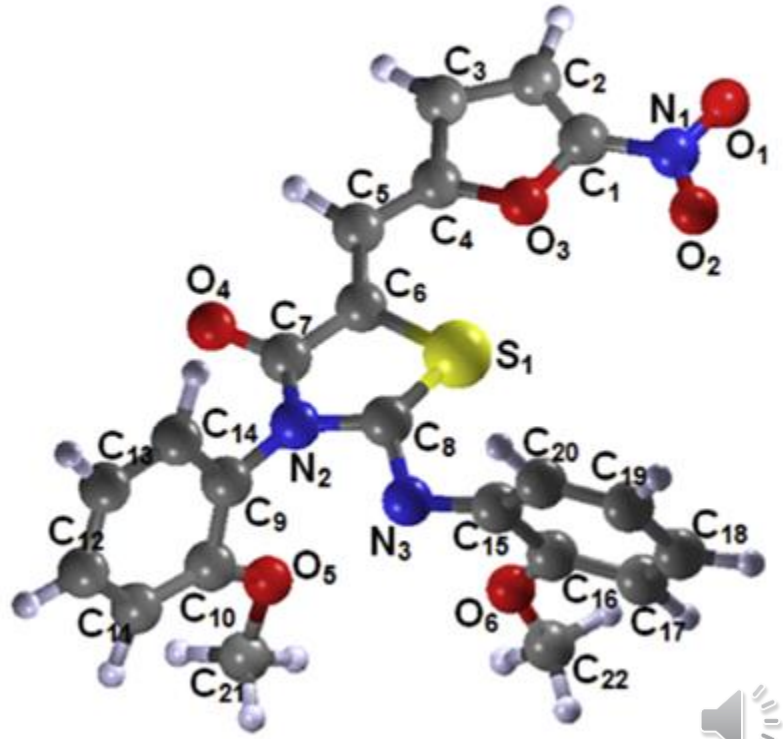
triclinic, *P*-1, cell parameters: *a*=11.476, *b*=10.912, *c*=8.809 Å, α=103.663, β=91.490, γ=84.140°

RES=1.34Å; NA-noH=32; Number of reflections: 919; IR=349; IRP=38%; IR/NA-noH =10.9

Low<Success rate<High



a-posteriori analysis: R_F=46%



Solution by Direct Methods in EXPO: 5 minutes

[Intel(R) Core(TM) i7-4510U CPU @ 2.00 GHz 2.60GHz]

Structure solution in the reciprocal space

2-(5,6-dimethylimidazo[2,1-b]thiazol-3-yl)-1-morpholinoethanone

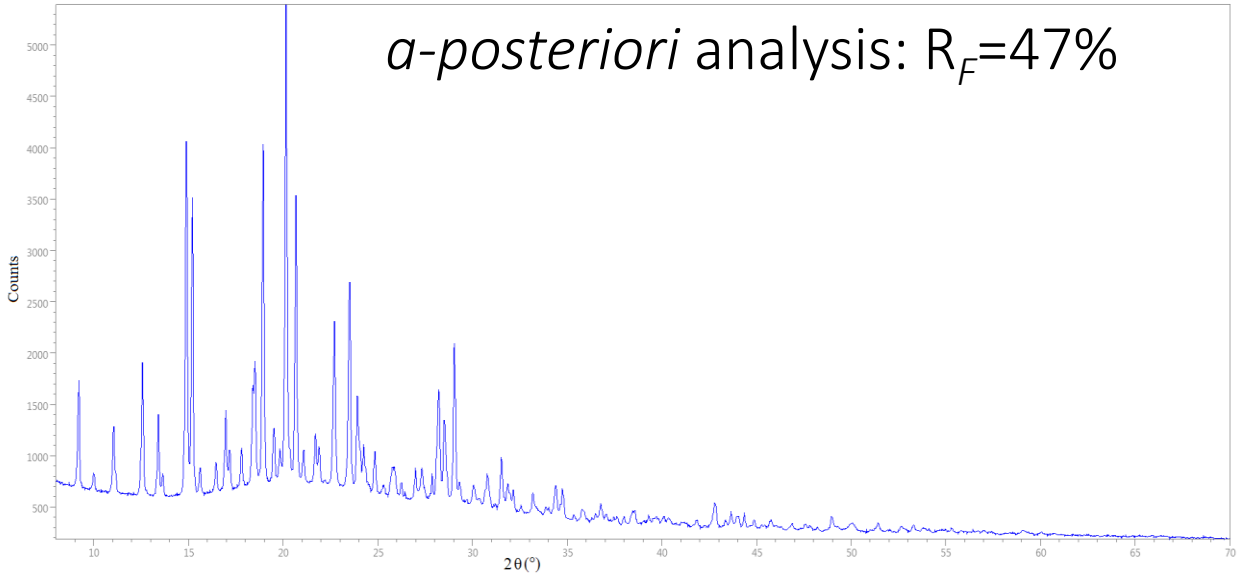
$C_{13}H_{17}N_3O_2S$

X-ray laboratory data

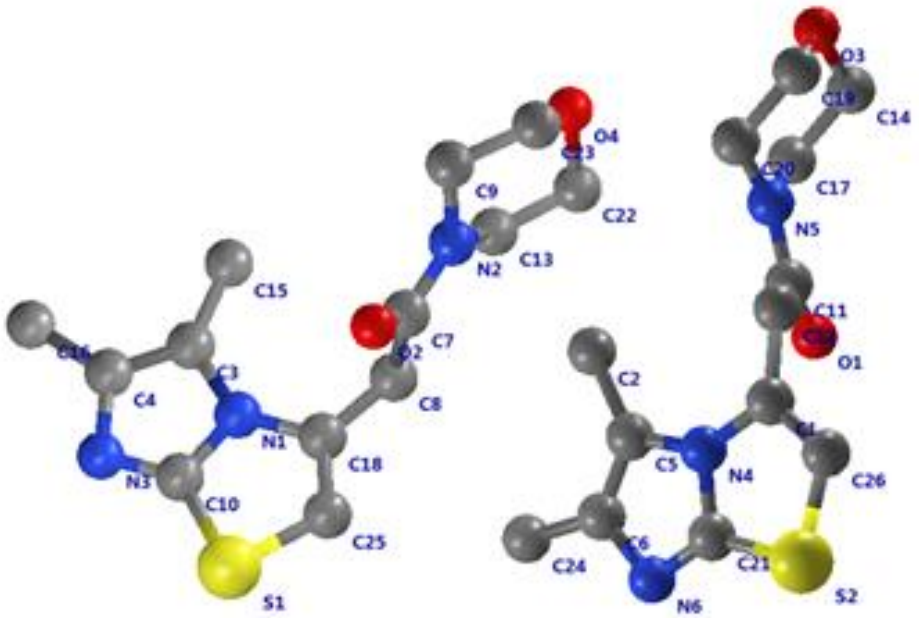
Monoclinic, $P2_1/c$, cell parameters: a=14.237, b=19.197, c=10.085 Å, β=99.082°

RES=1.34Å ; NA-noH=38; Number of reflections: 1175; IR=331; IRP=28%; IR/NA-noH =8.7

Low<Success rate<High

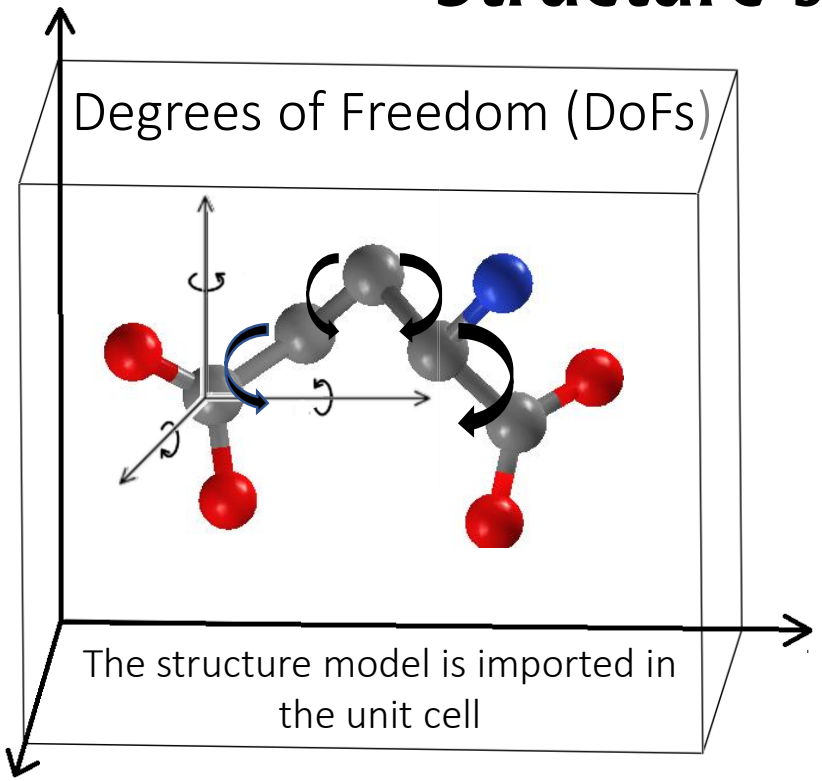


a-posteriori analysis: R_F=47%

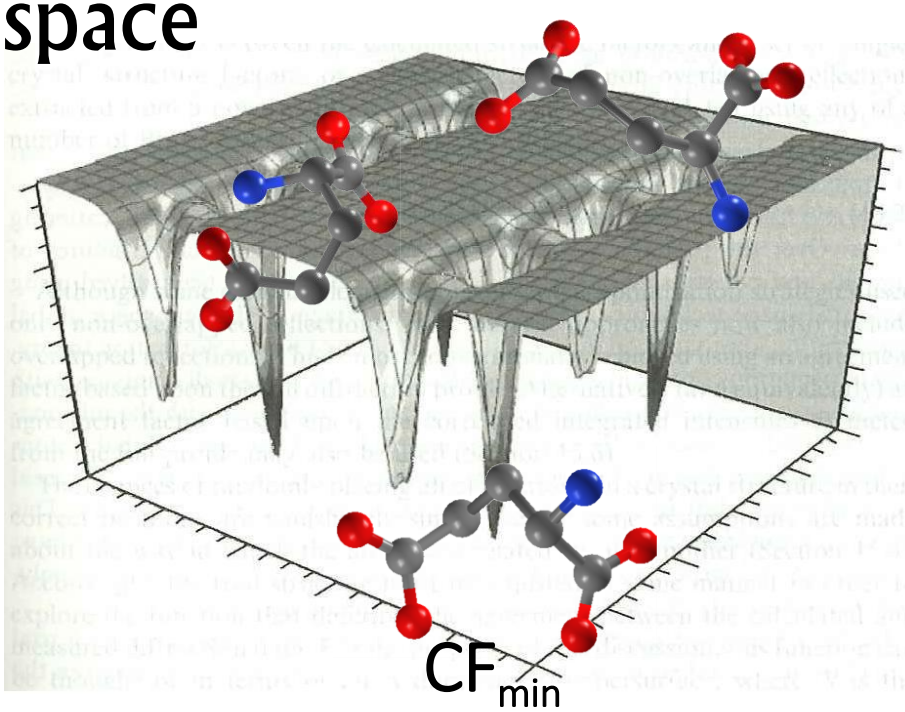


Unsolved by Direct Methods in EXPO

Structure solution in the direct space



$$\mathbf{CF} = \sqrt{\frac{\sum_i w_i \left(y_{obs}(\theta_i) - y_{calc}(\theta_i)\right)^2}{\sum_i w_i \, y_{obs}(\theta_i)^2}}$$



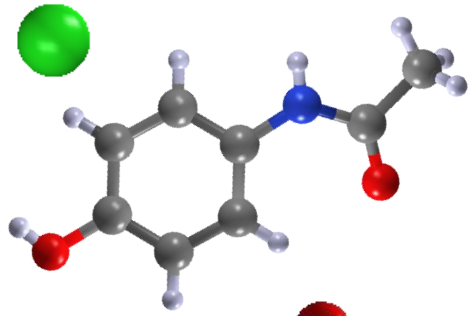
The molecular connectivity must be known (well known bond distances and angles).

Crystal structure can be described as a combination of building blocks: atoms, molecules, polyhedrons.

- Similar molecules in databases and/or in the literature are searched.
- Molecule editors are used. Molecules are sketched in 2D or 3D format. Their geometry is optimized by force field method. The removal of H atoms during the structure solution process (they do not significantly contribute to X-ray diffraction) is advisable for reducing the number of atoms and DoFs, and decreasing the computational time to evaluate CF for each trial structure.

Structure solution in the direct space: Simulated Annealing

$\Delta CF = CF_{current} - CF_{previous}$
RND = random number



Starting random model

Trial generation of structure models by variation of DoFs

CF computation corresponding to the trial structure

Metropolis: is the new configuration better than the previous one?

Yes (**ΔCF** < 0) The new configuration is kept

No (**ΔCF** > 0)

The trial model is accepted if $\exp(-\Delta CF/T) > RND$

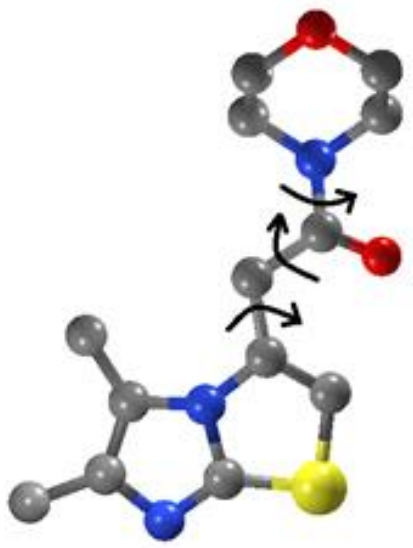
Annealing

Structure solution in the direct space

The solution in the direct space is particularly effective for the organic compounds.

If **DoFs≤15**, results by standard direct space solution are usually successful.

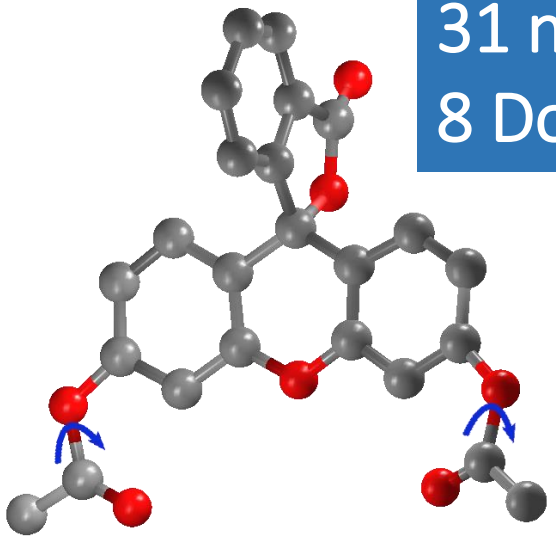
The execution time increases by increasing the number of DoFs and the number of fragments of the structure model.



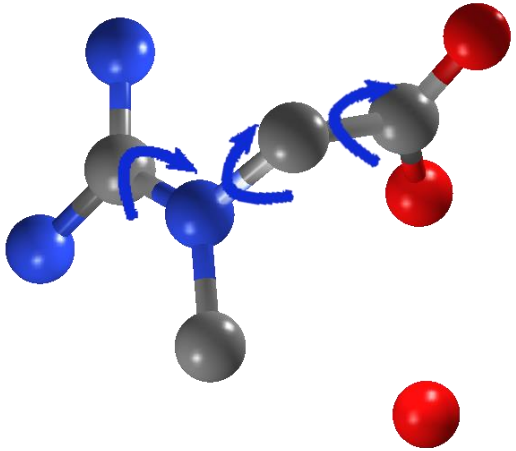
2-(5,6-dimethylimidazo[2,1-b]thiazol-3-yl)-1-morpholinoethanone $C_{13}H_{17}N_3O_2S$
X-ray laboratory data
Monoclinic, $P2_1/c$, cell parameters: a=14.237, b=19.197, c=10.085 Å, β=99.082°
RES=2.0Å; 18 DoFs (12 external and 6 torsion angles for the two molecules)

Solution by Simulated Annealing in EXPO: 277 hours (Intel(R) Xeon(R) CPU E5-2690 @ 2.90GHz).

Reciprocal space solution (Direct Methods) *versus* Direct space solution (Simulated Annealing)

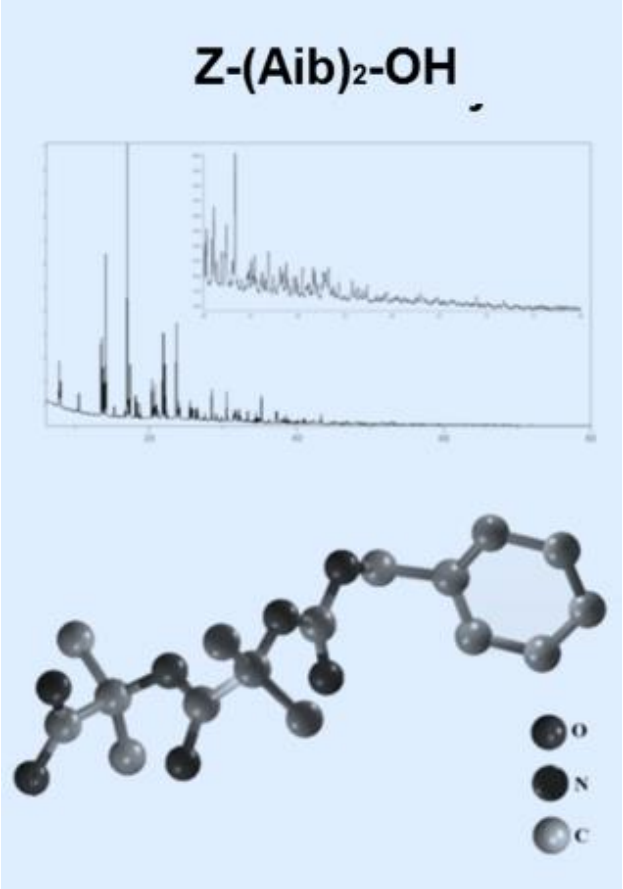


31 non-H atoms
8 DoFs



10 non-H atoms
2 fragments
12 DoFs

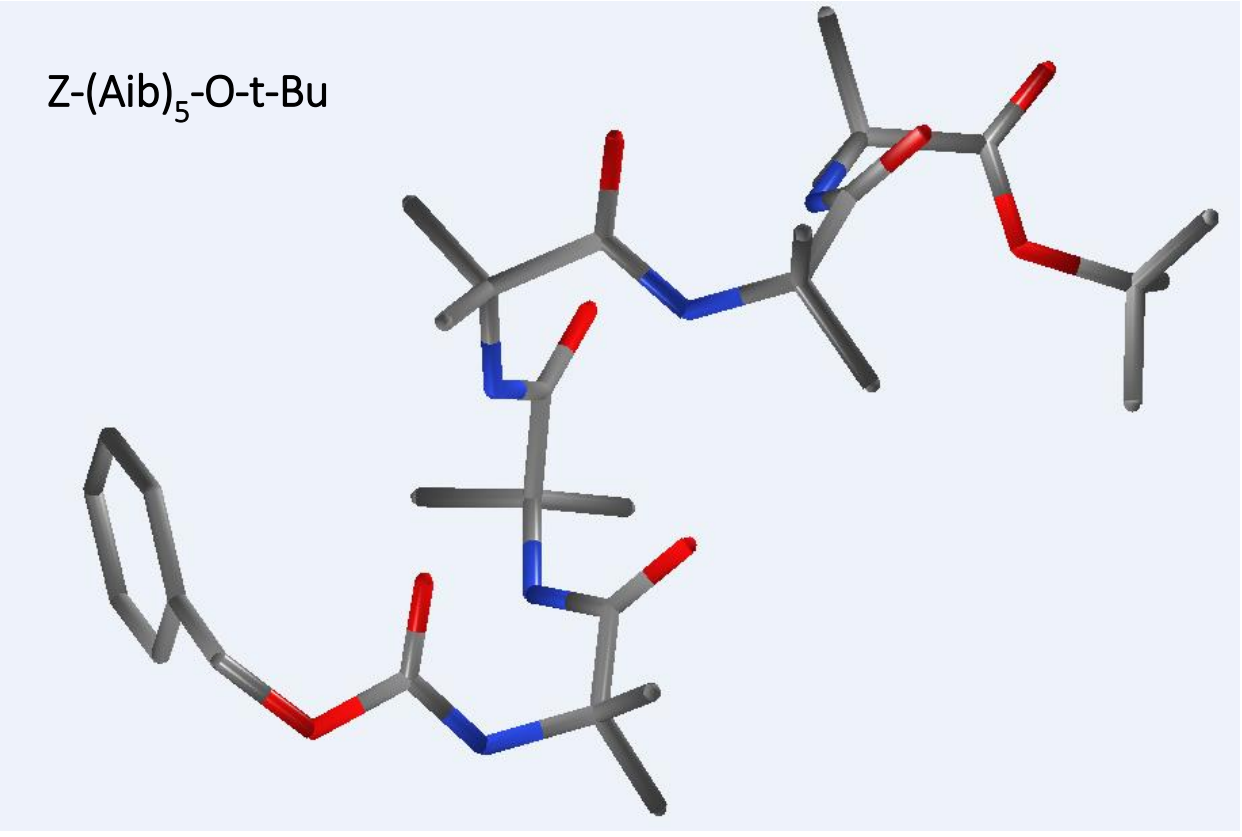
23 non-H atoms in the asymmetric unit
15 DoFs



Direct Methods → 14m 57s

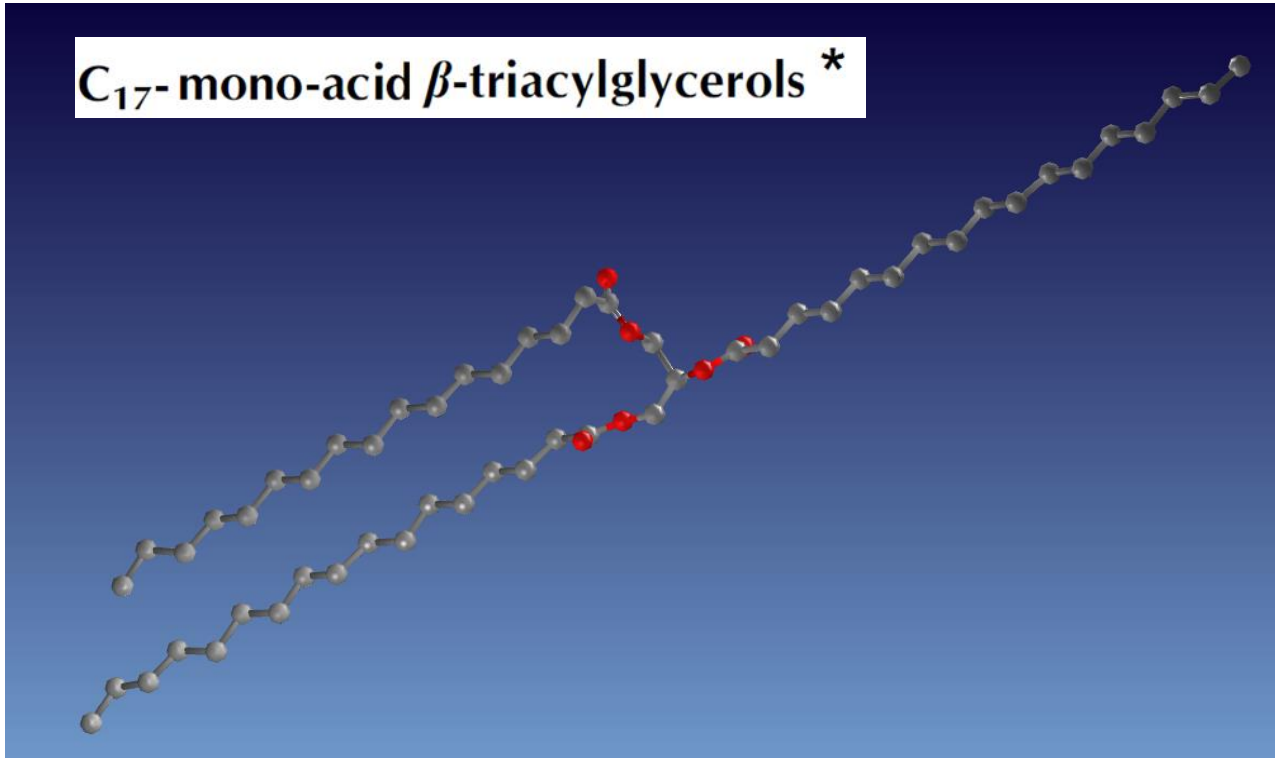
Simulated Annealing → 164m 40s

Structure solution in the direct space: Simulated Annealing in EXPO



Number of non-H atoms in the asymmetric unit: 45

DoFs
Internal: 20
External: 6



Number of non-H atoms in the asymmetric unit: 60

The parallel version (MPI protocol)
Time
20 CPU-cores≈290 h

DoFs
Internal: 53
External: 6

*Helmholdt et al. Acta Cryst. (2002). B58, 134-139.

The combination of Direct Methods and Simulated Annealing

Heterogeneous & Homogeneous & Bio- & Nano-
CHEMCATCHEM
CATALYSIS
ChemPubSoc Europe

Divergent Multicomponent Tandem Palladium-Catalyzed Aminocarbonylation-Cyclization Approaches to Functionalized Imidazothiazinones and Imidazothiazoles

Dr. Lucia Veltri, Dr. Raffaella Mancuso, Dr. Angela Altomare, Prof. Dr. Bartolo Gabriele

First published: 10 June 2015

2-(5,6-Dimethylimidazo[2,1-*b*]thiazol-3-yl)-1-morpholinoethanone

$C_{13}H_{17}N_3O_2S$

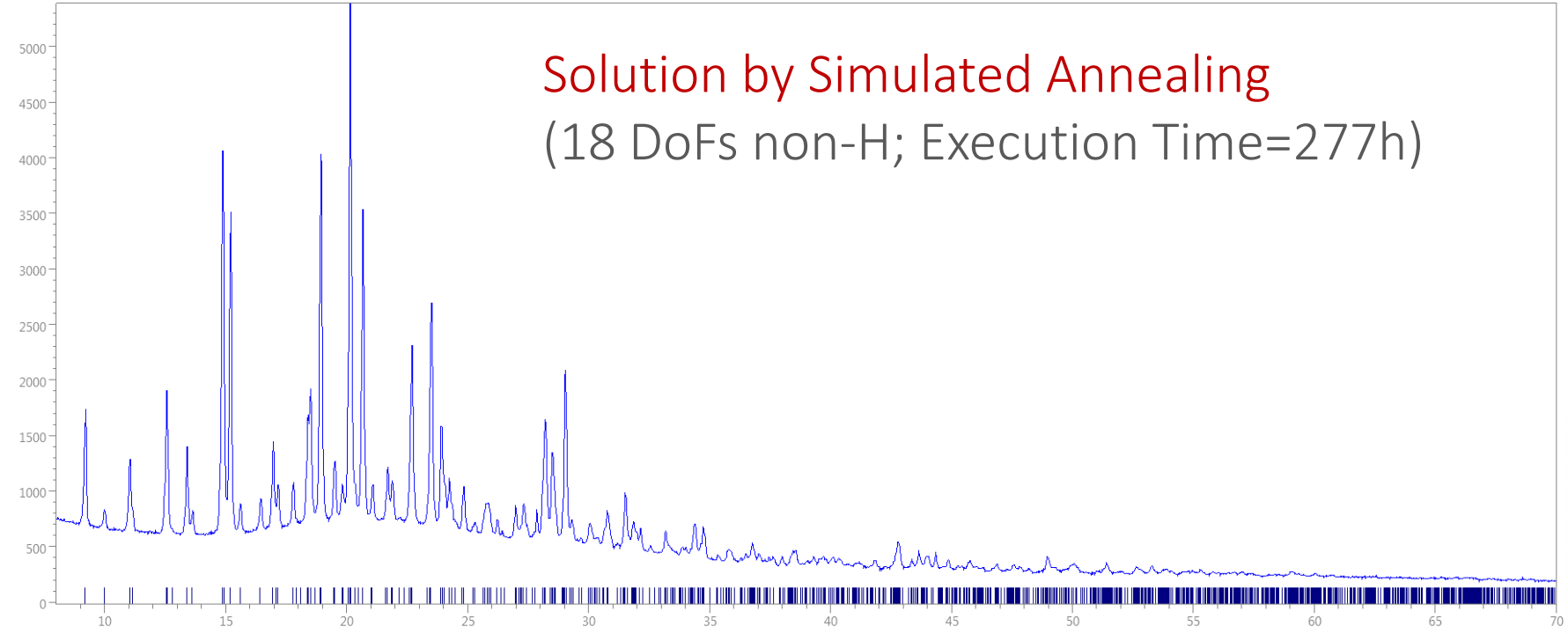
Monoclinic, P21/c

a = 14.252 (7) Å

b = 19.243 (9) Å

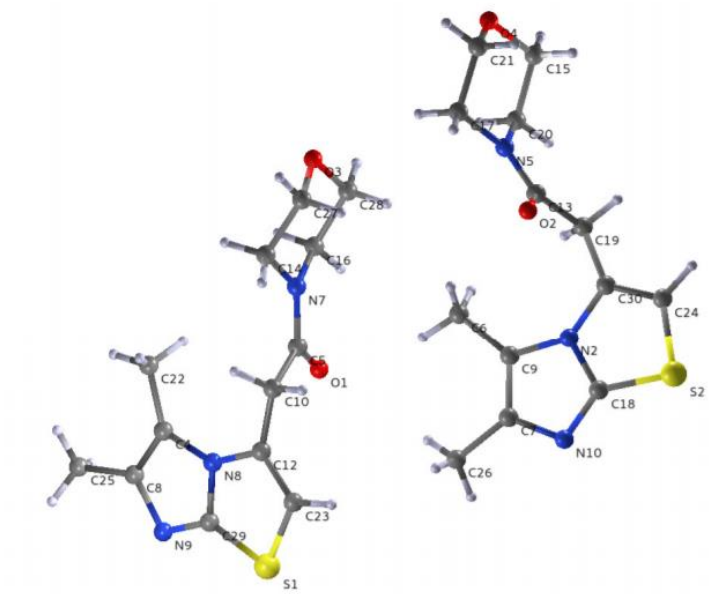
c = 10.0878 (18) Å

β = 99.12 (3)°

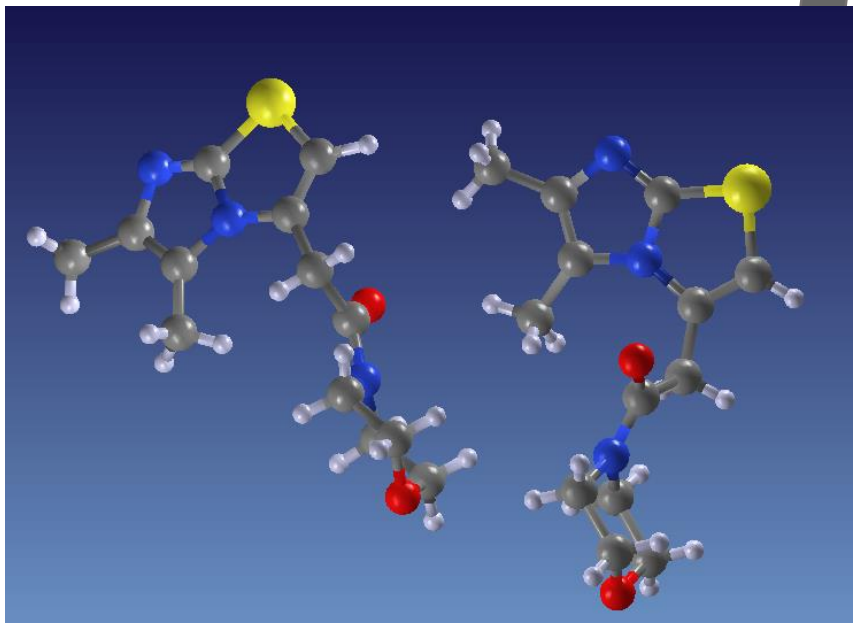


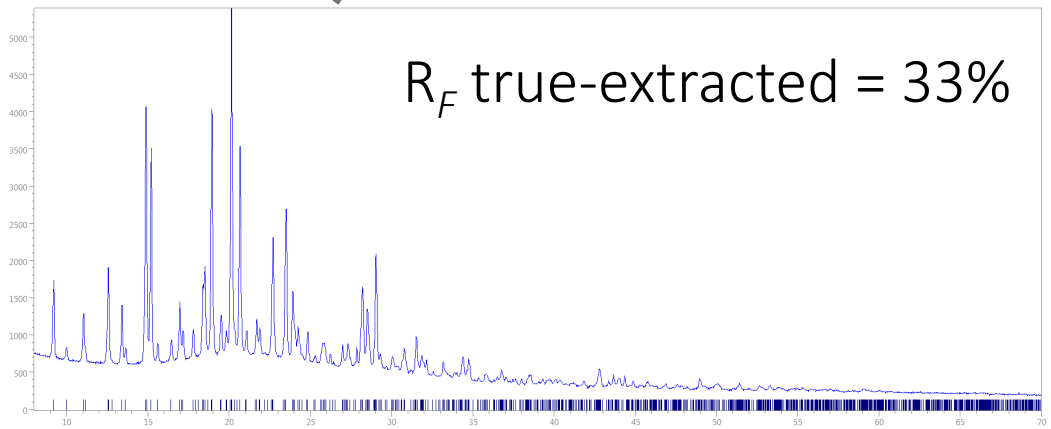
Solution by Simulated Annealing

(18 DoFs non-H; Execution Time=277h)



The combination of Direct Methods and Simulated Annealing





Solution by Direct Methods

Solutions superimposable → Correct solution → Rietveld refinement

Examples of structure solution by EXPO software

Journal of Molecular Structure 1189 (2019) 8–20

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Synthesis, PXRD structural determination, Hirshfeld surface analysis and DFT/TD-DFT investigation of 3N-ethyl-2N'-(2-ethylphenylimino) thiazolidin-4-one

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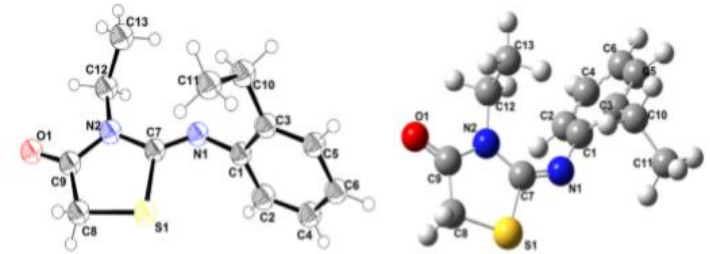

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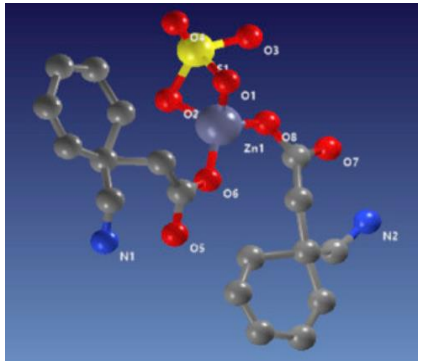
Volume 1199, 5 January 2020, 126951

Zinc ternary complexes with gabapentin and neurotransmitters: Synthesis, spectral, thermal and molecular docking studies

M.A. Mahmoud [a], M.A. Helal [b, c], A.M. Ammar [d, 1]



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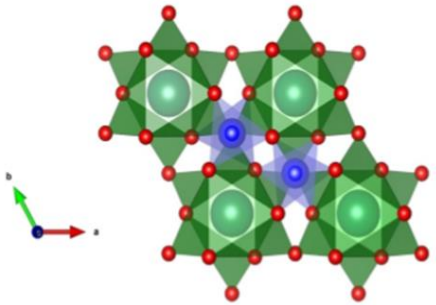
Magnetic oxygen stored in quasi-1D form within $BaAl_2O_4$ lattice

Martina Vrankić [1,7*], Ankica Šarić [1], Sanja Bosnar [2], Damir Pajić [3,7], Jure Dragović [3], Angela Altomare [4], Aurelia Falcicchio [4], Jasminka Popović [5], Marijana urić [2], Mladen Petravić [5], Ivana Jelovica Badovinac [5] & Goran Dražić [6]



Inorganic Chemistry
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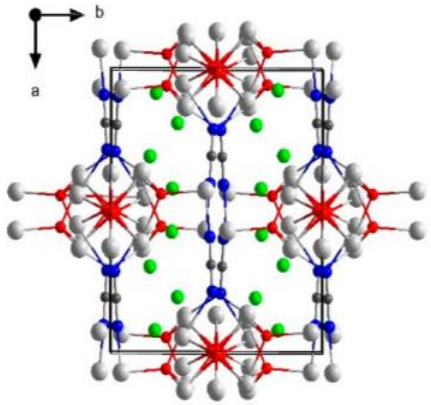
Synthesis, Structure, and Electronic Properties of $Sn_9O_5Cl_4(CN_2)_2$

Manuel Löber,[†] Chris Steve Geißenhöner,[†] Markus Ströbele,[†] Sylvio Indris,[‡] Carl P. Romao,[†] and Hans-Jürgen Meyer*[,†]



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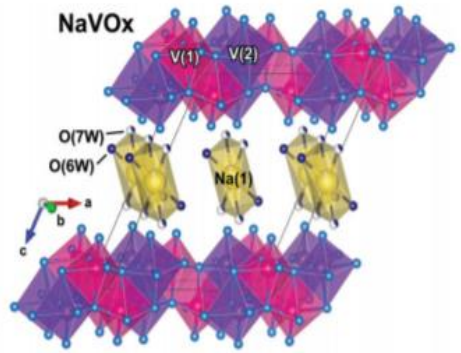
Exploring new hydrated delta type vanadium oxides for lithium intercalation†

Joseba Orive, [a,b] Roberto Fernández de Luis, [c] Edurne S. Larrea, [d] Ana Martínez-Amesti, [e] Angela Altomare, [f] Rosanna Rizzi, [f] Luis Lezama, [d] María I. Arriortua, [c,d] Juan Luis Gómez-Cámer, [g,h] María Jauregui, [h] Montse Casas-Cabanas [h] and Judit Lisoni [b,i]



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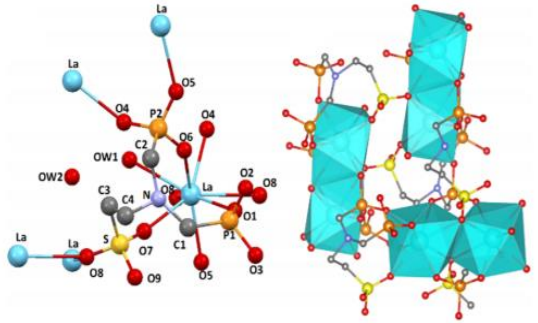
Layered Lanthanide Sulfophosphonates and Their Proton Conduction Properties in Membrane Electrode Assemblies

Montse Bazaga-García,[†] Inés R. Salcedo,[†] Rosario M. P. Colodrero,[‡] Konstantinos Xanthopoulos,[§] Didier Villemin,[⊥] Norbert Stock,[∥] Mar López-González,[#] Carmen del Río,[#] Enrique R. Losilla,[†] Aurelio Cabeza,[†] Konstantinos D. Demadis,*[,§] and Pascual Olivera-Pastor*[,†]



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Altomare, A.; Corriero, N.; Cuocci, C.; Falcicchio, A.; Rizzi, R.
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Registration and Download of EXPO software

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EXPO2013: a kit of tools for phasing crystal structures from powder data
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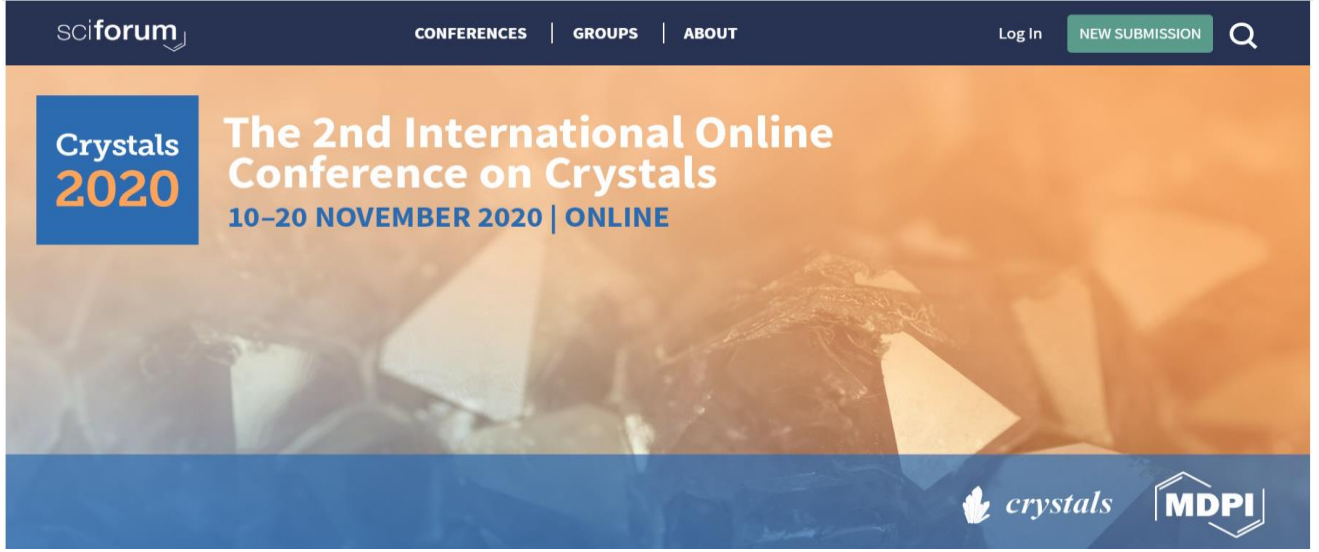

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