Monitoring in situ experiments with RootProf

Marco Milanesio

Dipartimento di Scienze e Innovazione Tecnologica, Università degli Studi del Piemonte Orientale, viale T. Michel, 11 - 15121 Alessandria, Italy
E-mail: marco.milanesio@uniupo.it
Introduction: PCA, MED, OCCR and kinetics and dynamics analysis in simulated in situ XRPD data

Sub-structure solution by PCA- and OCCR-assisted dynamic analysis of Xe into Y zeolite in situ XRPD data

Kinetics retrieval by PCA-assisted analysis

The real world: three case studies where PCA is applied to real world data
MOTIVATION

Back 1999 SNBL@ESRF
in situ experiment
20-100 XRPD patterns

Back 2009 SNBL@ESRF
in situ Raman/XRPD experiment
200-1000 Raman and 200-2000 XRPD patterns

2019 SNBL (Raman/XRPD) PSI (UV-Vis/Raman/XRPD
BNL(XRPD/PDF) multiprobe experiments:
2000-10000 pattern each probe
But also lab XRPD can be used for in situ XRPD
experiment with 1 min time resolution!

2029? 100000-1000000 patterns each experiment?
Are there alternative/complementary approaches to Rietveld refinement?

The case study: Xe absorption into an MFI zeolite

The target: speed, efficiency, selectivity, no need of crystal structure, robustness vs. Preferred Orientation, disorder, limited resolution, low data quality...
PCA, MED, OCCR and kinetics/dynamics in simulated in situ XRPD data

The playground: Xe occupancies are changed from 0 to 1 and the corresponding XRPD data calculated

The case study: Xe absorption into an MFI zeolite
Fourier analysis (PSD-MED) can retrieve both kinetics ($1\Omega$) and substructure ($2\Omega$).

MED analysis of theoretical in situ XRPD data

Simulated in situ XRPD data.

PSD-MED analysis of dynamic XRPD data gives a virtual XRPD that can be indexed by EXPO retrieving the original MFI unit cell and space group.

MED analysis of theoretical in situ XRPD data

EXPO can solve the substructure of Xe into a MFI zeolite perfectly: **Chemical selectivity in X-ray diffraction!**

Going to real data, the good news are finished! - I

Figure SI-5: Simulated by a sinus stimulus (green) vs. experimental (blue) $2\Omega$ demodulated pattern from the T1 experiment.

MED $2\Omega$ (Blue) fails in real world data on Xe-MFI case study: real data $2\Omega$ is different from simulated $2\Omega$. L. Palin et al., Phys.Chem.Chem.Phys., 2015, 17, 17480.
We realized that some theoretical requirement of MED:

- Clear distinction between active (Xe) and spectator part (MFI zeolite)
- Linear response of the system to the stimulus
- Absence or limited lattice variations
- Stimulus shape should be sinusoidal

Not easy to implement in the real world on real samples. Many limitations.
Other routes than Fourier-based PSD-MED? analysis?
Principal Component Analysis (PCA) as alternative to PSD-MED approach

“Only” a coordinate change able to reduce dimensionality, BUT with huge power of unraveling trends in large dataset

http://setosa.io/ev/principal-component-analysis/
PCA vs. MED on in situ XRPD SIMULATED data

- Introduction
- Simulated data
- The PCA approach
- Case study n. 1
- Case study n. 2
- Case study n. 3

PC1 = 1Ω (PSD-MED) → PCA can be interesting for kinetic analysis

The good news are finished! - II

**PC2 ÷ 2Ω in simulated data**

Modulated Enhanced Diffraction (MED) vs Principal Component Analysis (PCA) for (sub)structure solution

**PSD-MED:**
- Fourier
- Analysis by Phase
- Sensitive Detection

MED can in principle retrieve a kinetic and solve the «active» substructure in a dynamic experiment.

**PCA:**
- Variance analysis and data dimens. reduction

PCA can retrieve with a good approximation $1\Omega$ and only roughly estimate $2\Omega$


New hints on Maya Blue formation process by PCA-assisted in situ XRPD and optical spectroscopy

M. Milanesio

03/10/2019
Problems and solutions

PSD-MED has limitations in real world

PC2 \neq 2\Omega in simulated data

Adapt PSD_MED to real data Escape Lane n. 1

Use PCA to analyze the data instead of PSD-MED, especially for kinetics dynamics Escape Lane n. 2

Use OCCR, i.e.a constrained PCA «instructed» to search for «2\Omega like» information and use it for structure solution Escape Lane n. 3
Escape lane n. 1: Real world low amplitude modulation and PSD-MED

Fig. 7 Real MED data powder diffraction data on Xe occupancy variation inside a TS-1 zeolite, by a triangular small amplitude stimulus (experiment T3 in Table 1), before (a) and after (b) normalization toward beam decay.

MED 2Ω succeeded in real world data on Xe-MFI case study as in simulated data BUT unique success → we moved to PCA!

Escape lane n. 2: OCCR can reveal structural details with improved selectivity from in situ powder and single crystal

Scores from PCA or OCCR vs. 2Θ are a virtual XRPD pattern containing the information active atoms only

Guccione, L. et al., PCCP, 2018, 20, 2175-2187. From themed collection 2018 PCCP HOT Articles;
The OCCR virtual pattern was refined by Topas TA and gives experimental information on Xe only with improved chemical selectivity from in situ powder XRPD data

Two new Xe adsorption sites unraveled by PCA-OCCR assisted XRPD data analysis

POWDERs: Guccione, L. et al., PCCP, 2018, 20, 2175-2187. From themed collection 2018 PCCP HOT Articles;
Escale lane n. 3: PCA can be used to analyse in situ XRPD data

Scores from PCA give the reaction kinetics of the solid-state reactions with good agreement with Rietveld refinement

By the way, PCA can be applied also to in situ single crystal of CO$_2$ into a Y zeolite

Standard refinement

PCA scores

Three real world case studies about the PCA-assisted retrieval of the kinetics in in situ experiments

Case 1: in situ XRPD study of BaSO$_4$ sedimentation during epoxy resin curing

Case 2: Evolution of MOF phases whose structure is unknown

Case 3: Transformation of low ordered phases, a multitechnique approach
Case study n. 1: in situ XRPD study of BaSO4 sedimentation during epoxyresin curing

Radiopaque composites made of an epoxy resin additivate with BaSO4

During curing (24 hours), because of gravity, BaSO4 stratifies
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XRPD data collection on lab diffractometer

Ad hoc sample holder
(courtesy of Panero Elevatori srl)

In situ XRPD lab data. Limited angular range to collect data in 3 min/pattern
PCA analysis of in situ XRPD: scores describes the dynamics of the event i.e. process advancement vs time.

No structure needed, no problems about limited angular range, few minutes after data collection.
PC loadings tell us WHAT is happening

A clear drift of the peak is observed that $\text{BaSO}_4$ is decanting down in the sample
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Rietveld refinement by Mattia@EXPO hands on session after knowing the result by PCA analysis

The zero shift measure the BaSO₄ decantation during curing

Rietveld refinement is difficult because of the limited 2Θ range and correlation between sample transparency and displacement
Rietveld refinement by Mattia@EXPO hands on session after knowing the result by PCA analysis

EXPO refinement of 16 pattern (1 out of 10) half an hour. Clear physical meaning

PCA analysis of 150 patterns: few minutes Dynamic extracted no direct physical meaning
Case study n. 1 TAKE HOME message

PCA analysis is much faster and more efficient in extracting the kinetics from the whole pattern changes (peak position and intensity) BUT no physical meaning can be obtained directly, only inferred.

EXPO refinement require more time but a clear physical meaning (limited to zero shift) is obtained.

PCA is then a powerful analysis method to be used for online experiment monitoring and optimization. Besides PCA can highlight which pattern and what effect to look for in the post experiment traditional experiment.
Case study n. 2: Evolution of MOF phases whose structure is unknown

Structure and topology in the P2₁/n stable polymorph was solved
Pure P$_{21}/n$ product with high area expected

XRPD refined against SC structure

Observed
Calculated
Difference

26 (°) Cu Kα
Intensity (a.u.)

P21/n structure after «graphic» DMA removal

In silico optimized structure after DMA removal
The bad... or good (for the crystallographer only) news

- Thermal activation gave mixtures of phases with small or no surface area
- Chemical exchange of DMA produced new phases
- Exposure to air moisture or water impregnation cause new phases togheter with degradation

A magic space – the polymorph landscape -, was studied by oven treatments, TGA, SC- and P-XRD@Lab .......

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Monoclinic P21/n

- Air moisture
- ACN washing
- 150-200°C
- Dry atm
- 300°C dry atm or water impregnation at RT

In silico optimized structure with void channels!!!!!
PCA-assisted in situ synchrotron XRPD to study the «intermediate» phase at 120-200 °C

PCA was used to get «online and onsite» the dynamic of the process and to optimize the experiment setup and conditions.
PCA analysis of *in situ* XRPD allowed to obtain the stability range of the phases and find the \( \varepsilon \) phase.

The limitation of not knowing the structures is overcome: the phase are now isolated as pure and standard structure solution can be attempted.
Case study n. 2 TAKE HOME message

PCA analysis is much faster and more efficient in extracting the Dynamic without knowing the crystal structure BUT no physical meaning can be obtained directly, only inferred.

Traditional structure solution and refinement approach is needed to characterize the unknown phases.

PCA powerful on line analysis method for experiment optimization. PCA can highlight what to look for in the post experiment traditional data analysis.
Case study n. 3: Transformation of low ordered phases, a multitechnique approach

“Musicians and dancers” Ancient nanostructured material

The intriguing peculiarities:
- Brightness
- hue, ranging from a bright
- turquoise to a dark greenish blue
- remarkable durability
- chemical stability

The MB “technology” went lost and Maya Blue became an intriguing puzzle

Palygorskite Maya Blue Indigo

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- **Thermogravimetric analysis (TGA):** water adsorption/desorption, thermal stability
- **In situ X-ray powder Diffraction (XRPD):** long range order of water/indigo into the tunnels
- **In situ Pair Distribution Function (PDF):** short range order into the tunnels
- **In situ Fiber Optic Reflectance Spectroscopy (FORS):** optical properties of Indigo

Pre-heating in the range 105-200°C of the mixtures modify tunnel content, ordering and optical features
The collected data, 2 day@synchrotron, 5 day@lab
- About 2000 XRPD pattern
- About 2000 PDF patterns
- About 1000 in situ FORS optical spectra

HOW TO DEAL WITH?
Statistical methods to deal with complementary data

- *Principal component analysis to analyse the kinetic trends in a fast and efficient way*

- *Correlation analysis to analyze and «align» data from different probes (XRPD/PDF, XRPD/FORS ...)*

**The used tool: Rootprof**

“*general purpose tool for processing unidimensional profiles with specific applications to diffraction and spectroscopic measurements*”

http://users.ba.cnr.it/ic/crisrc25/RootProf/RootProf_help.html

Set A: Mayan materials explored by in situ XRPD to explore long range order

<table>
<thead>
<tr>
<th>Mixture</th>
<th>sample number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Paly_indigo_2%</td>
<td>0</td>
</tr>
<tr>
<td>Paly_indigo_3%</td>
<td>1</td>
</tr>
<tr>
<td>Paly_indigo_4%</td>
<td>2</td>
</tr>
<tr>
<td>Paly_isatin_4%</td>
<td>3</td>
</tr>
<tr>
<td>Paly_isatin_6%</td>
<td>4</td>
</tr>
<tr>
<td>Paly_isatin_8%</td>
<td>5</td>
</tr>
<tr>
<td>Paly_methblue_2%</td>
<td>6</td>
</tr>
<tr>
<td>Paly/fuchsin 2%</td>
<td>7</td>
</tr>
<tr>
<td>SAP110A_indigo_4%</td>
<td>8</td>
</tr>
<tr>
<td>Zeo-A_indigo_4%</td>
<td>9</td>
</tr>
<tr>
<td>HSZ-320_NAA(Y-type)/indigo4 %</td>
<td>10</td>
</tr>
<tr>
<td>Halloysite/indigo 4%</td>
<td>11</td>
</tr>
<tr>
<td>Cloisite_indigo_4%</td>
<td>12</td>
</tr>
<tr>
<td>NaSap(Al)_110/indigo 4%</td>
<td>13</td>
</tr>
</tbody>
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13 In situ XRPD data collected at variable temperature
After excluding the three outliers, $\text{PCA}_{\text{SEL}}^2$ in situ XRPD gave info on Indigo ordering in the channels:

- Channel 0, 1: «typical MayaBlue reaction»
- Channel 3, 6, 7, 8: similar to 0 and 1
- Channel 2, 10: reversible reaction

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In situ Fiber Optical Reflectance Spectroscopy (FORS) of Palygorskite indigo mixtures

Optical spectroscopy allows evaluating the color of the Maya Blue samples and the environment of Indigo

Preheating in the oven of the mixtures changes the optical features
Evolution of Indigo optical reflectance during the heating dwell at 200C and cooling to RT
Are structural (in situ XRPD) and optical (in situ FORS) data correlated for the NT sample treated from RT to 200°C?

Low angles XRPD peaks correlate with FORS: water elimination is correlated with optical features.

PDF correlates with FORS in region corresponding at about 10, 20, 30 Å, i.e. multiples of indigo molecule length.
Long (XRPD) vs. short (PDF) range order by PCA

- r<4 Å, all T range
  \[
  \text{PDF} = \text{XRPD}
  \]

- T<110°
  \[
  \text{PDF} \neq \text{XRPD}
  \]

- T<110°
  PDF: no more variations

Indigo < 110C occupy channels in a disordered behaviour!

R. Caliandro et al., *New hints on Maya Blue formation process by PCA-assisted in situ XRPD and optical spectroscopy analysis*, *Chem Eur. J.* 2019
Case study n. 3 TAKE HOME message

PCA and statistical analysis allowed managing successfully 5000 experimental patterns

Correlation analysis allowed to align and correlate signals from different probes (FORS, XRPD, PDF)

Traditional structure refinement is hampered by the inability of tracking the subtle changes of the low crystallinity palygorskite sample

Moreover the traditional «manual» approach is unfeasible with 5000 patterns by different probes
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