Can multivariate curve resolution be used for quantitative purposes?

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Outline

- **Introduction to MCR-ALS method**
- Quantitative MCR-ALS for two-way data
- Quantitative MCR-ALS for three-way data
- Conclusions and Acknowledgements

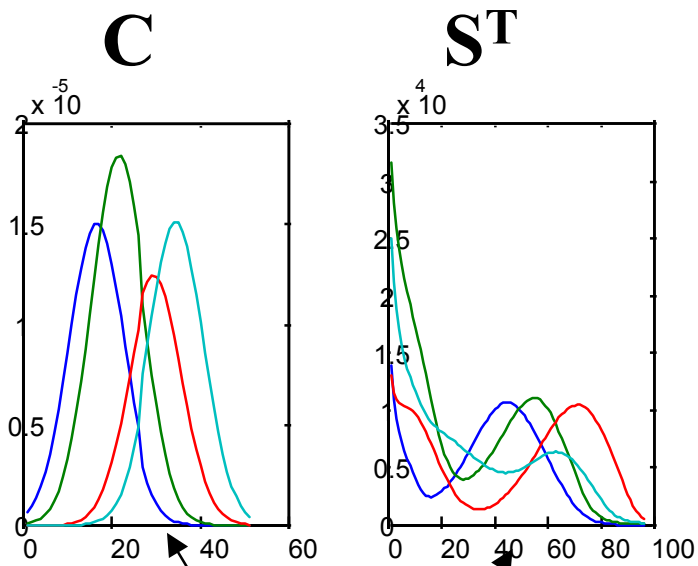
Multivariate Self Modeling Curve Resolution

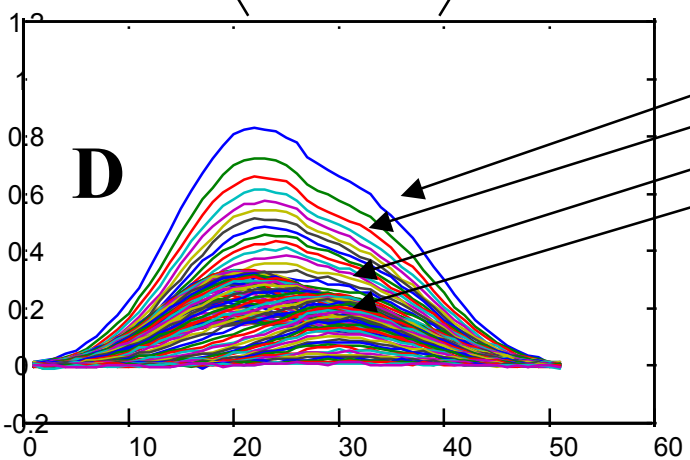
Group of techniques which intend the recovery of the response profiles (spectra, pH profiles, time profiles, elution profiles,....) of more than one component in an unresolved and unknown mixture (*obtained from evolutionary processes*) when no prior or little information is available about the nature and composition of these mixtures.

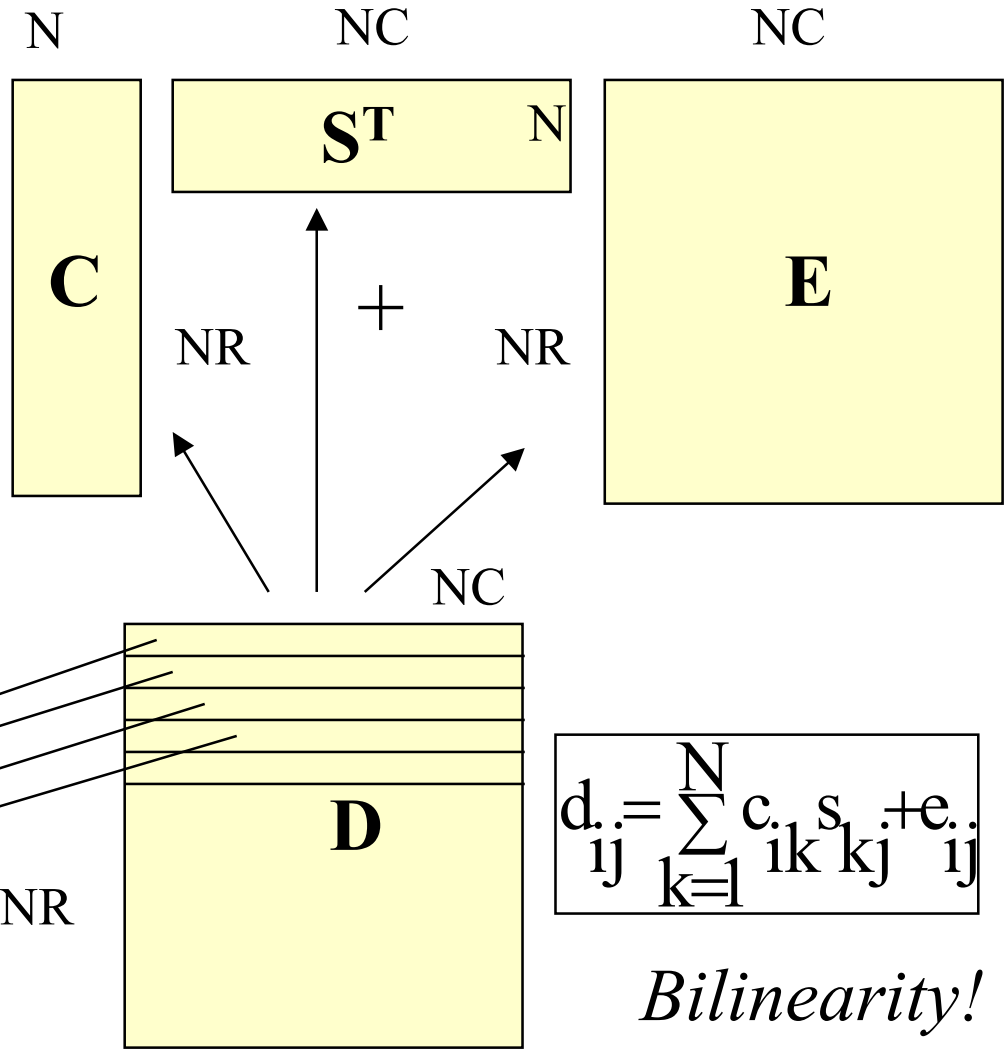
What problems can be solved with MCR?

- **Mixture Analysis problems using multivariate detection methods (spectrometry, voltampero-metry,…)**
- **Chromatographic coelution problems**
- **Industrial process monitoring and process mixture analysis problems**
- **Resolution of chemical reaction based systems (equilibria and kinetics)**
- **Resolution of macromolecular conformations; polynucleotide chemistry; protein folding**
- **Resolution of environmental pollution sources**
- .....

Multivariate Curve Resolution





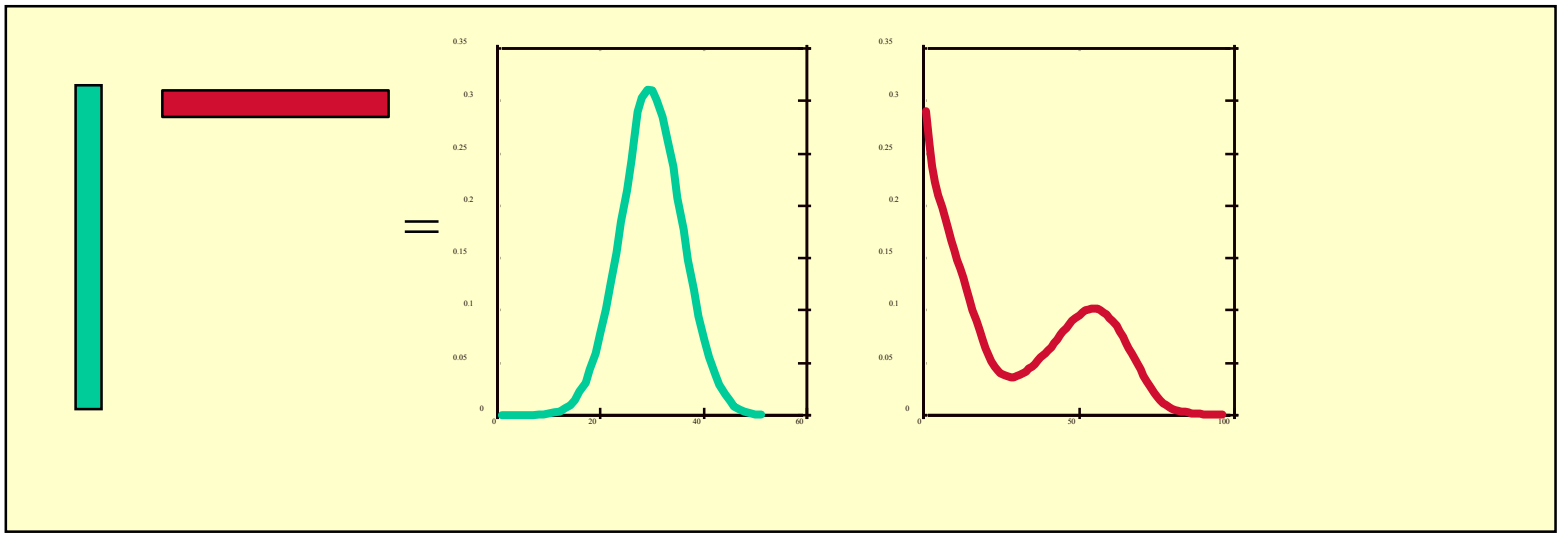


$$d_{ij} = \sum_{k=1}^{N} c_{ik} s_{kj} + e_{ij}$$

Bilinearity!

LC-DAD coelution problem

GOALS OF MCR



- **Recovery of the responses of every component (chemical species) in the different orders of measurement**

- **Is it possible to recover quantitative information?**

Rotational Ambiguities

$$\mathbf{D = C\,S^T + E = D^* + E}$$

$$\underset{(N,NC)}{\mathbf{S^T_{new}}} = \underset{(N,N)}{\mathbf{T}}\ \underset{(N,NC)}{\mathbf{S^T}}$$

$$\underset{(NR,N)}{\mathbf{C_{new}}} = \underset{(NR,N)}{\mathbf{C}}\ \underset{(N,N)}{\mathbf{T^{-1}}}$$

$$\mathbf{D^* = C\,S^T = C\,T^{-1}T\,S^T = C_{new}S^T_{new}}$$

Matrix decomposition is not unique!

T(N,N) is any non-singular matrix

Rotational freedom for any **T**

How to break (*at least partially*!) rotational ambiguities?

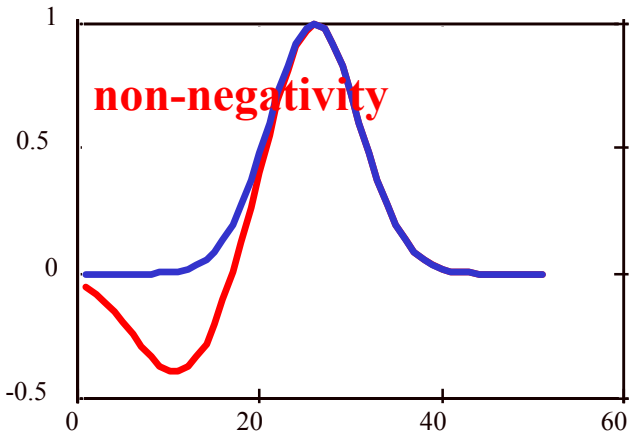
- ✓ **By using natural and shape constraints**
- ✓ By using selective variables and/or local rank information (equality constraints)
- ✓ **By matrix augmentation (three-way data analysis)**

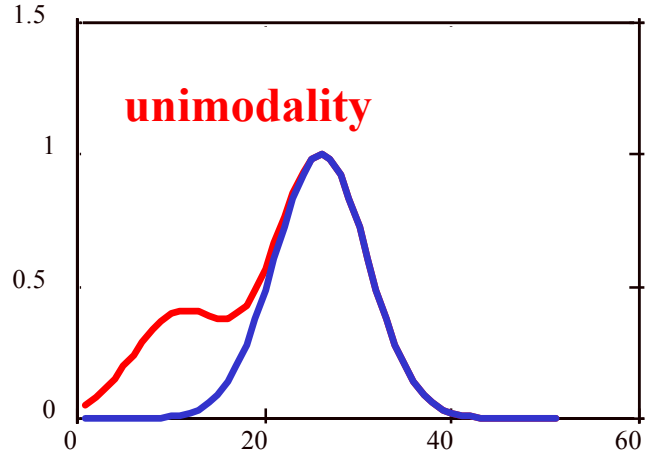
Tauler R, Izquierdo-Ridorsa A. and Casassas E., Chemom. Intell. Lab. Systems, 1993, 18, 293-300.

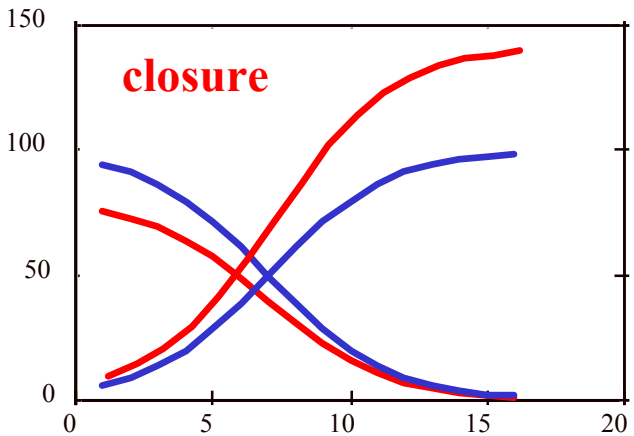
Tauler R. , Smilde A. and Kowalski B. R., J.of Chemometrics, 1995,9,31

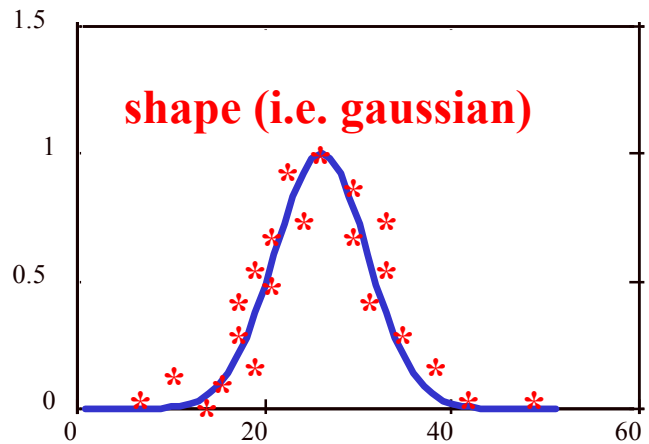
Tauler R. Chemom.Intell.Lab.Sys., 1995, 30, 133

Natural and shape constraints (graphical explanation)





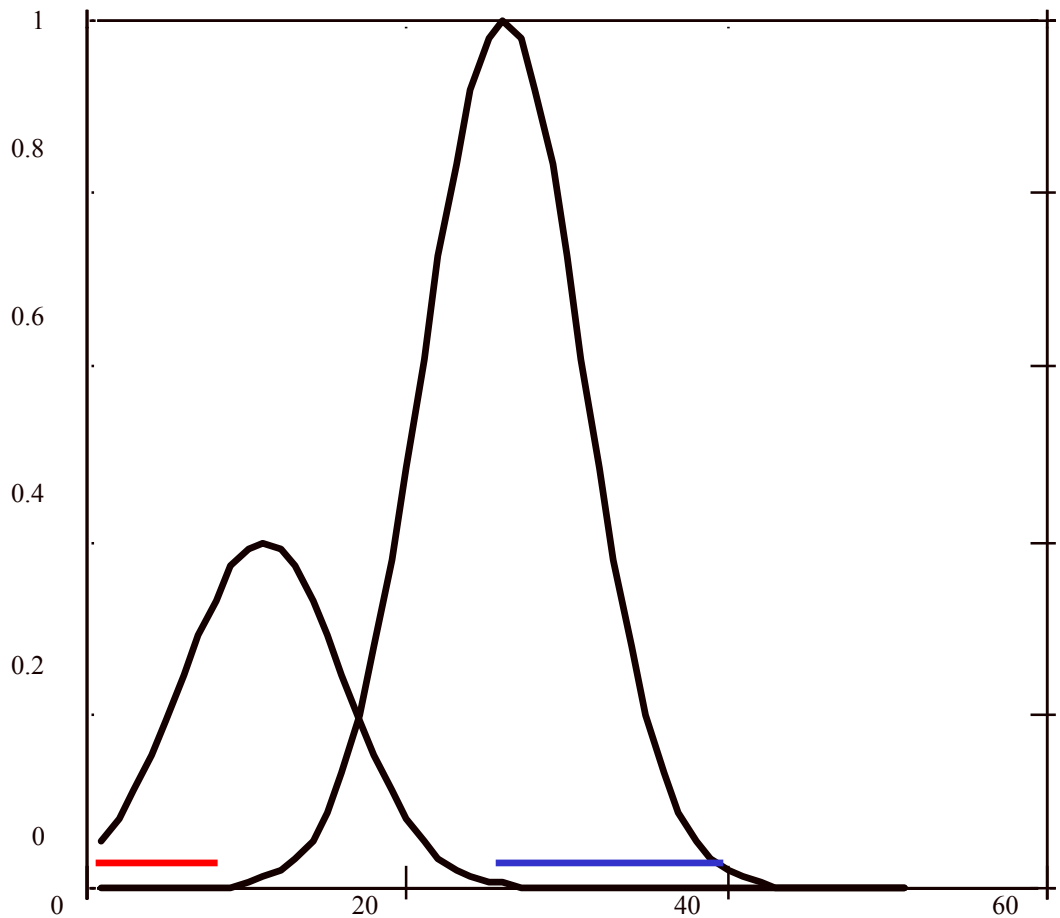




Selectivity constraints

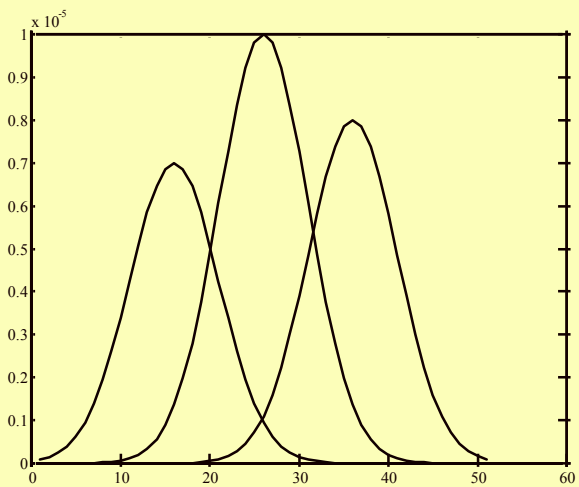
Selective regions are regions where only one component is present

In these regions rotational ambiguities are solved easily

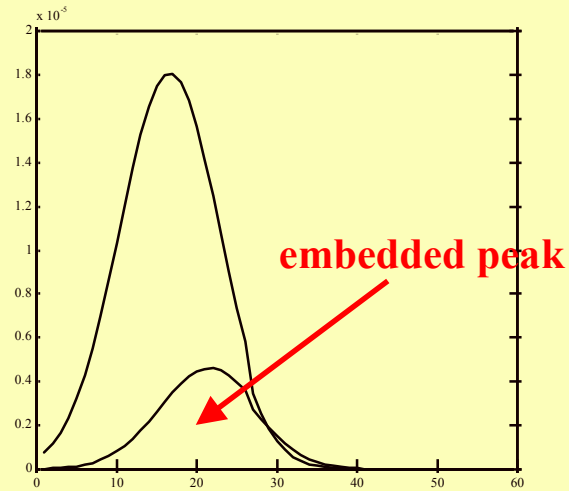


Resolution Based on Local Rank Information

Rolf Manne, Chemometrics and Intelligent Laboratory Systems, 27, 1995, 89-94



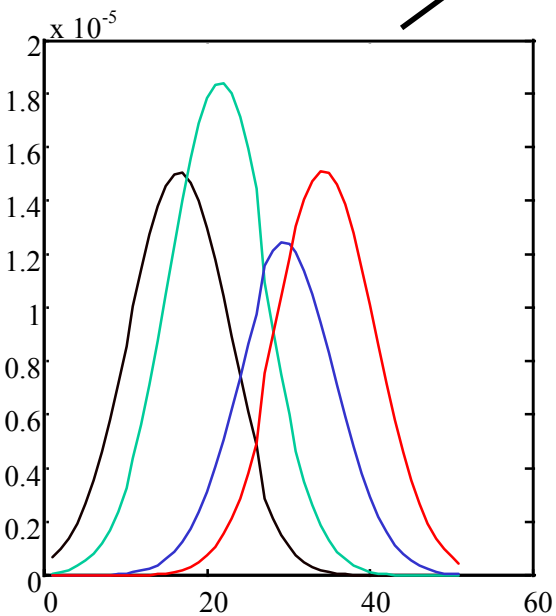
this system may be resolved without ambiguities

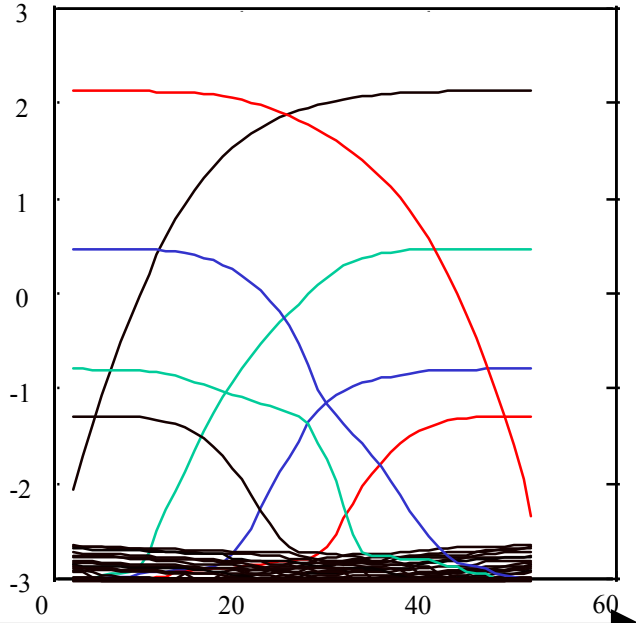


this system cannot be resolved without ambiguities

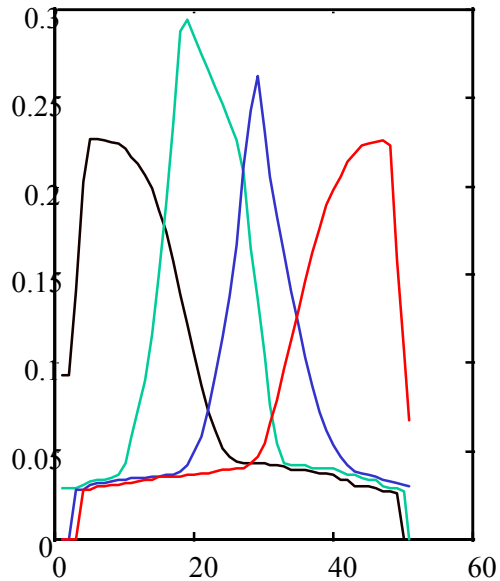
Selectivity and Local Rank detection

EFA

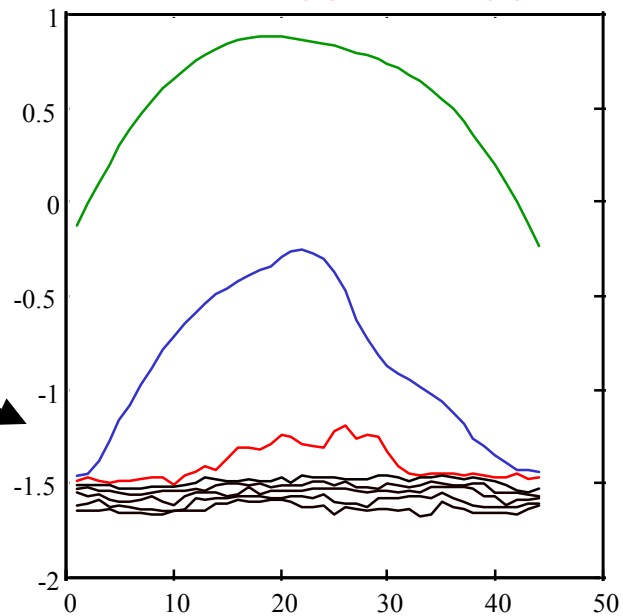




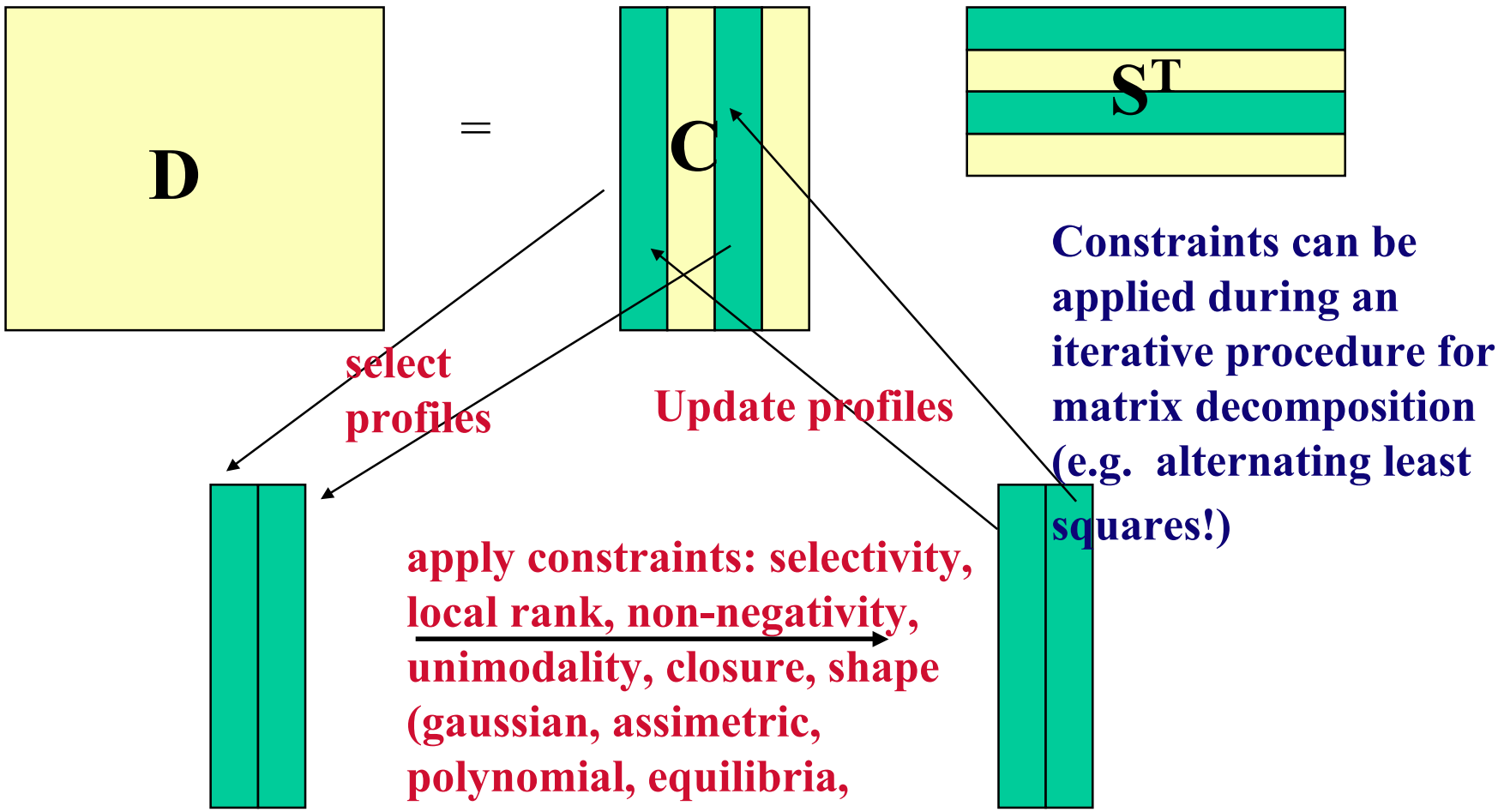
initial estimates



FSMWEFA



Application of constraints



Multivariate Curve Resolution Alternating Least Squares (MCR-ALS)

- Initial estimates of C or S^T are obtained from EFA or from pure variable detection methods
- **Optional constraints are applied at each ALS iteration !**

Alternating Least Squares (ALS) solution

$$\mathbf{D} = \mathbf{C}\,\mathbf{S}^{\mathbf{T}} + \mathbf{E}$$

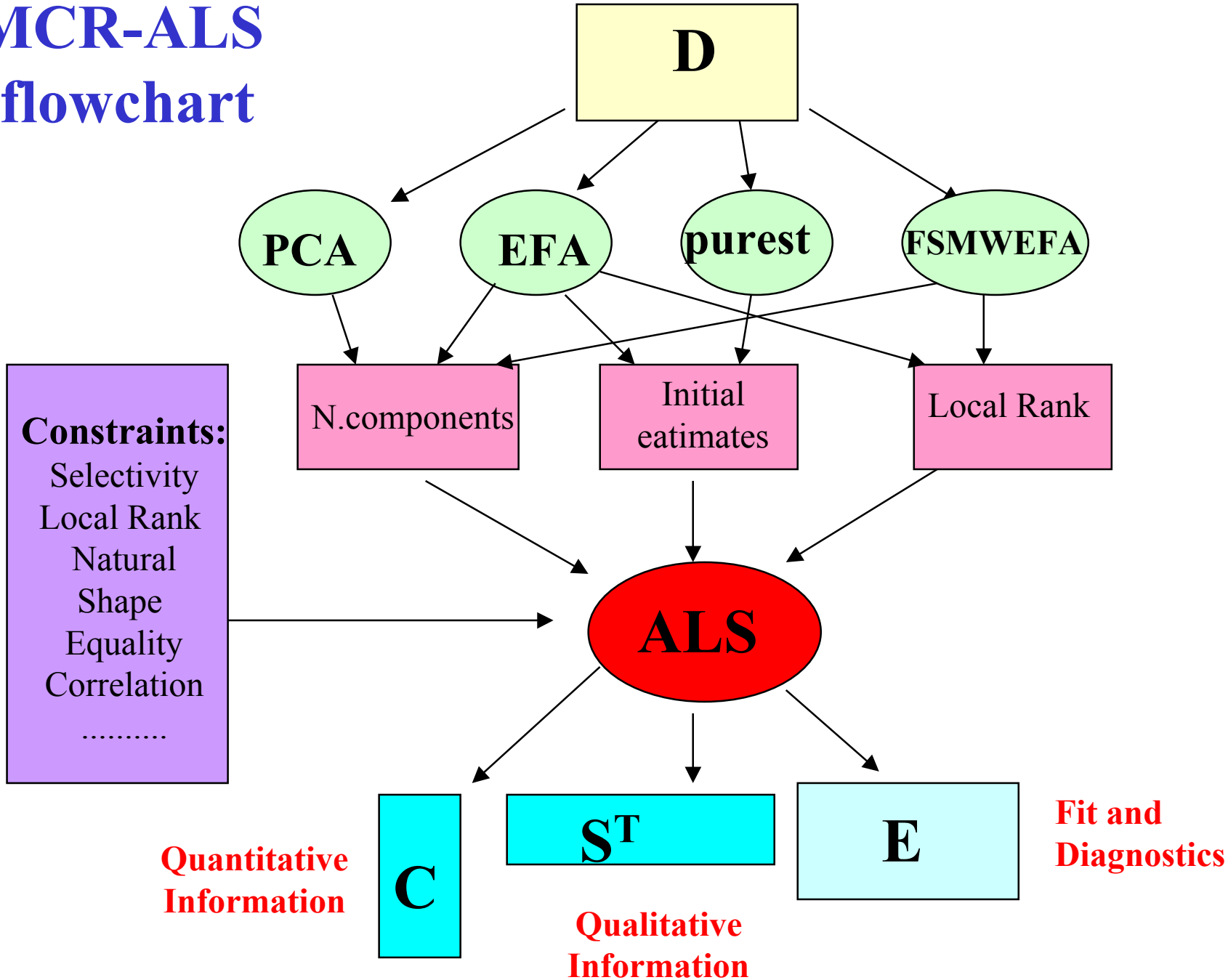
$$1)\ \min_{\mathbf{S}^{\mathbf{T}}\ constrain} \left\| \mathbf{D} - \mathbf{C}\,\mathbf{S}^{\mathbf{T}} \right\|$$

$$\mathbf{C}^{+}\,\mathbf{D} = (\mathbf{S}^{\mathbf{T}})_{uncons} \Rightarrow_{constrain} \mathbf{S}^{\mathbf{T}}$$

$$2)\ \min_{\mathbf{C}\ constrain} \left\| \mathbf{D} - \mathbf{C}\,\mathbf{S}^{\mathbf{T}} \right\|$$

$$\mathbf{D}\,(\mathbf{S}^{\mathbf{T}})^{+} = (\mathbf{C})_{uncons} \Rightarrow_{constrain} \mathbf{C}$$

MCR-ALS flowchart



Quantitative Information from MCR and Scale (intensity) Ambiguities:

$$d_{ij} = \sum_n c_{in} \; s_{nj} = \sum_n \mathrm{k} c_{in} \; \frac{1}{\mathrm{k}} s_{nj}$$

k is arbitrary. How to find the right one?

- Once rotational ambiguities are solved for the species of interest (analyte), how to break intensity ambiguities?
- Is it possible to recover quantitative information using MCR-ALS?

Solving intensity ambiguities in MCR-ALS

Two-way data:

In the analysis of a single data matrix intensity-scale ambiguities can be solved using:

a) scale/normalization/closure constraints

b) external knowledge and equality/correlation constraints

Three-way data

In the simultaneous analysis of multiple data matrices intensity/scale ambiguities can be solved

a) in relative terms (directly)

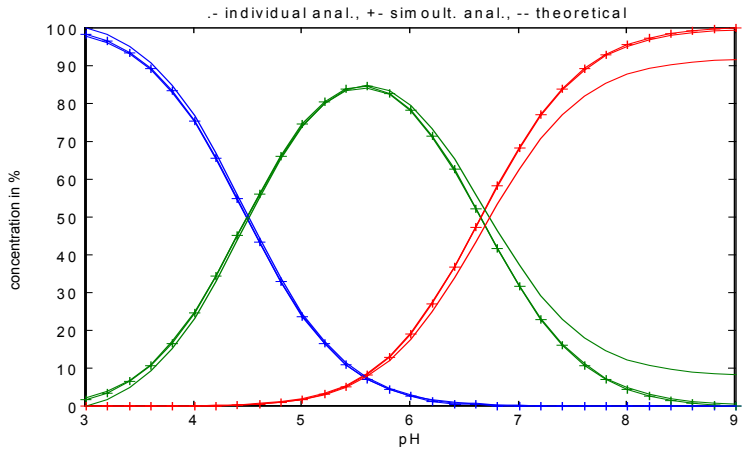
b) in absolute terms using external knowledge

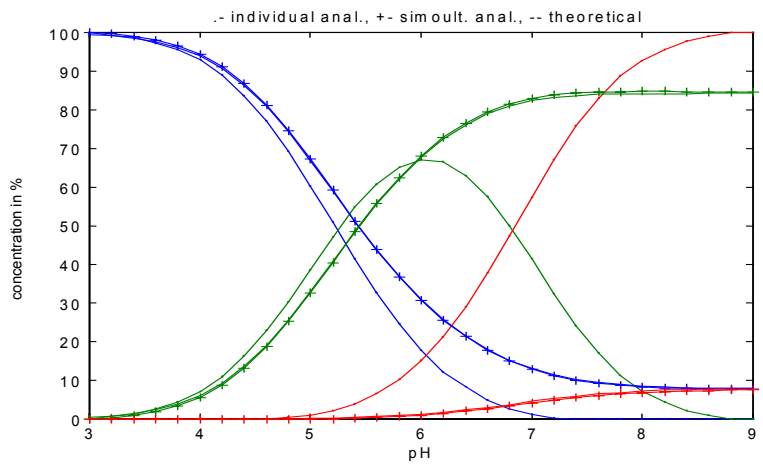
Outline

- Introduction to quantitative MCR-ALS method
- **Quantitative MCR-ALS for two-way data**
- Quantitative MCR-ALS for multiway data
- Conclusions and Acknowledgements

Solving intensity ambiguities using normalization/closure constraints

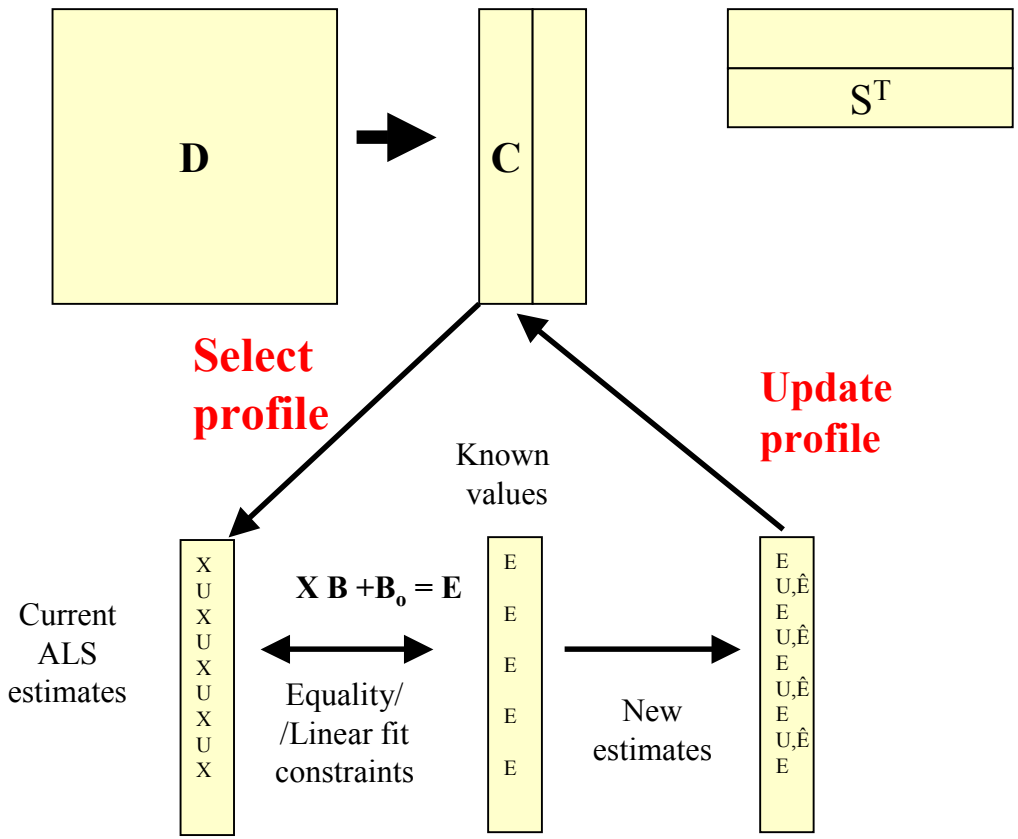
When rotational ambiguities are totally solved, closure constraints give the correct quantitative relationships between the components involved in the closure constraint





Solving intensity ambiguities using equality/ correlation constraints

ALS decomposition

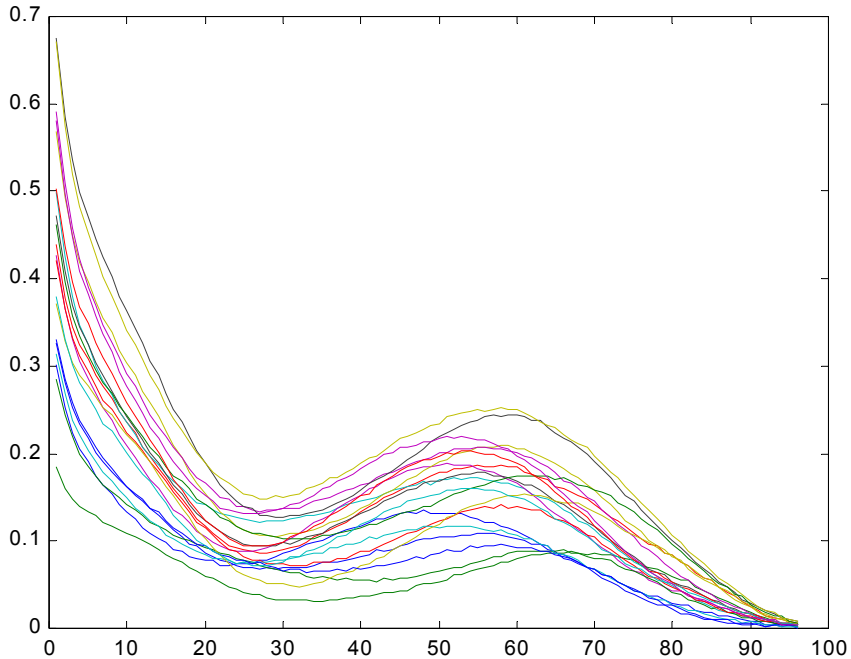


During the ALS decomposition, concentration profiles may be updated using equality constraints or accordingly to their correlation with previously known values (E)

Equality constraints: update X values by corresponding known E values

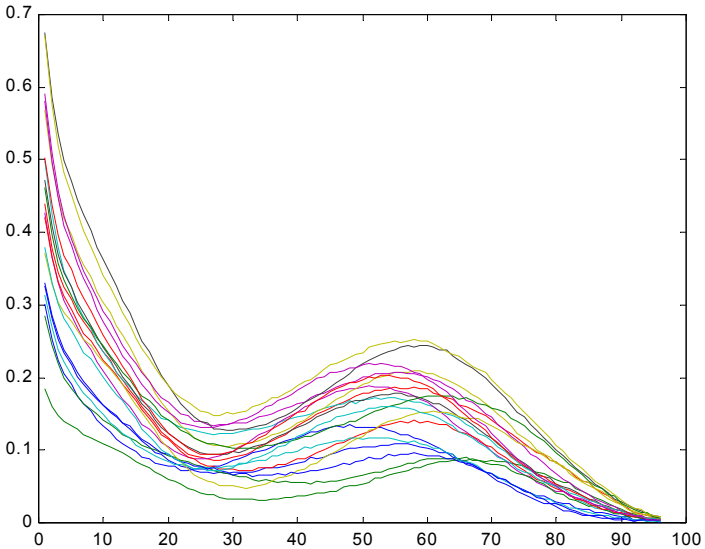
Correlation constraints: update X and U values by calculated Ê values deduced from correlation with known K values, $\mathbf{X\,B + B_0 = E;\ U\,B + B_0 = \hat{E}}$

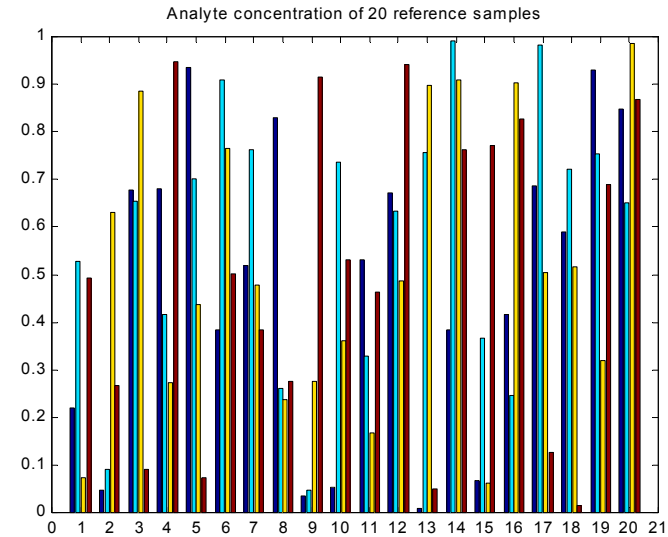
Example of application of equality constraints to two-way data (simulated data study



Problem to solve: predict the concentration of one nucleic base in a mixture of four of them (one analyte in the presence of three interferents)

Building the calibration data set



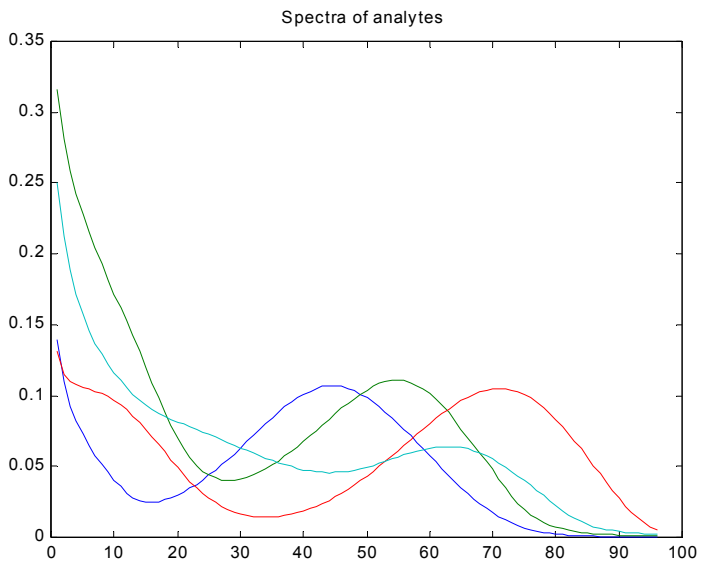


20 calibration samples with random concentrations of 4 bases between 0-1

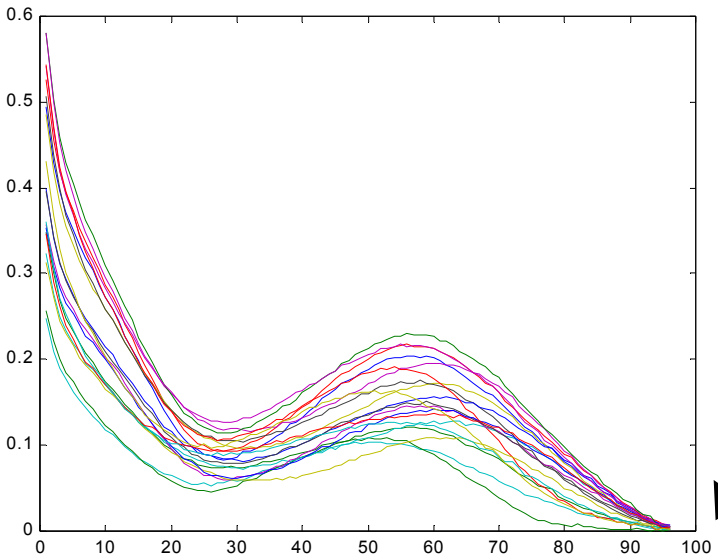
lof (%) = 0.6458

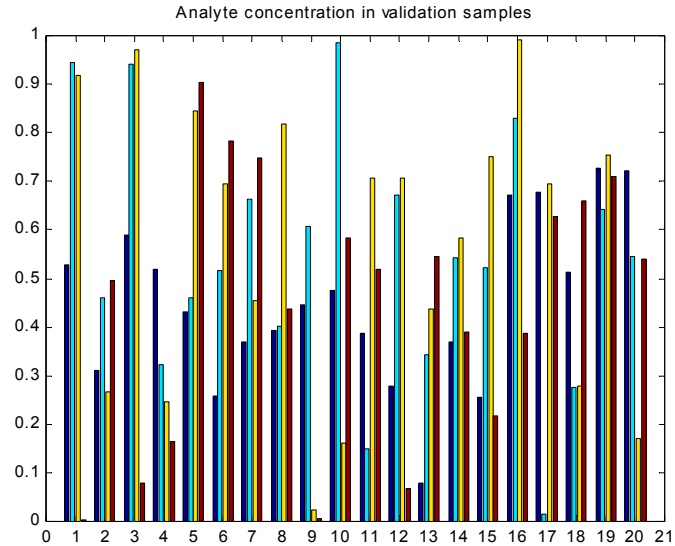
R^2 = 0.99996

sd white noise 0.001 units



Building the validation data set



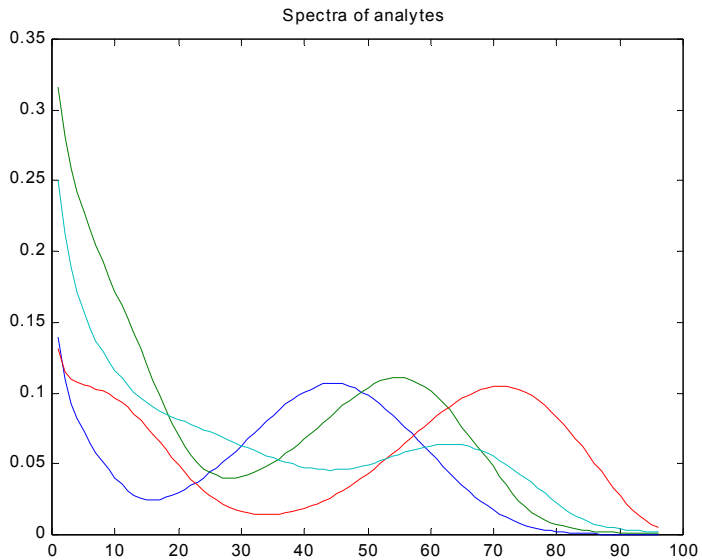


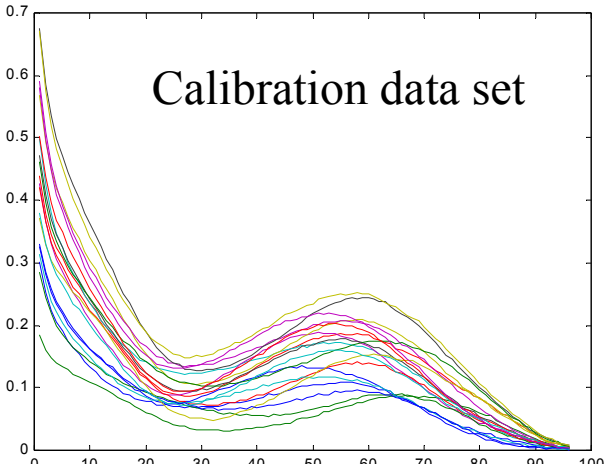
20 validation samples with random concentrations of 4 bases between 0-1

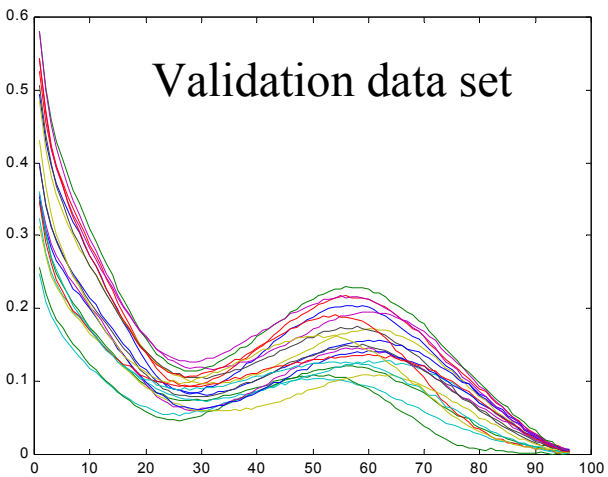
lof (%) = 0.679

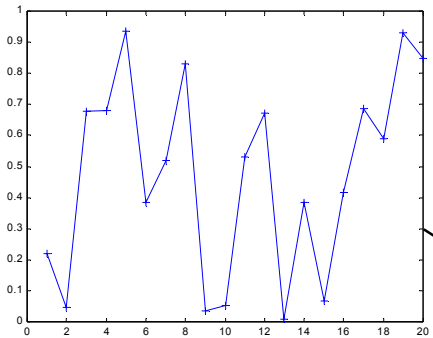
R^2 = 0.99995

sd white noise 0.001 units





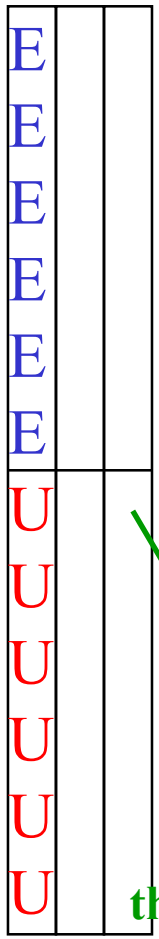




constraints: 1) non-negativity
2) concentration of the analyte in the calibration set (equality constraint)

Built a MCR-ALS Model

?????
What is the concentration of analyte in the validation data set?



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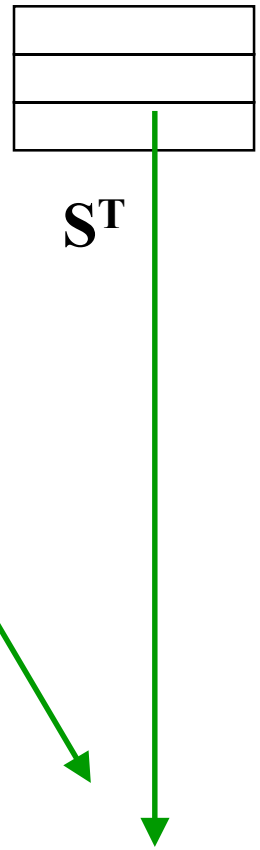


S^T

the other profiles are only constrained to be non-negative

Proposed strategy/procedure:

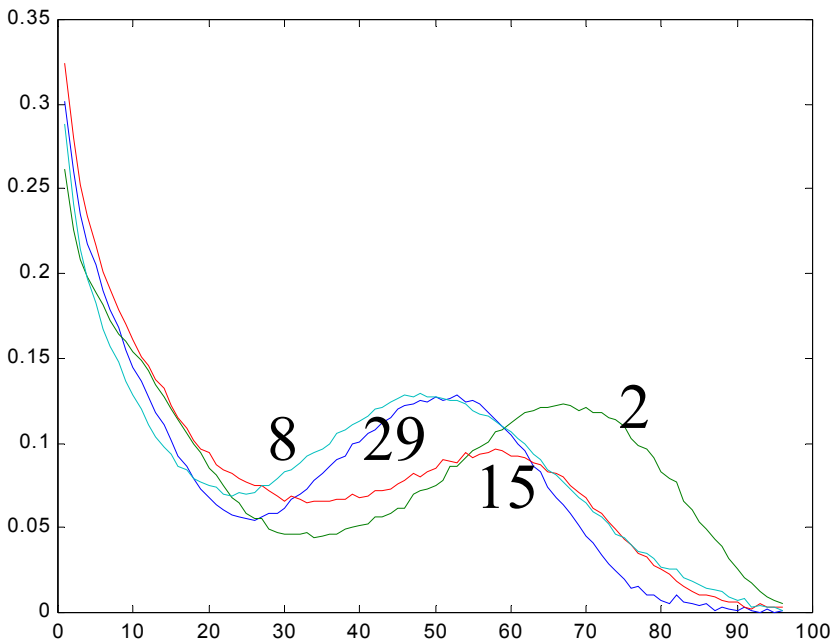
Apply MCR-ALS using the following constraints:

- ✓non-negativity
- ✓known concentrations of analyte in the calibration data set (equality/correlation constraints)

Initial estimates for ALS optimization:

- **✓from 'purest' spectra of the data set (using an approach similar to SIMPLISMA)**

Initial estimations of pure spectra are obtained from the purest samples (key set) number 2, 15, 8 and 29

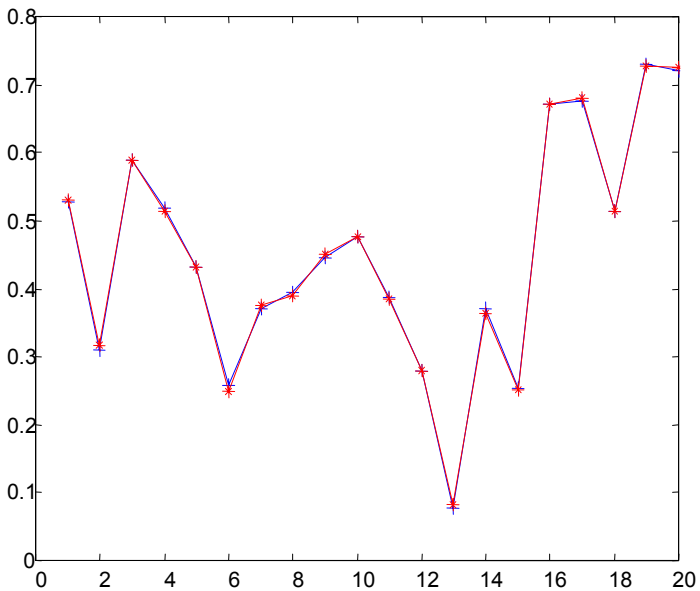


Correlation between true and initially estimated spectra

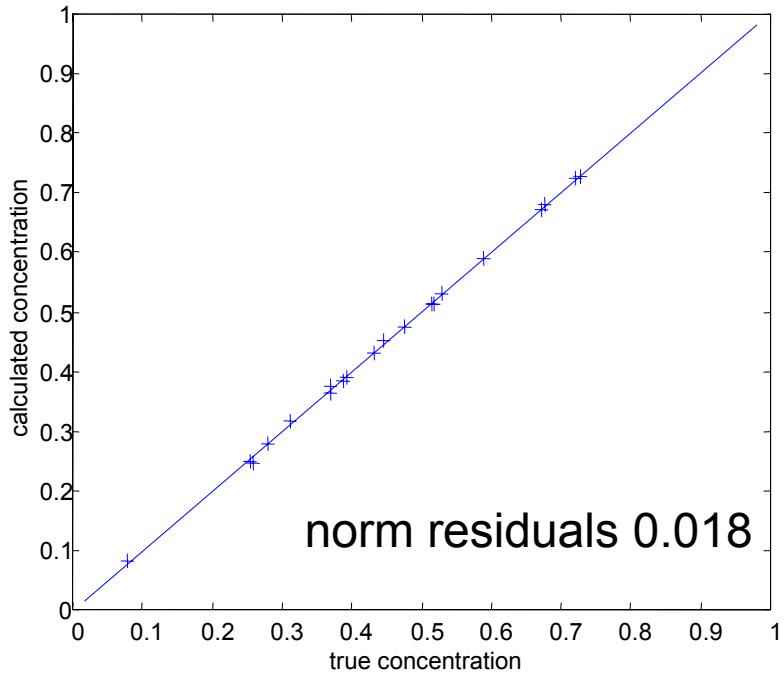
	analyte			
spectrum	1	2	3	4
2	0.0470	0.0920	**0.6316**	0.2661
8	**0.8310**	0.2625	0.2378	0.2771
15	0.0668	0.3653	0.0606	**0.7702**
29	0.4469	**0.6056**	0.0221	0.0063

MCR-ALS concentration prediction for analyte 1

predicted (red) versus
true (blue) concentrations of analyte 1



y=-0.0023+1.0044x



RECOVERED CONCENTRATIONS FOR ANALYTE 1 IN THE VALIDATION DATA SET USING MCR-ALS AND PLS (without any data pretreatment)

	CONCENTRATIONS			% Error	
	ALS	PLS	'true'	ALS	PLS
1	0.5295	0.5298	0.5285	0.1708	0.2405
2	0.3159	0.3160	0.3107	1.6500	1.7056
3	0.5882	0.5885	0.5881	0.0127	0.0646
4	0.5144	0.5142	0.5181	-0.7200	-0.7459
5	0.4317	0.4316	0.4308	0.1917	0.1650
6	**0.2478**	**0.2478**	**0.2588**	**-4.2732**	**-4.2555**
7	0.3759	0.3761	0.3702	1.5321	1.5840
8	0.3898	0.3898	0.3930	-0.8076	-0.8169
9	0.4505	0.4501	0.4469	0.8052	0.7304
10	0.4763	0.4767	0.4759	0.0850	0.1647
11	0.3840	0.3838	0.3878	-0.9876	-1.0488
12	0.2783	0.2786	0.2793	-0.3624	-0.2369
13	**0.0818**	**0.0819**	**0.0783**	**4.5376**	**4.5876**
14	0.3646	0.3647	0.3697	-1.3929	-1.3524
15	0.2501	0.2503	0.2539	-1.5048	-1.4455
16	0.6703	0.6704	0.6718	-0.2247	-0.2005
17	0.6812	0.6820	0.6762	0.7274	0.8485
18	0.5132	0.5129	0.5139	-0.1471	-0.1981
19	0.7268	0.7267	0.7286	-0.2542	-0.2584
20	0.7247	0.7245	0.7208	0.5459	0.5220

Formulas for Results Validation

RMSEP = Root Mean Square Error in Prediction

$$\text{RMSEP} = \sqrt{\frac{\sum_i \sum_j (\hat{c}_{ij} - c_{ij})^2}{NR}}$$

SEP = Standard Error in Prediction (bias corrected)

$$\text{SEP} = \sqrt{\frac{\sum_i \sum_j (\hat{c}_{ij} - c_{ij} - \text{bias})^2}{NR - 1}}$$

bias = systematic deviations

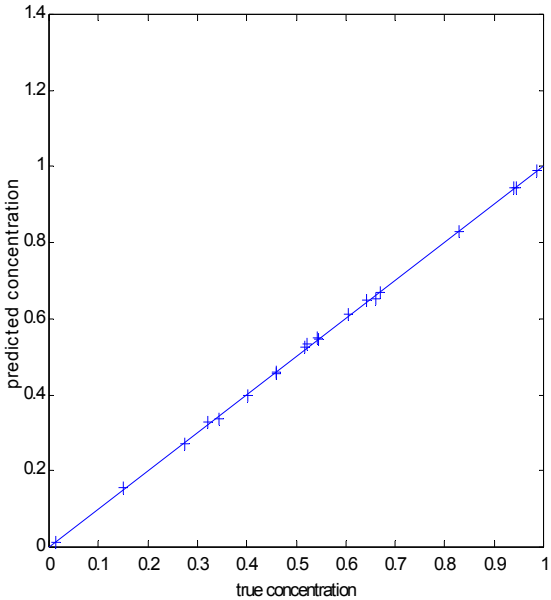
$$\text{bias} = \sqrt{\frac{\sum_i \sum_j (\hat{c}_{ij} - c_{ij})}{NR}}$$

RE = Overal % relative error in the prediction

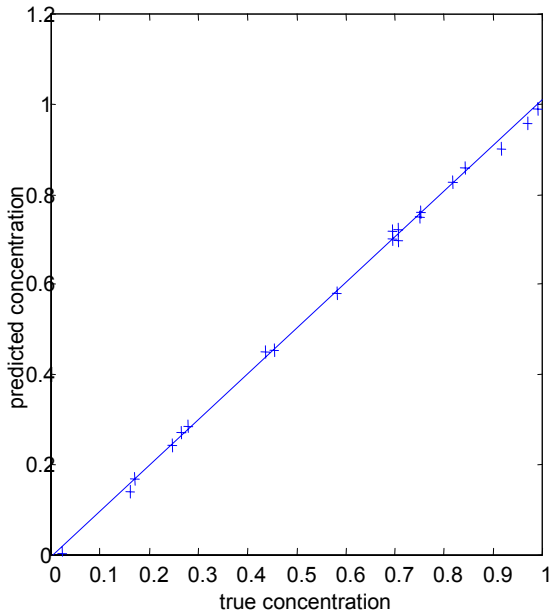
$$\text{RE} = 100 \sqrt{\frac{\sum_i \sum_j (\hat{c}_{ij} - c_{ij})^2}{\sum_i \sum_j (c_{ij})^2}}$$

MCR-ALS concentration prediction for other analytes

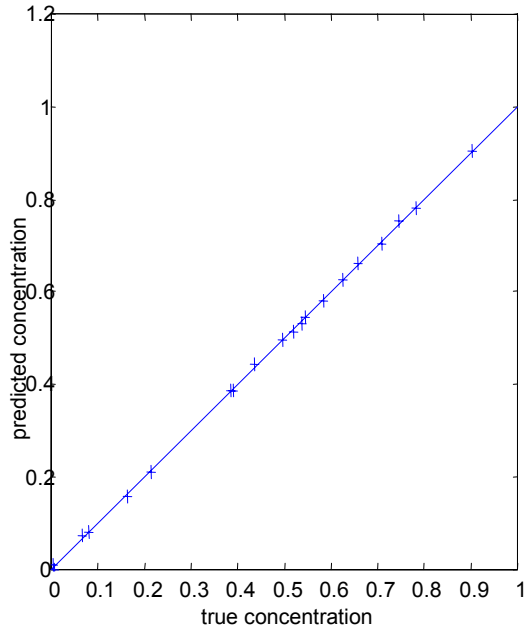
Analyte 2



Analyte 3

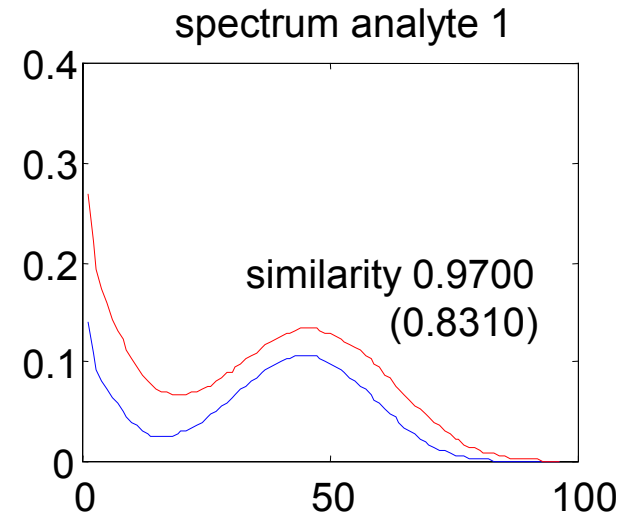


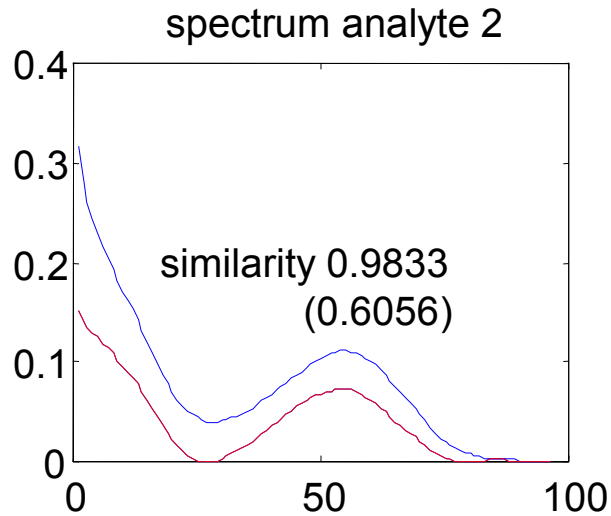
Analyte 4

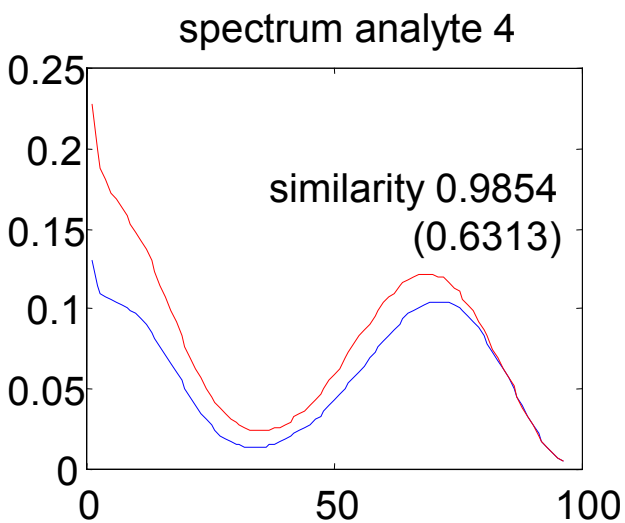


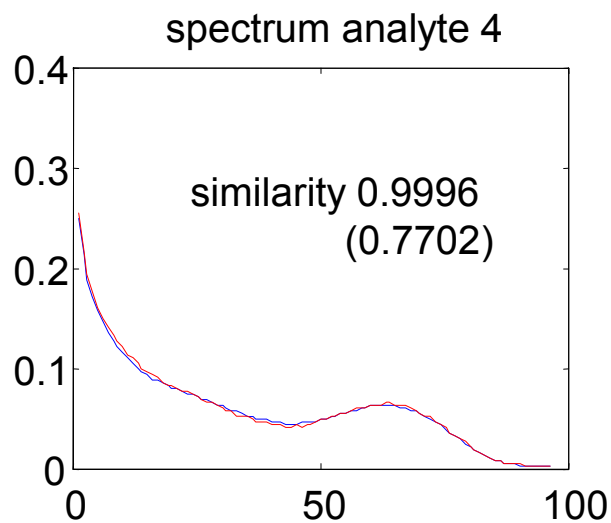
analyte	RMSEP	SEP	bias	RE %	slope	offset	corcoef	sdres
1.0000	0.0041	0.0042	0.0003	1.7714	1.0044	-0.0023	0.9997	0.0179
2.0000	0.0050	0.0050	-0.0012	1.4081	1.0019	0.0002	0.9998	0.0217
3.0000	0.0117	0.0120	-0.0001	2.8427	1.0092	-0.0052	0.9992	0.0511
4.0000	0.0046	0.0047	0.0007	1.7384	1.0010	-0.0011	0.9999	0.0205

MCR-ALS spectra prediction









In parenthesis correlation (similarity) respect initial estimates

red predicted, blue 'true'

Example of application (real data study):

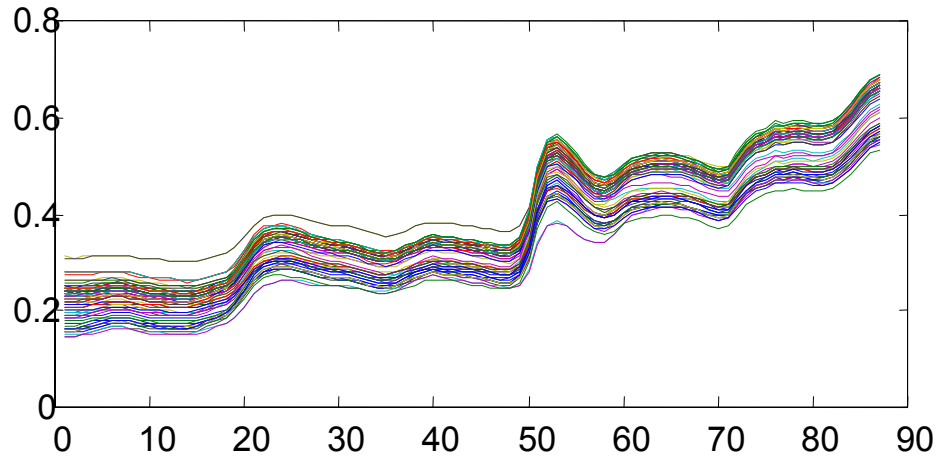
Quantitation of forrage samples using NIR spectroscopy and MCR-ALS with known concentration constraints

Problem to solve: Determination of moisture and protein content using a calibration and a validation real data sets

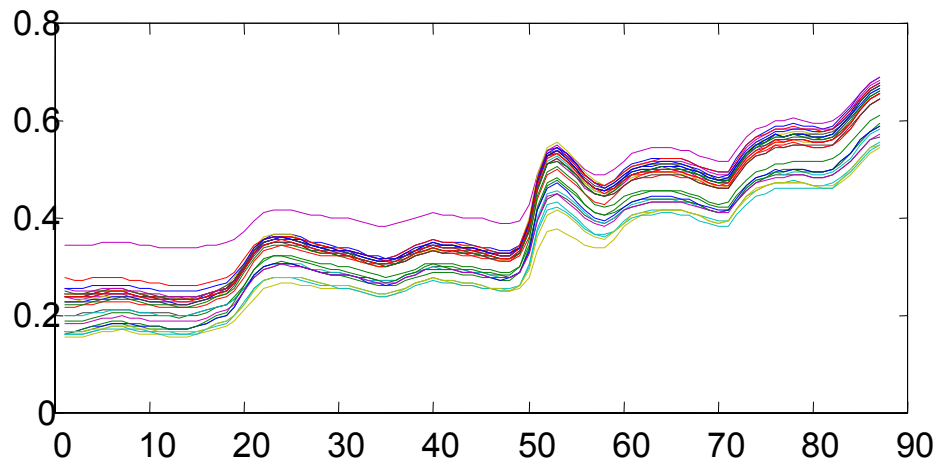
Comparison with results obtained using PLS multivariate calibration

Example of application: NIR real data

Calibration data set
86 samples
87 wavelengths
no-pretreatrment

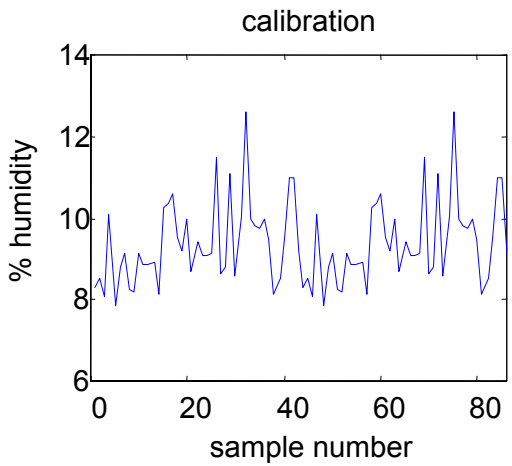


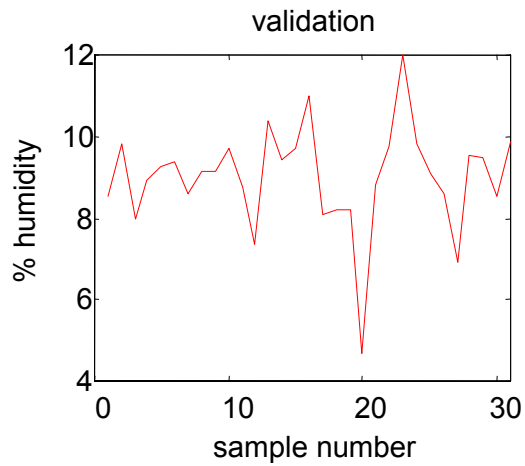
Validation data set
31 samples
87 wavelengths
no-pretreatment



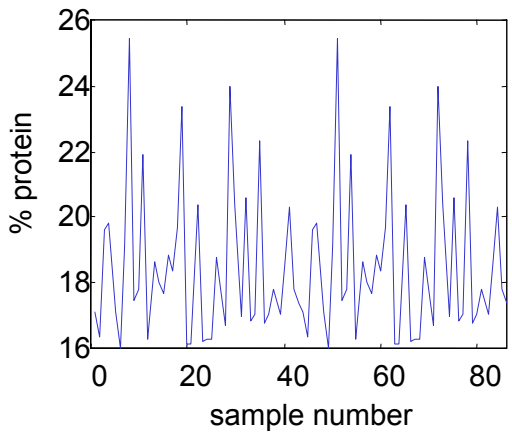
Determination of moisture and protein

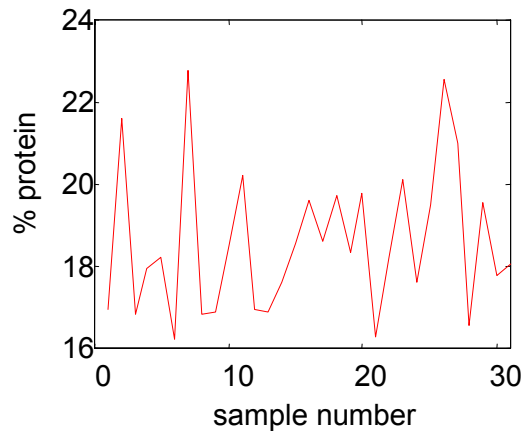
Moisture concentrations in the calibration and validation data sets





Protein concentrations in the calibration and validation data sets





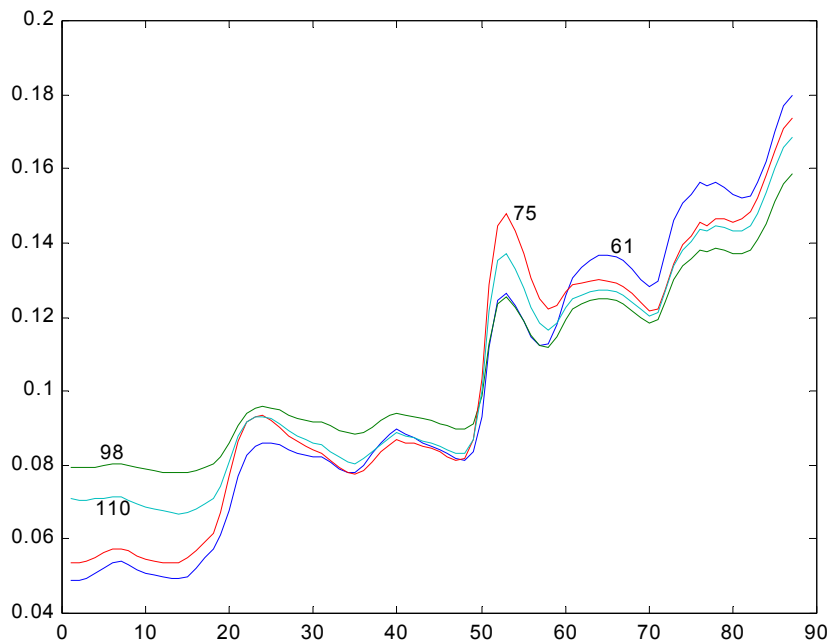
NIR Data structure:

Singular Values	*PCA lof*
39.8310	**2.68%**
0.9829	**1.06%**
0.3629	**0.55%**
0.1889	**0.28%**
0.0736	0.21%
0.0562	0.15%
0.0334	0.13%
0.0314	0.10%
0.0227	0.09%
0.0205	0.07%

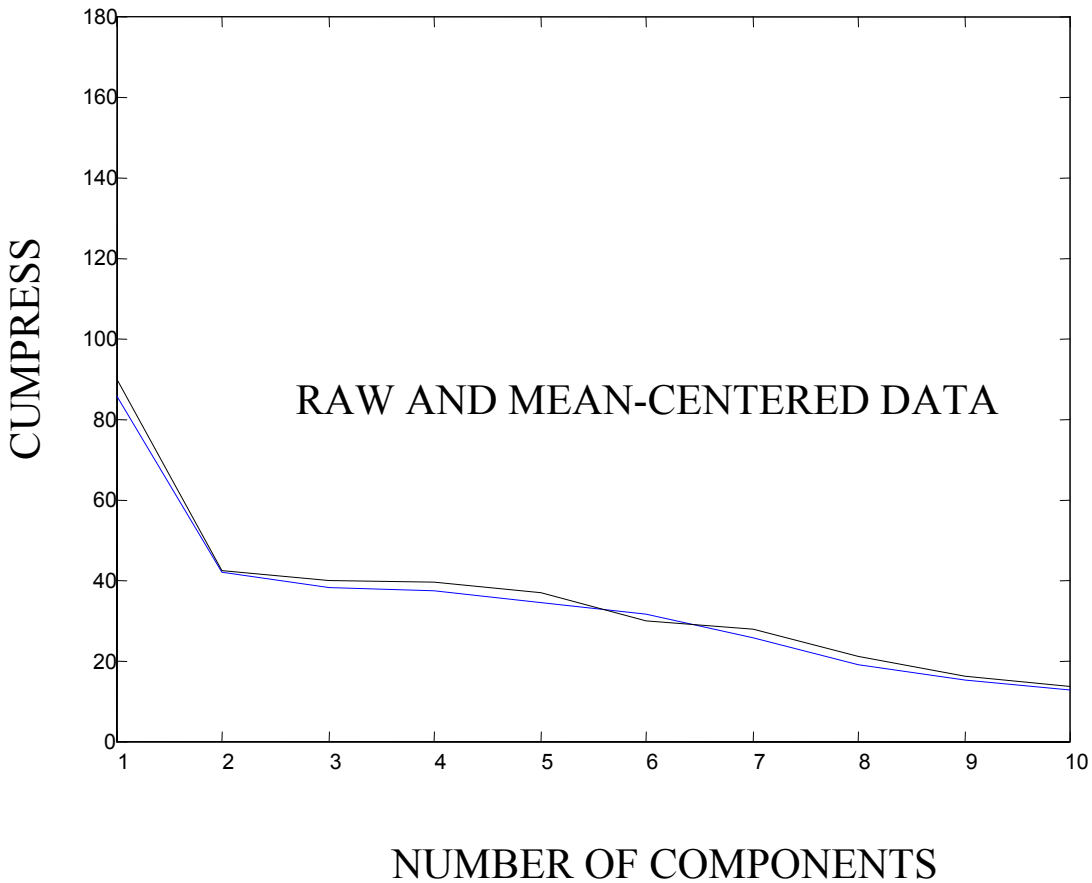
Raw data

Detection of purest spectra

num	moist	protein
61	9.51	19.7
98	7.33	16.93
75	**12.6**	20.58
110	9.80	17.60

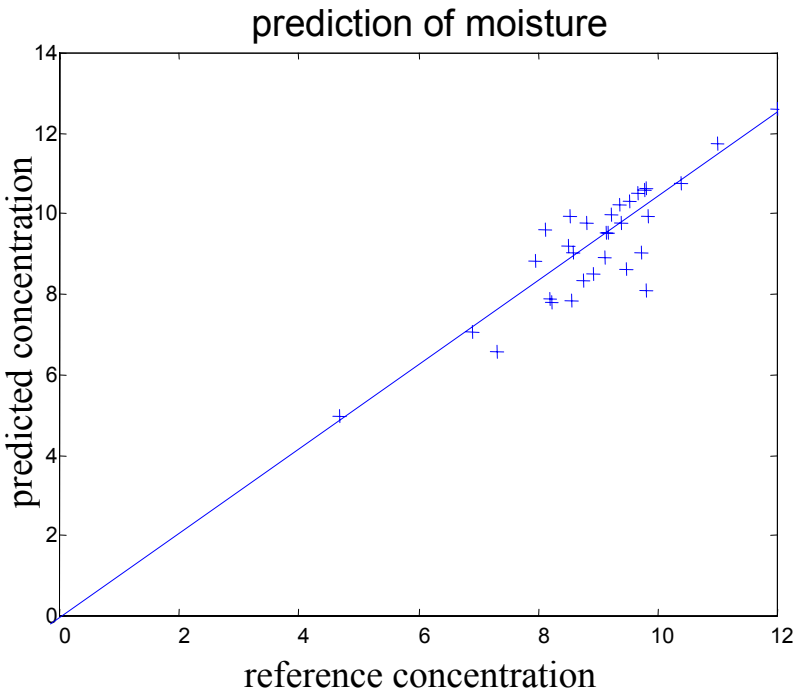


PLS CROSS-VALIDATION
MOISTURE

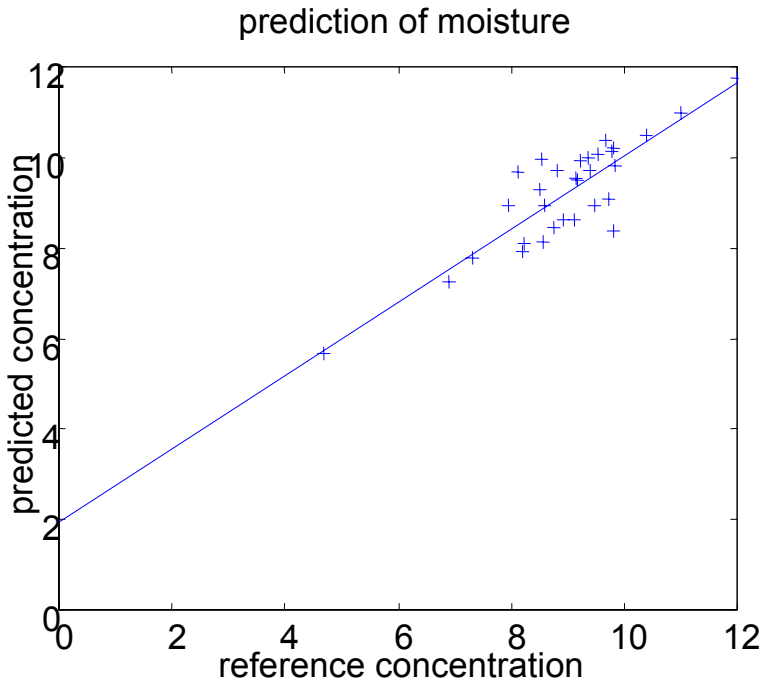


Prediction of moisture (raw data)

ALS predictions



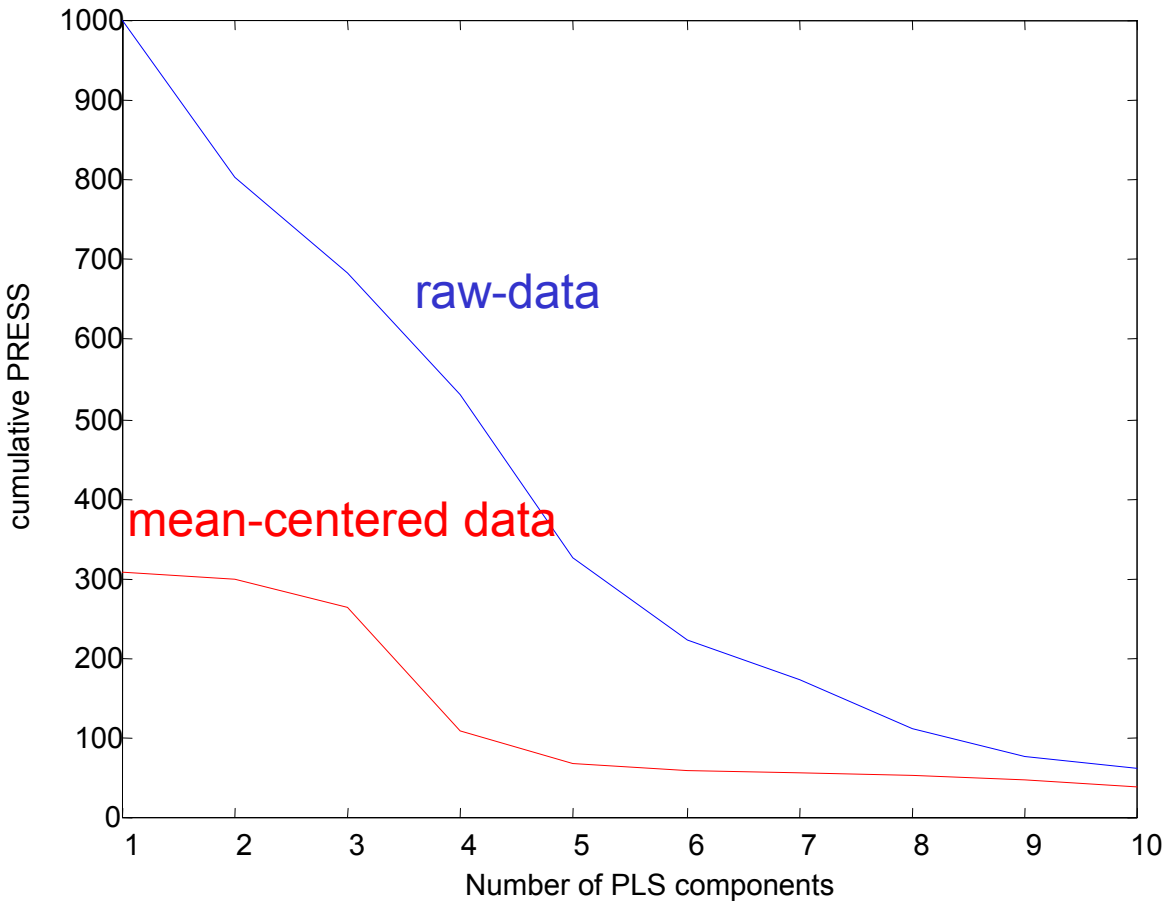
PLS predictions



method	analyte	RMSEP	SEP	bias	RE %	slope	offset	corcoef	sdres
ALS(4)	moisture	0.7470	0.7227	-0.2291	0.9071	1.0531	-0.2478	0.8827	3.94
PLS(4)	moisture	0.6760	0.6433	-0.2375	0.8208	0.8097	1.9475	0.8677	3.26
PLS(3)	moisture	0.6771	0.6621	-0.1849	0.8222	0.8569	1.4711	0.8656	3.48

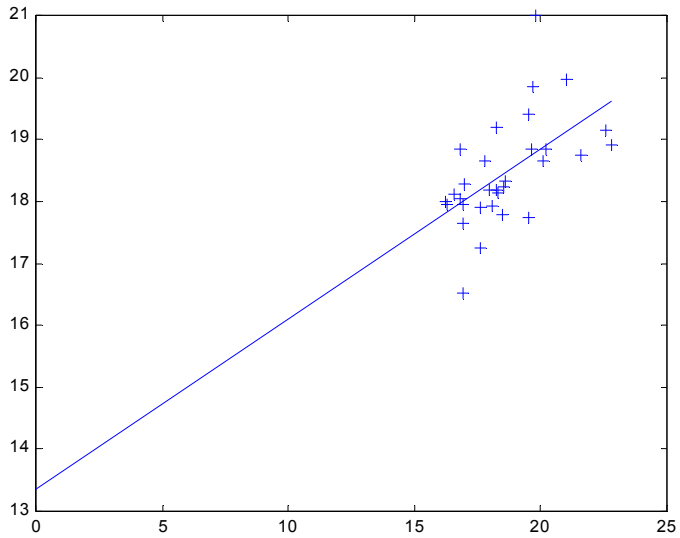
Results did not improve significantly with mean centering nor with 2nd derivative!

PLS CROSS-VALIDATION
PROTEIN

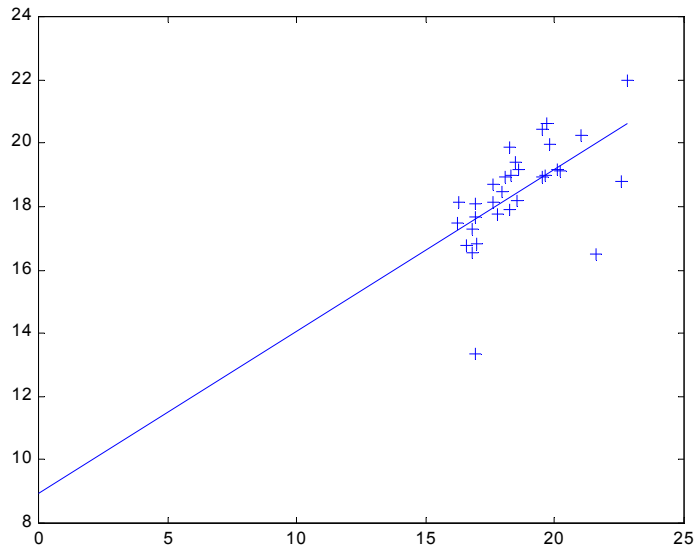


Prediction of protein (mean centered data)

ALS 4 components



PLS 4 components



method	analyte	RMSEP	SEP	bias	RE %	slope	offset	corcoef	sdres
ALS(4)	protein	1.4548	1.4732	0.1259	0.4174	0.2743	13.363	0.5673	3.881
PLS(4)	protein	1.5388	1.5590	0.1259	0.4415	0.5116	8.951	0.5754	7.088
PLS(8)	protein	0.9865	0.9946	0.1259	0.2830	0.7033	5.388	0.8295	4.616
PLS(6)	protein	0.8572	0.8620	0.1259	0.2459	0.7006	5.438	0.8787	3.711
2nd der.									

Provisory conclusions on the use of MCR-ALS for quantitative two-way data analysis

✓MCR-ALS can be used for the resolution and quantitation of those components which contribute significantly to the signal (i.e. usually for the major constituents of mixtures)

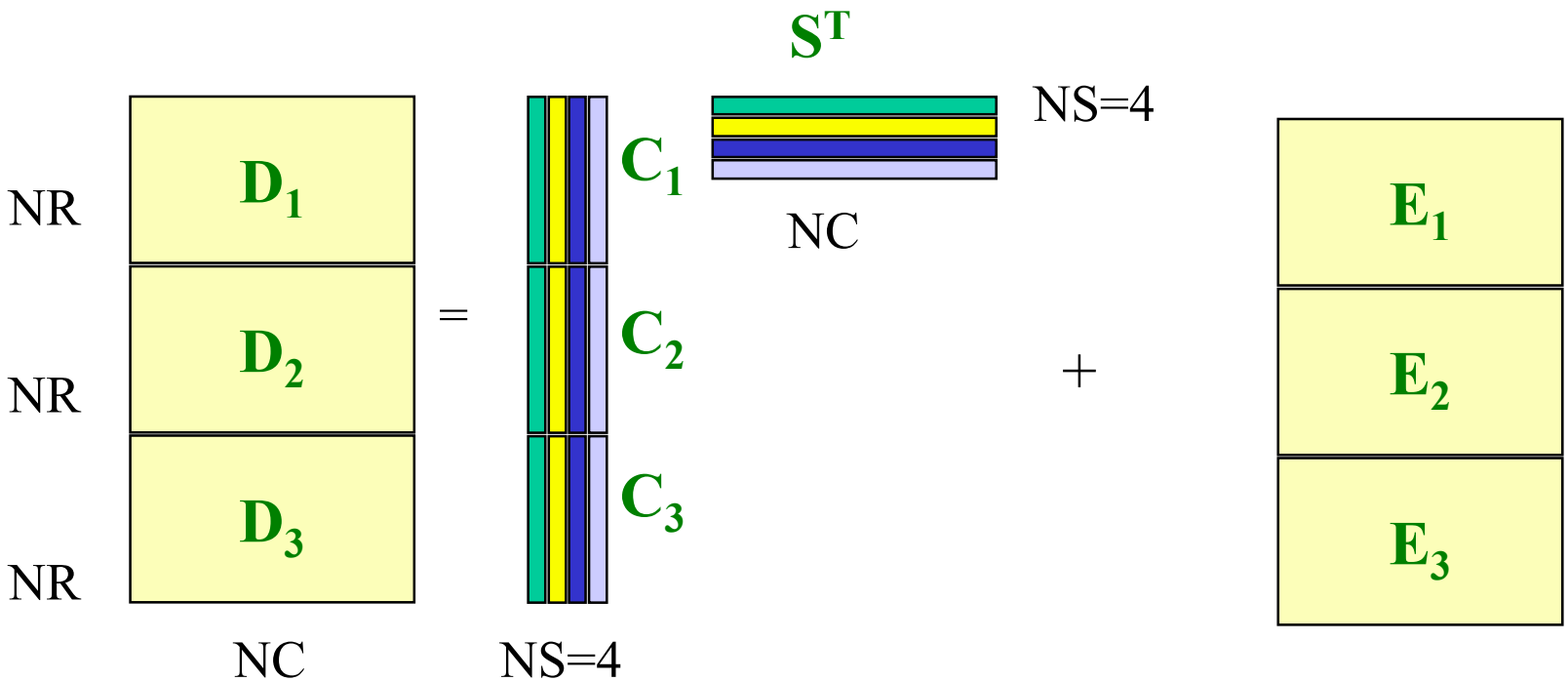
✓However, it is not recommended for

- ➢components contributing little to the signal
- ➢when the previous knowledge of the system is minimal (natural samples)
- ➢when nearly no constraints can be applied (i.e. for mean centered 2nd derivative data)

Outline

- Introduction to MCR-ALS method
- Quantitative MCR-ALS for two-way data
- **Quantitative MCR-ALS for three-way data**
- Conclusions and Acknowledgements

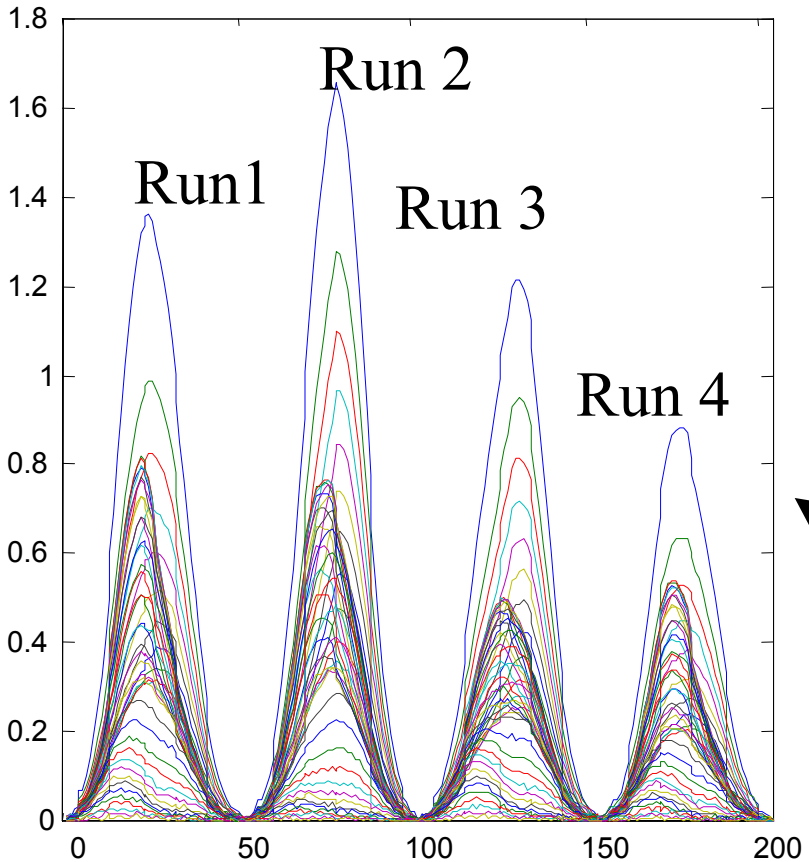
MCR-ALS can be easily extended to three-way (bilinear) data!

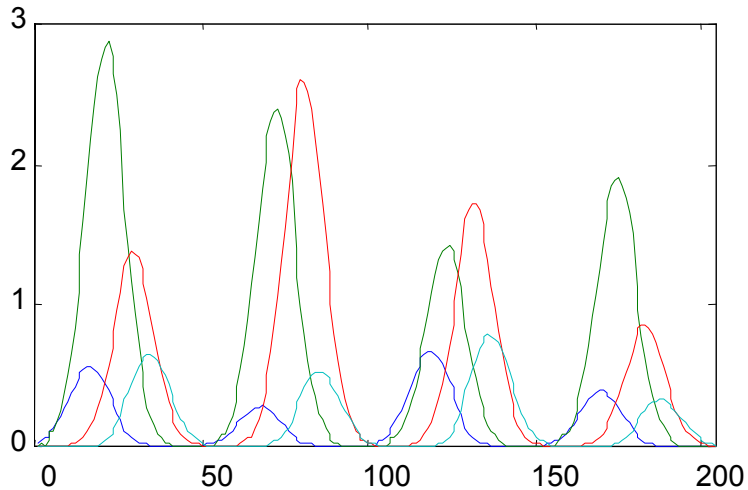


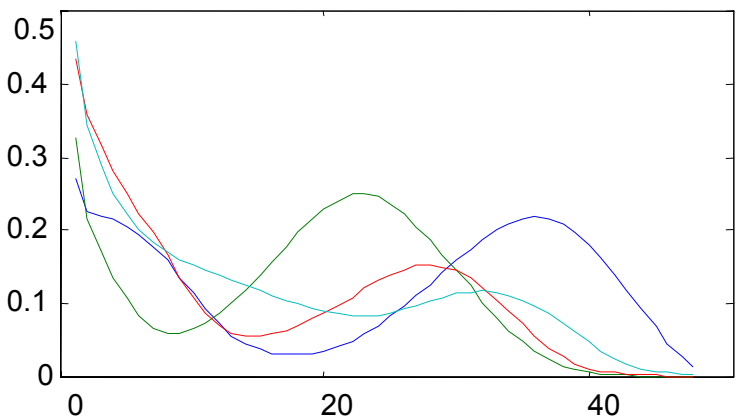
Column-wise Data Matrix Augmentation constraints may be applied independently to each concentration species profile in each submatrix C_1, C_2, C_3

Trilinear data

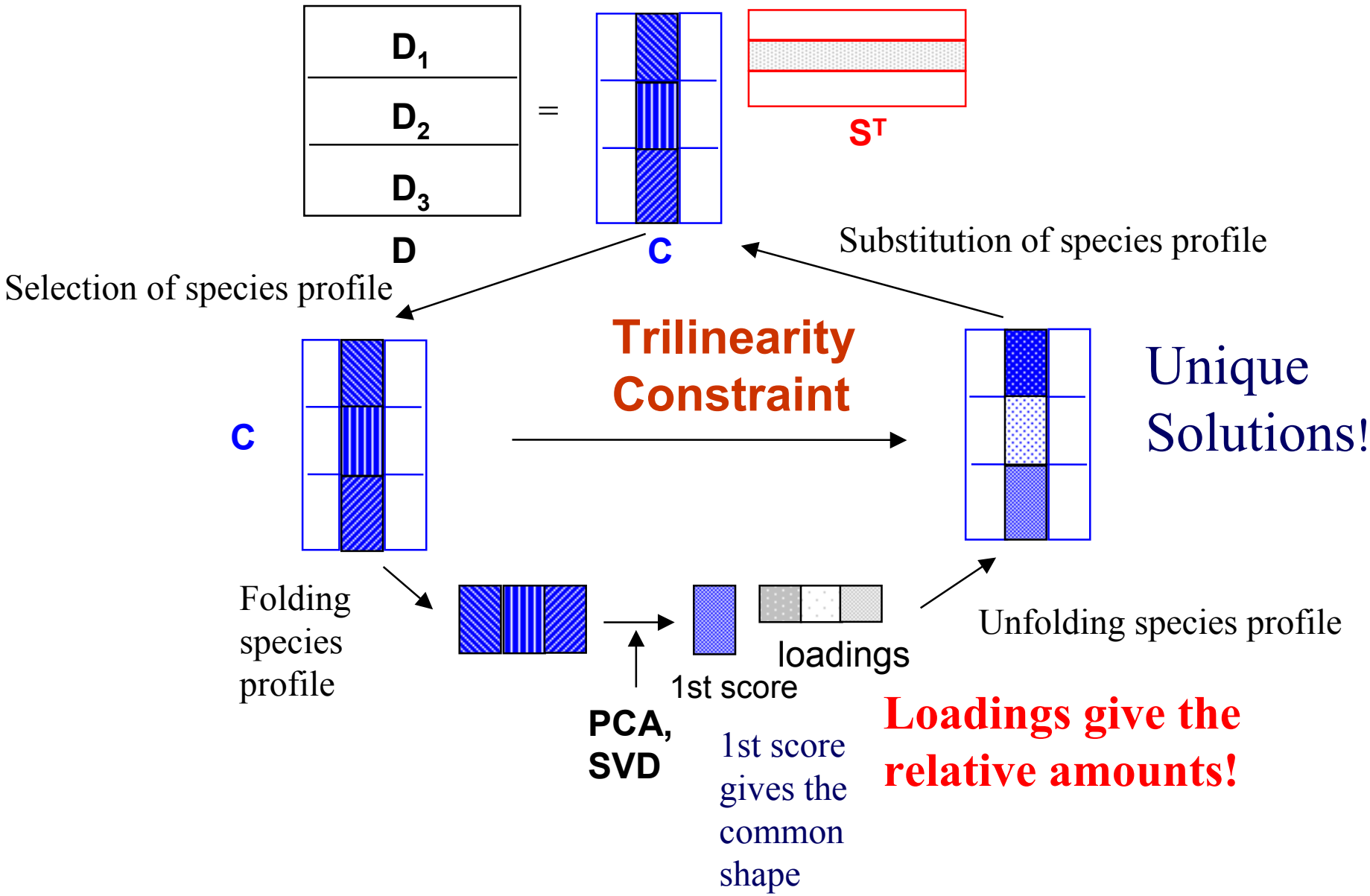
$$d_{ijk} = \sum_{n=1}^{N} c_{in} s_{jn} t_{kn} + e_{ijk}$$





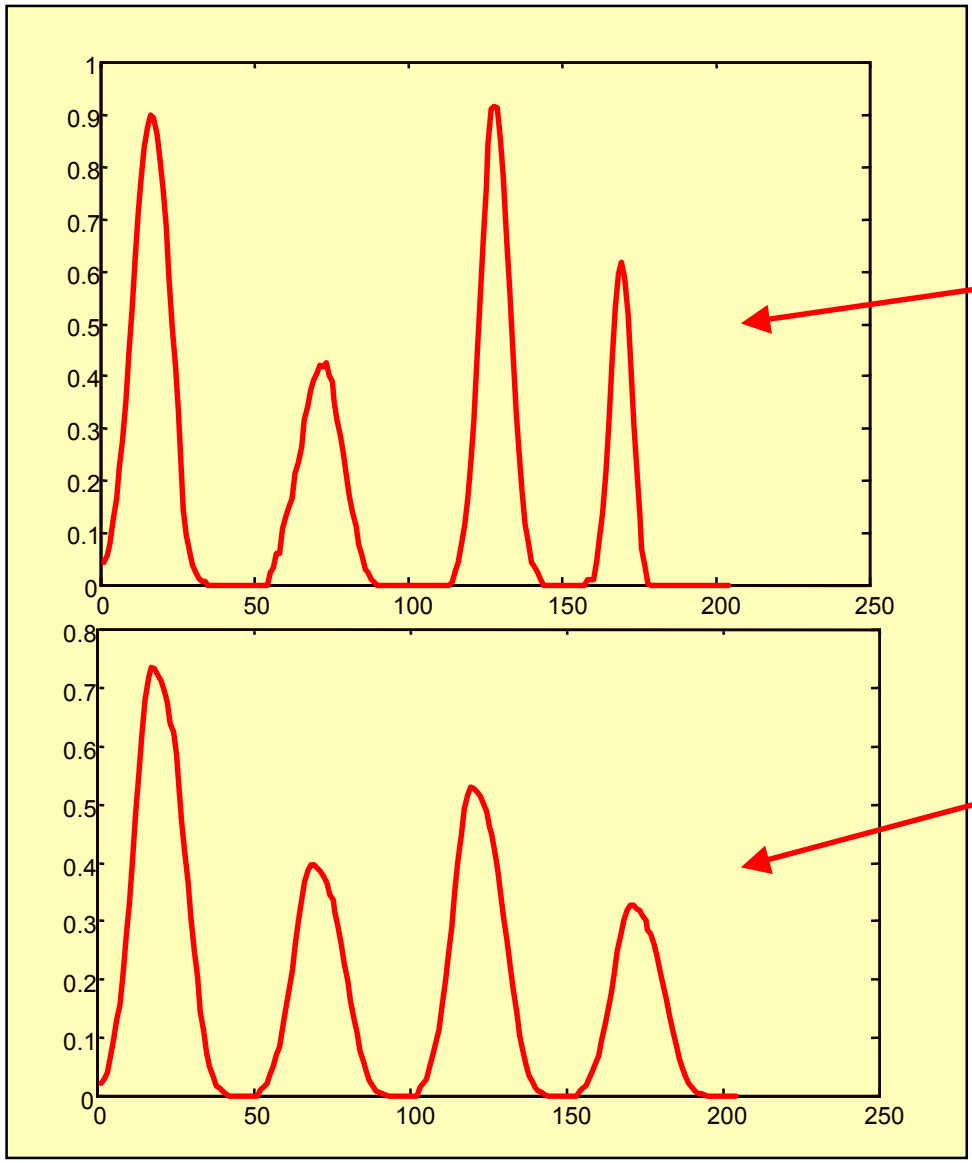


Trilinearity can be implemented independently for each component (chemical species) in MCR-ALS!



Effect of application of a trilinearity constraint

Trilinearity constraint



Profiles with different shape

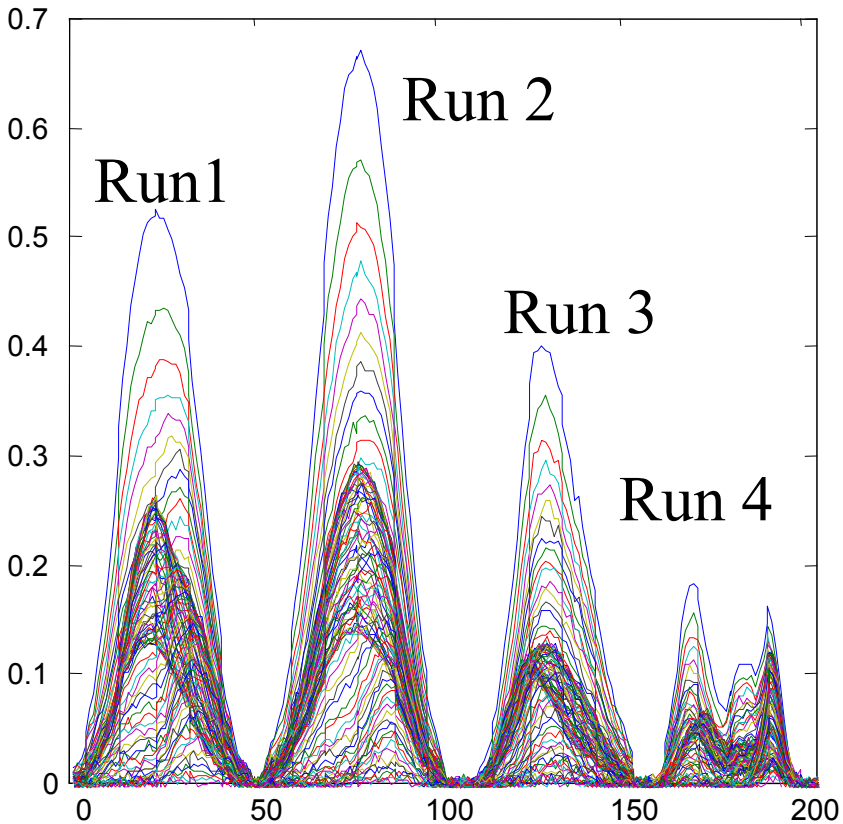
Profiles with equal shape

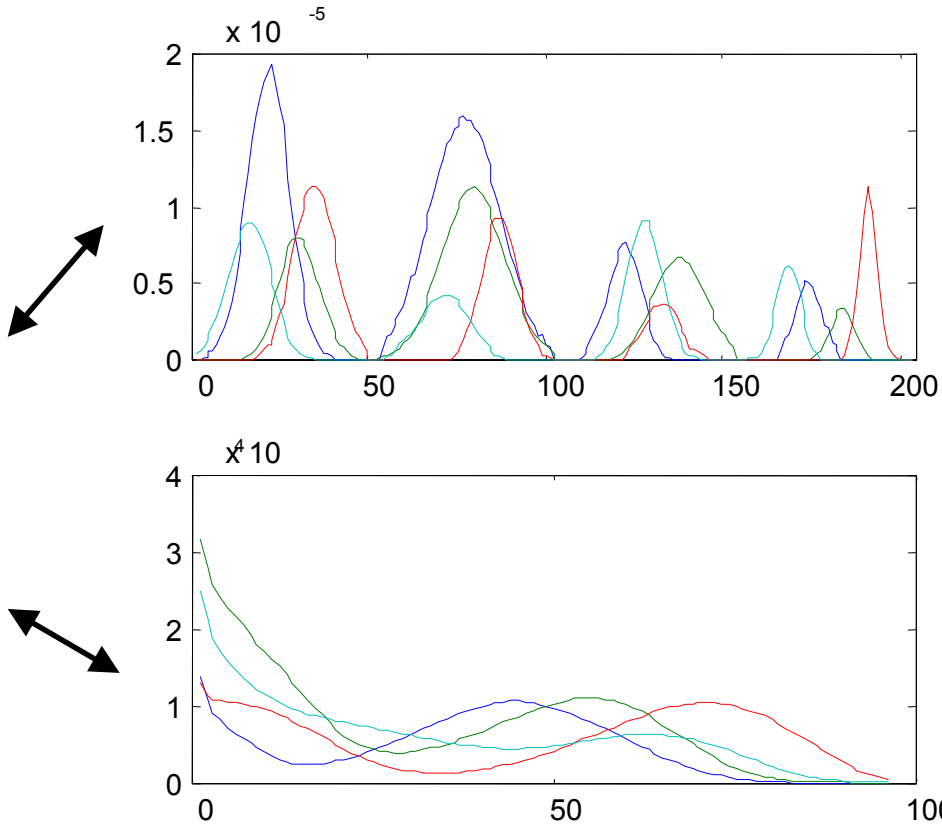
Trilinear data: spectra recovery

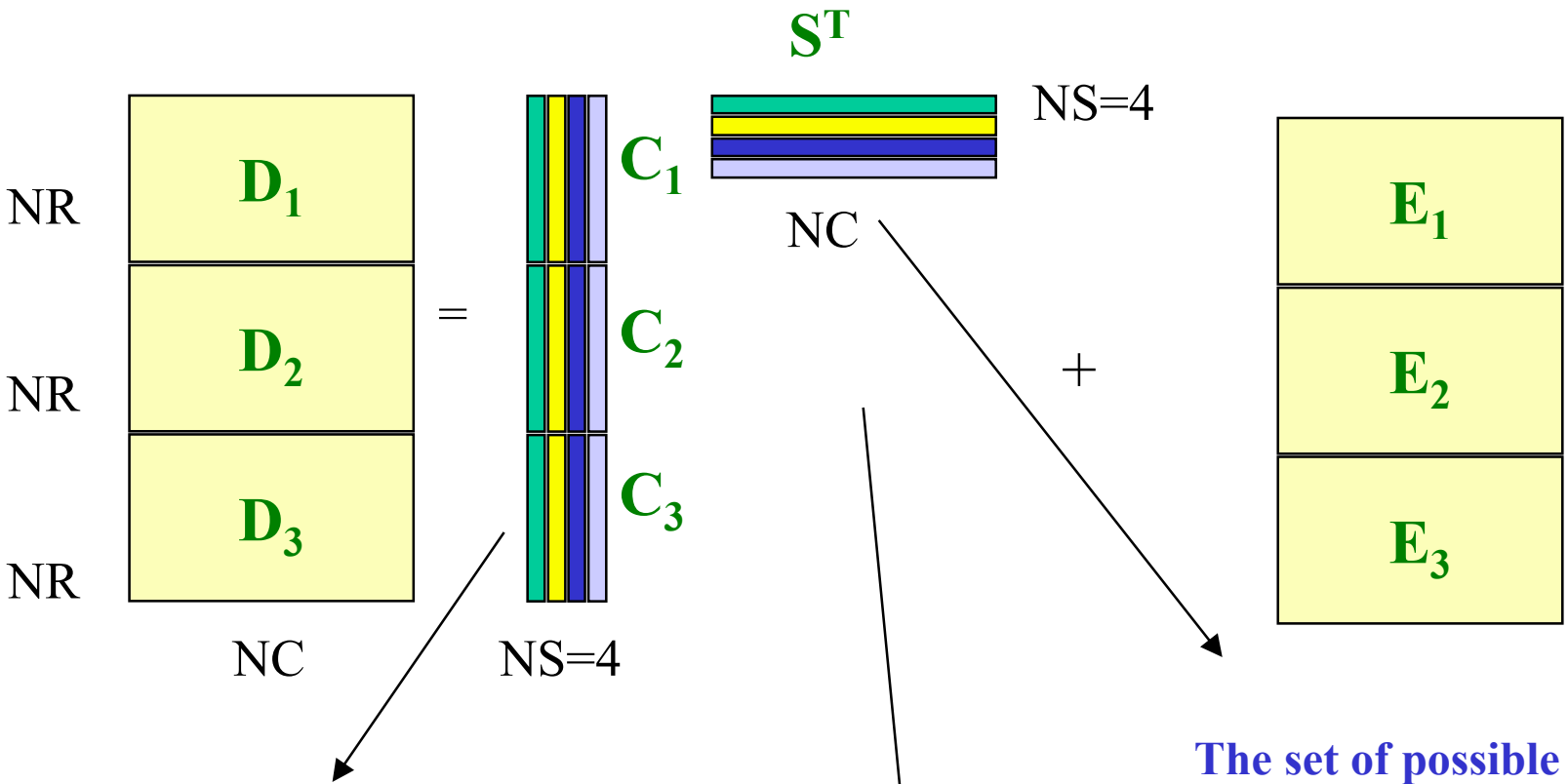
species	TLD (cos)	ALS (cos)	TLD (sin)	ALS (sin)
1	0,9995	0,9999	0,033	0,0107
2	1	1	0,0069	0,0068
3	0,9998	0,9999	0,0221	0,0136
4	0,9999	1	0,0124	0,0086

Non-trilinear data

$$d_{ijk} \neq \sum_{n=1}^{N} c_{in} s_{jn} t_{kn} + e_{ijk}; \quad d_{ijk} = \sum_{p=1}^{Np} \sum_{q=1}^{Nq} \sum_{r=1}^{Nr} g_{pqr} c_{ip} s_{jq} t_{kr} + e_{ijk}$$







When selectivity or local rank resolution conditions are fulfilled for the concentration profile of one species in one matrix, resolution will be also achieved for the concentration profiles of the same species in the other matrices simultaneously analyzed

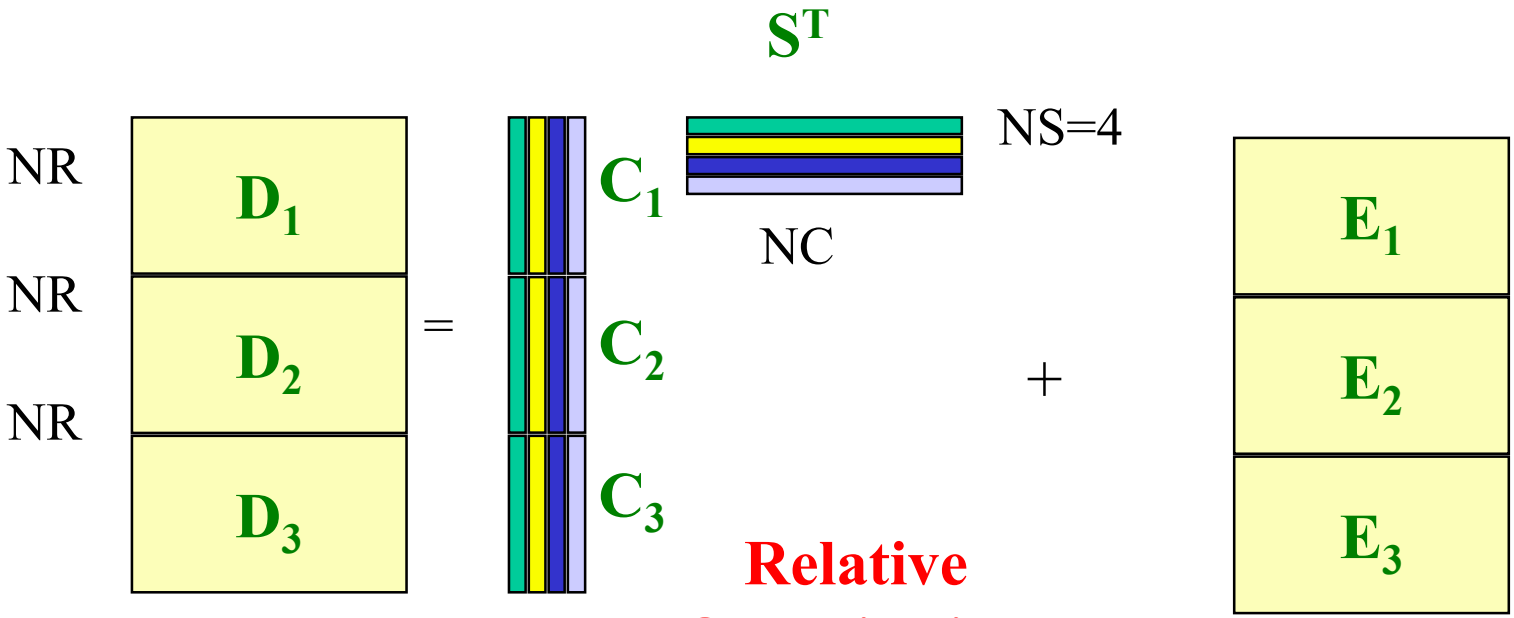
The set of possible LS solutions for S^T are now more restricted

appropriate experimental design of experiments included in augmented matrices may allow total resolution!

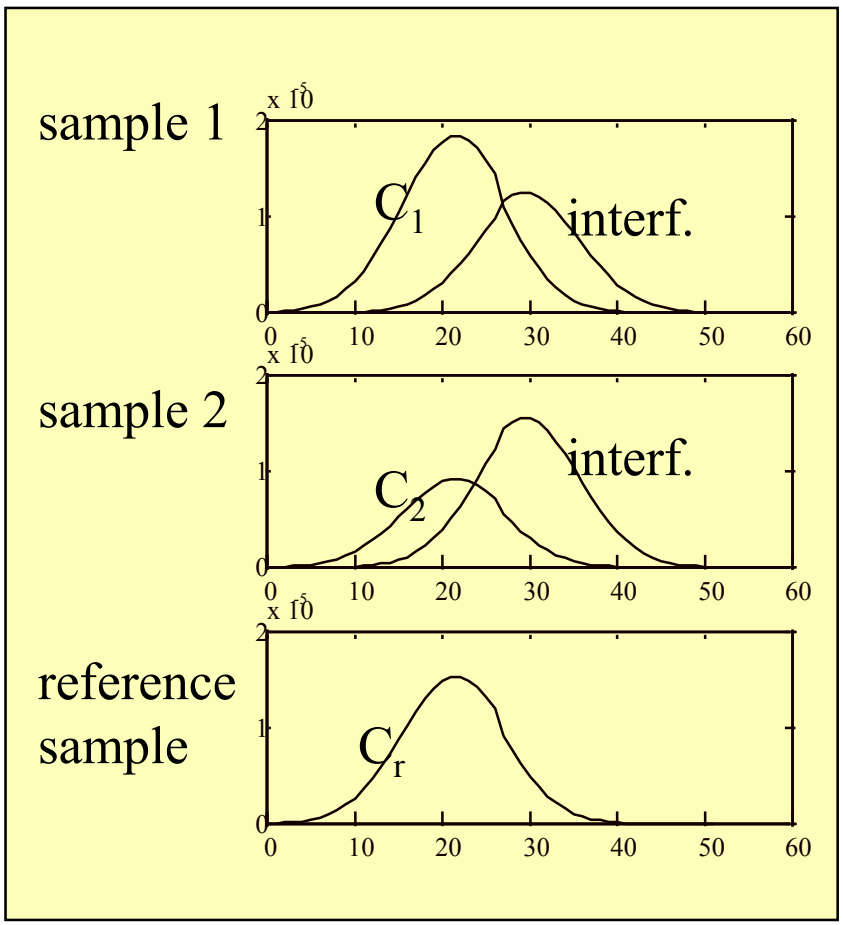
Non-trilinear data: spectra recovery

Species	TLD	ALS (cos)	ALS (sin)
1	complex	0,9984	0,0567
2	complex	0,9997	0,0246
3	complex	1	0,008
4	complex	1	0,008

Quantitative MCR-ALS for three-way data



Recovery of quantitative information



- **Relative Quantitation**

reference C_r unknown

Rel Conc(C_1) = Area(C_1)/(Area(C_r)

Rel Conc(C_2) = Area(C_2)/(Area(C_r)

- **Absolute Quantitation**

reference C_r known

Conc(C_1) =

[Area(C_1)/Area(C_r)] Conc(C_r)

Conc(C_2) =

[Area(C_2)/Area(C_r)] Conc(C_r)

Trilinear data: quantitative recovery

Species	Matrix	theoretical	TLD	ALS
1	2	0,5	0,5	0,5
	3	1,2	1,2	1,2
	4	0,7	0,7	0,7
2	2	0,8	0,85	0,84
	3	0,5	0,48	0,5
	4	0,66	0,67	0,67
3	2	1,87	1,85	1,87
	3	1,25	1,24	1,25
	4	0,62	0,62	0,62
4	2	0,8	0,82	0,81
	3	1,2	1,21	1,2
	4	0,5	0,5	0,5

Non-trilinear data: quantitative recovery

Species	Matrix	theoretical	ALS
1	2	0,61	0,55
	3	0,81	0,84
	4	0,38	0,39
2	2	1,34	1,39
	3	0,34	0,31
	4	0,18	0,17
3	2	2,13	2,2
	3	1	1,07
	4	0,27	0,25
4	2	0,68	0,68
	3	0,27	0,26
	4	0,4	0,41

Determination of triphenyltin in sea-water by excitation-emission matrix fluorescence and multivariate curve resolution

A method for the determination of triphenyltin (TPhT) in sea-water is proposed:

1) Solid phase exctraction (SPE) of sea-water samples;
2) Reaction with a fluorogenic reagent (flavonol in a micellar medium);
3) Excitation-emission fluorescence measurements (giving an EEM data matrix);
4) MCR-ALS analysis of EEM data matrices
5) Quantitation of TPhT

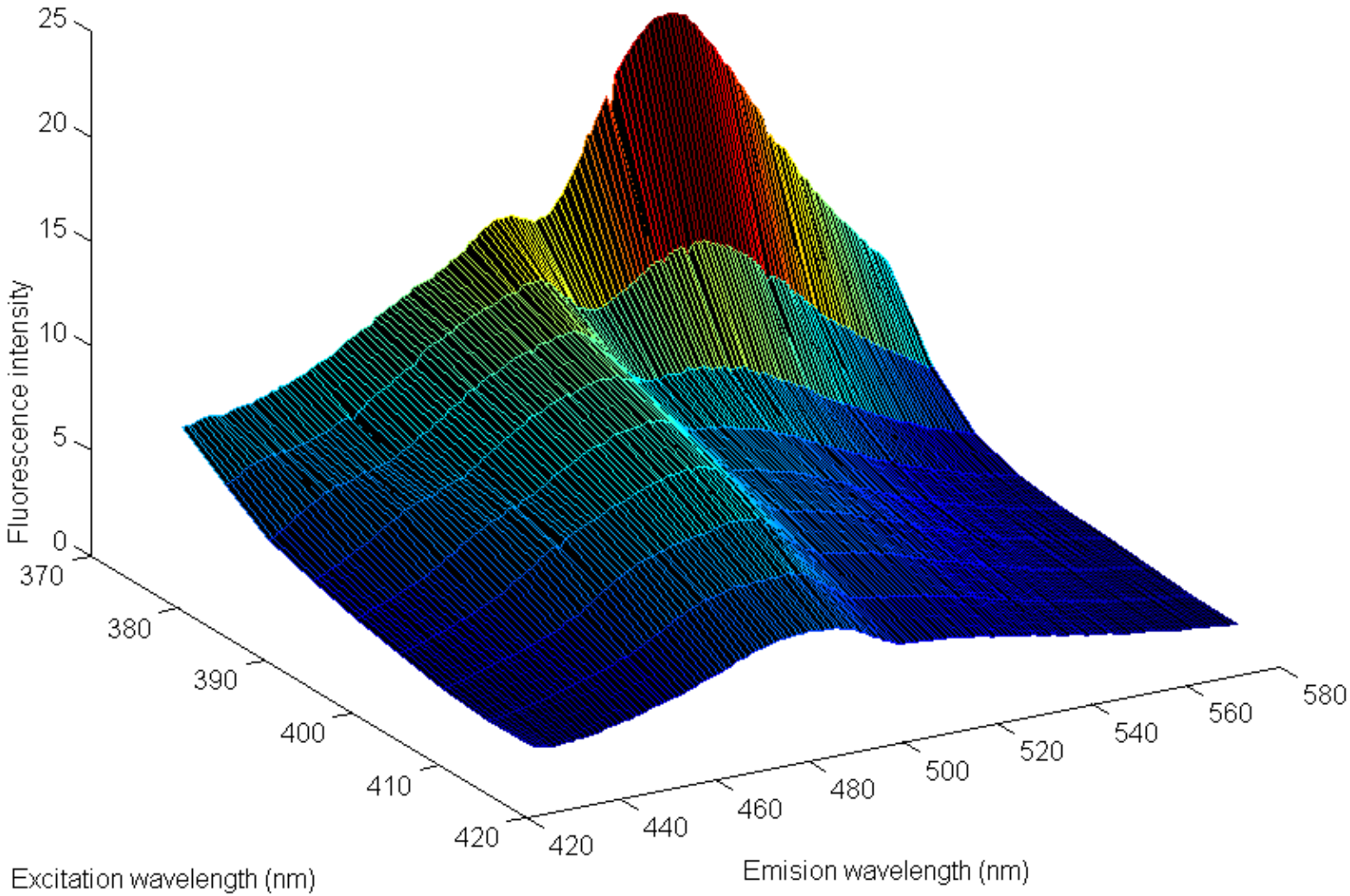
J.Saurina, C.Leal, R.Compañó, M.Granados, R.Tauler and M.D.Prat. Analytica Chimica Acta, 2000, 409, 237-245

Determination of triphenyl in sea-water by excitation-emission matrix fluorescence and multivariate curve resolution.

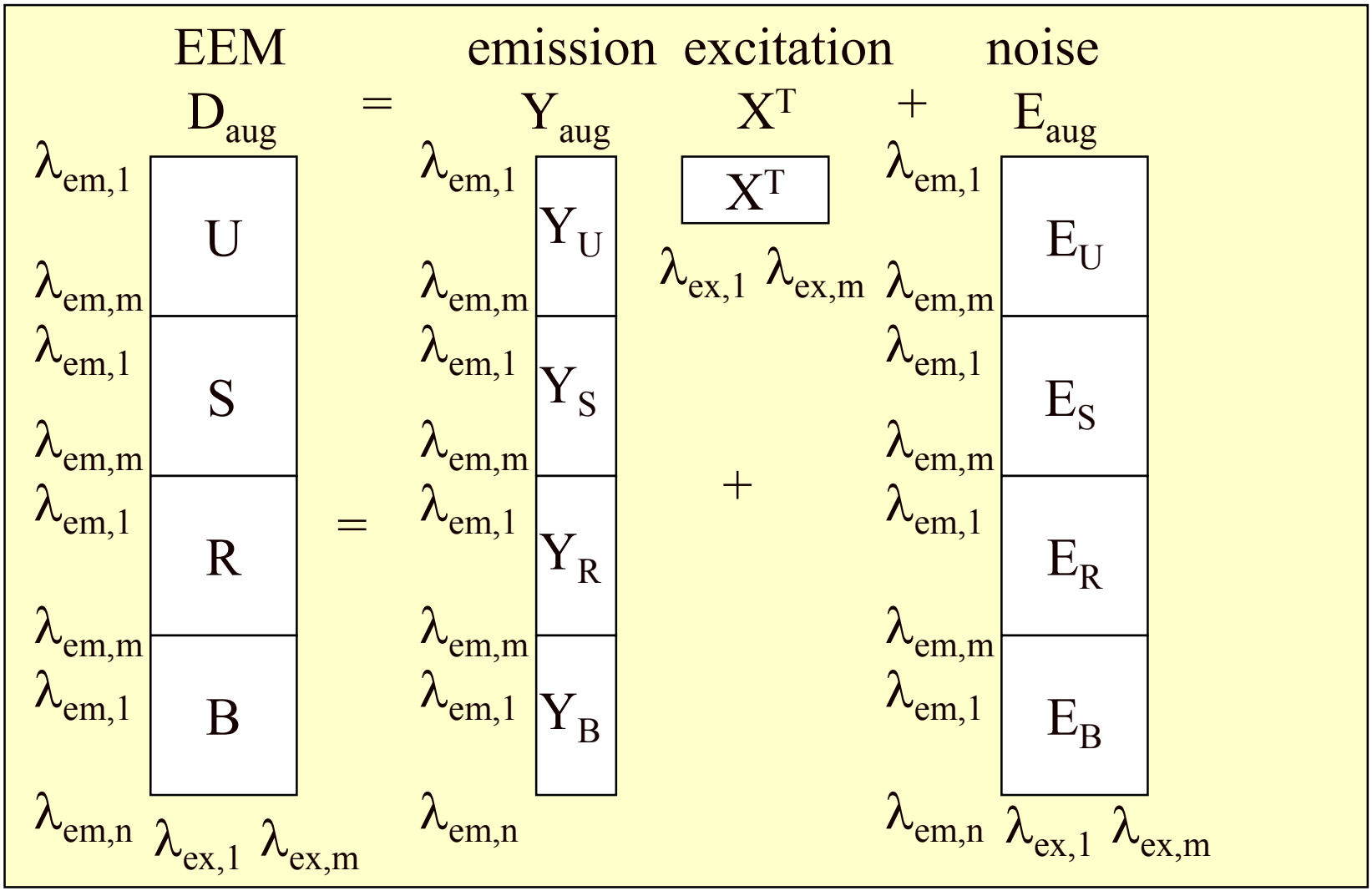
Difficulties were:

- low concentrations of TPht (ng/l)
- strong background (fulvic acids) emission
- strong reagent emission
- lack of selective emission/excitation wavelengths
- to have sea-water TPhT standards available

Excitation-Emission spectra for an unknown sea-water sample



MCR-ALS resolution of EEM data



U unknown sea water; S TPhT pure standard;
R reagent (flavonol); B sea-water background (fulvic acids)

MCR-ALS resolution of EEM data

a) Model:

$$[\mathbf{U};\mathbf{S};\mathbf{R};\mathbf{B}] = \mathbf{D}_{aug} = \mathbf{Y}_{aug}\mathbf{X}^{T} + \mathbf{E}_{aug}$$

b) Resolution:

(emission) $\mathbf{Y}_{aug} = \mathbf{D}_{aug}(\mathbf{X}^{T})^{+}$

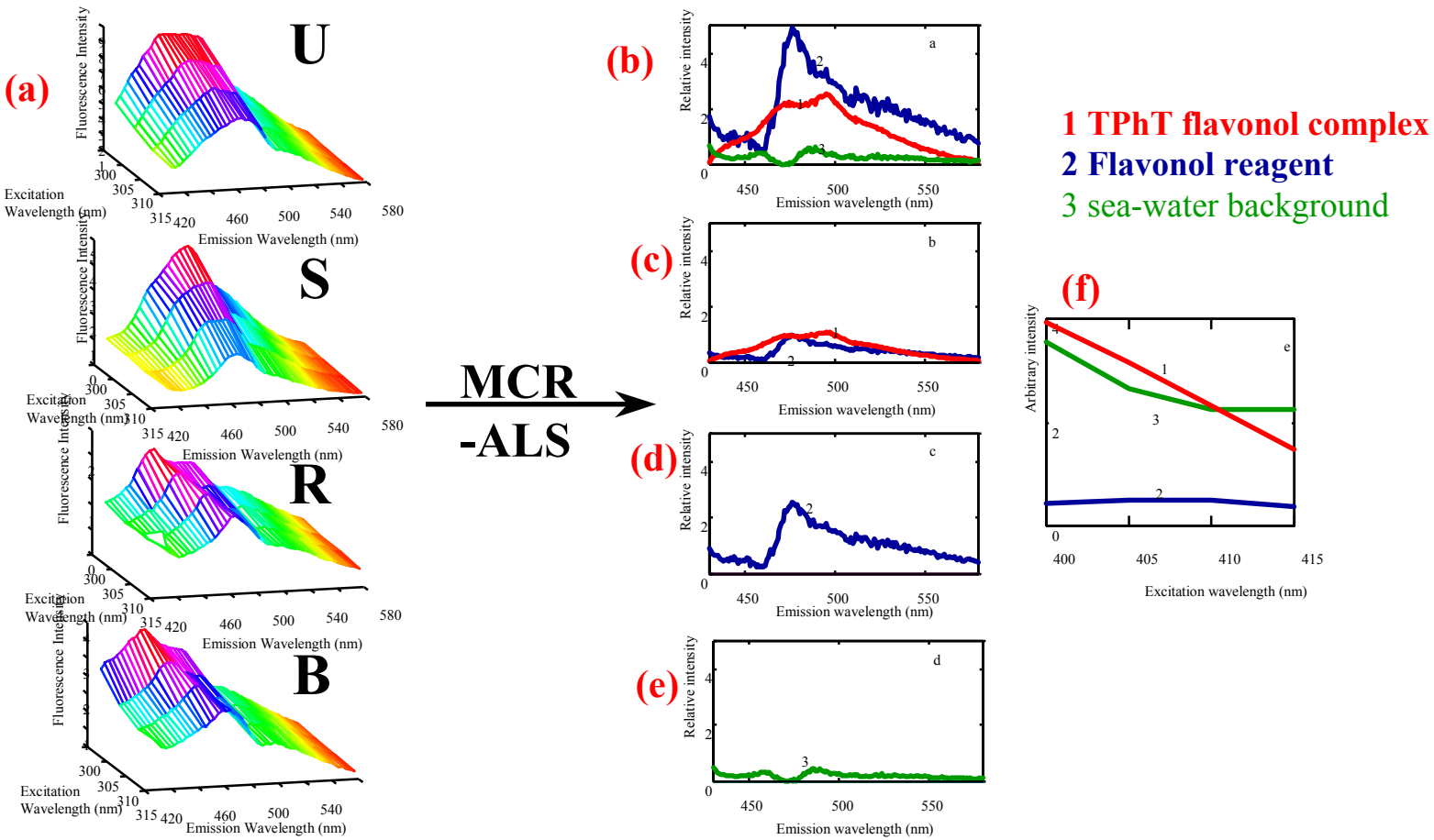
(excitation) $\mathbf{X}^{T} = (\mathbf{Y}_{aug})^{+}\mathbf{D}_{aug}$

Constraints:
- non-negativity
- trilinearity

c) Quantitation:

$$c_{TPhT,U} = [Area(\mathbf{y}_{\mathbf{TPhT,U}}) / Area(\mathbf{y}_{\mathbf{TPhT,S}})]\, c_{TPhT,S}$$

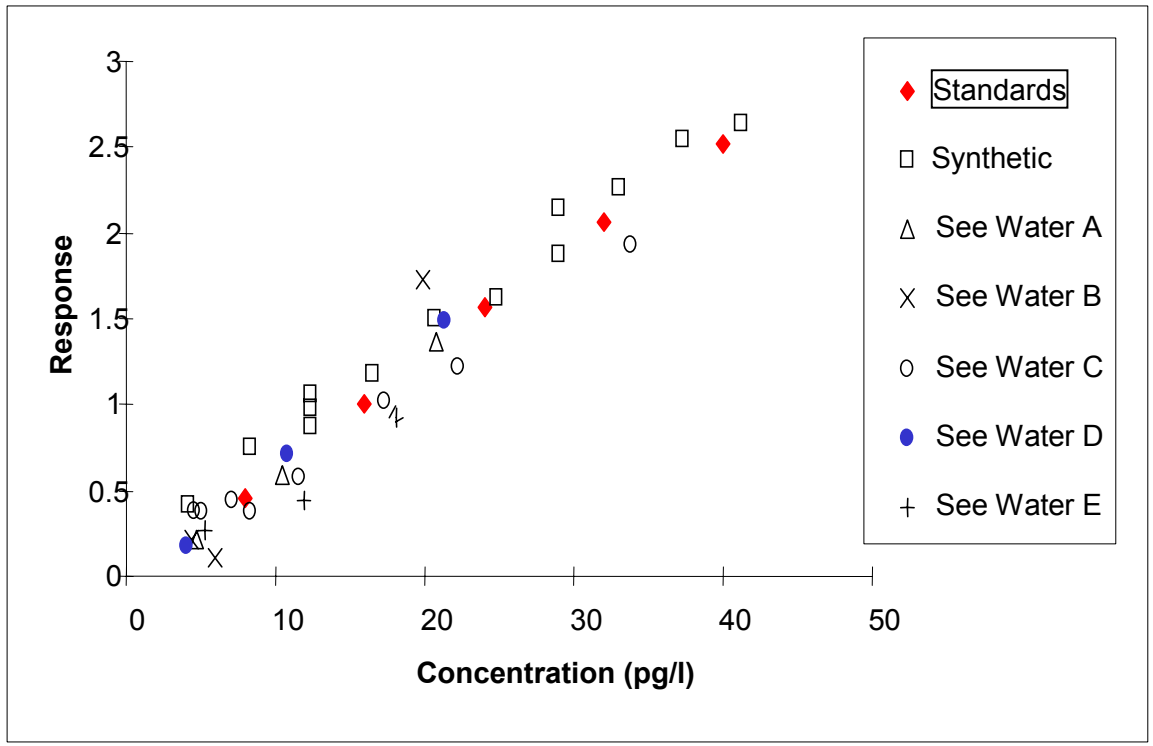
MCR-ALS resolution of [U;S;R;B] augmented matrix



a) 3-D plots of the EEM fluorescence of the unknown sample U, standard S, flavonol reagent R and sea-water background B;

b) emission spectra for the unknown sea-water sample; **c)** emission species spectra for the standard; **d)** emission species spectra for flavonol reagent; **e)** emission species spectra for sea-watere background; **f)** excitation spectra

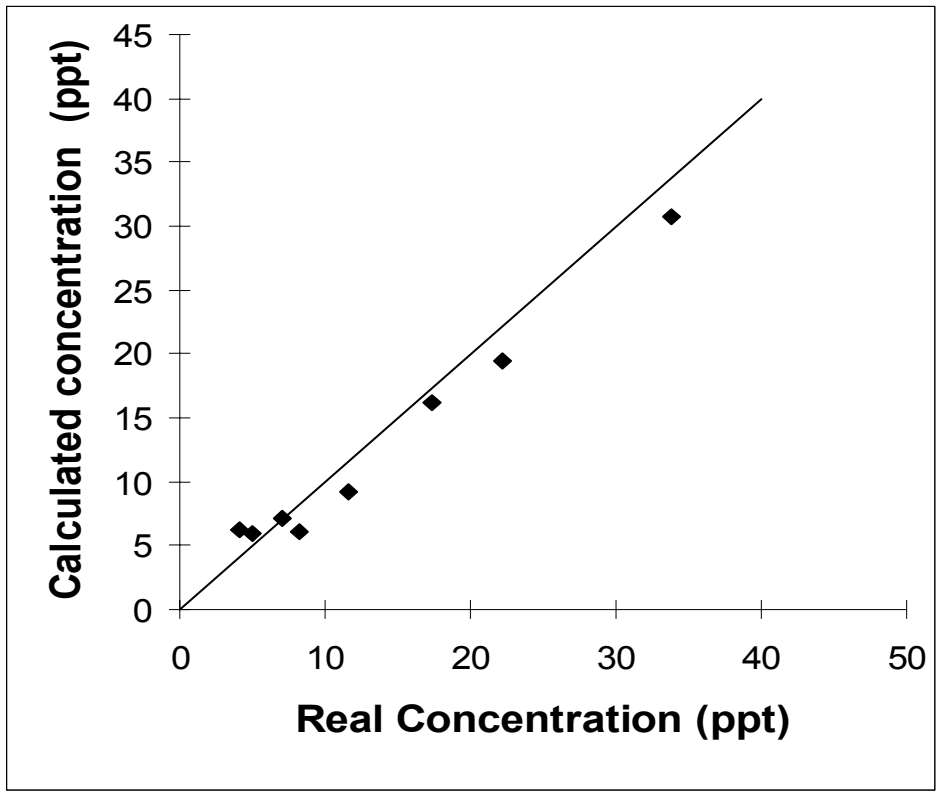
MCR-ALS resolution/quantitation of EEM data



Plot of the emission profiles areas for TPhT species in standards, synthetic and sea-water samples respect the analyte concentration

Comparison between 'true' and MCR-ALS calculated TPhT concentrations in sea-water samples

Quantitation: $c_U = [\text{Area}(y_U) / \text{Area}(y_S)]\, c_S$



overall prediction errors were always below 13%!

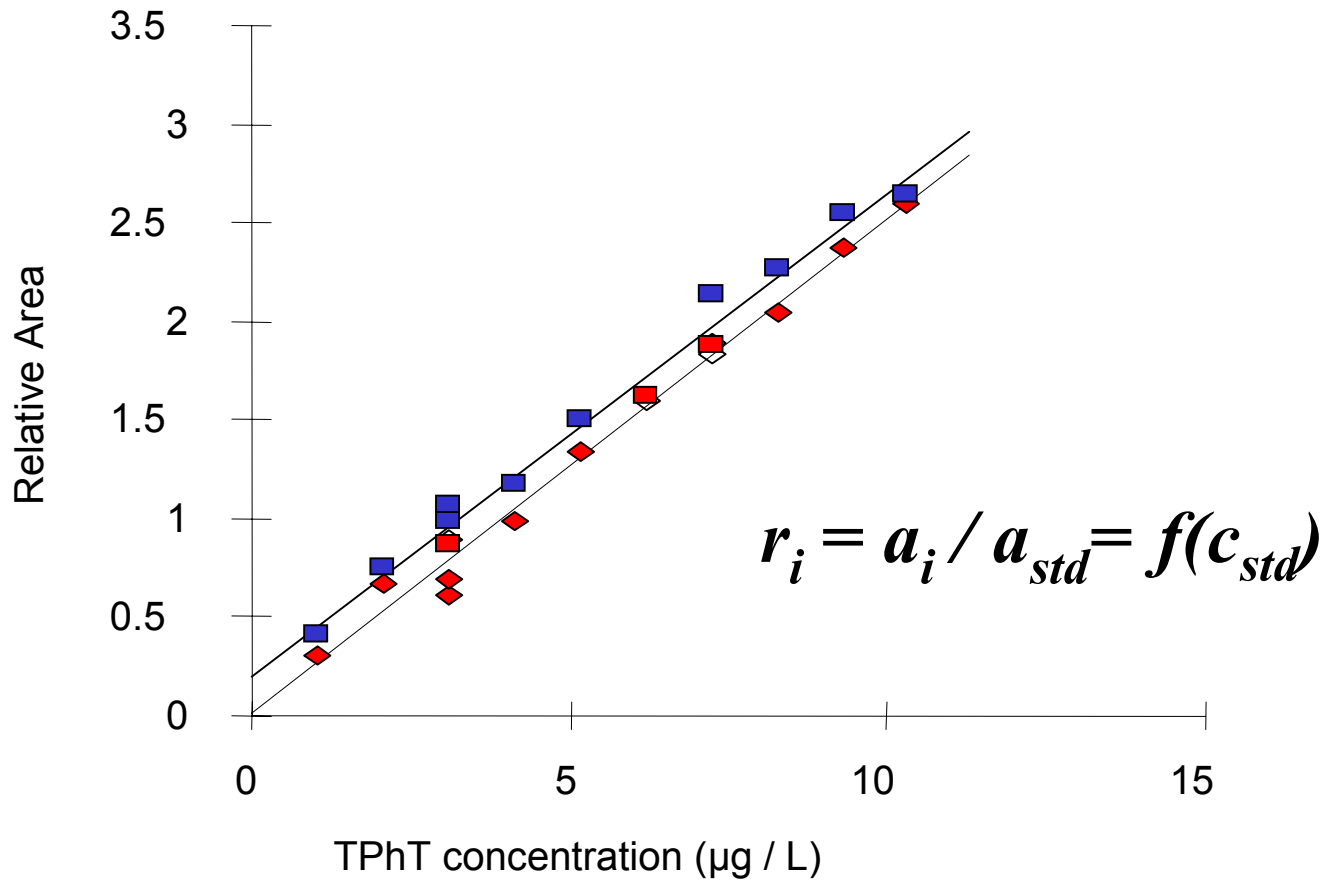
FIGURES OF MERIT IN SECOND ORDER MULTIVARIATE CURVE RESOLUTION

• From MCR-ALS resolution of the pure response profiles of the analyte in different known and unknown mixures (data matrices), a ***Calibration Curve*** is built.

• Figures of merit such as ***Limit of Detection, Sensitivity, Precision and Accuracy*** are calculated from the calibration curve

like in univariate calibration!

Building the Calibration Curve and Sensitivity



- Approach (a) [U;S2;R] $r_i = 0.260\ c_i + 0.014$ (r = 0.998)
- Approach (b) [U1;U2;U3;U4;U5;U6;U7;U8;U9;U10;U11;U12;S2;R;B]
  $r_i = 0.244\ c_i + 0.201$ (r = 0.987)

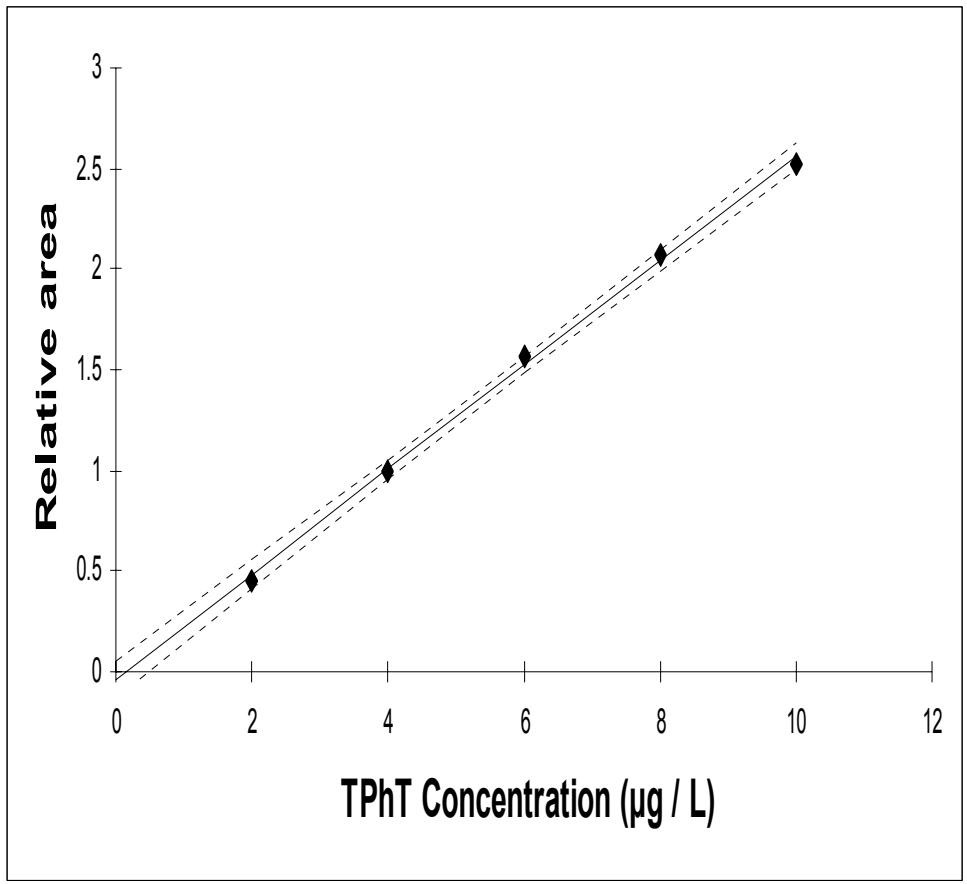
Precision:

$$s_R = \sqrt{\frac{\sum_{i=1}^{n}(\hat{r}_i - r_i)^2}{n-1}}$$

(a) and (b) $s_R = 0.0404$

Precision bands

$$\pm s_R t \left(1/m + 1/n + (r_i - \bar{r})^2 / \Sigma(c_i - \bar{c})^2 \right)^{1/2}$$

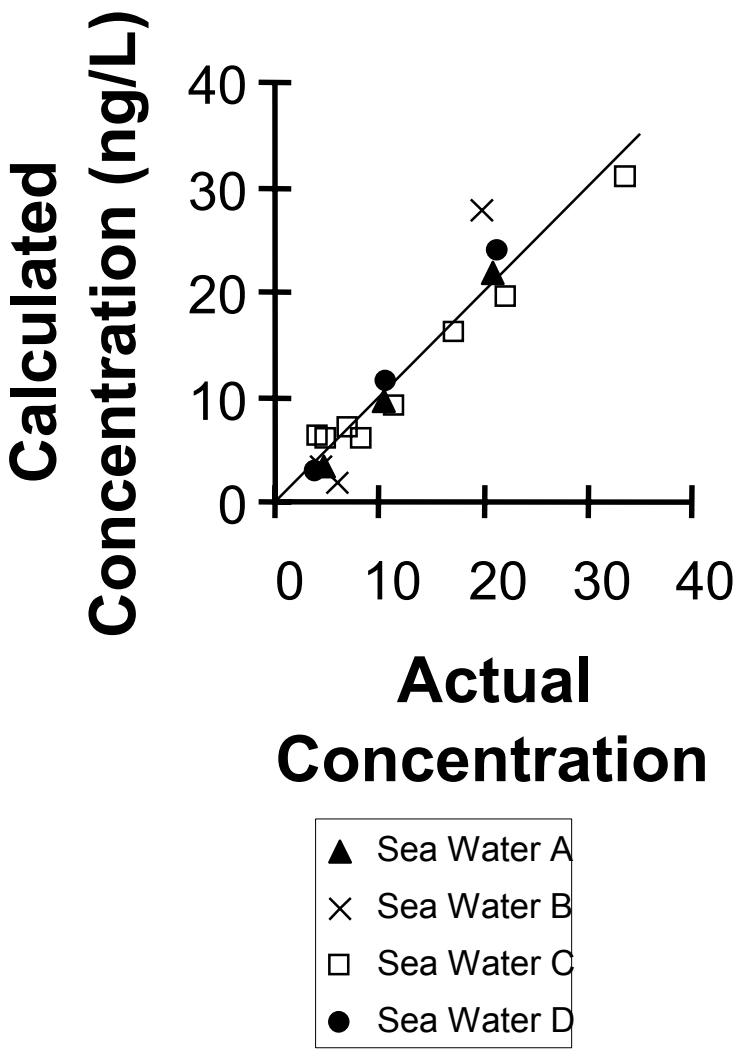


Limit of detection

$$\text{LOD} = + t\, s_R / b \left(1/m + 1/n + \right.$$
$$\left. + ((r_i - \bar{r}) / b)^2 / \Sigma(c_i - \bar{c})^2 \right)^{1/2}$$

(a) and (b) LOD = 0.7 µg l^{-1}

Accuracy of the method in the prediction of TPhT in real samples



overall prediction error

$$\text{Error}(\%) = \frac{\sqrt{\sum_{i=1}^{\text{Samples}} (c_i - \hat{c}_i)^2}}{\sqrt{\sum_{i=1}^{\text{Samples}} (c_i)^2}} \times 100$$

Error % = 5.5 % for strategy (A)

Error % = 12.7 % for strategy (B)

Solving matrix effects

Three strategies were compared for the recovery of the analyte response in the sea-water samples:

i. using pure standards
ii. using sea-water standards
iii. using the standard addition method

J.Saurina and R.Tauler, The Analyst, 2000, in press

Standard addition strategy:

For each unknown sample, MCR-ALS is applied to the following augmented matrices (i.e A4, the same for the other A1, A2, A3, A5 and A6)

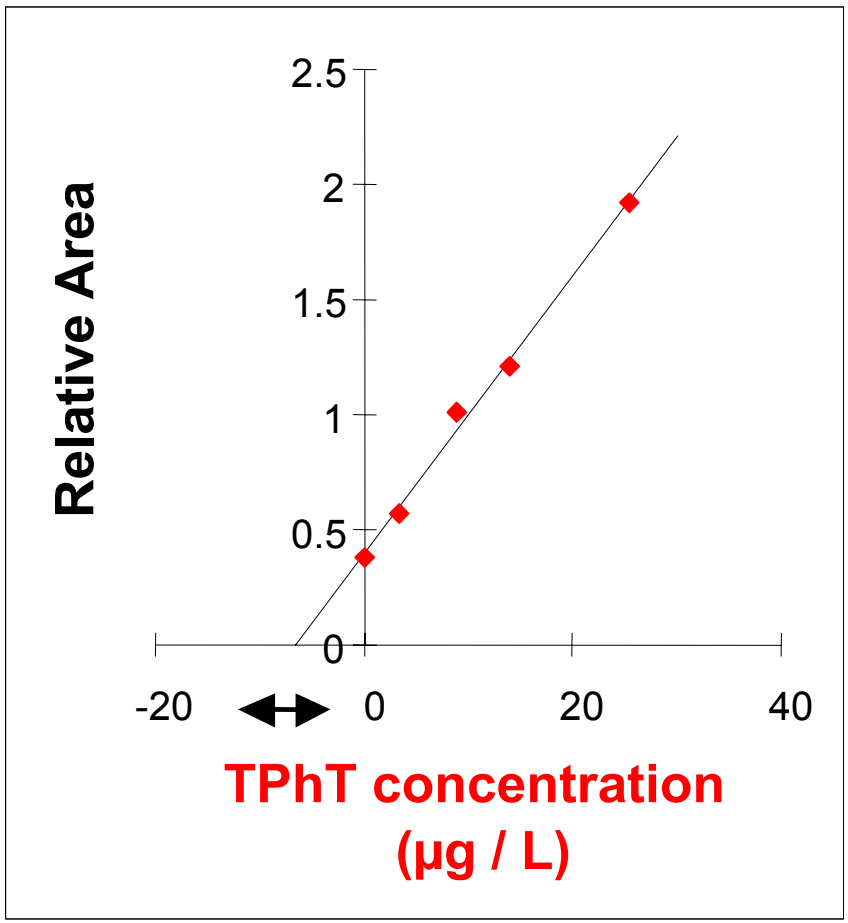
augmented matrices		*identification*
[A4;S2;R;B]	=>	A4 unknown sample
[A4SA1;S2;R;B]	=>	A4SA1 = A4 + 0.20 µg l^{-1} TPhT
[A4SA2;S2;R;B]	=>	A4SA2 = A4 + 0.75 µg l^{-1} TPhT
[A4SA3;S2;R;B]	=>	A4SA3 = A4 + 1.05 µg l^{-1} TPhT
[A4SA4;S2;R;B]	=>	A4SA4 = A4 + 1.87 µg l^{-1} TPhT
[A4SA5;S2;R;B]	=>	A4SA5 = A4 + 3.30 µg l^{-1} TPhT
[A4SA6;S2;R;B]	=>	A4SA6 = A4 + 4.52 µg l^{-1} TPhT
[A4SA7;S2;R;B]	=>	A4SA7 = A4 + 7.42 µg l^{-1} TPhT

S2 EMM response matrix of an standard of TPhT

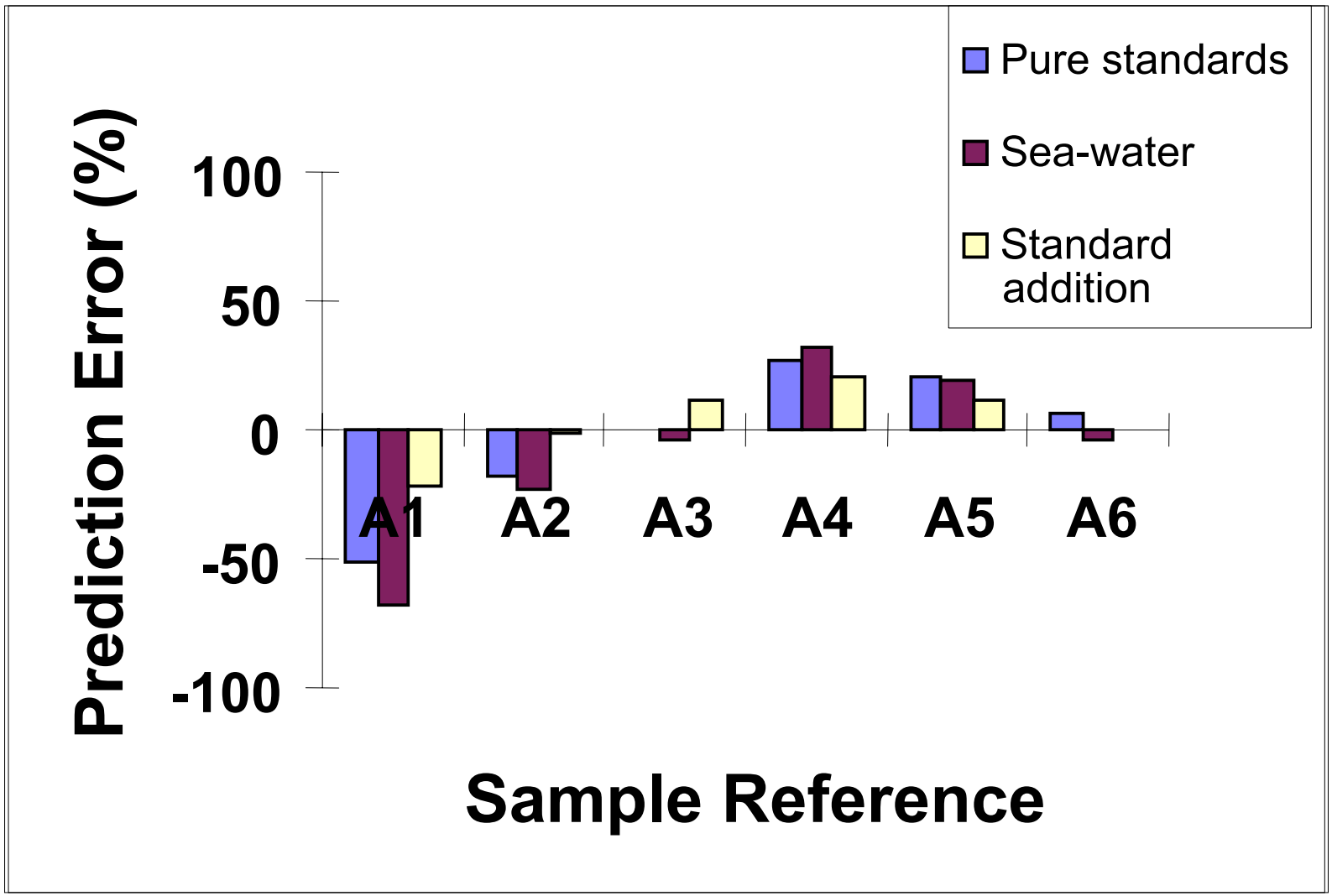
R EMM response matrix of the reagent

B EMM response matrix of the background

Standard addition calibration graph in a sea-water analyte determination (sea-water sample A4)



Prediction errors in the determination of TPhT in sea-water samples A1-A6 using MCR-ALS and three calibration approaches:



Provisory conclusions on the use of MCR-ALS for quantitative three-way data analysis

✓Quali- and Quantitative information may be recovered simultaneously using MCR-ALS for three-way data

✓Calculation of figures of merit is possible from resolved profiles (using same methods as in univariate calibration)

✓The combination of standard addition with multivariate curve resolution method improved the accuracy of predictions in the presence of matrix effects.

✓Limitations will appear for analytes contributing very little to the whole signal and for systems with a high chemical rank

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