One-shot tensor decomposition of full-scale GC×GC-VUV datasets for resolving petrochemical groups

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UNIVERSITY OF COPENHAGEN

Acknowledgements

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Sent: 10. marts 2025 13:15
To: Rasmus Bro <rb@food.ku.dk>
Subject: Question regarding PARAFAC (for GCxGC-VUV data of gas-oils)

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Outline of the presentation

All-samples-at-once shift-invariant tri-linear decomposition provides a simple and robust data analysis strategy to group-level analysis of petrochemicals, using GC×GC-VUV.

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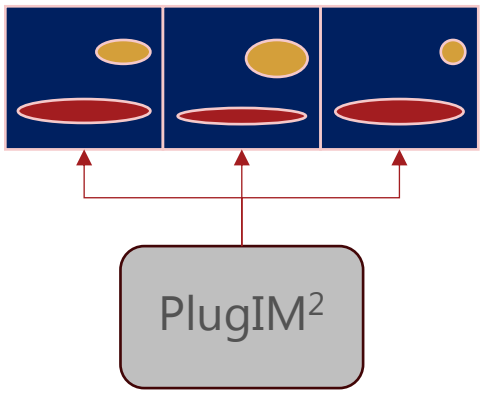
Model properties

Shift-invariant tri-linearity is an efficient method to deconvolute shifted, co-eluting peaks.

Overview: Data analysis workflow

Data analysis workflow

GC×GC-VUV measurements



[1]Schneide P-A, Bro R, Gallagher NB. *Journal of Chemometrics*. 2023; 37(8):e3501
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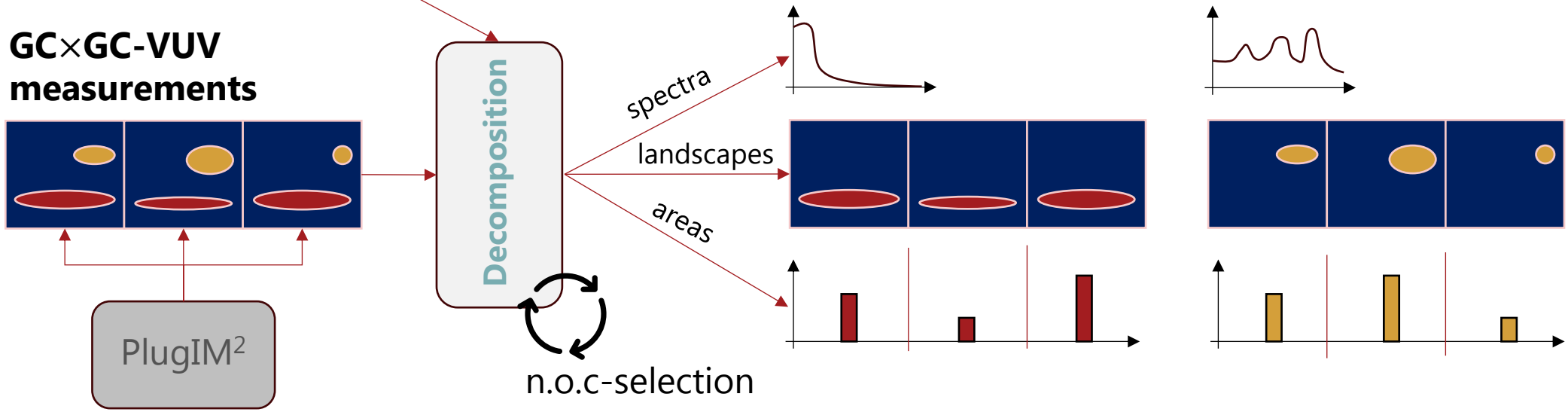

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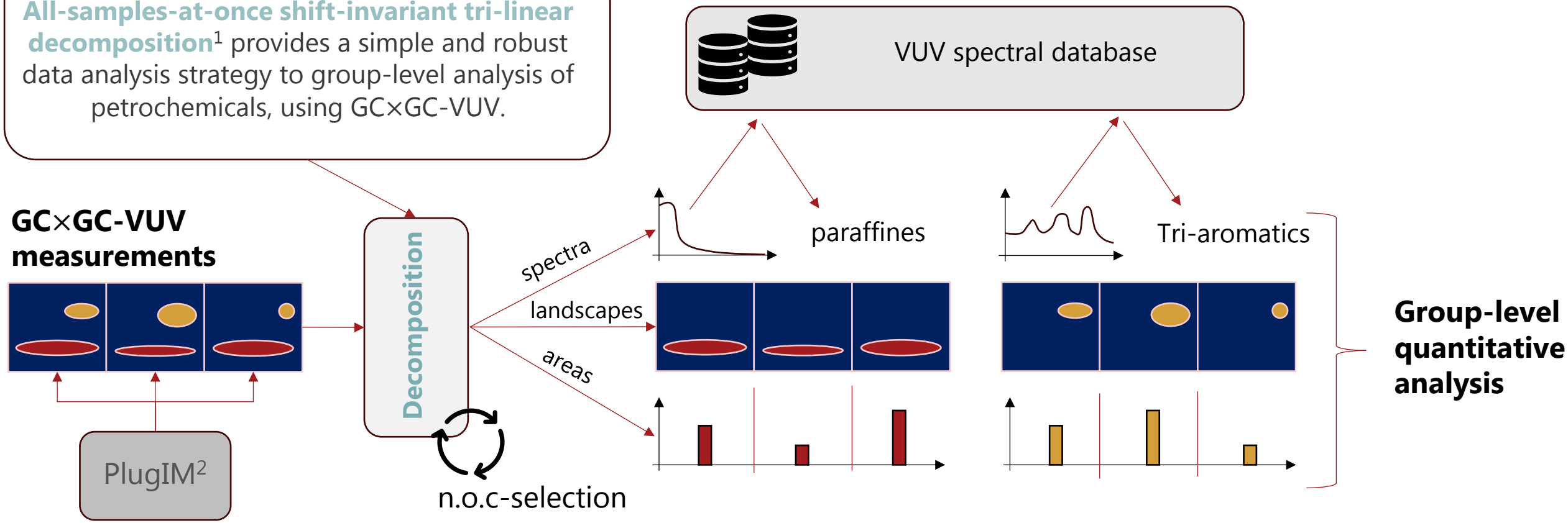

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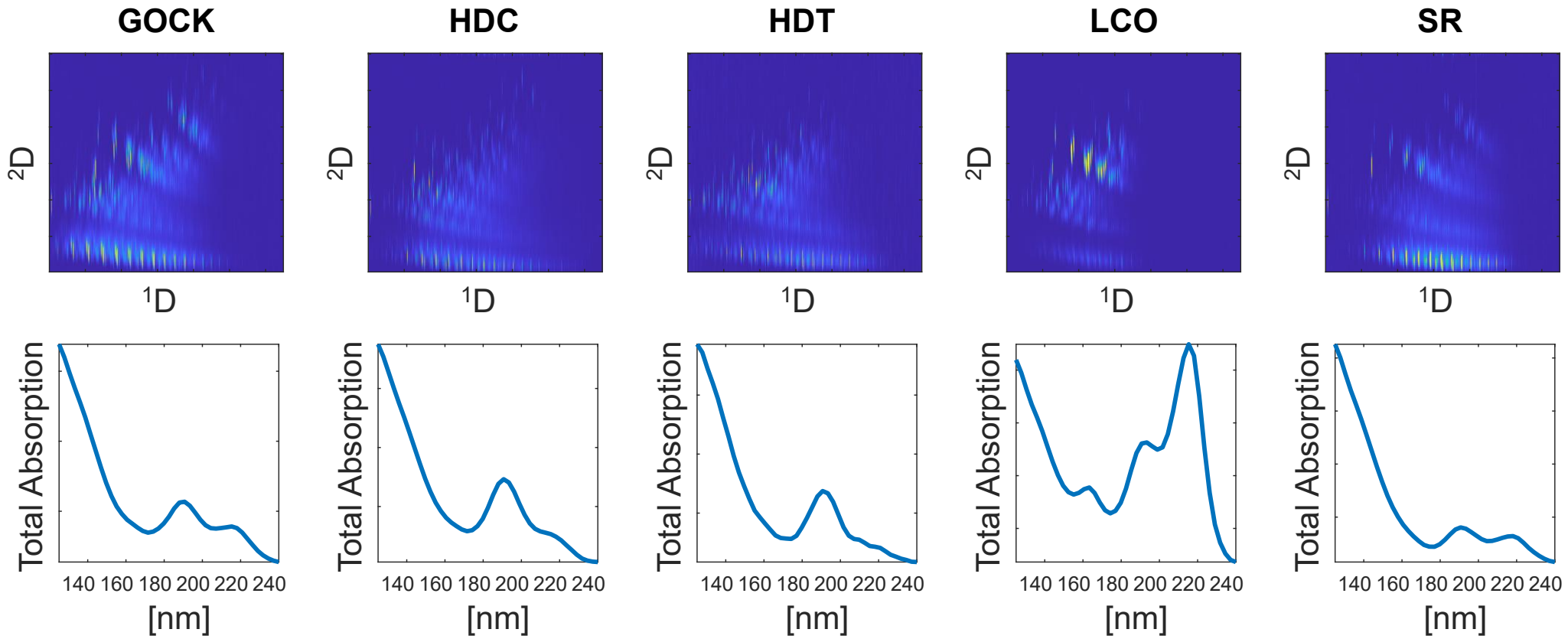
Case study: Petrochemical samples

- GC×GC-VUV data: 14 gas oil samples, cocker gas oils (GOCK), hydroconverted (HDC), hydrotreated (HDT), light cycle oils (LCO), straight run gas oils (SR), 24 measurements[3]

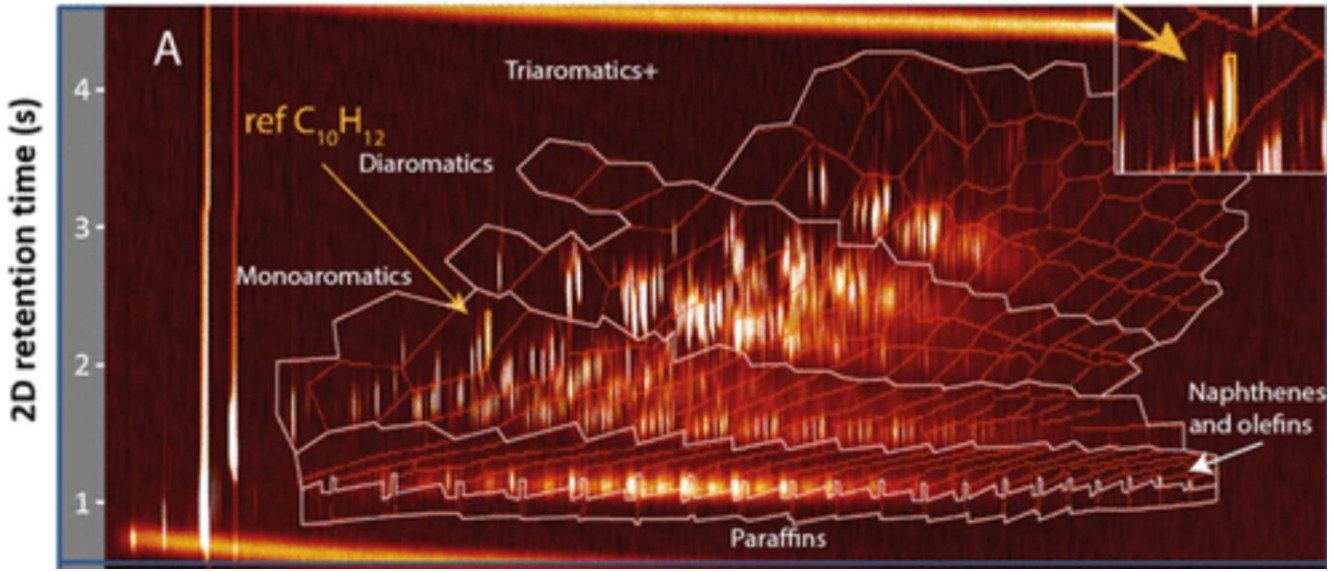


[3]Lelevic et al *Energy & Fuels* 2022 *36* (18), 10860-10869 DOI: 10.1021/acs.energyfuels.2c01960

Case study: Problem specification and benchmark

Characterizing and semi-quantifying chemical groups: *saturates, olefines, mono-aromatics, di-aromatics, tri-aromatics*.

Benchmark: *Template-based approach*[3,4], *pixel-based approach*[5]



Template-based approach has been compared to, and showed good agreement with[1]*:*

- *GC-MS derived from ASTM D2425.*
- *GC×GC-FID with prefractionation.*
- *Bromine Number (ASTM D1159).*

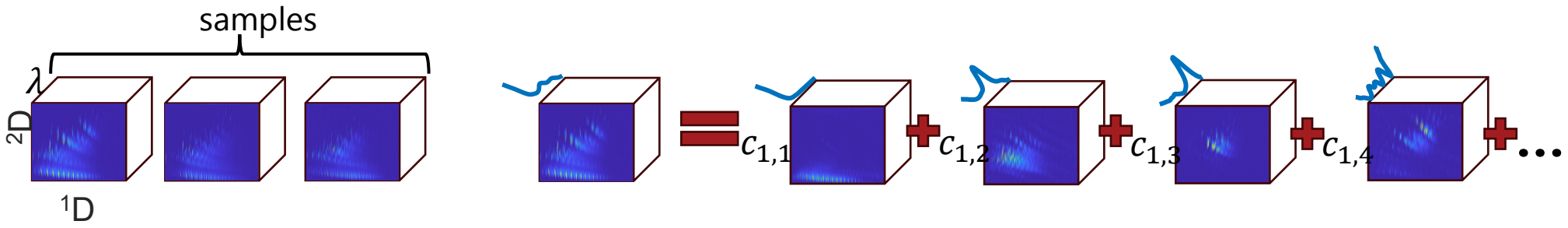
Limitations: sensitive to retention time shifts → manual adjustment of template required, resolving co-eluting signals requires *a priori* knowledge

[3]Lelevic et al *Energy & Fuels* 2022 *36* (18), 10860-10869 DOI: 10.1021/acs.energyfuels.2c01960
[4]Lelevic et al *Energy & Fuels 2021* 35 (17), 13766-13775 DOI: 10.1021/acs.energyfuels.1c01910
[5]Lelevic *Journal of Separation Science 2025* 48 (12), e70318. https://doi.org/10.1002/jssc.70318

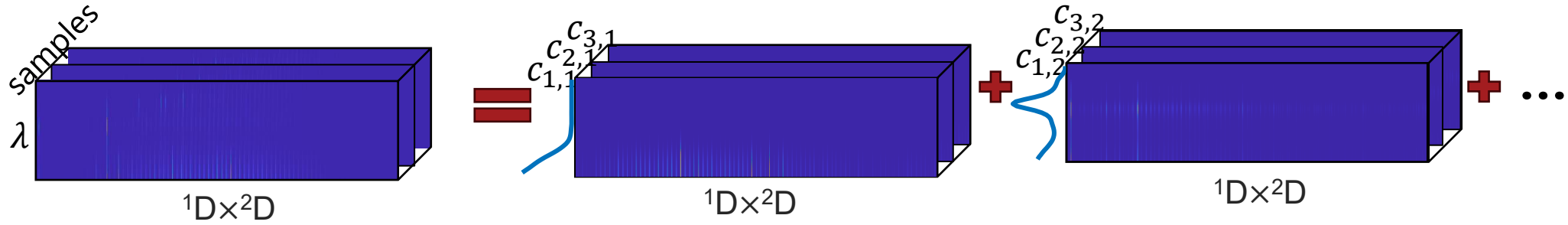
The proposed method: Overview

Shift-invariant tri-linear decomposition → **Exploiting Lambert-Beers law**

Strategy 1:



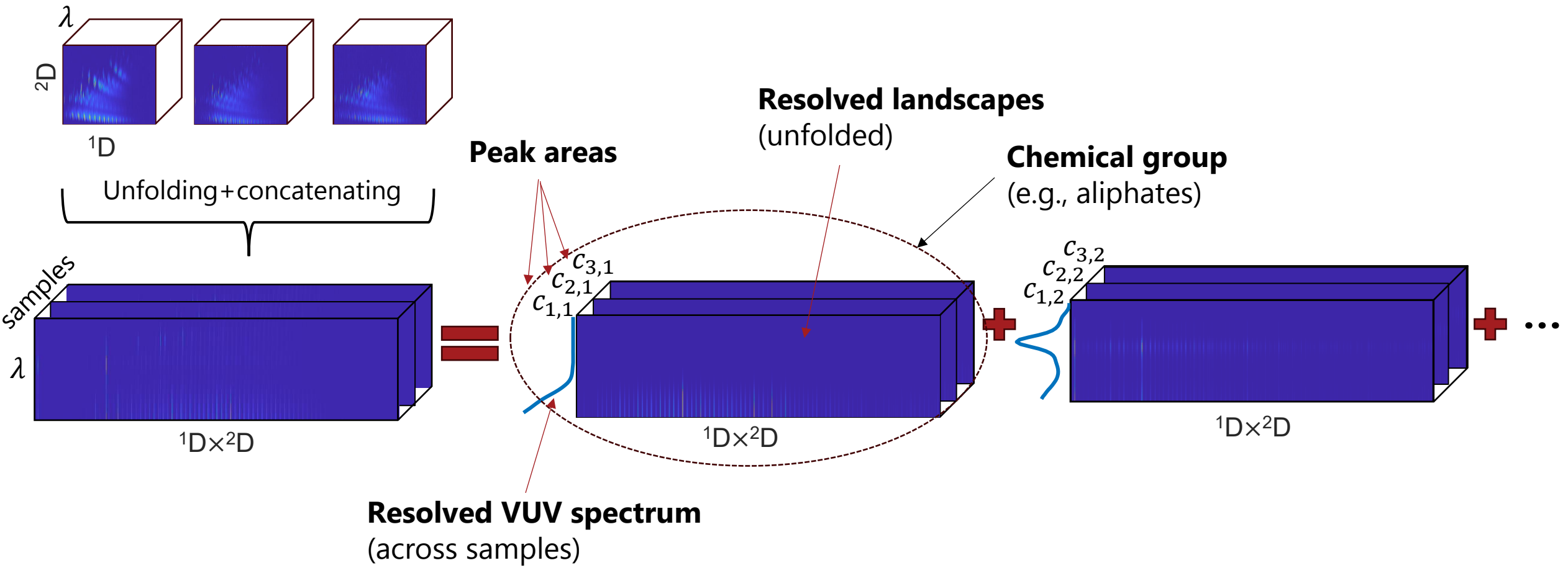
Strategy 2:



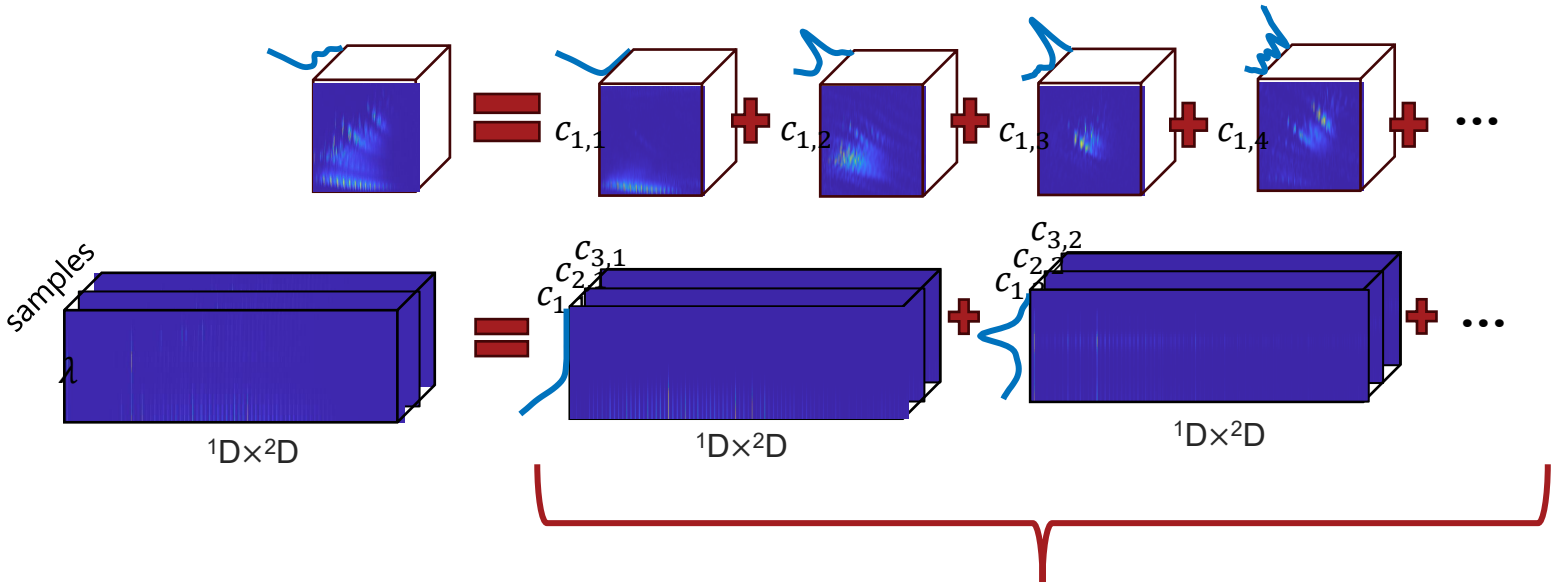
Conceptually: Doing Parallel Factor Analysis (PARAFAC)[6] / Multivariate Curve Resolution (MCR)[7] on the whole GC×GC-VUV dataset instead of decomposing selected Regions of Interest (ROIs).

[6]Hoggard et al. *Analytical Chemistry* 2007 *79* (4), 1611-1619
[7]Parastar et al. *Analytical Chemistry* 2014 *86* (1), 286-297

How does it work: Strategy 2 (all-samples-at-once)



Data Properties: Low-rank-structure of GC×GC-VUV data



We need to get a "good" approximation of the raw data for a "small" number of terms.

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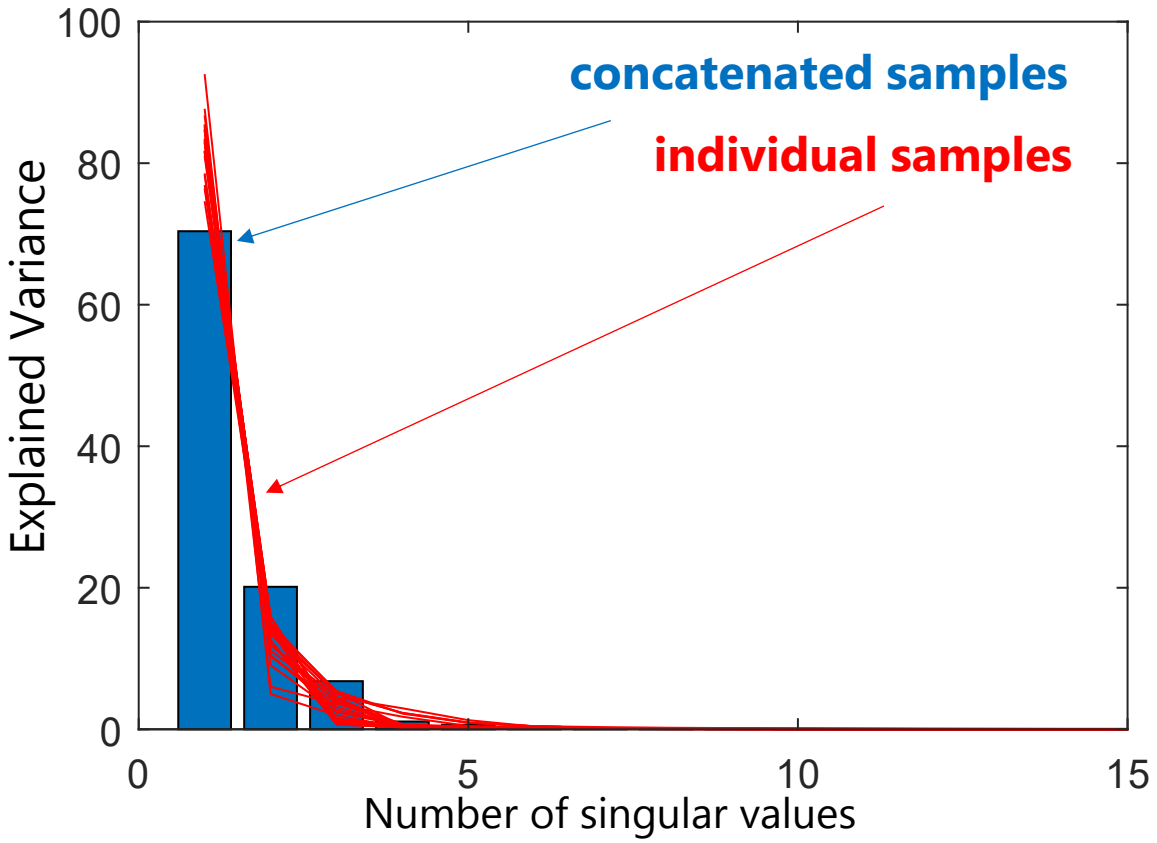
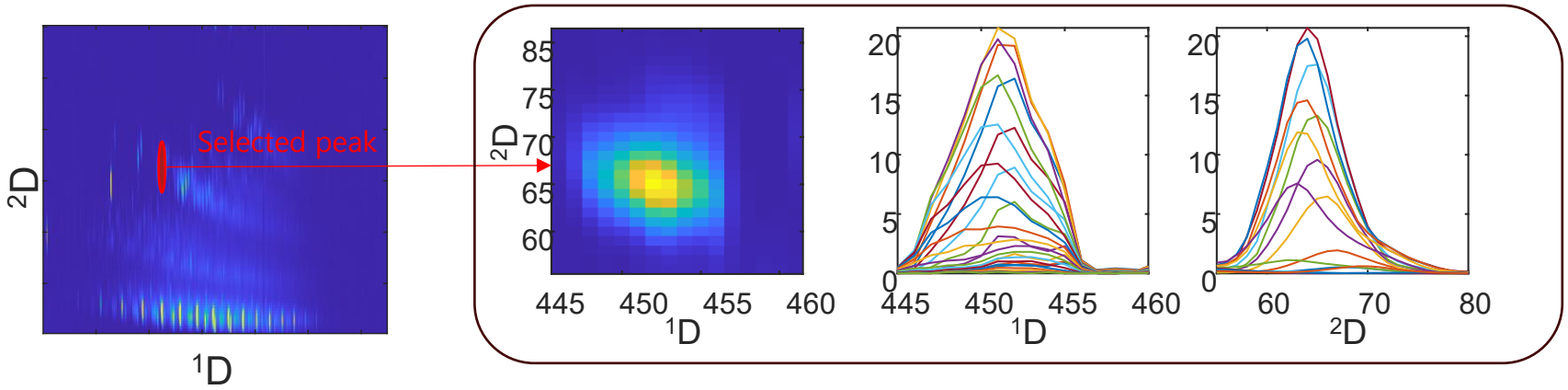


Singular value decay curves show that **< 10 components explain > 99.9 % of the variance** for all individual samples.

Model Properties: shift-invariant, tri-linear decomposition



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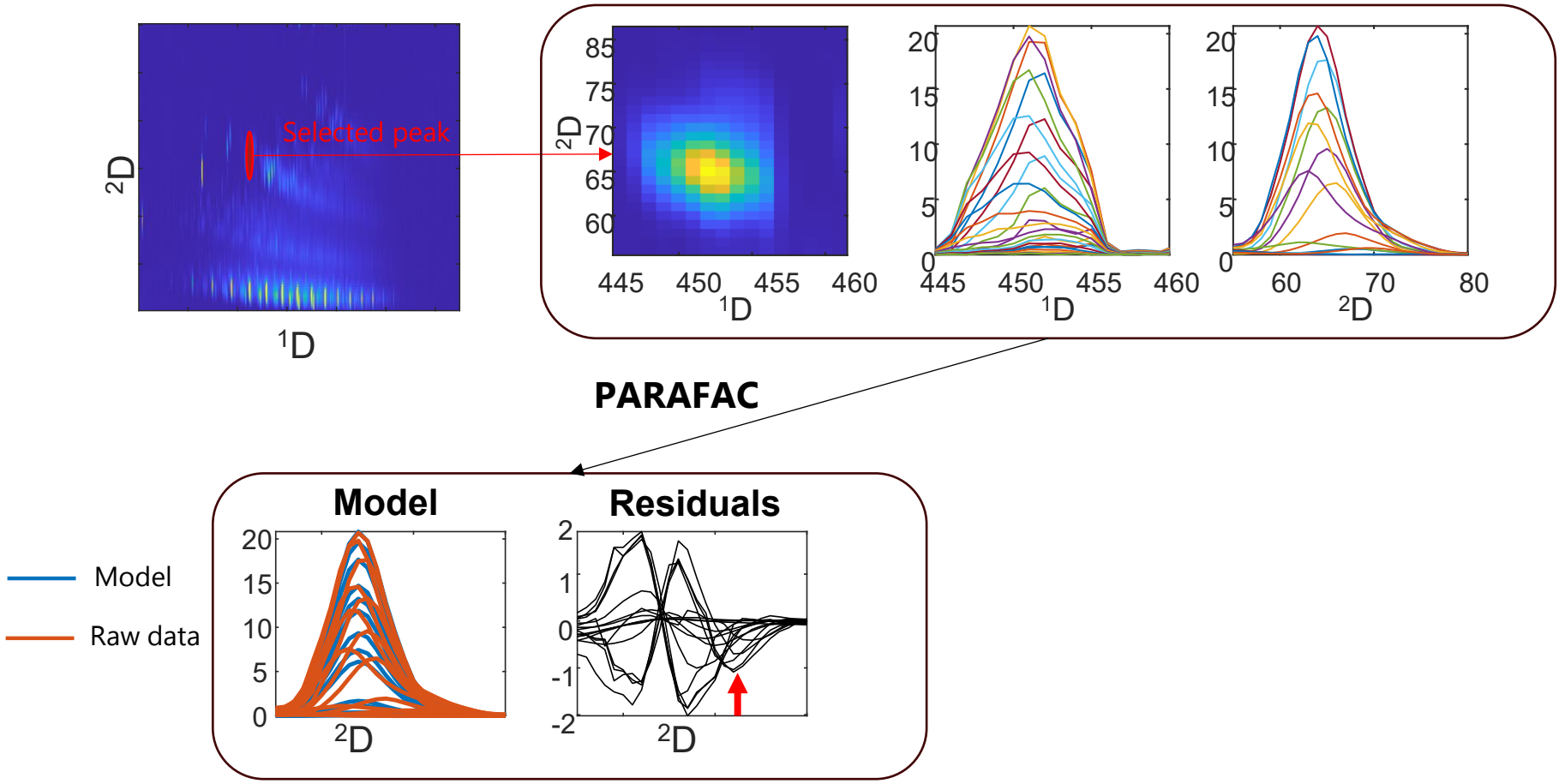
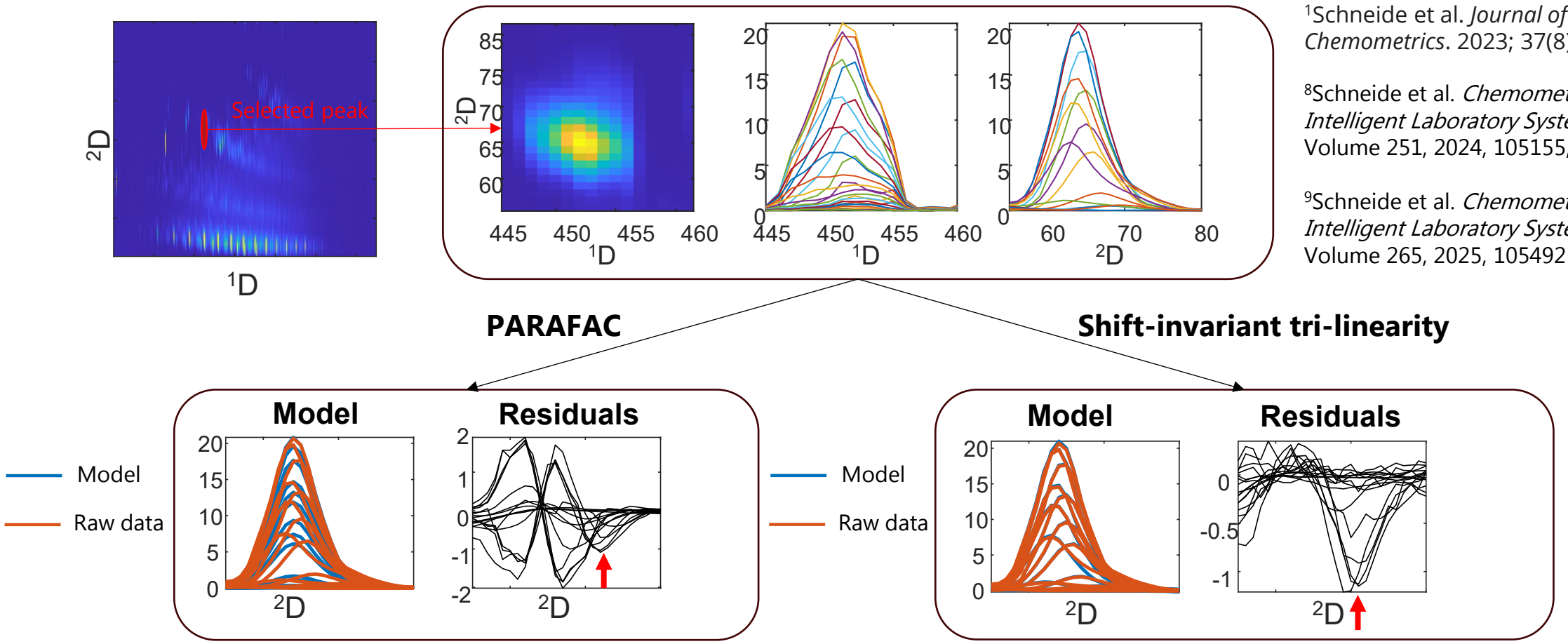


Problem: Residuals from unmodelled shift overshadow residuals from an unresolved peak

Model Properties: shift-invariant, tri-linear decomposition



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[8]Schneide et al. *Chemometrics and Intelligent Laboratory Systems*, Volume 251, 2024, 105155,

[9]Schneide et al. *Chemometrics and Intelligent Laboratory Systems*, Volume 265, 2025, 105492

Improvement: Agnostic towards retention time shift, facilitating extraction of chemically interpretable information.[1,8,9]

Model Properties: Math

- We use FFT to model shift.
- It's faster than PARAFAC2

Matricizing $\underline{\mathbf{X}}$:

$\underline{\mathbf{X}} \in \mathbb{R}^{I \times J \times K} \rightarrow \mathbf{X}_{(1)} \in \mathbb{R}^{I \times JK}$
$\underline{\mathbf{X}} \in \mathbb{R}^{I \times J \times K} \rightarrow \mathbf{X}_{(2)} \in \mathbb{R}^{IK \times J}$
$\underline{\mathbf{X}} \in \mathbb{R}^{I \times J \times K} \rightarrow \mathbf{X}_{(3)} \in \mathbb{R}^{IJ \times K}$

Tri-linearity constrained NNMF (MCR):

$\mathbf{X}_{(2)} \approx \mathbf{C}'\mathbf{S}^{\mathrm{T}}, s.t. \mathbf{C}'_r = \mathbf{u}_{1,r}\boldsymbol{\sigma}_{1,r}\mathbf{v}_{1,r}^{\mathrm{T}}$
$\mathbf{u}_1 = \mathbf{c}_r$
$\left(\boldsymbol{\sigma}_1\mathbf{v}_1^{\mathrm{T}}\right)^{\mathrm{T}} = \mathbf{f}_r$

$\mathbf{C}' \in +\mathbb{R}^{IK \times R}$
$\mathbf{S} \in +\mathbb{R}^{J \times R}$
$\mathbf{C}'_r \in +\mathbb{R}^{I \times K}$
$r \in \{1, \ldots, R\}$
$\mathbf{u}_{1,r}\boldsymbol{\sigma}_{1,r}\mathbf{v}_{1,r}^{\mathrm{T}}$ is a rank-one SVD decomposition.

$\mathbf{X}_{(2)} \approx \mathbf{C}'\mathbf{S}^{\mathrm{T}}, s.t. \left|\tilde{\mathbf{C}}'_r\right| = \mathbf{u}_{1,r}\boldsymbol{\sigma}_{1,r}\mathbf{v}_{1,r}^{\mathrm{T}}$

$\mathbf{C}' \in +\mathbb{R}^{IK \times R}$
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$\tilde{\mathbf{C}}'_r \in \mathbb{C}^{I \times K}, \tilde{\mathbf{c}}'_{r,k} = \mathcal{F}(\mathbf{c}'_{r,k})$
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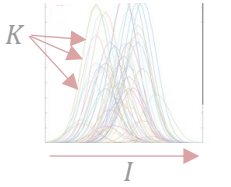
$\mathbf{u}_{1,r}\boldsymbol{\sigma}_{1,r}\mathbf{v}_{1,r}^{\mathrm{T}}$ is a rank-one SVD decomposition.

The general idea is that the amplitude spectrum $\mathbf{a}_{r,k}$ of a time-domain signal is shift-invariant!

How to make shift invariant tri-linearity [32]

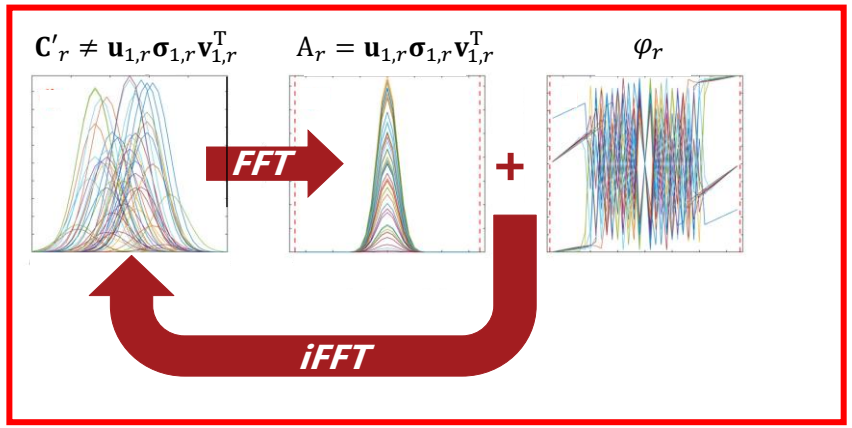
$\mathbf{C}'_r \neq \mathbf{u}_{1,r}\boldsymbol{\sigma}_{1,r}\mathbf{v}_{1,r}^{\mathrm{T}}$



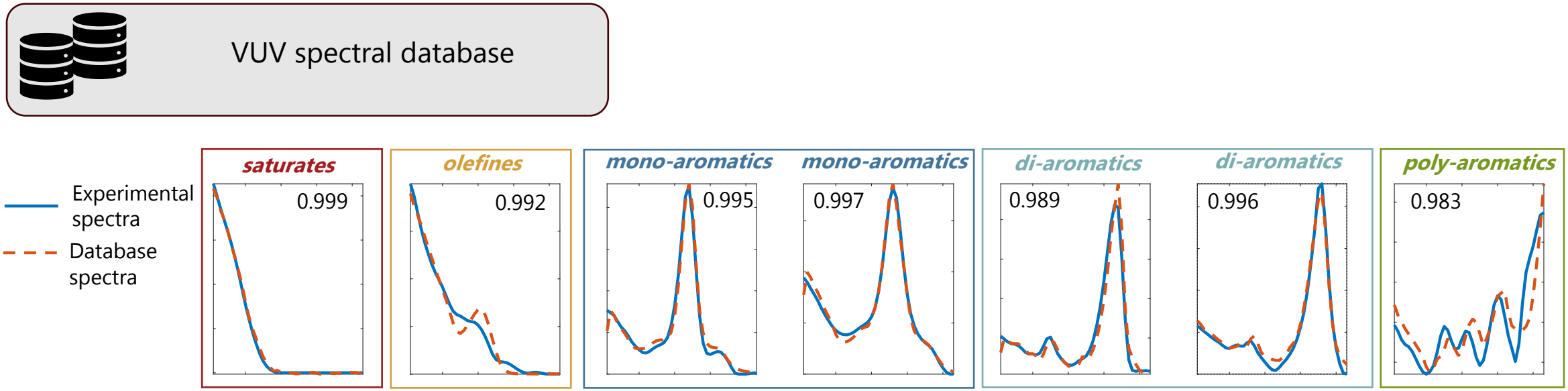
Looking at the shifted signal in the frequency domain:

$\tilde{\mathbf{c}}'_{r,k} = \mathcal{F}(\mathbf{c}'_{r,k})$
$\tilde{\mathbf{c}}'_{r,k}[i] = \mathbf{a}_{r,k}[i]e^{j\varphi_{r,k}[i]}$
$\mathbf{a}_{r,k} = \sqrt{Re\left(\tilde{\mathbf{c}}'_{r,k}\right)^2 + Im\left(\tilde{\mathbf{c}}'_{r,k}\right)^2} = \left|\tilde{\mathbf{c}}'_{r,k}\right|$
$\varphi_{r,k} = \arctan\left(\frac{Im(\tilde{\mathbf{c}}'_{r,k})}{Re(\tilde{\mathbf{c}}'_{r,k})}\right)$

[32] P.-A. Schneide, N. Gallagher, and R. Bro, Shift-invariant tri-linearity—A new model for resolving untargeted gas chromatography coupled mass spectrometry data , J. Chemometrics, 37, (2023)

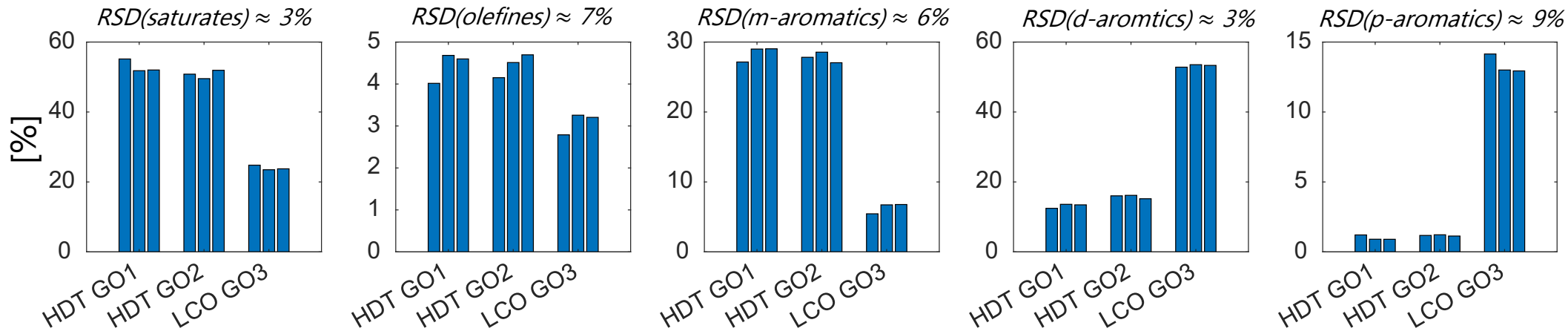


Results: Spectral similarity



Extracted VUV spectra show high similarity to reference spectra → assigning components to chemical groups.

Results: Quantitative performance



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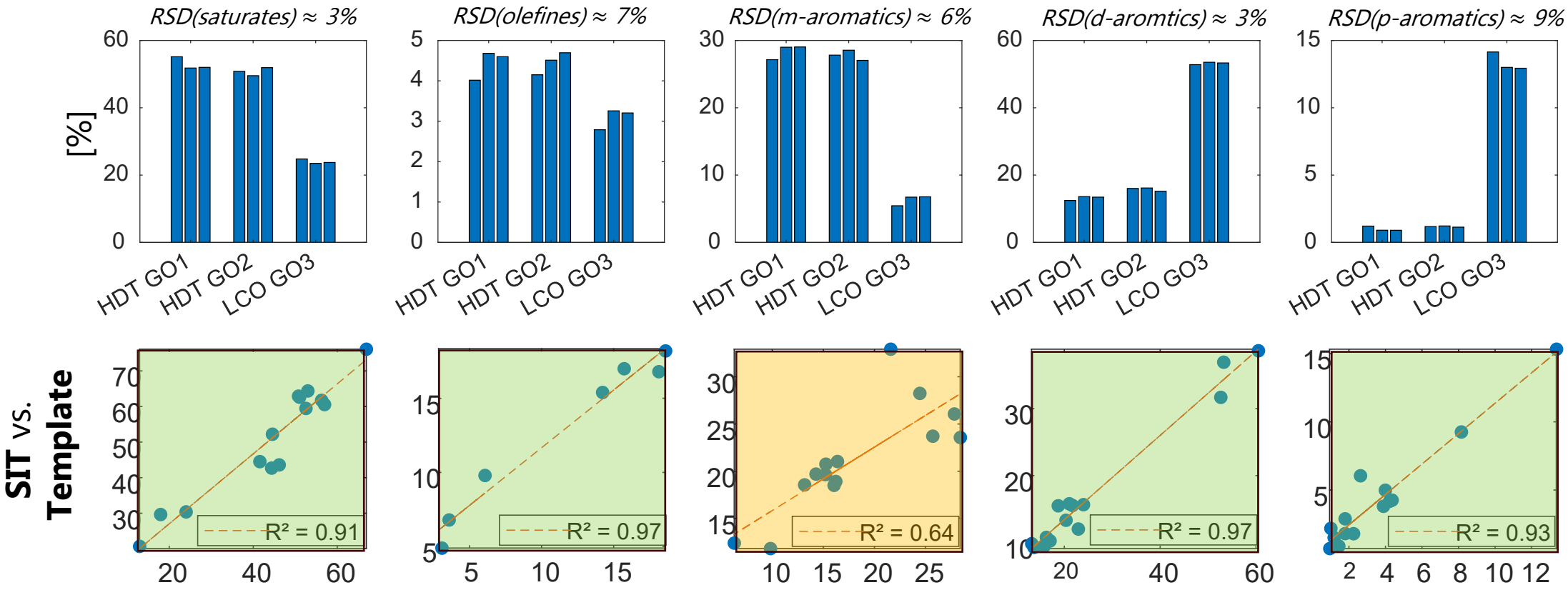

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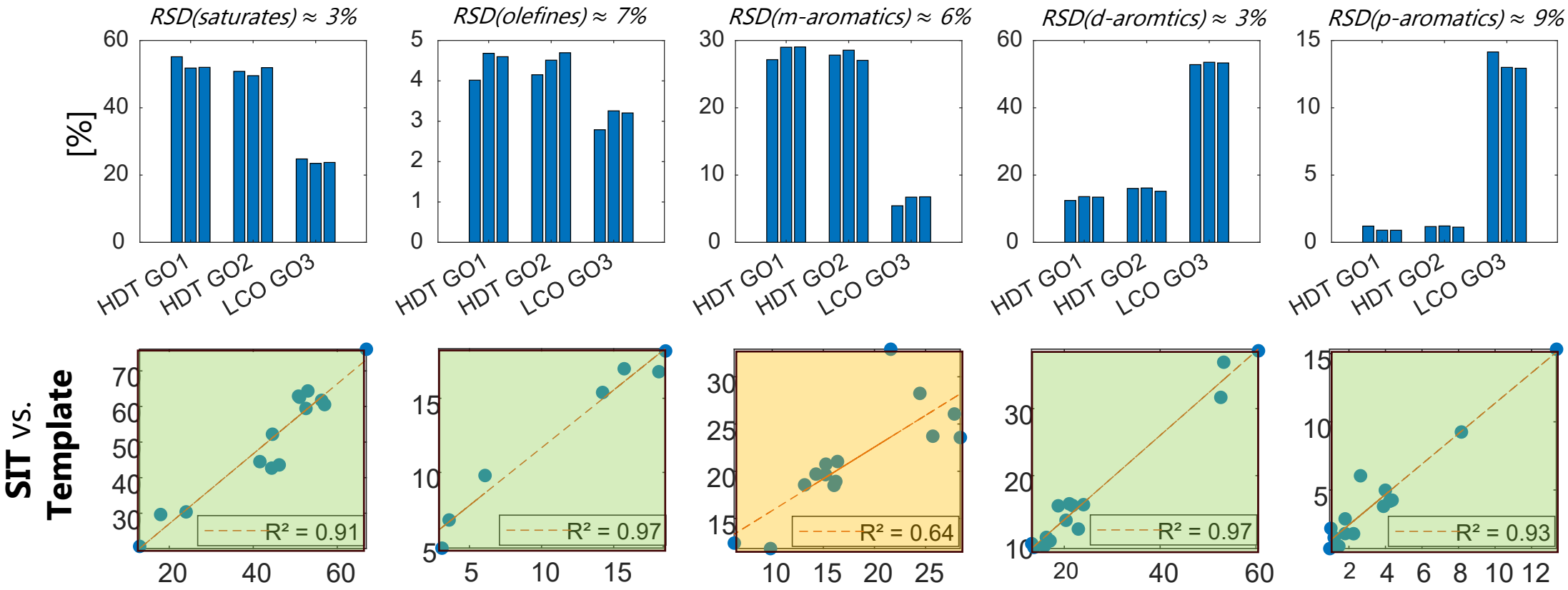

Quantitative results obtained from a 7-component model show **high repeatability for replicates** and **high correlation with template-based reference method**.

Summary

Next steps

- ❑ Running models on individual samples
- ❑ Automating number of component selection in pipeline (e.g., split-half, cross validation)
- ❑ Understand where deviations for mono-aromatics come from
- ❑ Maybe integrate pipeline in existing project, e.g. GCDuo (?) ☺☺

Thank you very much for your attention!

I am happy to connect with you:

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