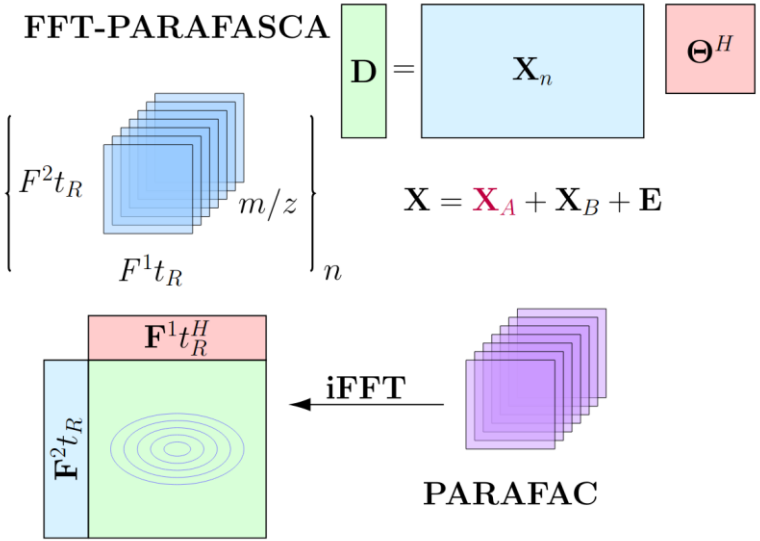
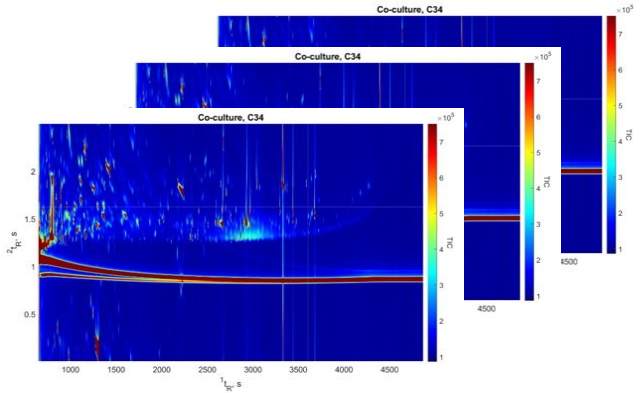
Comparative analysis of comprehensive 2D gas chromatography-time-of-flight mass spectrometry data in time and frequency domains

Michael Sorochan Armstrong [1]
José Camacho [1]
Court Sandau [2]



1-Computational Data Science Lab, Department of Signal Theory, Telematics and Communications, University of Granada, Spain
2-Chemistry Matters, Calgary, Alberta Canada

Raw Data



Peak Table

PKS	var1	var2	var3	var4	var5
cls1					
cls2					
cls1					
cls2					
cls1					

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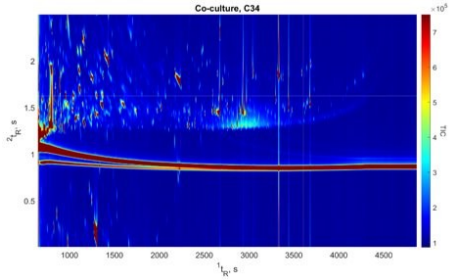
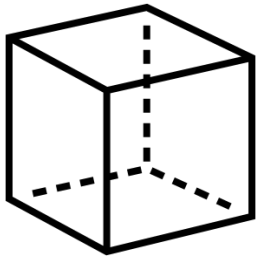
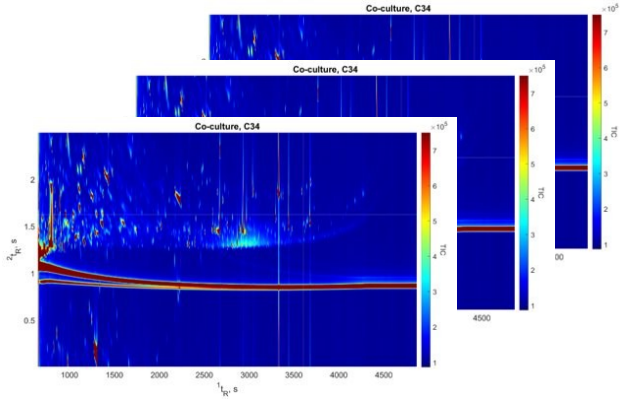
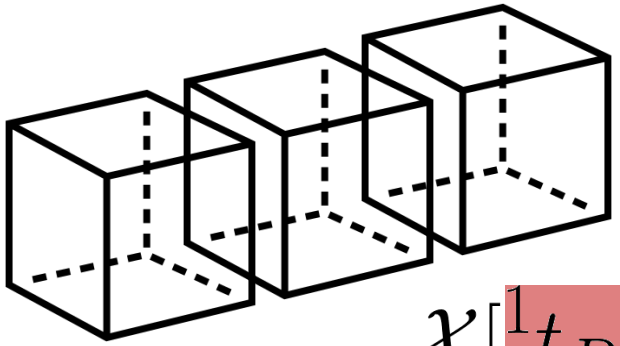
Data Structure

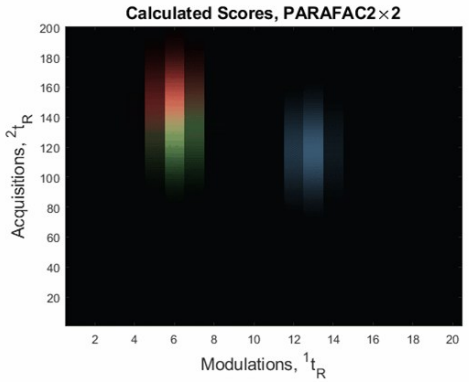




$$\mathcal{X}[{}^1t_R, {}^2t_R, m/z]$$







$$\mathcal{X}[{}^1t_R, {}^2t_R, m/z, smpl]$$

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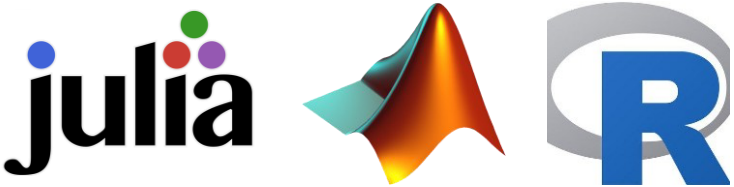
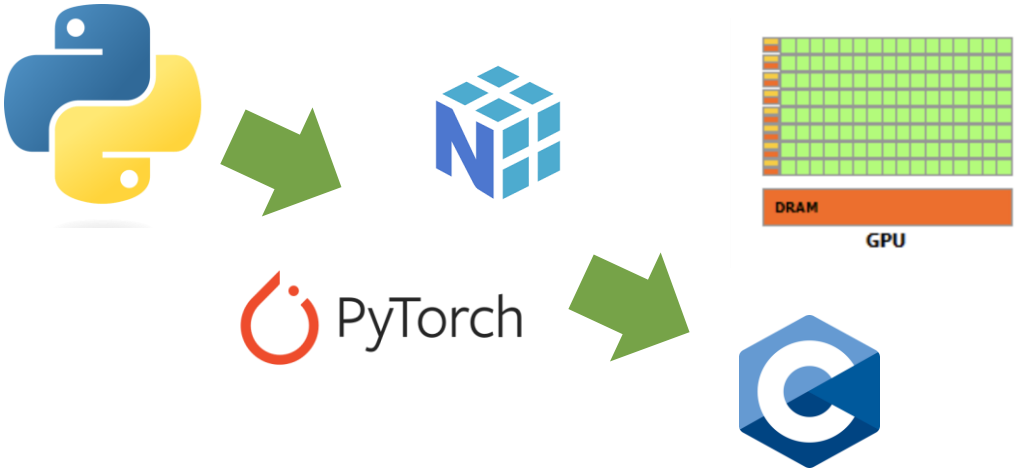
Why Python?

Python	Rating
Open Source	**yes**
Widespread	**10/10**
Ease of use	**5-9/10 ****
Efficiency	**5-9/10 ****





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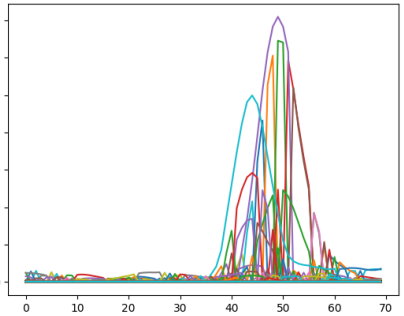
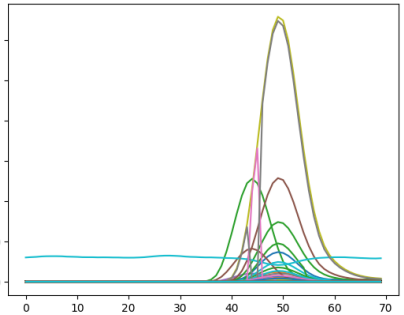
Mass alignment

At resolution m/z = +/- 0.001

Before alignment



After alignment



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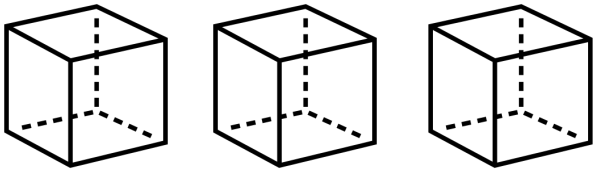
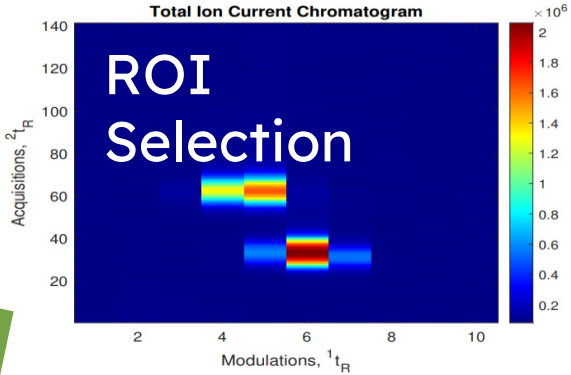
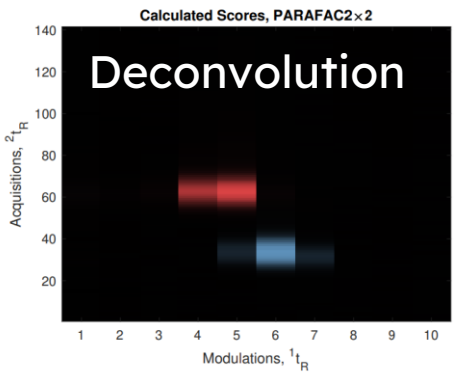
What's our proposed solution?

Feature engineering

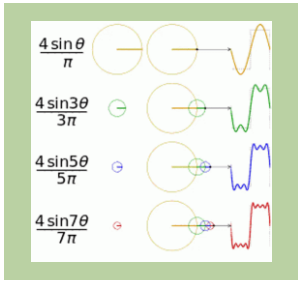
Load



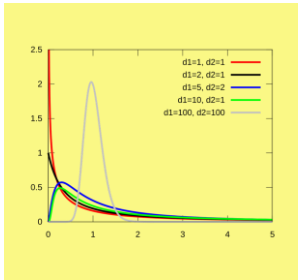




FFT



GLM



Factorization

$$\mathbf{X} = \mathbf{X}_A + \mathbf{X}_B + \mathbf{E}$$

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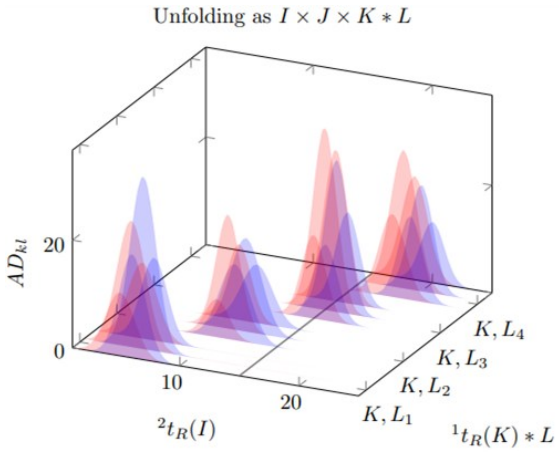
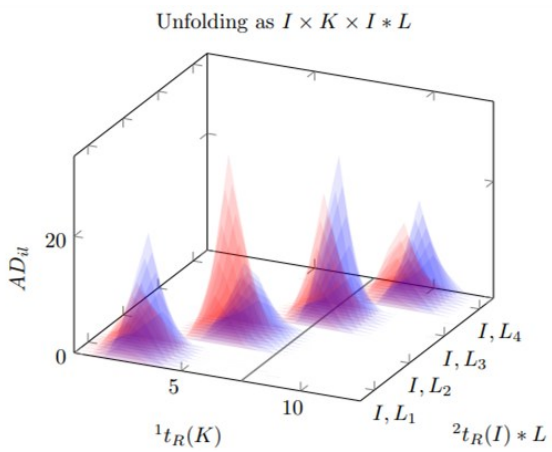
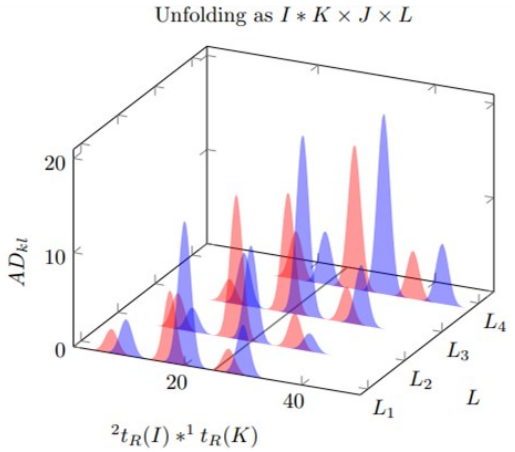
Deconvolution







ELSEVIER
Analytica Chimica Acta
Volume 1249, 8 April 2023, 340909

PARAFAC2×N: Coupled decomposition of multi-modal data with drift in N modes

Michael D. Sorochan Armstrong [a], Jesper Løve Hinrich [b], A. Paulina de la Mata [a], James J. Harynuk [a]

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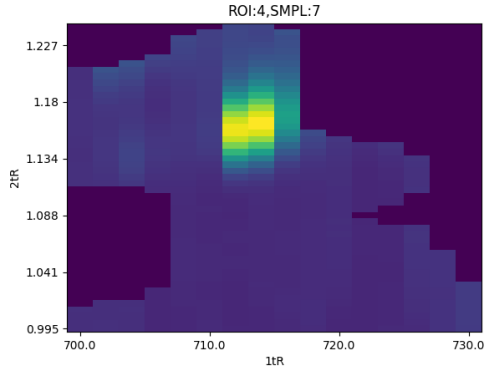
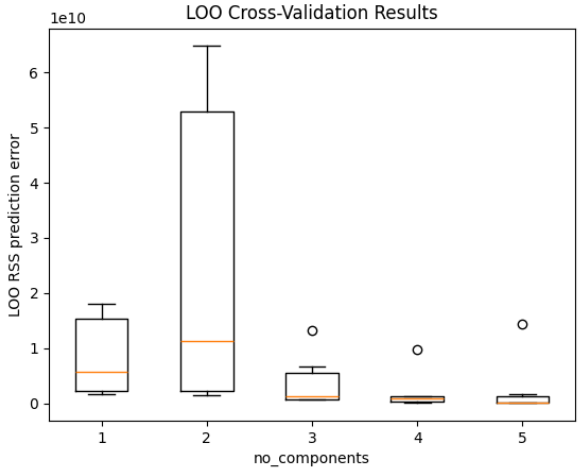
Component Number Selection (LOO)

Figure 10: One iteration of a LOO cross-validation routine. The efficacy of the model with a particular component number is tested on the sum of squared residuals on the test set.





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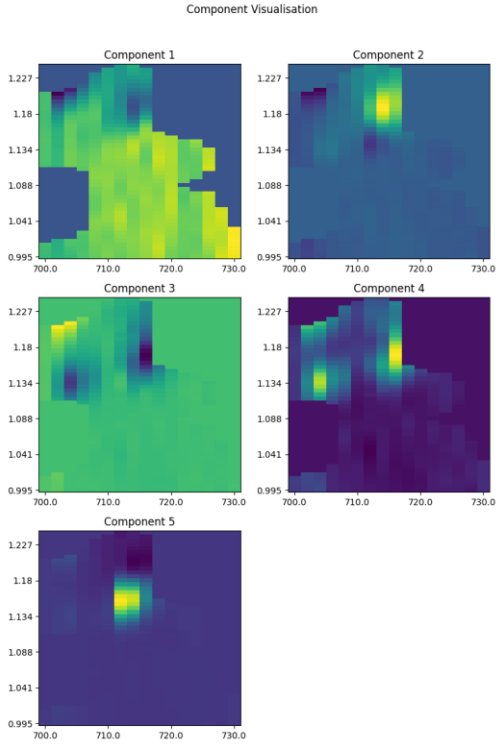
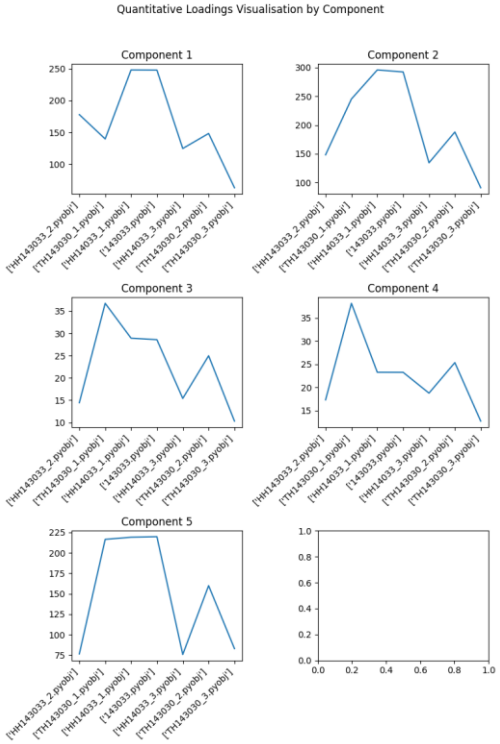
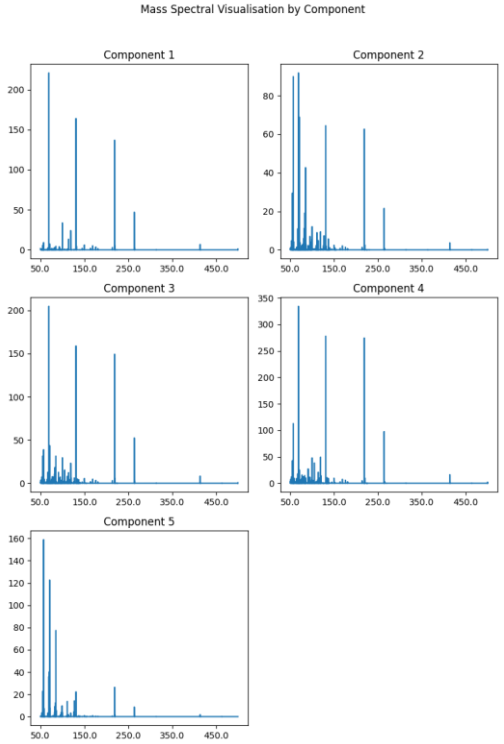
Deconvolution Results







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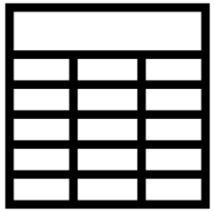
Peak Table Creation

raw2table.py

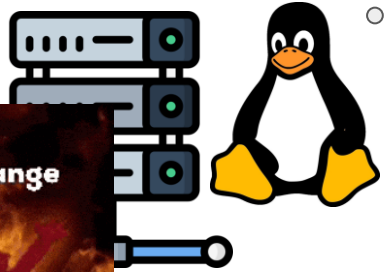
docker

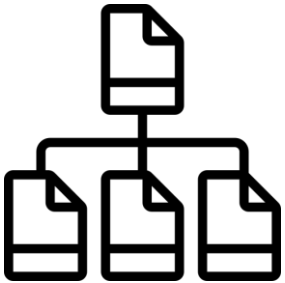
domdfcoding / pynist



pandas

Peak Table





File Structure

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MS Search Results (Reverse)

roi1_1	roi1_2	roi1_3
Perfluorotributylamine (687)	Perfluorotributylamine (570)	Perfluorotributylamine (534)
Perfluoro(dibutylmethylamine) (679)	Perfluoro(dibutylmethylamine) (563)	Perfluoro(dibutylmethylamine) (507)
Tris(trifluoromethyl)phosphine (562)	Tris(trifluoromethyl)phosphine (439)	3-[4-Chromanyl]-2-oxazolidinone (431)
Nonafluoro-1-bromobutane (528)	Pentadecafluorooctyl butanesulfonate (431)	Chloromethyl-phenylethoxy-silacyclohexane (428)
Pentadecafluorooctyl butanesulfonate (524)	Nonafluoro-1-bromobutane (430)	3-Phenylpropionic acid, morpholide (419)

	roi001_1	roi001_2	roi001_3	roi001_4	roi001_5
TH143030_1.cdf	94.74	96.83	23.53	7.02	110.66
HH14033_3.cdf	89.73	159.22	29.13	4.38	64.36
HH143033_2.cdf	89.01	139.61	32.63	56.03	166.69
143033.cdf	89.01	139.61	32.63	56.03	166.69
HH14033_1.cdf	76.33	84.73	16.76	7.61	80.48
TH143030_2.cdf	102.50	130.82	24.66	6.51	66.17
TH143030_3.cdf	44.88	49.93	10.12	1.25	29.95
fvals	0.05	1.01	1.99	191.58	4.39
pvals	0.84	0.42	0.29	0.005	0.17

Quantitative Peak Table w/ 1-way ANOVA results

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Better deconvolution w/ FFT

Computational Data Science (CoDaS) Lab
UNIVERSIDAD DE GRANADA

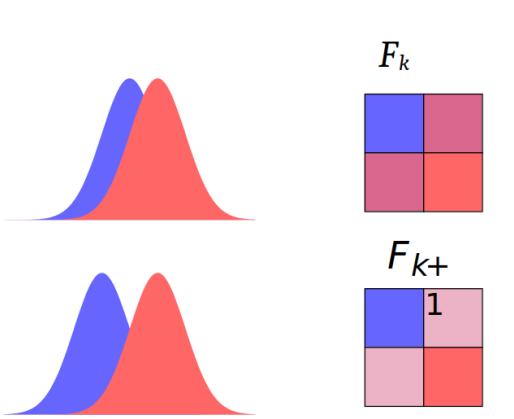
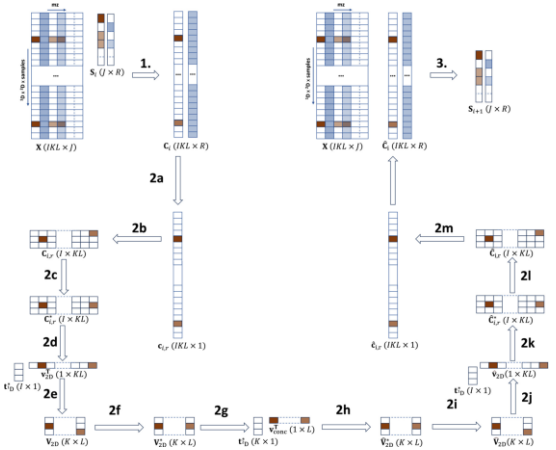
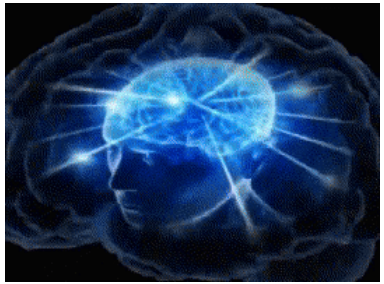


Figure 1: The effect of independent peak drift on the coupling matrix, F



Paul-Albert Schneide

Shift-Invariant Multi-Linearity



Journal of CHEMOMETRICS

RESEARCH ARTICLE | Full Access

Unlocking New Capabilities in the Analysis of GC × GC-TOFMS Data With Shift-Invariant Multi-Linearity

Paul-Albert Schneide, Michael Sorochan Armstrong, Neal Gallagher, Rasmus Bro

First published: 05 December 2024 | https://doi.org/10.1002/cem.3623

Funding: This work was supported by BASF SE. Michael Sorochan Armstrong is funded by an MSCA grant (number 101106986).

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Topological Data Analysis

Computational Data Science (CoDaS) Lab
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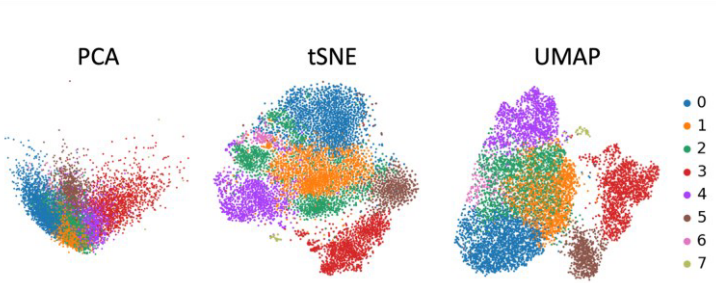


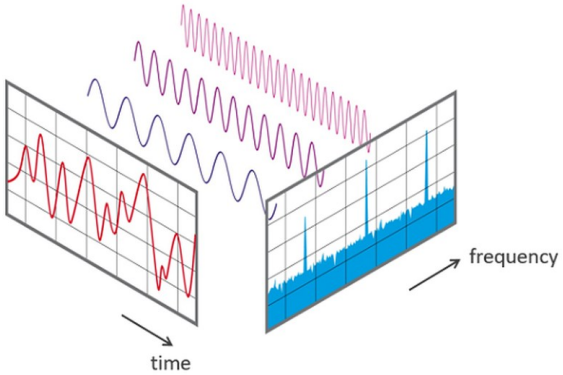
Manifold learning

- Slow
- More meta-parameters, more problems
-Non-unique solutions

- Wavelet selection

Wavelet transform

$$F(\tau, s) = \frac{1}{\sqrt{|s|}} \int_{-\infty}^{+\infty} f(t)\, \psi^* \left(\frac{t-\tau}{s} \right) dt$$



Fourier analysis

- Algebra is a little different

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FFT-ASCA

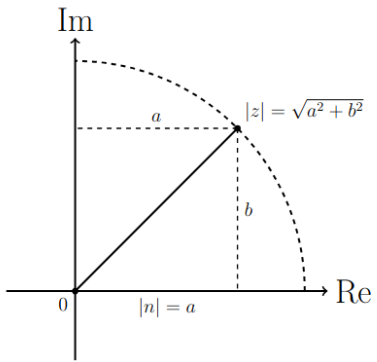
Journal of CHEMOMETRICS

RESEARCH ARTICLE | Full Access

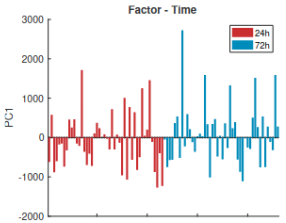
An Alignment-Agnostic Methodology for the Analysis of Designed Separations Data

Michael Sorochan Armstrong | José Camacho

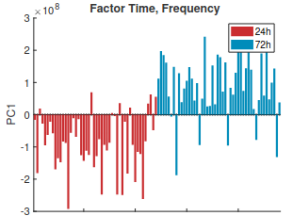
First published: 25 January 2025 | https://doi.org/10.1002/cem.70002



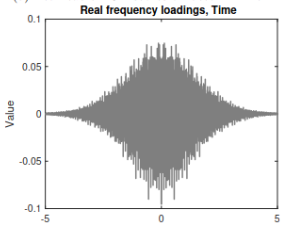
FFT, mean-centered	SumSq	PercSumSq	df	MeanSq	*F*	*p*-value
Mean	5.84e+14	5.09	1	5.84e+14	—	—
Time-1	1.54e+15	13.4	1	1.54e+15	19.5	**0.000999**
Treatment-2	7.79e+14	6.78	2	3.89e+14	4.92	**0.00599**
Sex-3	8.7e+14	7.57	1	8.7e+14	11	**0.00599**
Order-4	7.13e+14	6.2	7	1.02e+14	1.29	0.25
Interaction 1-2	4.51e+14	3.93	2	2.26e+14	2.85	0.0569
Residuals	6.49e+15	56.5	82	7.92e+13	—	—
Total	1.15e+16	100	96	1.2e+14	—	—



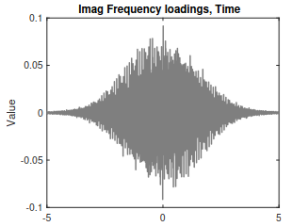
(a) Peak table PCA scores of factor "Time".



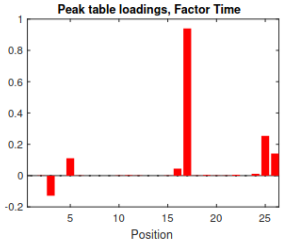
(b) Real-valued PCA scores for factor "Time" from FFT transformed data. Mean-centred.



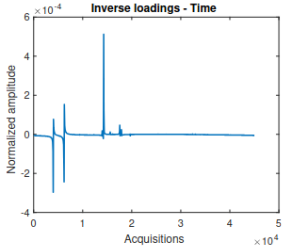
(c) Loadings for factor "Time" from the peak table representation of the data. 26 targeted metabolites were included in the analysis.



(d) Complex-valued loadings in the frequency domain for factor "Time".



(e) Real-valued loadings in the time domain for factor "Time".



(f) Real-valued loadings in the time domain for factor "Time".

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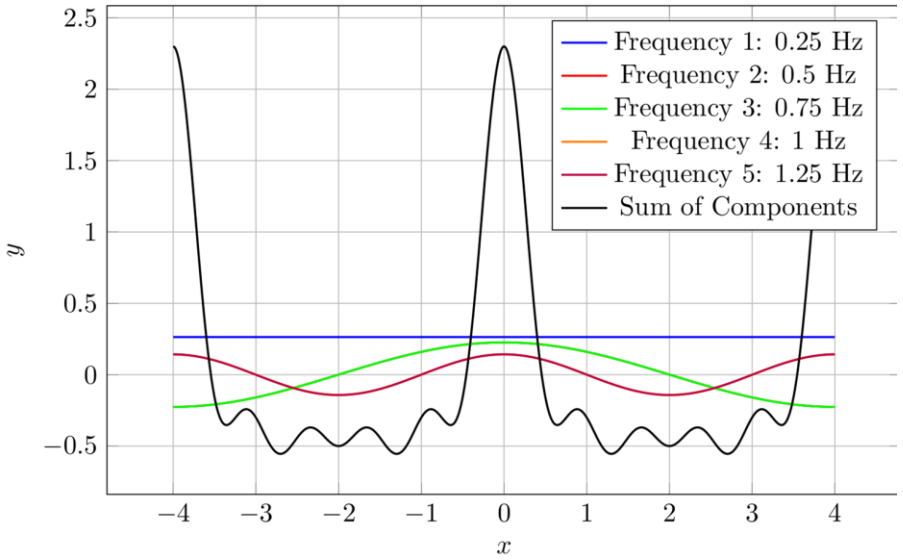

Amplitude - real part

Shift - imaginary part

Both - complex domain

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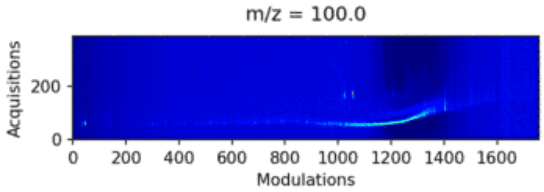
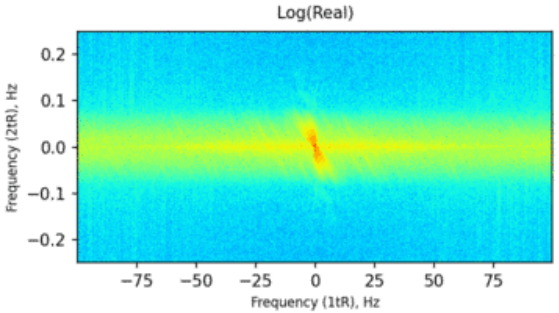
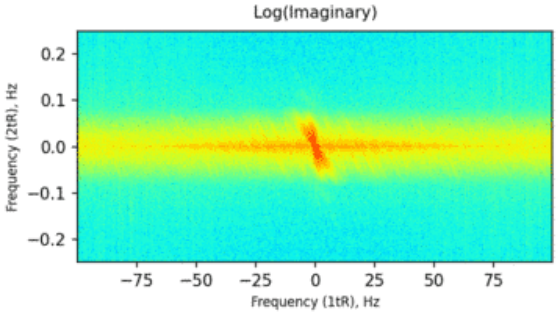
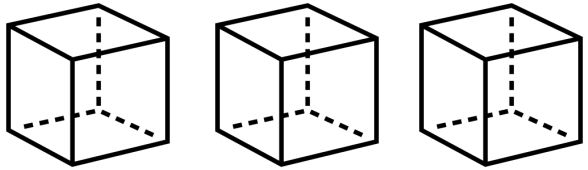
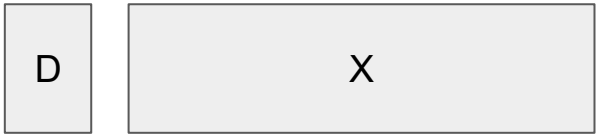








$$\mathcal{F}\left({}^{1}t_R, {}^{2}t_R\right) | \; m/z$$



$$\mathbf{X} = \mathbf{X}_A + \mathbf{X}_B + \mathbf{E}$$

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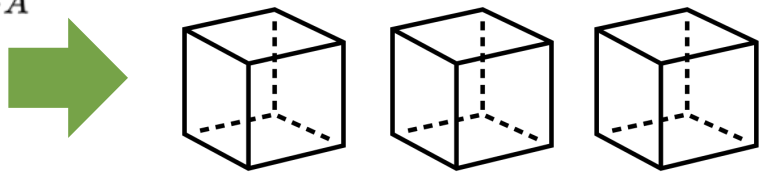
Tensor algebra - array indexing

$\mathbf{X}_A$



TensorLy
Tensor Learning in Python

$$\mathbf{X}_A = \mathbf{A}_{1t_R} \times \left(\mathbf{B}_{2t_R} \otimes \mathbf{C}_{m/z} \otimes \mathbf{D}_{smpls}\right)^H$$

$$\mathbf{X}_{[n]} = \mathbf{U}^{(n)}\mathbf{G}_{[n]}\left(\mathbf{U}^{(1)} \otimes \cdots \mathbf{U}^{(n-1)} \otimes \mathbf{U}^{(n+1)} \otimes \cdots \otimes \mathbf{U}^{(N)}\right)^T$$

Python

$$\mathbf{X}_{[n]} = \mathbf{U}^{(n)}\mathbf{G}_{[n]}\left(\mathbf{U}^{(N)} \otimes \cdots \mathbf{U}^{(n+1)} \otimes \mathbf{U}^{(n-1)} \otimes \cdots \otimes \mathbf{U}^{(1)}\right)^T$$

MATLAB, R

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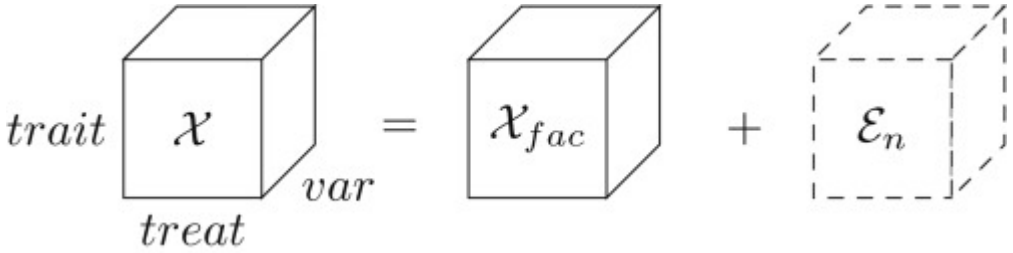
http://jeankossaifi.com/blog/unfolding.html

What else can we do with PARAFASCA?



Project the error tensor for uncertainty estimation

$$Z_{|I} = F_M \otimes F_L \otimes F_K$$
$$^{I}X_A^* \in \mathbf{R}^{I \times K * L * M}$$
$$F_I = ^{I} X_A^* Z_{|I} (Z_{|I}^T Z_{|I})^{-1}$$

Replicate analysis for uncertainty estimation in PARAFAC and PARAFASCA analyses of factorial metabolomics data

Michael Sorochan Armstrong[a,b], José Camacho[a]

[a] *Computational Data Science (CoDaS) Lab, C. Periodista Daniel Saucedo Aranda, Granada, 18071, Andalucia, Spain*
[b] *Lifewatch ERIC, Instituto Interuniversitario De Investigación Del Sistema Tierra En Andalucía, University of Granada, Av. del Mediterráneo, Granada, Granada, 18006, Andalucia, Spain*

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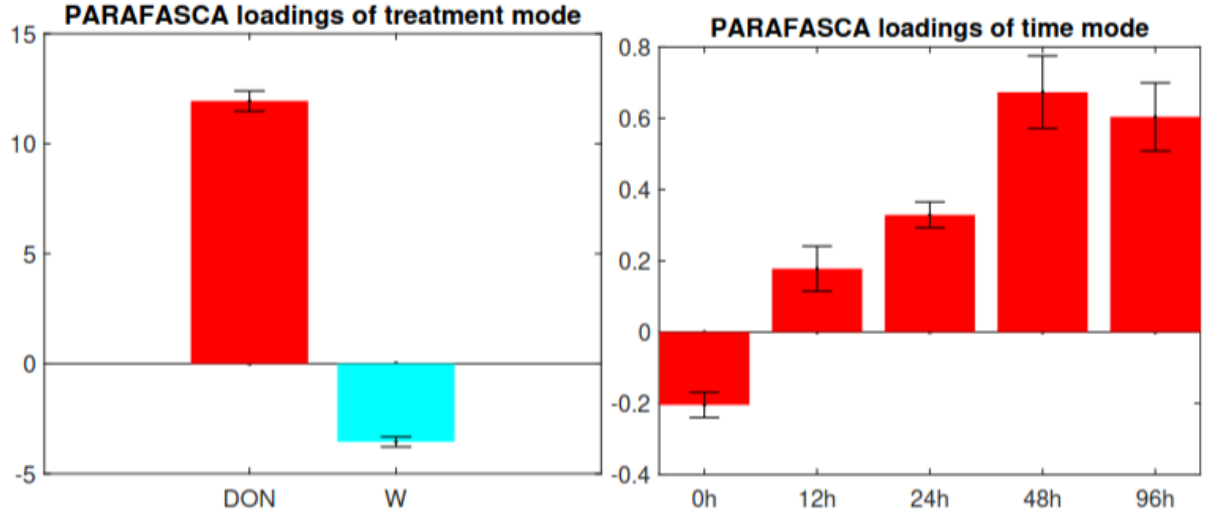
PARAFASCA example



We can visualize the uncertainty per experimental level

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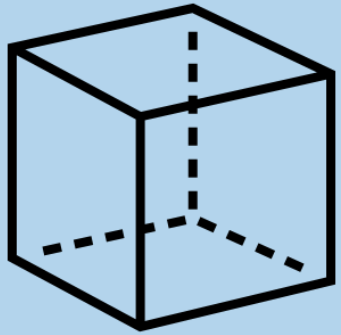
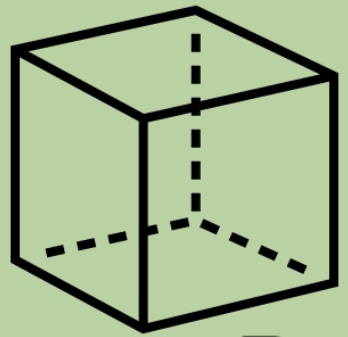
Recovering the retention scores

NOMINAL $\mathbf{X}_A$

$\mathbf{C}_{m/z}$  $\times$ $\mathbf{D}_{smpls}$

$\mathbf{A}_{1t_R}$ $\mathbf{B}_{2t_R}$

w/ ERROR $\mathbf{X}_A + \mathbf{E}$

$\mathbf{C}_{m/z} + \mathbf{E}$  $\times$ $\mathbf{D}_{smpls} + \mathbf{E}$

$\mathbf{A}_{1t_R} + \mathbf{E}$ $\mathbf{B}_{2t_R} + \mathbf{E}$

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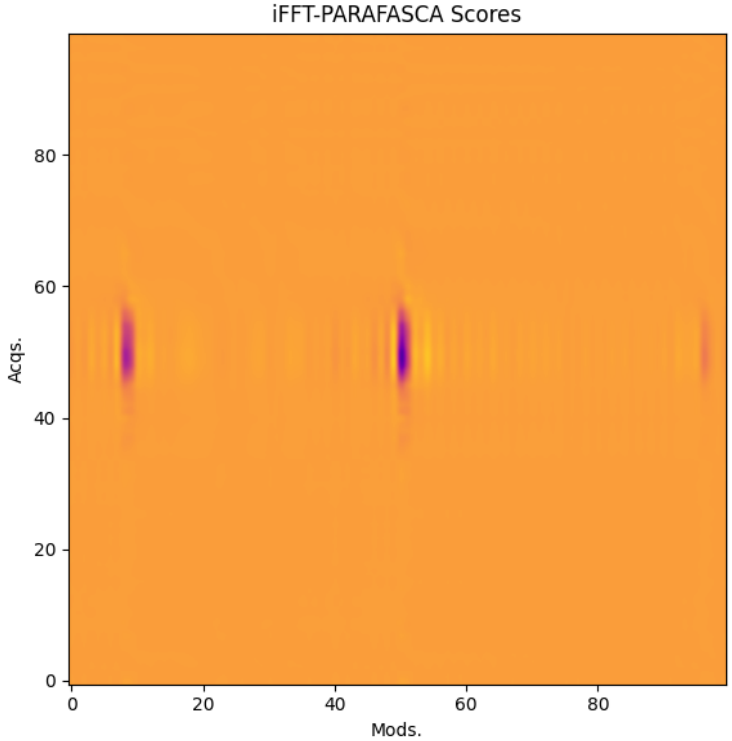
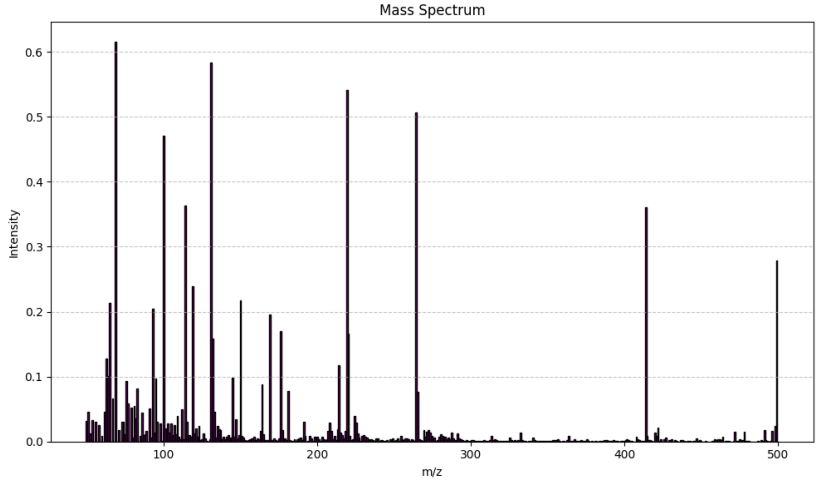
Results of 2DFFT-PARAFASCA





Results are localized by retention patterns, not individual peaks.

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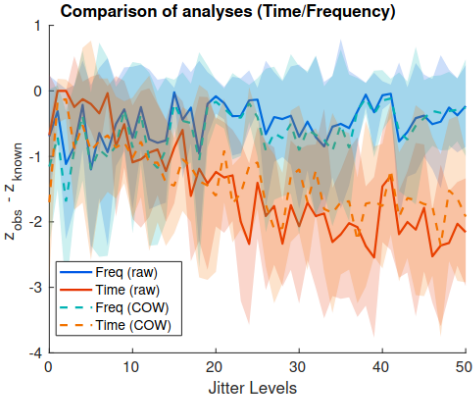
Further yet...

Heterogeneous data analysis - what if the peaks are in completely different locations?



Same colour := same factor

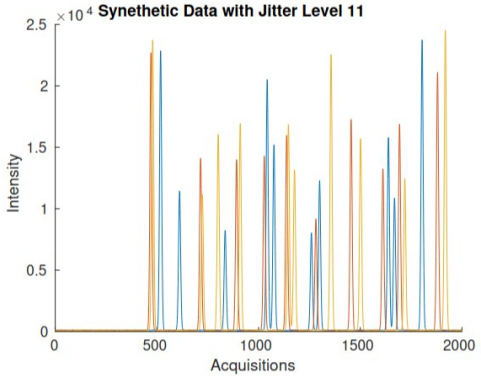


Figure A.16: 3 samples for jitter level 11

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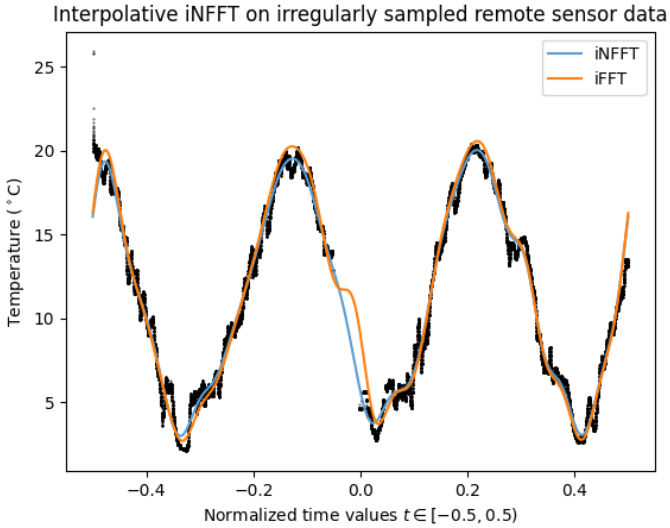
$$\hat{h}_k = Af(x_j)\left(W_k - W_k L\left(I + UW_k L\right)^{-1} UW_k\right)$$



A direct solution to the interpolative inverse non-uniform fast Fourier transform (i-iNFFT) problem for spectral analyses of non-equidistant time-series data

Michael Sorochan Armstrong, José Carlos Pérez-Girón, José Camacho *Member, IEEE*, Regino Zamora

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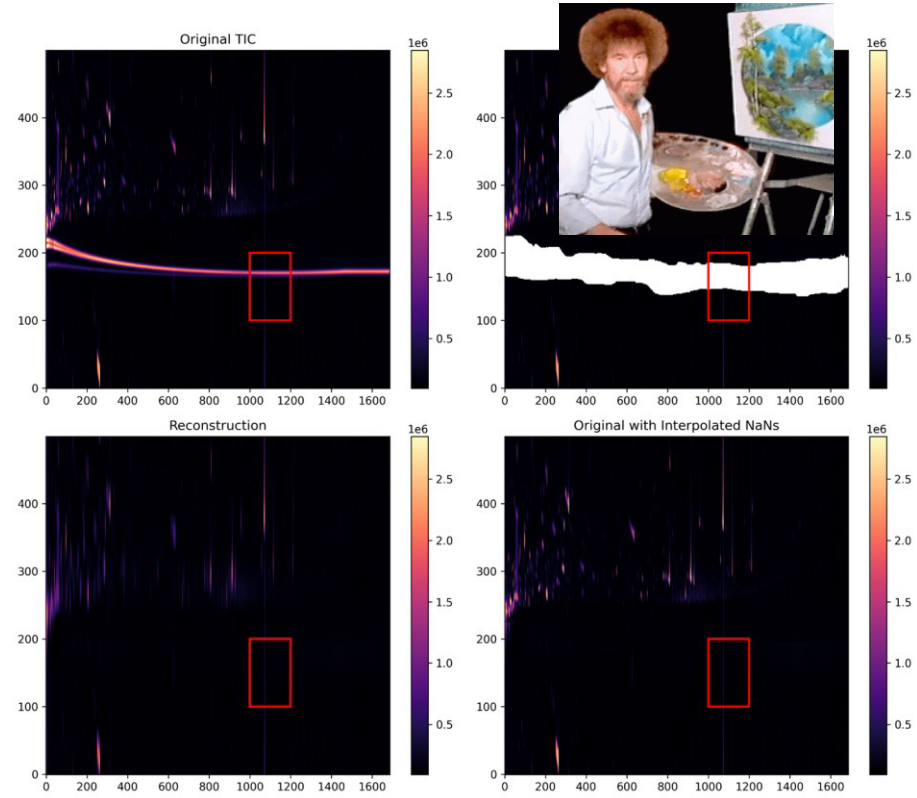
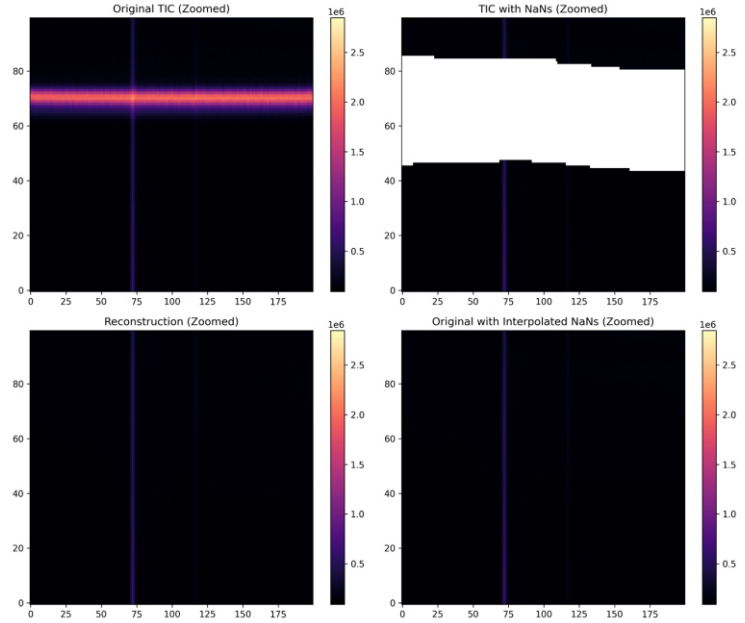
Source: Star Wars

Interpolative transforms





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Applications of Frequency Analysis

Heterogeneous data analysis

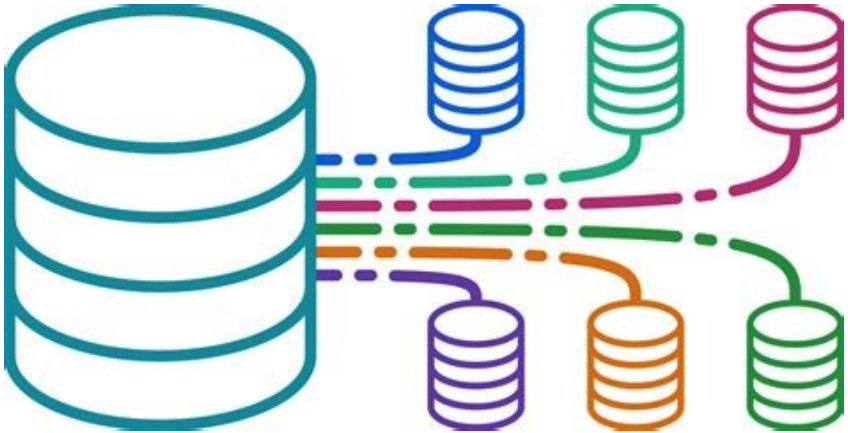
Process control

Interpolating irrelevant information

Extrapolation for saturated masses

Exploratory data analysis

Statistical analysis



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Acknowledgements

Computational Data Science (CoDaS) Lab

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mustard
multi-scale spatio-temporal analysis of research data



MARIE CURIE ACTIONS

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Dr. Regino Zamora

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chemistry matters

Dr. Courtney Sandau
Dr. Ifeoluwa Grace Idowu

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