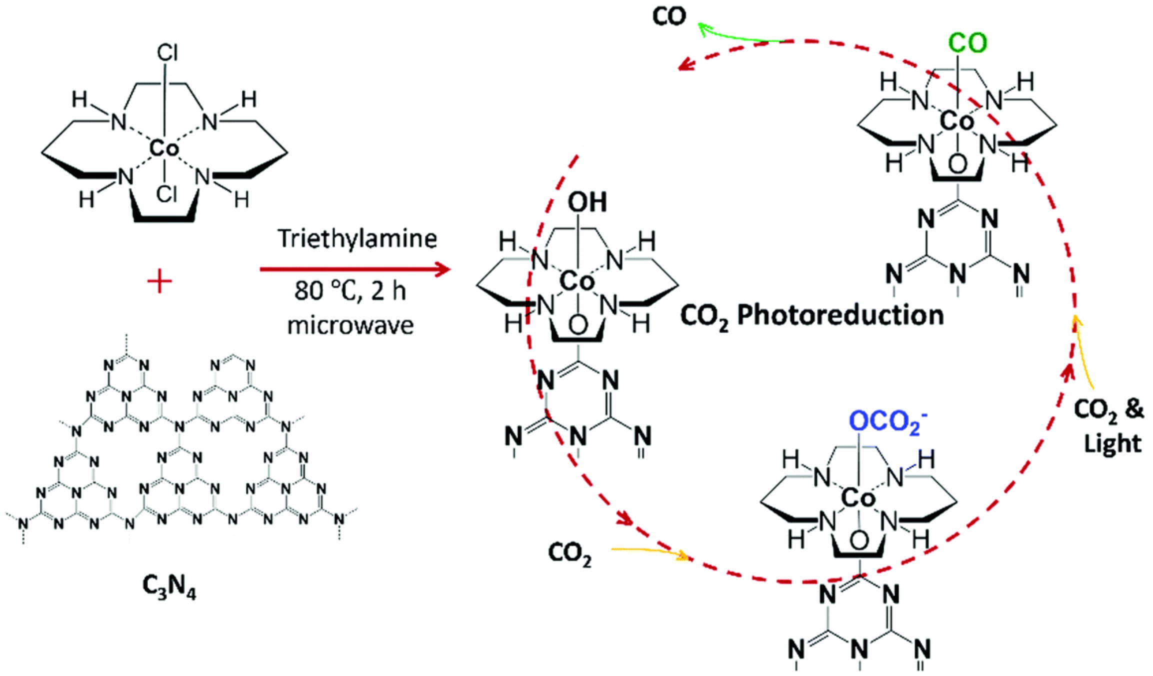
Resolving Spectra Mixtures: XANES data analysis by LCF, PCA and MCR-ALS:

- Prahlad K. Routh, Ph.D.

Examples of Mixtures

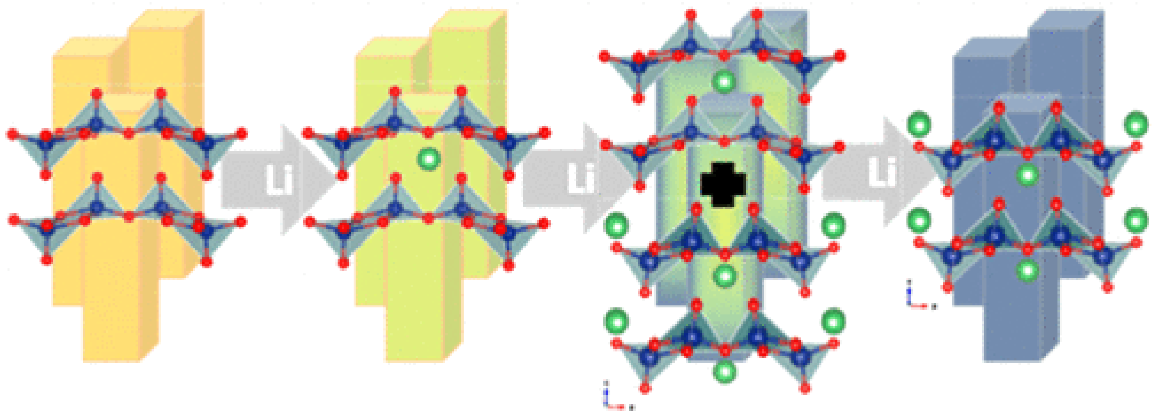
In-situ studies: Photocatalysis using Co-Single Atom Catalysts



S. Xiang..Frenkel et al., PCCP (2022)

Composition dependent changes

Lithiation of V_2O_5: Mixture of $Li_xV_2O_5$



Horrocks, Gregory A., et al. *The JPCC* (2016)

How to deal with Spectral Mixtures?

The goal is to determine:

- Number of components in the mixture
- Concentrations of the components
- Spectra of the components: Pure Species
- Identity of Pure Species

Case-1: Mixtures of Known Samples

- Spectra of the components are known
- Concentration of the components are fitted

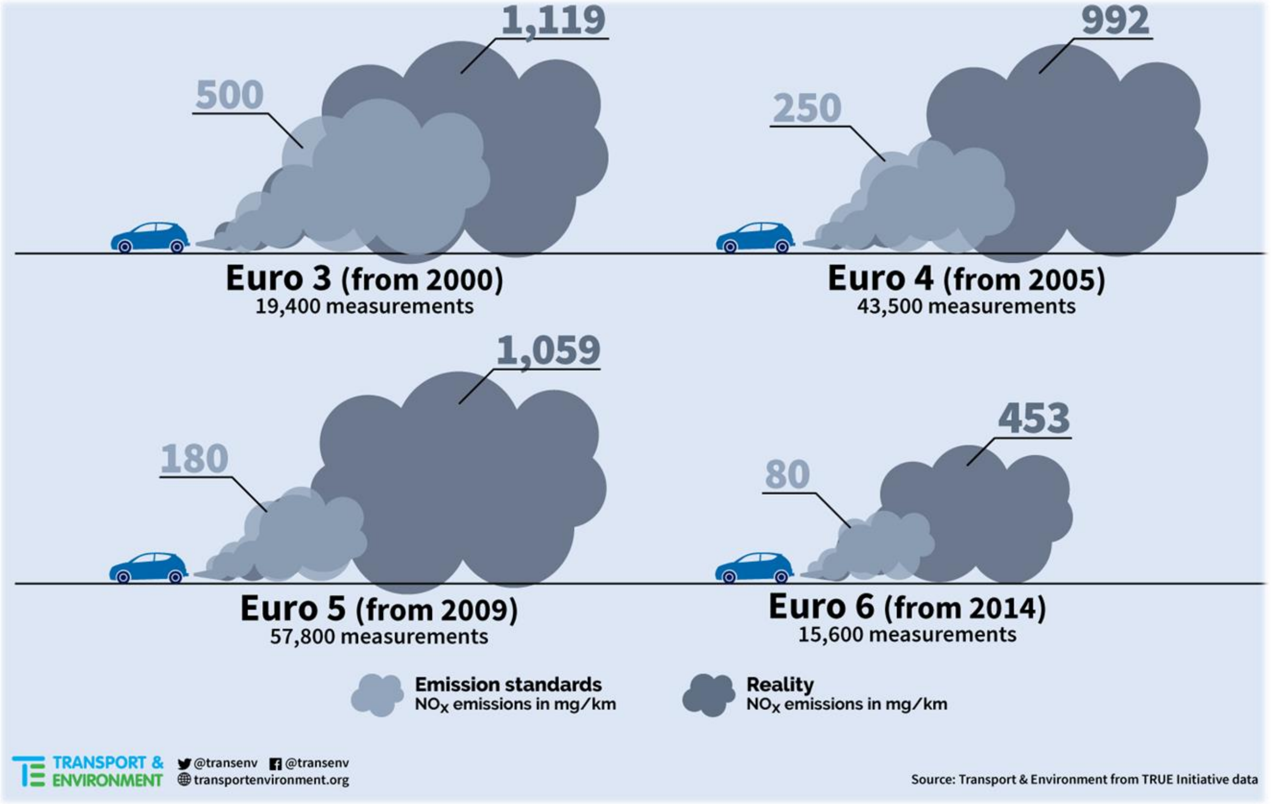
$$\mu^{exp}(E) = \sum_{\mathrm{i}} w_i \, \mu_i \, (E)$$

$\boxed{\text{Linear Combination Fitting}}$

Case Study-: Cu-Zeolites

Cu-CHA zeolite: novel highly efficient SCR catalyst

NO_x emissions: eco standards will grow much stricter



NH_3-assisted Selective Catalytic Reduction (SCR) of NO_x

$$4NO + 4NH_3 + O_2 \longrightarrow 4N_2 + 6H_2O$$

F. Giordanino, et al., *J. Phys. Chem. Lett.* **2014**, 5, 1552
E. Borfecchia, et al., *Chem. Sci*. **2015**, 6, 548
T.V.W. Janssens et al., *ACS Catal*., **2015**, 5, 2832
K.A. Lomachenko, et al., *J. Am. Chem. Soc*. **2016**, 138, 12025
A. Martini, et al., *Chem. Sci*. **2017**, 8, 6836
E. Borfecchia, et al., *Chem. Soc. Rev*. **2018**, 47, 8097.
E. Borfecchia, et al., *React. Chem. Eng*. **2019**, 4, 1067.
C. Negri, et al., *ChemCatChem* **2019**, 11, 3828
…

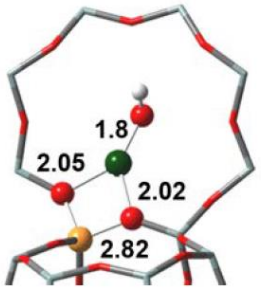
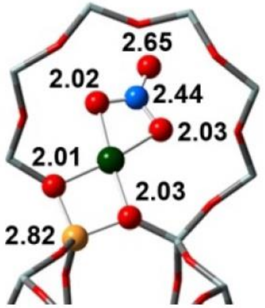
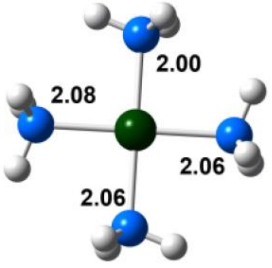
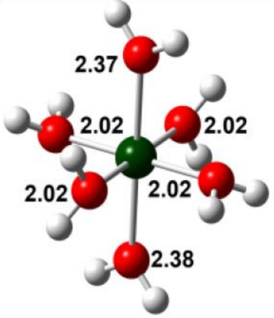
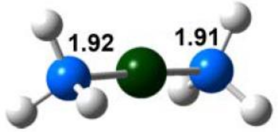
in-situ XAS

J|A|C|S JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Communication
pubs.acs.org/JACS

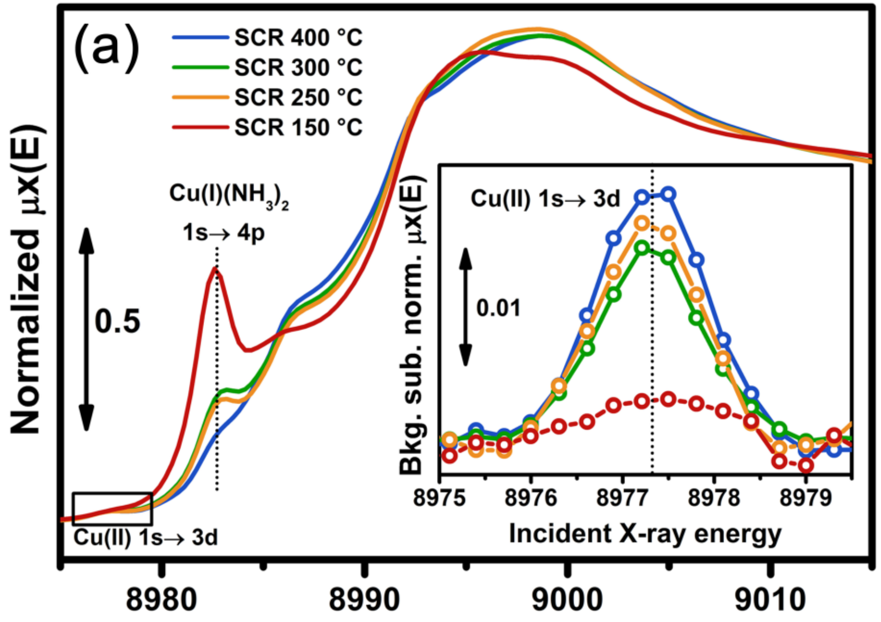
The Cu-CHA deNO$_x$ Catalyst in Action: Temperature-Dependent NH_3-Assisted Selective Catalytic Reduction Monitored by Operando XAS and XES

Kirill A. Lomachenko,[†,‡] Elisa Borfecchia,[*,†] Chiara Negri,[†] Gloria Berlier,[†] Carlo Lamberti,[†,‡] Pablo Beato,[§] Hanne Falsig,[§] and Silvia Bordiga[†]

Cu-type	***Z-Cu(II)***		***m-Cu(II)***		***m-Cu(I)***
(Dominant) Cu-species	**Z-[Cu(II)OH]$^-$**	**Z-[Cu(II)NO_3^-](*)**	**[Cu(II)$(NH_3)_4$]$^{2+}$**	**[Cu(II)$(H_2O)_6$]$^{2+}$(**)**	**[Cu(I)$(NH_3)_2$]$^+$**
Molecular geometry					
XAS data collection conditions	50%O_2/He 400 °C	1000 ppm NO/10%O_2/He 200 °C	Solution phase RT	Solution phase RT	Solution phase RT
Pertinent Cu-CHA *in situ* states	50%O_2/He 400 °C ca. 80% total Cu	1000 ppm NO/10%O_2/He 200 °C	1200 ppm NH_3/He 200 °C ca.75% total Cu	Hydrated, RT ca. 100% total Cu	1000 ppm NO/ 1200 ppm NH_3/He 200 °C ca. 100 % total Cu

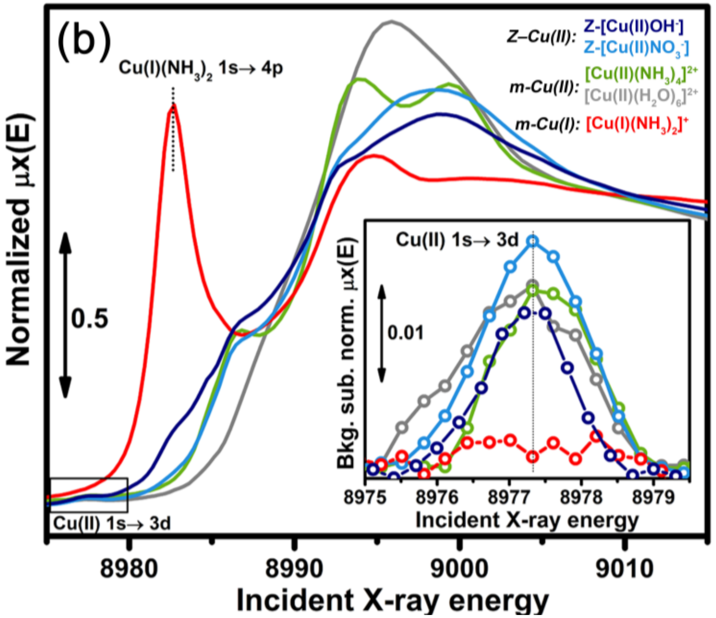
Lomachenko, Kirill A., et al. JACS, (2016)

Cu-K-edge operando study of Cu species



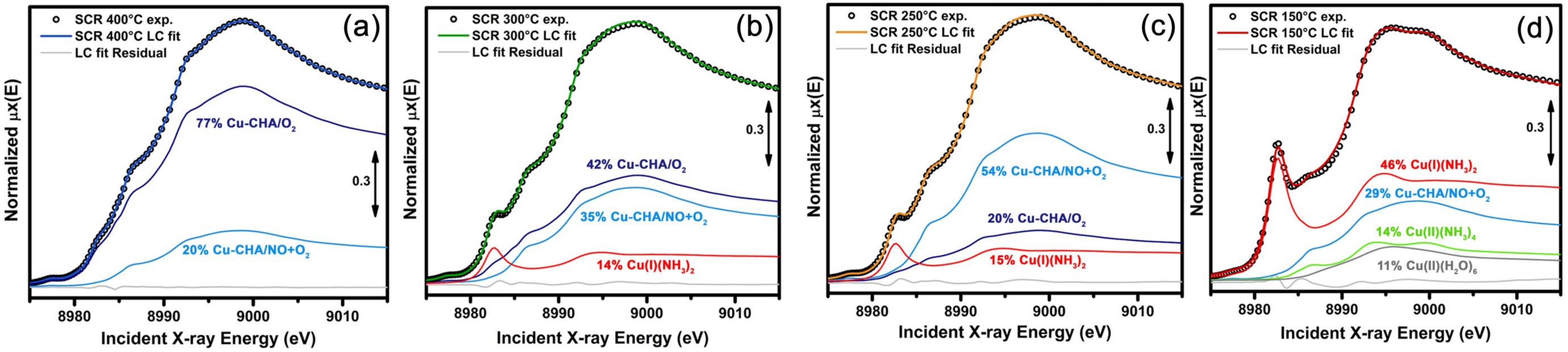
- 500 ppm NO 500 ppm NH_3
- 10% O_2
- 5% H_2O
- Si/Al: 15
- Cu/Al: 0.48

Known reference compounds of Cu Species



Lomachenko, Kirill A., et al. JACS, (2016)

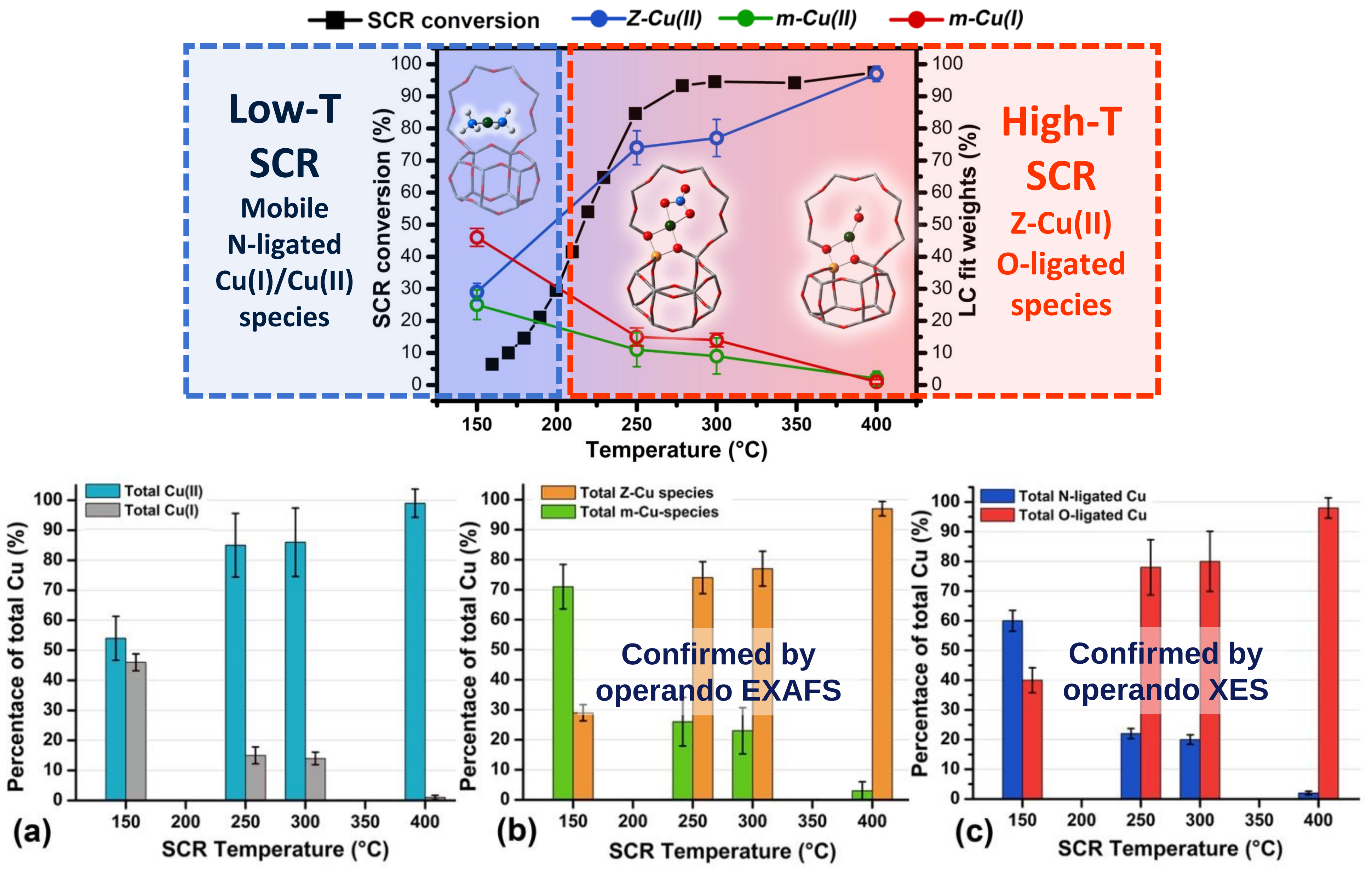
LCF Results



LCF weights

T (°C)	R-factor	Z-[Cu(II)OH$^-$]	Z-[Cu(II)NO$_3^-$]	[Cu(II)(NH$_3$)$_4$]$^{2+}$	[Cu(II)(H$_2$O)$_6$]$^{2+}$	[Cu(I)(NH$_3$)$_2$]$^+$
400	0.00001	77 ± 1	20 ± 2	1.0 ± 0.5	1 ± 1	1.0 ± 0.5
300	0.00005	42 ± 3	35 ± 3	6 ± 1	3 ± 1	14 ± 1
250	0.00006	20 ± 3	54 ± 3	7 ± 1	4 ± 1	15 ± 1
150	0.00030	0.0 ± 0.5	29 ± 3	14 ± 3	11 ± 1	46 ± 3

Lomachenko, Kirill A., et al. JACS, (2016)



Lomachenko, Kirill A., et al. JACS, (2016)

LCF: Summary

Advantages:

- Works fine quite often
- No problem with the interpretation of the components
- Available in Athena

Main problem: choice of references

<u>Often the references are not readily available at all</u>…

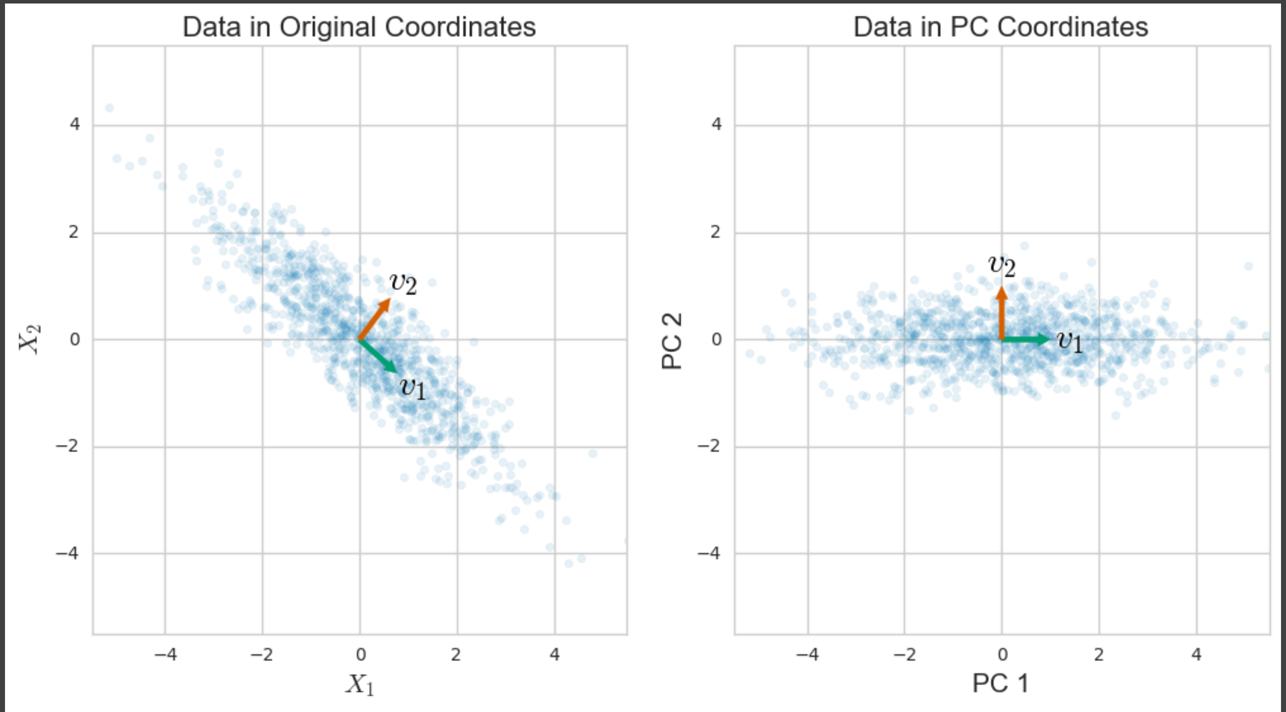
Case-2: Number of Species is not known

- Number of pure components is not known
- Spectra of most of the pure components are not readily available

Apply PCA + MCR−ALS

Principal Component Analysis (PCA):
A dimensionality reduction technique

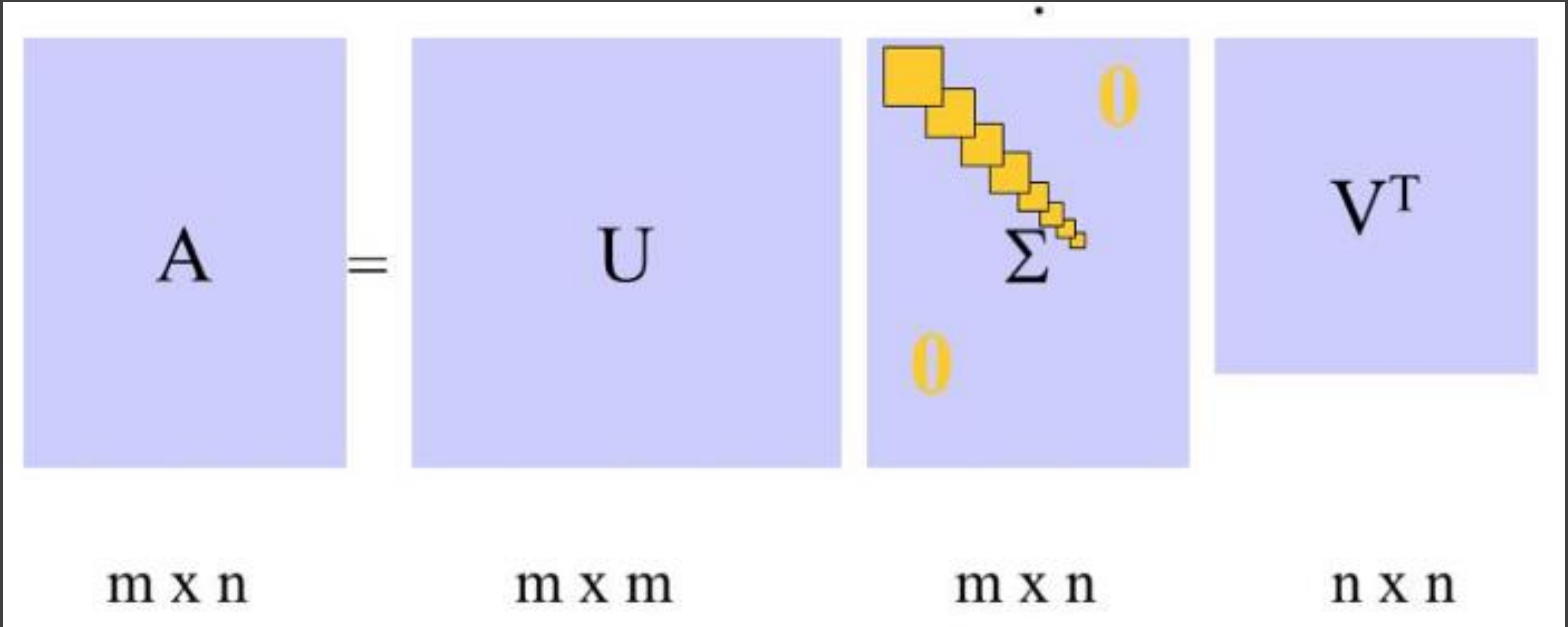
- Coined in 1901 by Pearson
- Main Attraction
  - Reduce the number of variables to a manageable number
  - Retaining most of the information
  - doesn’t need any information outside of spectral data



Excellent tool for Discovery and Exploratory Analysis

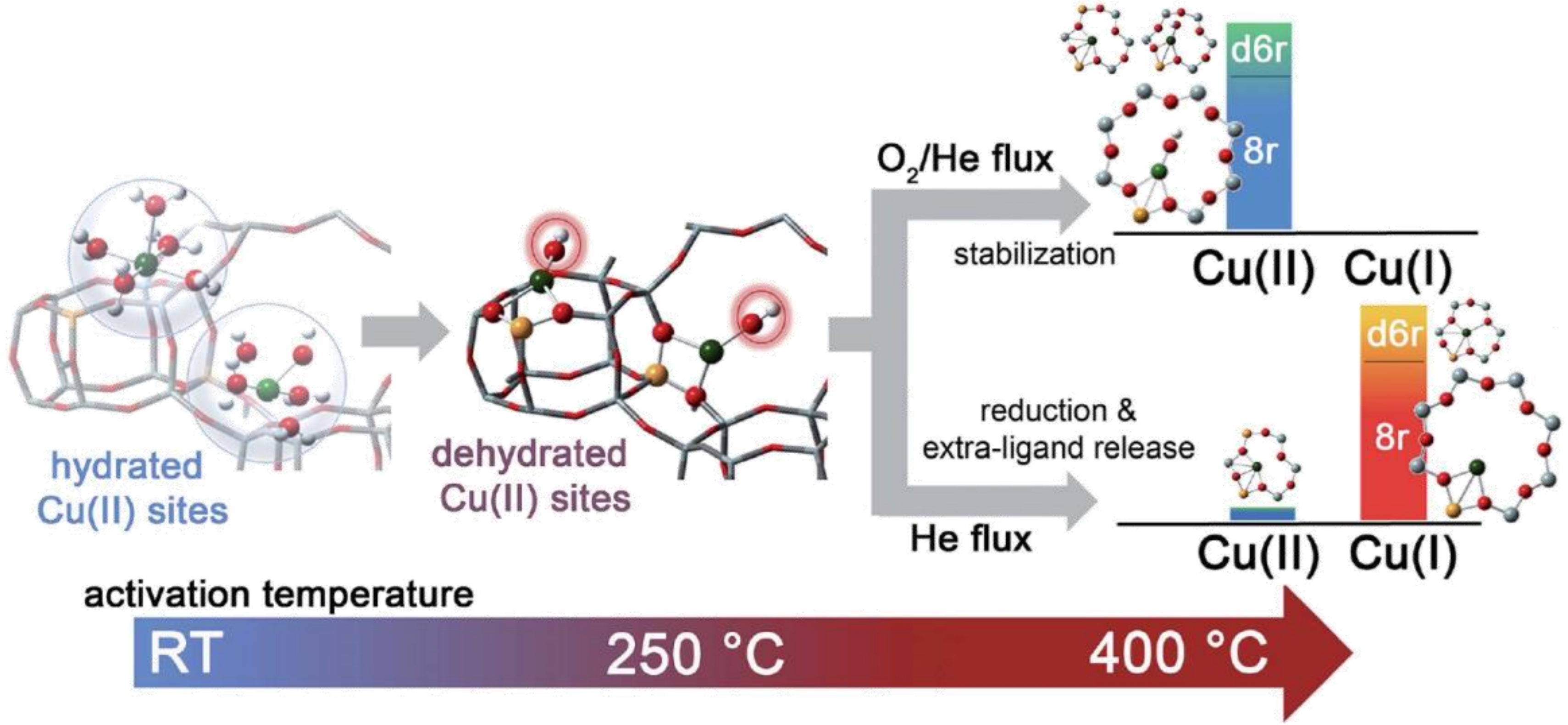
Goal: to determine the minimum number of pure components in the mixture, that adequately reproduce the whole dataset

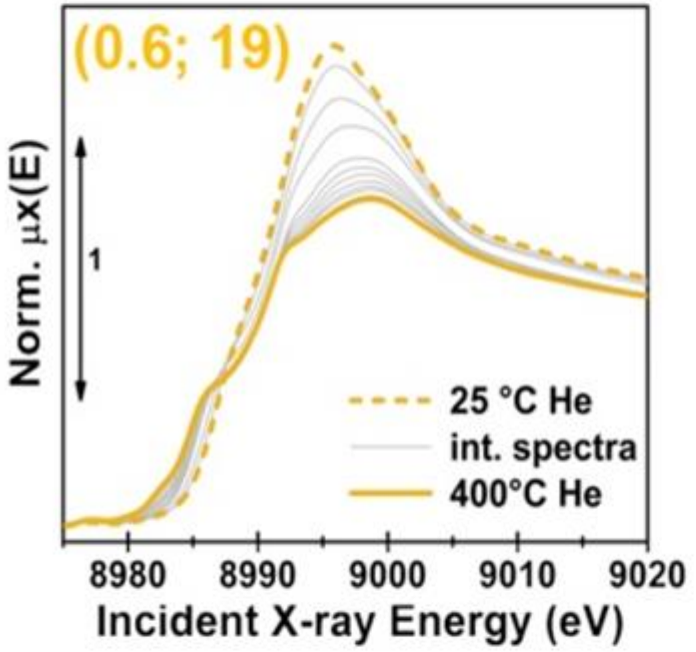
Solution: singular value decomposition (SVD) algorithm



Continuing with Cu-CHA: self-reduction

- **Reference composition:**
Cu/Al = 0.44, Si/Al = 13
- **Multi-technique approach:**
  XAS & XES + FTIR + DFT
- **Activation in O_2 and He**





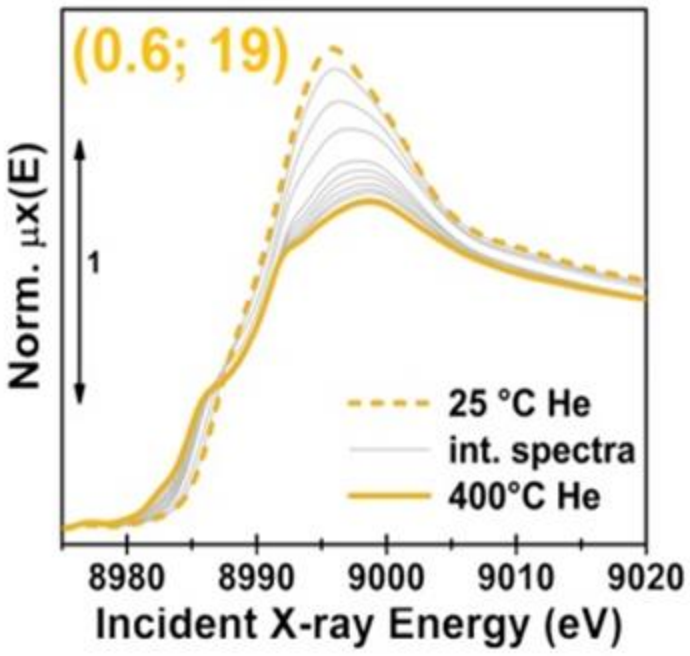
Borfecchia *et al.*,
Chem Sci. 2015, **6**, 548.

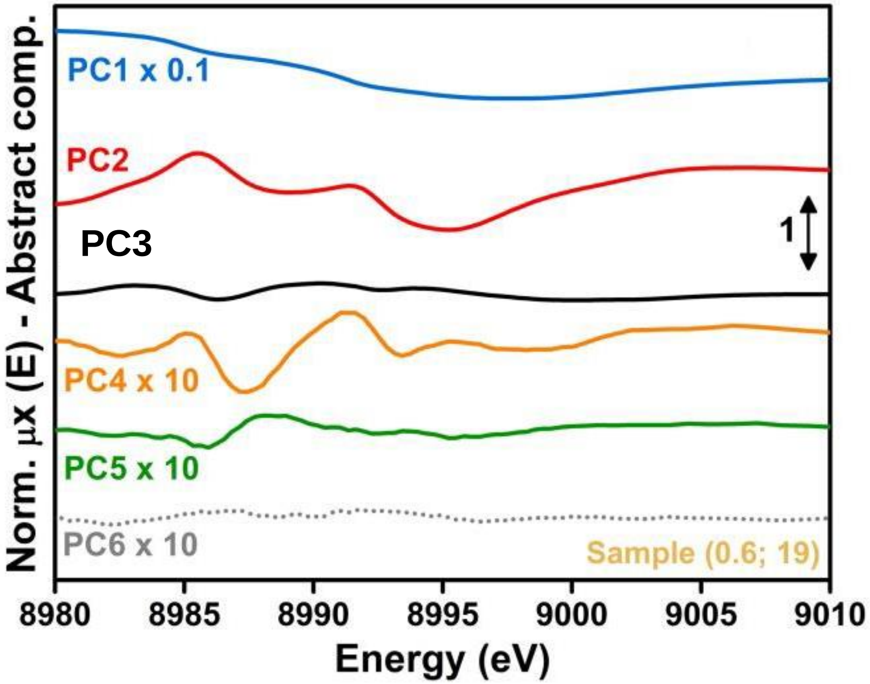
Determining the number of components

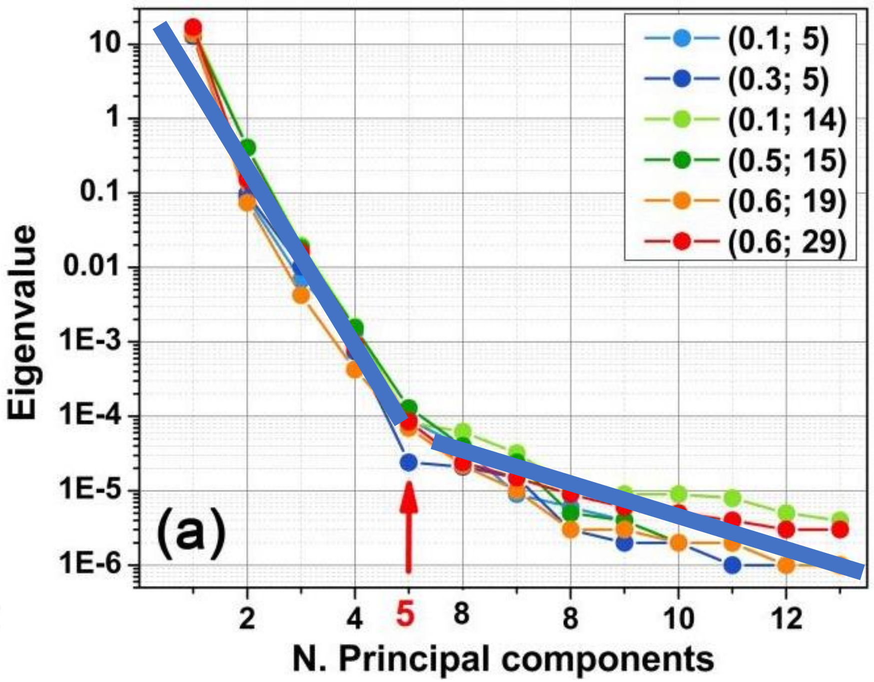
Spectra

Principal components

Scree plot







Starting from PC6, the variance described by the components is very low

5 ± 1 components is a reasonable choice

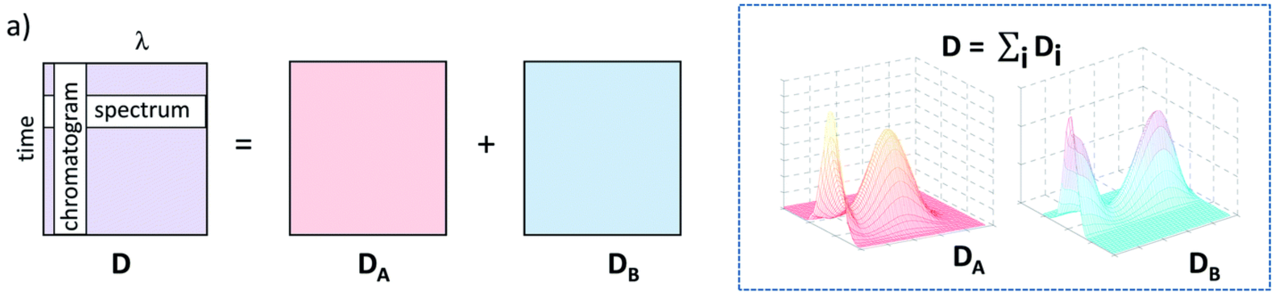
Goal: Recovering Spectra of Pure Species

$$\mu^{\exp}\left(\frac{\mathrm{Cu}}{\mathrm{Al}};\frac{\mathrm{Si}}{\mathrm{Al}},T,E\right)=\sum_{i=1}^{\boxed{N_{\text{pure}}}} w_i^{\text{pure}}\left(\frac{\mathrm{Cu}}{\mathrm{Al}};\frac{\mathrm{Si}}{\mathrm{Al}},T\right)\times\boxed{\mu_i^{\text{pure}}(E)}$$

UNKNOWN

Goal: Recovering Spectra of Pure Species

Solution: Multivariate Curve Resolution-Alternate Least Square

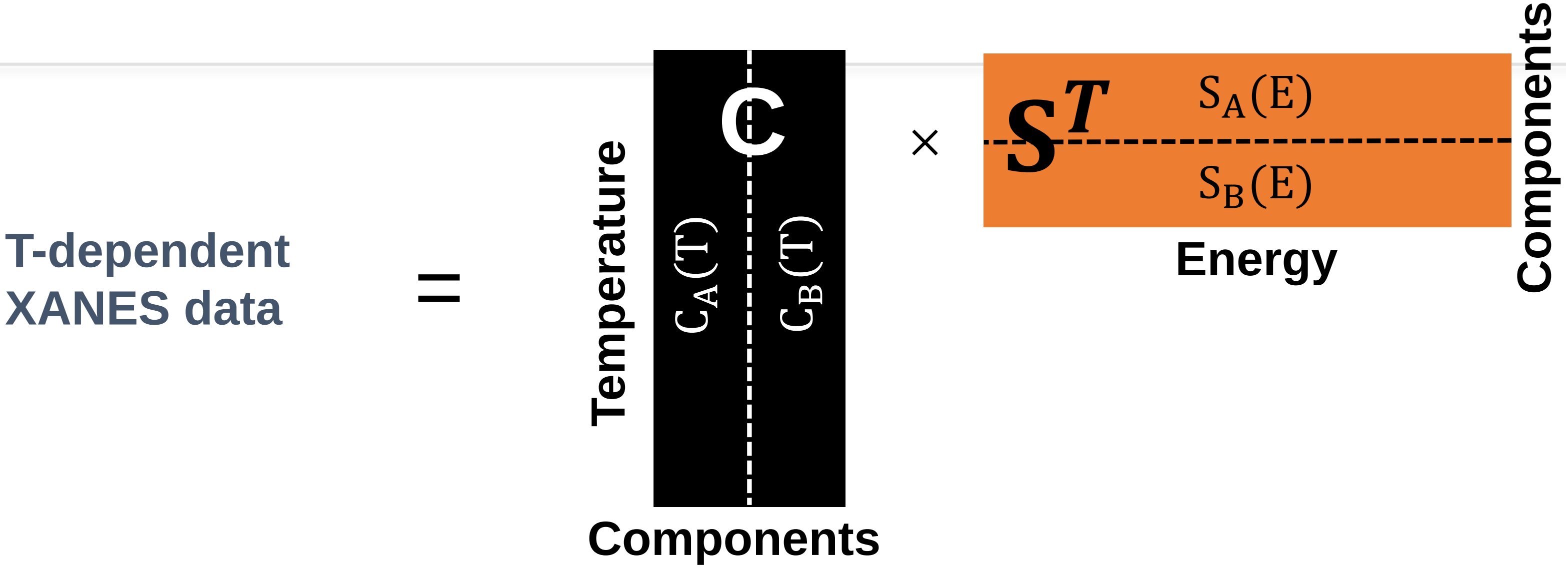


Multivariate Curve Resolution (MCR). Solving the mixture analysis problem

de Juan et al, Anal. Methods, 2014, 6, 4964-4976
J. Jaumot et al, Chemometrics Intell. Lab. Syst., 2005, 76, 101-110

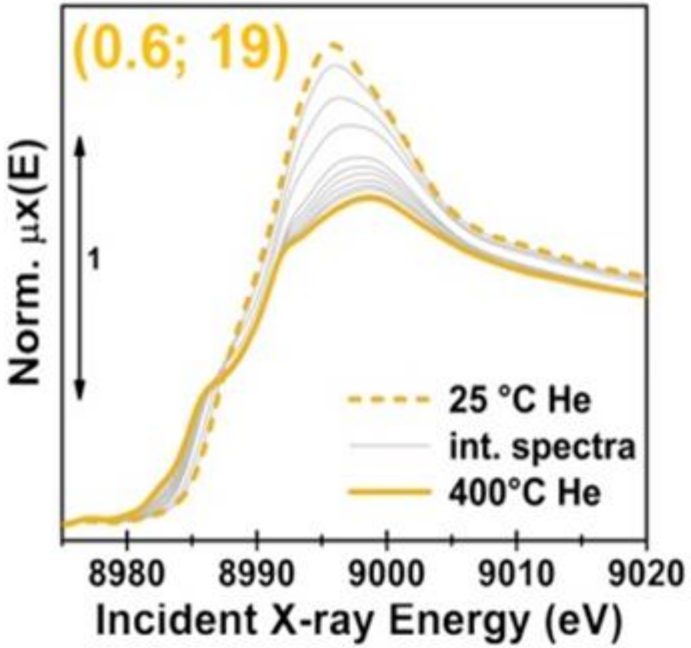
Idea: reconstruct the spectra of pure species from the set of experimental data.

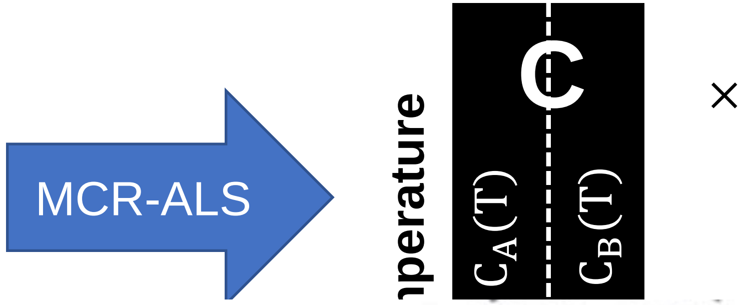
$$\boxed{D = CS^T + E}$$

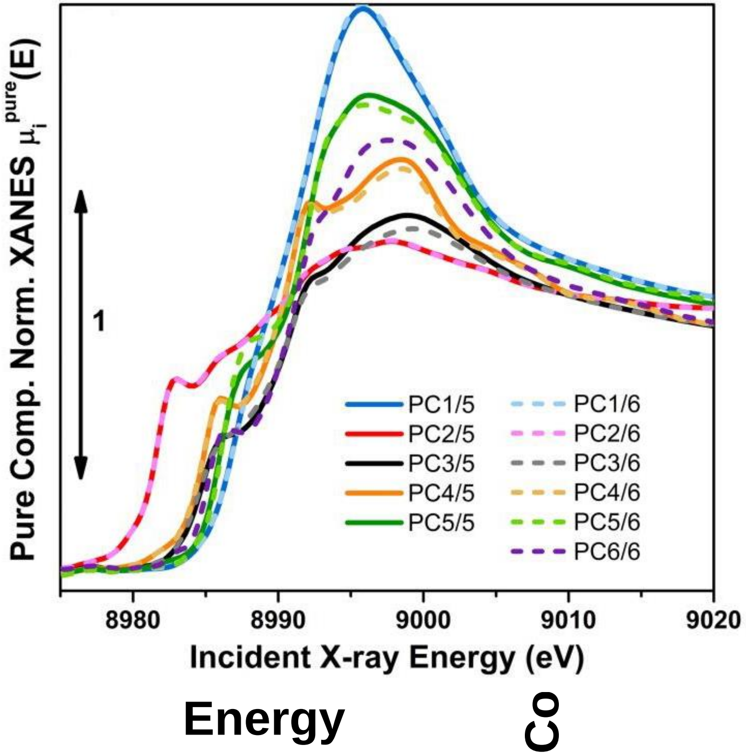


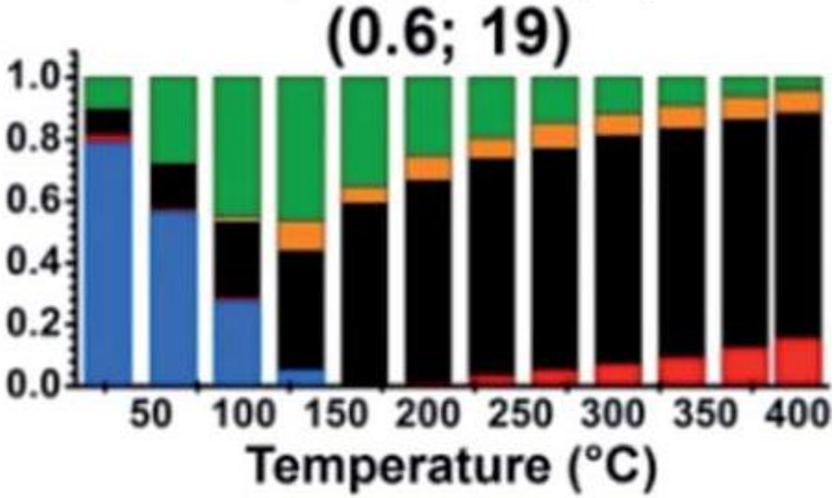
- Number of pure components is determined independently by PCA
- Spectra and concentrations of pure components are deduced iteratively using constraints for **C** and **S** matrices

MCR-ALS
Application in XAS



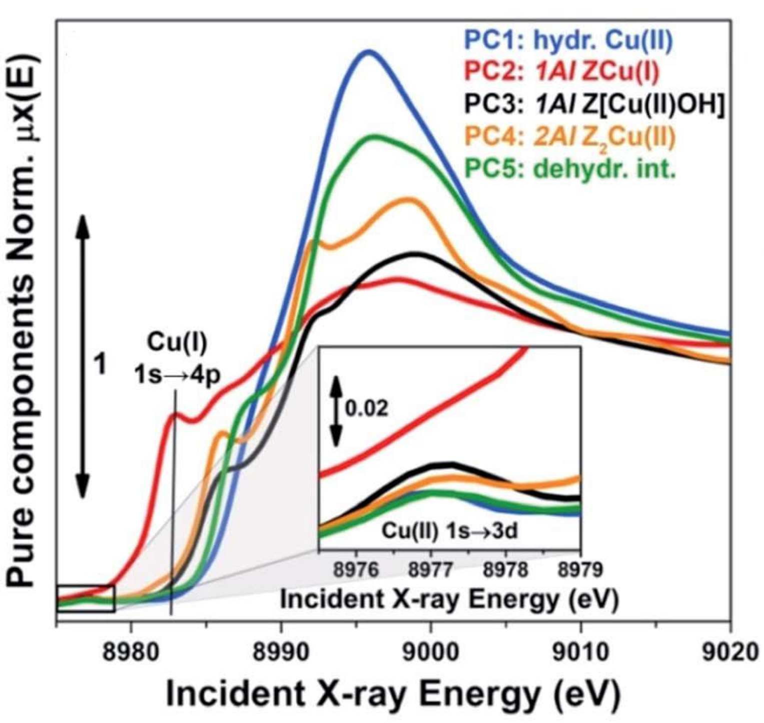


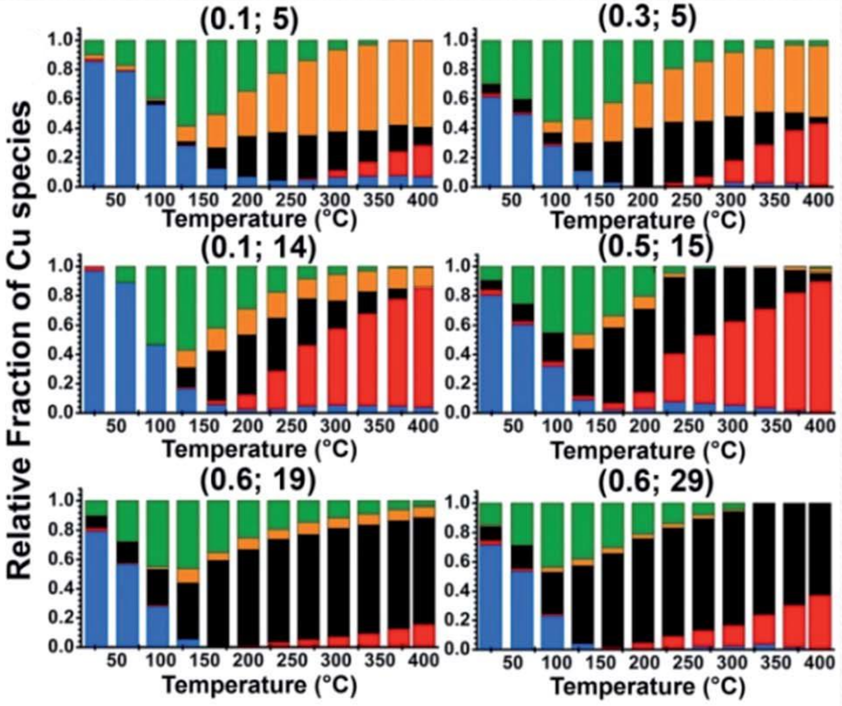




Martini, A. et al., *Chemical science*, (2017)

MCR ALS analysis of XANES allows to monitor the evolution of Cu speciation





MCR-ALS: Additional Constraints

- Concentration Non-Negativity
- Spectra Non-Negativity
- Closure to 1 for Concentrations

Chemometrics and Intelligent Laboratory Systems 140 (2015) 1–12

Contents lists available at ScienceDirect

Chemometrics and Intelligent Laboratory Systems

journal homepage: www.elsevier.com/locate/chemolab

Software Description

MCR-ALS GUI 2.0: New features and applications

Joaquim Jaumot [a,*], Anna de Juan [b], Romà Tauler [a]

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[b] Department of Analytical Chemistry, Universitat de Barcelona, Diagonal 645, Barcelona 08028, Spain

https://mcrals.wordpress.com/

Volume 124, Article No. 124018 (2019) https://doi.org/10.6028/jres.124.018
Journal of Research of National Institute of Standards and Technology

pyMCR: A Python Library for Multivariate Curve Resolution Analysis with Alternating Regression (MCR-AR)

https://github.com/usnistgov/pyMCR

MCR-ALS

Advantages:

- No need for reference spectra
- Less “subjective” than LCA

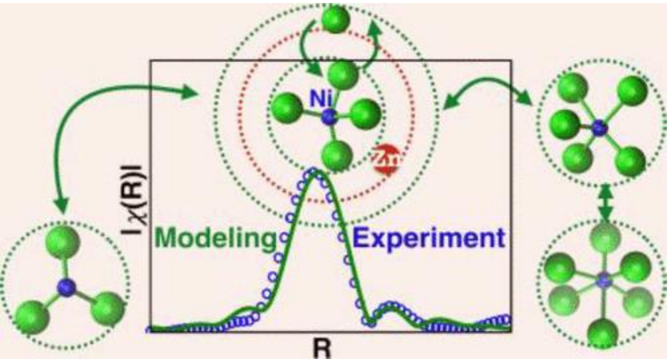
Difficulties:

- Results might depend on initial guess
- Interpretation of “pure spectra” can be challenging
- Very sensitive to data quality and alignment of the spectra

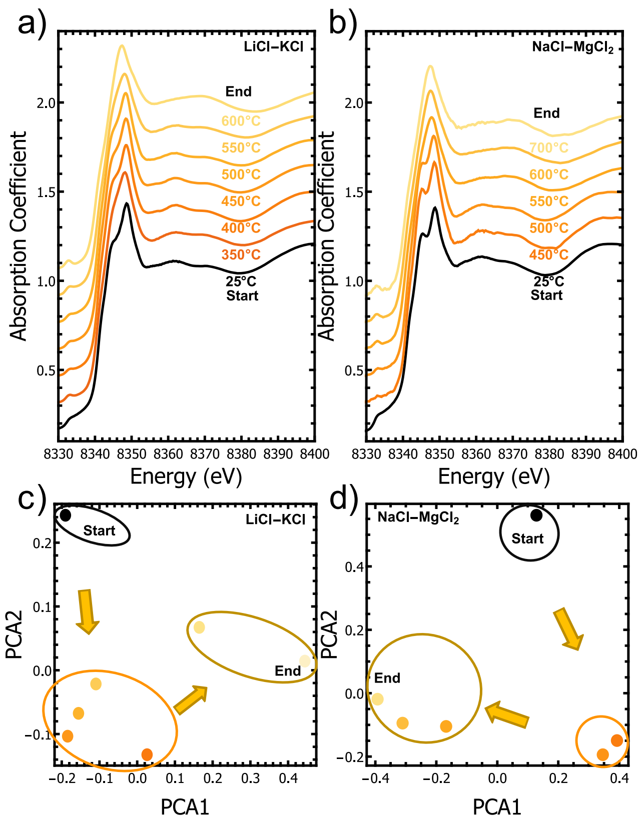
Case Study-2: Molten Salt

Dimensionality reduction and Scree Plot

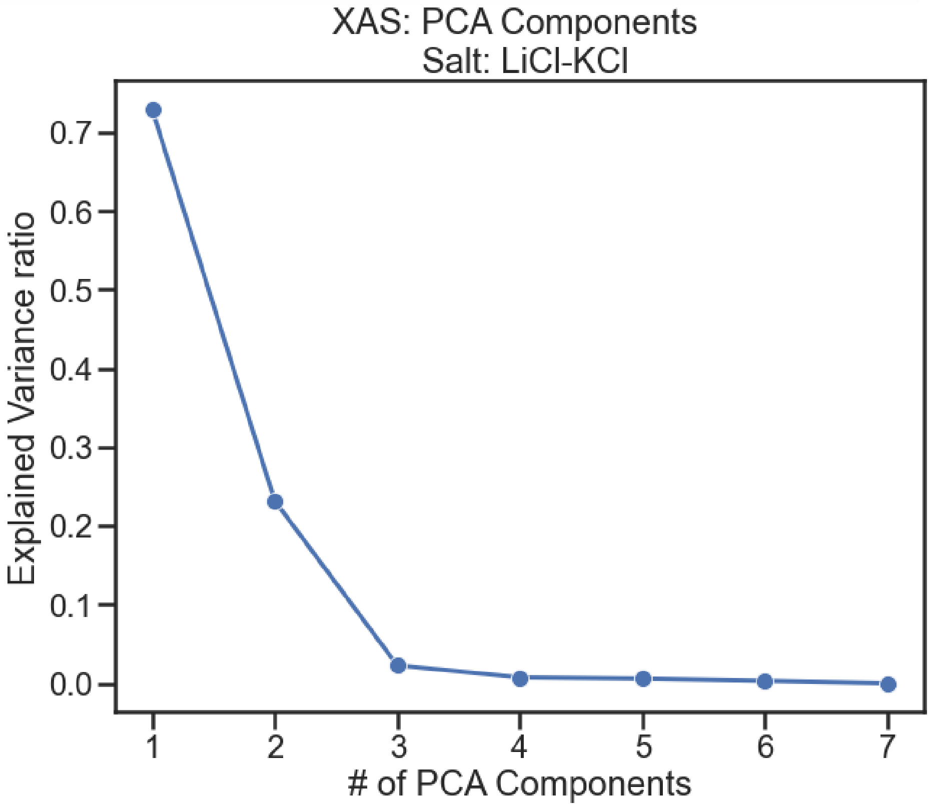
PCA shows the presence of 3 species



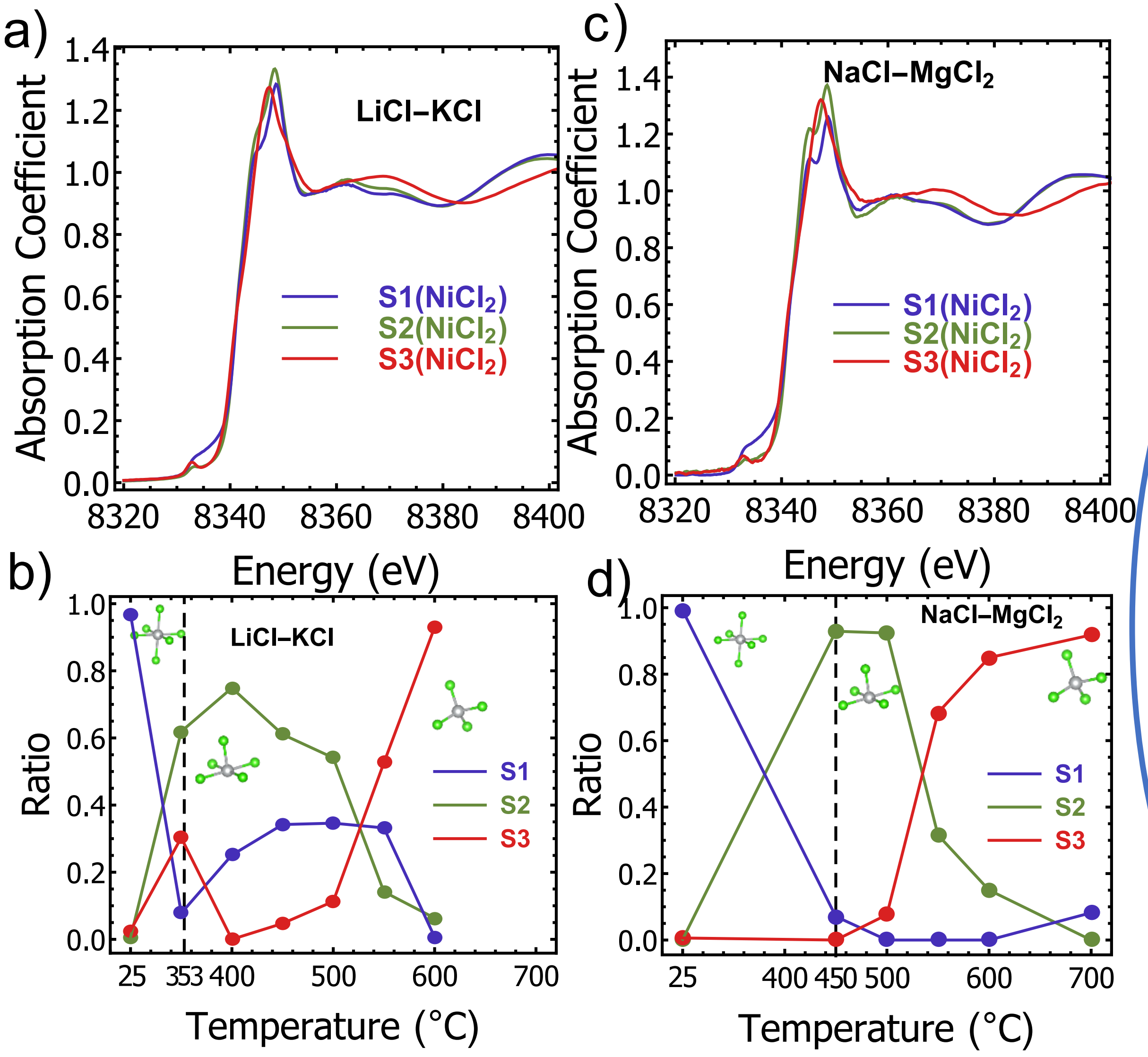
Roy et al. JACS (2021)

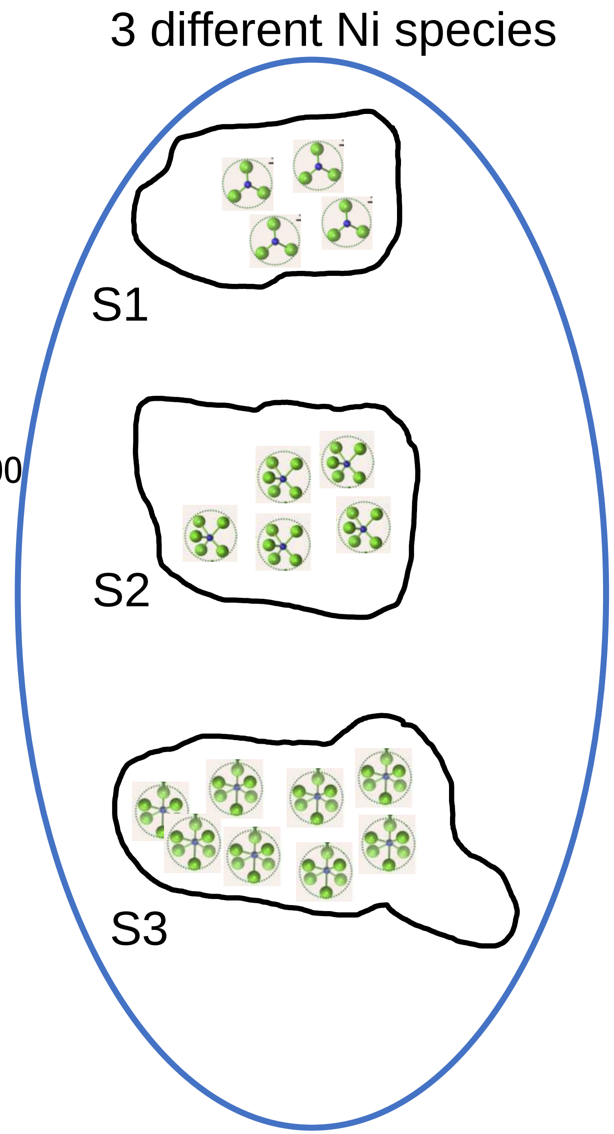


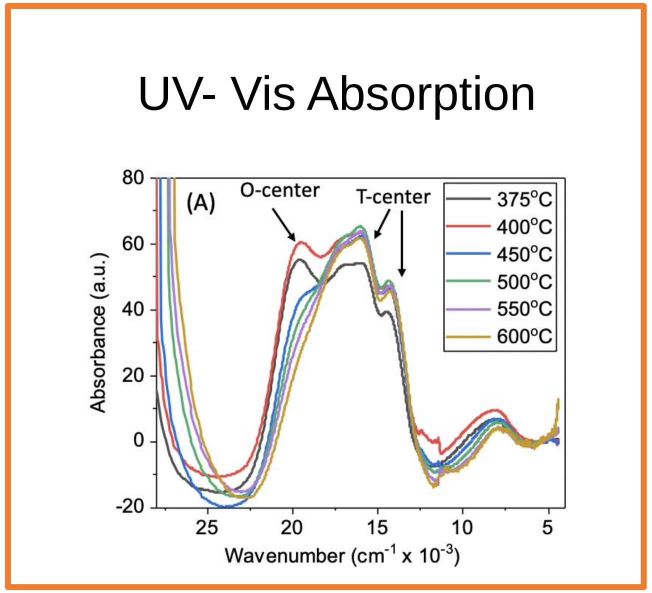
Frenkel et al. 2022



Mixture of Ni-complexes



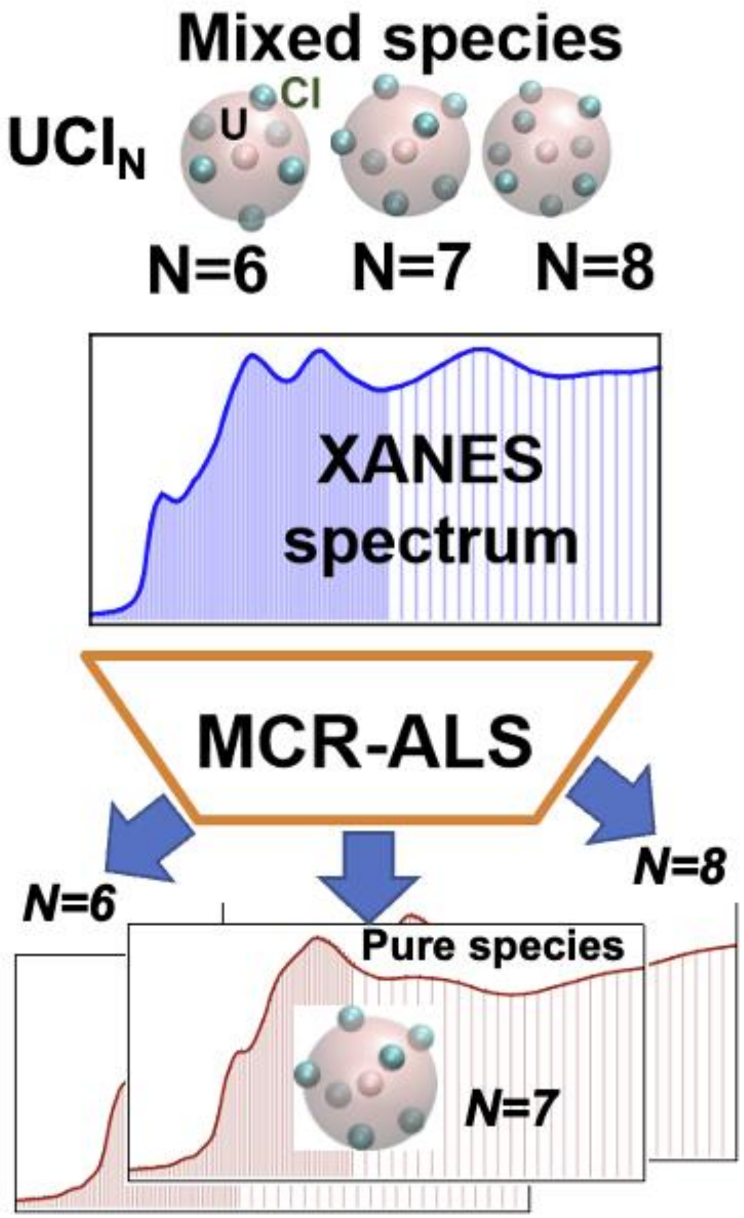




Frenkel et al. 2022

- If the standards are known:
    - Use LCF to obtain fractions
- If the standards and number of species is NOT known
    - Use PCA to learn the number of species.
    - MCR-ALS for extraction of pure species.

Summary



After the break: *XANES modeling using FEFF by F. Vila*

Questions?

Thank you for your attention!