NEW METHODS FOR INCREASING ACCURACY OF IN-SITU POWDER DIFFRACTION

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The method of \textit{in-situ} powder diffraction

„bottle necks“ and possible solutions

State of the art examples:
- Monitoring of mechanochemical milling reactions
- Gas adsorption in large pore MOF’s
- Advances in MEM analysis

Conclusions
THE METHOD OF CHOICE:
TIME RESOLVED ‘IN SITU’ POWDER DIFFRACTION

Phase transitions
• ‘Polymorph screening’
• Phase transitions of different order
• Reversibility of phase transitions (hysteresis, strain-order parameter coupling)

Chemical reactions
• solid/solid, liquid/liquid, solid/gaseous etc.
• Influence of external conditions (pressure, temperature, stress, Electric/magnetic field, Light, mechanical power, etc.)

Physical effects
• thermal expansion (change of bond lengths, cell volume, cell axes etc.)
• Compressibility (bulk modulus)
• structural changes
An early 'in-situ' powder xray diffraction experiment on the structure of $\alpha$-N$_2$

Debye-Scherrer film of $\alpha$-N$_2$ at 34K

Exposure time: 18h

Schematic drawing of the used cryo-camera

$\alpha$-N$_2$ Pa-3

THE BOTTLE NECKS

- Scanning Speed
- Instrumental Resolution
- Data Reduction Software
WHY BETTER RESOLUTION...

Stoe Stadi-P, Mo
(Ge(111) monochromator, PSD)

ESRF, ID31
(analyzer crystal)

NSLS, X7B
(image plate)

LiNa-triflate
WHY HIGHER SPEED

Radiation induced phase transition of Rubidium triflate measured at ID31, ESRF, July, 2005

- 5 minutes/scan
- 1 minute/scan
- 30 seconds/scan
Rendered images of a high pressure powder diffraction data set (left) and a high temperature powder diffraction data set (right) collected by a 2D-image plate detector.

The white spikes are high intensity peaks originating from larger grains within a fine grained matrix (left) or reflections of the high temperature sapphire capillary (right).
SOLUTION OF THE SPEED/RESOLUTION PROBLEM:
HIGH RESOLUTION PSD’S

The 30720-element Mythen II strip detector, covering 120° at the SLS

5* with 9 Si(111) analyzing crystals at I11, Diamond
The effect of fractile filtering on the diffraction image is shown:

**Green mask:** top 48%
**Blue mask:** bottom 2%
**Yellow mask:** beam stop
**Grey region:** used for integration
FeSb$_2$O$_4$ at 53 kbar

Final integrated powder patterns
REAL-TIME AND IN SITU MONITORING OF MECHANOCHEMICAL MILLING REACTIONS

Tomislav Friščić, Ivan Halasz, Patrick J. Beldon, Ana M. Belenguer, Frank Adams, Simon A.J. Kimber, Veijo Honkimäki, Robert E. Dinnebier

2013, Nature Chemistry 5, 66–73.
MECHANOCHEMISTRY: DIFFERENT WAYS OF INTRODUCING ENERGY INTO A REACTION:

Heat

Radiation/electricity

Grinding (mechanical force)

Applications in hydrogen storage, CO₂ sequestration and catalysis

Commercial materials: Basolite (BASF/Sigma-Aldrich)
LIQUID-ASSISTED GRINDING (LAG): SCREENING FOR METAL-ORGANIC ARCHITECTURES

ZnO + \( \text{HO} \text{O} \rightarrow \text{Zn} \text{O} \cdot 1.2\text{H}_2\text{O} \) Will not react by slurry stirring over 48 hrs (bottled oxide)

LAG (EtOH or MeOH)

LAG (4 eq. H_2O)

LAG (3 eq. H_2O)

3-D polymer
previously unknown

2-D polymer (sheets)
previously unknown

1-D polymer (zigzag inclusion host)
forms in solution

1-D polymer (linear chain)
forms in solution

We’d like:

ZnO + HOOC-\textcolor{red}{R}-COOH $\rightarrow$ LAG $\rightarrow$ MOF

We get:

30 min grinding replaces 2 days solvothermal synthesis in DMF, 160°C

(No rxn by neat grinding)

(with László Fábián CrystEngComm 2009, 11, 743)
**ILAG**: ion- and liquid-assisted grinding

\[
\text{ZnO} + \text{(≈0.1\%)}\text{NO}_3^- + \text{SO}_4^{2-} \xrightarrow{\text{ILAG}} \text{JUST ADD SALT! (300 ppm)}
\]

The bent geometry of the imidazole ligand, coupled with the tetrahedral coordination of Zn$^{2+}$ results in a metal-organic analogy of silicate/zeolite structures.

Normally obtained through solvothermal synthesis from zinc nitrate and imidazole ligand. Yields often below 40%.


EFFICIENCY AND TEMPLATING OF ZIF SYNTHESIS USING LAG/ILAG

MECHANISTIC STUDIES – LOOKING INTO THE REACTION

Modified Retsch MM200 mill
Visual observation is not very useful - switched to 90 keV X-ray beam at ID15, ESRF, Grenoble

(a) Proper handling of the two halves of the PMMA milling jar before snapping them together.
(b) The milling jar after snapping the two halves together. The left side contains the milling liquid and milling balls. The right side contains the reactants (white powder).
(c) Horizontal positioning of the PMMA milling jar on the milling station.
(d) The positioning of the mill and the milling jar with respect to the X-ray beam is verified using a teodolite.
In situ measurements will provide mechanistic detail on the formation, transformation and stabilization of different framework types.
THE NEED FOR PROPER SCALING...

INTERMEDIATES AND KINETIC ANALYSIS USING TIME-RESOLVED PXRD

ZnO + \text{Other species} \rightarrow \text{Intermediate} \rightarrow \text{Final product}

RHO ($T/V=1.9$ T/nm$^3$) \quad ANA ($T/V=2.5$ T/nm$^3$) \quad qtz ($T/V=3.8$ T/nm$^3$)

Conversion rates are different for each salt: control over reaction kinetics

More liquid

Less liquid

Direct monitoring of how reaction kinetics is affected by different parameters
PARTICLE SIZE EVOLUTION BY
TIME-RESOLVED PXRD

Direct monitoring of how particle size changes throughout milling
NOVEL CHARACTERIZATION OF THE ADSORPTION SITES IN LARGE PORE METAL-ORGANIC FRAMEWORKS: COMBINATION OF X-RAY POWDER DIFFRACTION AND THERMAL DESORPTION SPECTROSCOPY


2012, Physical Chemistry Chemical Physics 14, 37, 12892-12897
SELECTED MOF’S

HKUST-1

COF-102

MFU-41

ZIF-8
KR AND XE DESORPTION SPECTRA
UPTAKE AND DESORPTION TEMPERATURE

Microporous and Mesoporous Materials, 162 (2012) 64
ADSORPTIONS ISOTHERMEN

Graphs showing adsorption isotherms for HKUST-1 and MFU-4I with Xe and Kr at different temperatures (280 K, 290 K, 300 K, 310 K, 220 K, 230 K, 240 K, 250 K). The plots display the relationship between pressure (kPa) and volume (STP cm³ g⁻¹) for HKUST-1 and MFU-4I.

Graphs also show the heat of adsorption (Q̇_{ad}, kJ mol⁻¹) as a function of loading (mmol g⁻¹) for HKUST-1 and MFU-4I with Xe and Kr.
Methods:
1. Thermal desorption spectroscopy
2. In-situ X-ray powder diffraction
3. Quantum mechanical calculation
XE ADSORPTION ON MFU-4LARGE
In-situ X-ray Powder Diffraction on MFU-4l

- Loaded at 20mbar
- Different patterns at 110 and 150K
- Only one adsorption site for Xenon at $2/3,2/3,2/3$ (32f positions)
- Site Occupancy: at 110K$\approx$100% and at 150K=23%

![Graph showing observed pattern, best fit profile, and difference pattern](image)

![3D representation of MFU-4l structure](image)
Xenon Adsorption Energy:

**Large pore:** 96 KJmole\(^{-1}\)

**Small Pore:** Equal to Xe-Xe Van der Waals force

**Xenon does not adsorb in the small pores!**

Unpublished work
Xe sites from MEM-analysis

Xe sites from DFT calculations
ADVANCES IN THE ANALYSIS OF IN-SITU XRPD DATA USING THE METHOD OF MAXIMUM ENTROPY (MEM)

Oksana Magdysyuk, Ali Samy, Sander van Smaalen, Martin Jansen, Pavel Kazin, Robert E. Dinnebier


Introduction

MEM versus Fourier analysis

The effect of biasing

Selected Examples

Using the MEM to
- locate intercalated atoms with low occupancy
- analyse disorder

Conclusions
The maximum entropy method (MEM) can be used to extract the maximum amount of information from a limited set of data by maximizing the entropy in an iterative process:

$$S = - \sum_{i=1}^{N_{\text{pix}}} \rho_i \ln \frac{\rho_i}{\rho_{\text{prior}}}$$

- the electron density is sampled at the points of the grid over the unit cell
- the prior density

Prior density:
1) flat
2) any desirable distribution of the available electrons over the unit cell
The Problem of Powder Diffraction

- Summary -

Powder: Single crystal reciprocal lattice is smeared into spherical shells

→ $d \Rightarrow |d| = d \approx \sin \theta^{-1}$

→ Different degrees of overlap:
  - multiplicity (just a factor between 2 and 48)
  - systematic (e.g. 511, 333 in the cubic case)
  - accidental (depending on lattice parameters and scattering angle)

→ Not only the phases of the structure factors are unknown, but also many amplitudes
Example: single crystal and powder data of Pb₃O₄
THE GOAL OF THE MEM IS TO FIND THE ELECTRON DENSITY THAT MAXIMIZES THE ENTROPY S SUBJECT TO VARIOUS CONSTRAINTS

1) \[
\rho_{\text{total}} = \sum_{k=1}^{N_{\text{pix}}} \rho_k
\]
- normalization of the electron density

2) \[
C_F = -1 + \frac{1}{N_F} \sum_{i=1}^{N_F} w_i \left( \frac{|F_{\text{obs}}(H_i) - F_{\text{MEM}}(H_i)|}{\sigma(H_i)} \right)^2
\]
constraint \(C_F\) is based on the observed phased structure factors

3) \[
G^j = \sqrt{\sum_{k=1}^{N_G} m_k \left| F(H_k) \right|^2 / \sum m_k}
\]
constraint \(G\) is the “structure factor” of a group of overlapping reflections

\[
C_{FG} = -1 + \frac{1}{N_{\text{all}}} \sum_{i=1}^{N_F} w_i \left( \frac{|F_{\text{obs}}(H_i) - F_{\text{MEM}}(H_i)|}{\sigma(H_i)} \right)^2 + \frac{1}{N_{\text{all}}} \sum_{j=N_F+1}^{N_{\text{all}}} \left( \frac{|G_{\text{obs}}^j - G_{\text{MEM}}^j|}{\sigma(H_i)} \right)^2
\]
Maximize:

\[ Q(\rho) = S(\rho) - \sum_{j=1}^{N_e} \lambda_j C_j(\rho) , \quad \frac{\partial Q}{\partial \rho_i} = 0 \]

\[ \rho_i = \frac{N_{el} N_{pix}}{V} \tau_i \exp \left( -\lambda_F \frac{\partial C_F}{\partial \rho_i} \right) / \sum_{i=1}^{N_{pix}} \tau_i \exp \left( -\lambda_F \frac{\partial C_F}{\partial \rho_i} \right) \]

\[ \tau_i^{n+1} \approx \rho_i^n \]

Iteration:

\[ \rho_i^{n+1} = \frac{N_{el} N_{pix}}{V} \rho_i^{(n)} \exp \left( -\lambda_F \frac{\partial C_F}{\partial \rho_i} \bigg|_{\rho_i^{(n)}} \right) / \sum_i \rho_i^{(n)} \exp \left( -\lambda_F \frac{\partial C_F}{\partial \rho_i} \bigg|_{\rho_i^{(n)}} \right) \]

The iteration is started with \( \rho_i^{(1)} = \tau_i \) and the new density \( \rho_i^{(n+1)} \) is calculated from the prior density \( \rho_i^{(n)} \), the value of the constraint decreases each cycle until the condition of \( C_F \leq 1 \) is fulfilled.

- \( \rho_i \) Electron density
- \( \tau_i \) Prior density
- \( N_{pix} \) no of pixels of cell volume \( V \)
- \( N_{el} \) no of electron/unit cell = F000
- \( w \) weight factor
- \( \sigma(H) \) standard error of \( F_{obs} \)
- \( F_{obs} \) observed structure factors
- \( F_{MEM} \) MEM structure factors
- \( \lambda \) Lagrange multipliers
- \( N_c \) no of constraints

**BASICS OF THE MAXIMUM ENTROPY METHOD (MEM)**
POWDER DIFFRACTION: OVERLAPPING REFLECTIONS

K₂C₂O₄

Rietveld plot

Le Bail plot
Advantages of the Fundamental Parameters Approach (FPA):

In contrast to empirical/conventional profile fitting methods, the refined numerical parameters have physical meaning.

FPA greatly reduces the number of parameters refined and hence minimizes parameter correlation.

Example: quartz
Rietveld refinement:
- the peak area is proportional to the square of the structure-factor amplitude
- for overlapping peaks, the contribution for a given reflection is weighted by the calculated peak contribution for that reflection divided by the sum of the calculated peak values for each contributing reflection ("F_{obs}" might be wrong)

Le Bail fit:
- there is no initial structural model
- the values of the integrated intensities are determined iteratively after each refinement cycle
- for fully overlapping peaks, intensities are partitioned equally
MEM RECONSTRUCTION OF DIFFERENT TYPES
OF ELECTRON DENSITY MAPS FROM
POWDER DIFFRACTION DATA

1) $F_{\text{calc}}, f_{\text{calc}}$ → $\rho_{\text{calc}}$

2) $F_{\text{obs}}, f_{\text{calc}}$ → $\rho_{\text{obs}}$

3) $F_{\text{obs}} + G, f_{\text{calc}}$ → $\rho_{\text{obs}+G}$

4) $F_{\text{LeBail}} + G, f_{\text{calc}}$ → $\rho_{\text{LeBail}+G}$

Completely model biased
Least model biased

Fourier Reconstruction of Different Types of Electron Density Maps from Powder Diffraction Data

1) $F_{\text{calc}}, f_{\text{calc}}$ → $\rho_{\text{calc}}$ (Completely model biased)

2) $F_{\text{obs}}, f_{\text{calc}}$ → $\rho_{\text{obs}}$

3) $F_{\text{obs}} - F_{\text{calc}}, f_{\text{calc}}$ → $\rho_{\text{diff}}$ (Least model biased)
MODELED AND EXPERIMENTAL FOURIER MAPS

Fourier map of experimental data of silicon in the (110) plane obtained by a Fourier synthesis of the structure factors for which $\sin\theta/\lambda = 0.86$ Å$^{-1}$. Contour intervals are at $0.1e/\text{Å}^3$ (cutoff level $1.6e/\text{Å}^3$).

Fourier map of model data of silicon in the (110) plane obtained by a Fourier synthesis of the structure factors for which $\sin\theta/\lambda = 5.5$ Å$^{-1}$. Contour intervals are at $0.1e/\text{Å}^3$ (cutoff level $2.5e/\text{Å}^3$).

DETERMINATION OF THE ELECTRON-DENSITY DISTRIBUTION
FOURIER MAP ↔ MEM MAP

- a perfect Fourier map would require a complete set of structure factors up to at least $\sin \theta/\lambda = 5.0 \, \text{Å}^{-1}$
- allows the location of missing atoms
- may show strong peaks that do not correspond to atoms

- allows to incorporate prior information
- does not involve numerical Fourier transform => no series termination errors.
- can successfully work with structure factors from powder data with a resolution of $\sin \theta/\lambda \approx 0.6 \, \text{Å}^{-1}$.
- allows the location of missing atoms
- peaks that do not correspond to atoms in the current model always have the density of the noise level
MEM map of experimental data of silicon in the (110) plane obtained using the flat prior and the calculated structure factors for which $\sin \theta / \lambda = 0.86 \ \text{Å}^{-1}$. Contour intervals are at $0.1e/\text{Å}^3$ (cutoff level $2.5e/\text{Å}^3$).

Same as left side but $\sin \theta / \lambda = 1.04 \ \text{Å}^{-1}$.

→ just 2 more Bragg reflections !!!

MEM map of experimental data of silicon in the (110) plane obtained using the flat prior and the calculated structure factors for which $\sin q/l = 0.86 \, \text{Å}^{-1}$. Contour intervals are at $0.1e/\text{Å}^3$ (cutoff level $2.5e/\text{Å}^3$).

Same as left side but using the procrystal density (ISAM).

**ELECTRON-DENSITY DISTRIBUTION IN APATITES WITH INTERCALATED METAL ATOMS**

**Molecular formula**: Sr$_5$(PO$_4$)$_3$Cu$_x$O$_{2x}$(OH)$_{1-2x}$

**Space group**: P6$_3$/m (176)

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<th>Parameter</th>
<th>Value</th>
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<tbody>
<tr>
<td>Z</td>
<td>2</td>
</tr>
<tr>
<td>a / Å</td>
<td>9.77</td>
</tr>
<tr>
<td>c / Å</td>
<td>7.28</td>
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LOCALIZATION OF MISSING ATOMS IN THE INCOMPLETE CRYSTAL STRUCTURE OF APATITE

$\text{Ca}_5(\text{PO}_4)_3\text{Cu}_{0.05}\text{O}_{0.5}\text{H}_{0.45-\delta}\text{F}_{0.5}$

X-ray laboratory data

$\sin\theta/\lambda = 0.55 \ \text{Å}^{-1}$

Contour levels: from 1 to 50 e/Å³, step 1 e/Å³

There is no Fourier map that allows to locate the Cu atoms unambiguously.
LOCALIZATION OF MISSING_ATOMS IN THE INCOMPLETE CRYSTAL STRUCTURE OF APATITE

$\text{Ca}_5(\text{PO}_4)_3\text{Cu}_{0.05}\text{O}_{0.5}\text{H}_{0.45-\delta}\text{F}_{0.5}$

$\rho_{\text{obs}}^\text{MEM}$

$\rho_{\text{calc}}^\text{MEM}$

$\rho_{\text{obs}}^\text{MEM}$

$\rho_{\text{obs}+G}^\text{MEM}$

$\rho_{\text{Le Bail}+G}^\text{MEM}$

X-ray laboratory data

$\sin \theta/\lambda = 0.55 \text{ Å}^{-1}$

Contour levels: from 1 to 50 e/Å$^3$, step 1 e/Å$^3$
DETERMINATION OF THE EDD OF INTERCALATED COPPER ATOMS USING MEM MAPS

All compounds have the same content of Cu = 0.1, but different amount of peroxide molecules

1 – 1.9 % of peroxide
2 – 3 % of peroxide
3 – 15 % of peroxide
4 – >15 % of peroxide

The distribution of the electron density is distorted due to the increasing content of peroxide molecules

X-ray laboratory data
\[ \sin \theta / \lambda = 0.55 \, \text{Å}^{-1} \]

Contour levels: from 1 to 50 e/Å³, step 1 e/Å³
DETERMINATION OF THE EDD OF INTERCALATED COPPER ATOMS USING MEM MAPS

All compounds have the same content of Cu = 0.1, but different amount of peroxide:

1 – 1.9 % of peroxide
2 – 3 % of peroxide
3 – 15 % of peroxide
4 – >15 % of peroxide

The distribution of the electron density is distorted due to the increasing content of peroxide molecules.

Synchrotron data $\sin \theta / \lambda = 0.55 \, \text{Å}^{-1}$

Contour levels: from 1 to 50 e/Å³, step 1 e/Å³
\(-\text{RbAg}_4\text{I}_5\) ionic conductor P4$_1$32 $a=11.2500 \text{ \AA}$

Parameters of the Rietveld refinement:
Rwp = 7.13\%, Rp = 5.23\%, $R_I$ = 3.10\%, GooF = 1.64
SINGLE CRYSTAL EDD
↔ Rietveld from Powder
↔ MEM Map from Powder

Ag1
Ag2

single crystal EDD
anisotropic ADPs from Rietveld refinement
red – MEM reconstructed ED
yellow – ISAM
THE HIGH TEMPERATURE PHASES OF RUBIDIUM OXALATE BY IN SITU POWDER DIFFRACTION

T: 25°-450°-25°
200 scans in 3½ hrs


A. Samy, R. E. Dinnebier, S. van Smaalen, and M. Jansen, The Maximum Entropy Method and Charge Flipping, a powerful combination to visualize the true nature of structural disorder from \emph{in situ} X-ray powder diffraction data. (2010) \emph{Acta Cryt. B}. 
THE HIGH TEMPERATURE PHASES AND DECOMPOSITION PRODUCTS OF RUBIDIUM OXALATE

$\text{Rb}_2\text{C}_2\text{O}$

$P_{bam} \rightarrow P2_{1}c \leftrightarrow P_{nma} \leftrightarrow P_{63}/mmc$

$\text{Rb}_2\text{CO}_3$
RESULTS OF MEM-CALCULATIONS BASED ON MODEL-RIETVELD-REFINEMENT

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<tr>
<td>Strong-biased</td>
<td>All F biased</td>
<td>F&lt;sub&gt;obs&lt;/sub&gt; partially biased</td>
<td>Less biased</td>
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**δ-K<sub>2</sub>C<sub>2</sub>O<sub>4</sub> (Pbam)** ordered

\[ T = 295 \text{ K} \]

**α-Rb<sub>2</sub>C<sub>2</sub>O<sub>4</sub> (P6<sub>3</sub>/mmc)** disordered

\[ T = 683 \text{ K} \]

**α-Rb<sub>2</sub>CO<sub>3</sub> (P6<sub>3</sub>/mmc)** disordered

\[ T = 860 \text{ K} \]
**CHARGE FLIPPING + MEM**

\[
\begin{align*}
F_{\text{LeBail}} + G, \ f^{\text{Rietveld}} \quad &\xrightarrow{\text{MEM}} \quad \rho_{\text{LeBail} + G} \\
F_{\text{LeBail}} + G, \ f^{\text{Charge Flipping}} \quad &\xrightarrow{\text{MEM}} \quad \rho_{\text{LeBail} + G}
\end{align*}
\]

1) structure-factor amplitudes are obtained by Le Bail fit
2) structure-factor phases are determined by charge flipping with histogram matching

**Completely *ab-initio* electron-density distribution!!!**
Distribution of the electron densities from Rietveld refinement:

Distribution of the electron densities from Charge Flipping + MEM:
New detectors and better X-ray sources allow to fully track structural changes in the sub-second regime.

New software for data reduction (e.g. Powder3D-IP), visualization (e.g. Powder-3D) and sequential/parametric WPPF refinement (e.g. Topas 5.0) allow to handle (semi-)automatically huge numbers of powder patterns.

Rietveld refinement and MEM allow for the investigation of advanced structural features (inaccessible to Fourier analysis) like: disorder, diffusion pathways in ionic conductors or distribution of electron density.

The MEM is very well suited to locate even small amounts of intercalated atoms in crystal structures from XRPD.

Complex structure determination from XRPD by the combination of CF and MEM is possible.
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SOME HOUSE ADVERTISING...