Constrained optimization of feasible ranges for species profiles obtained by multivariate curve resolution

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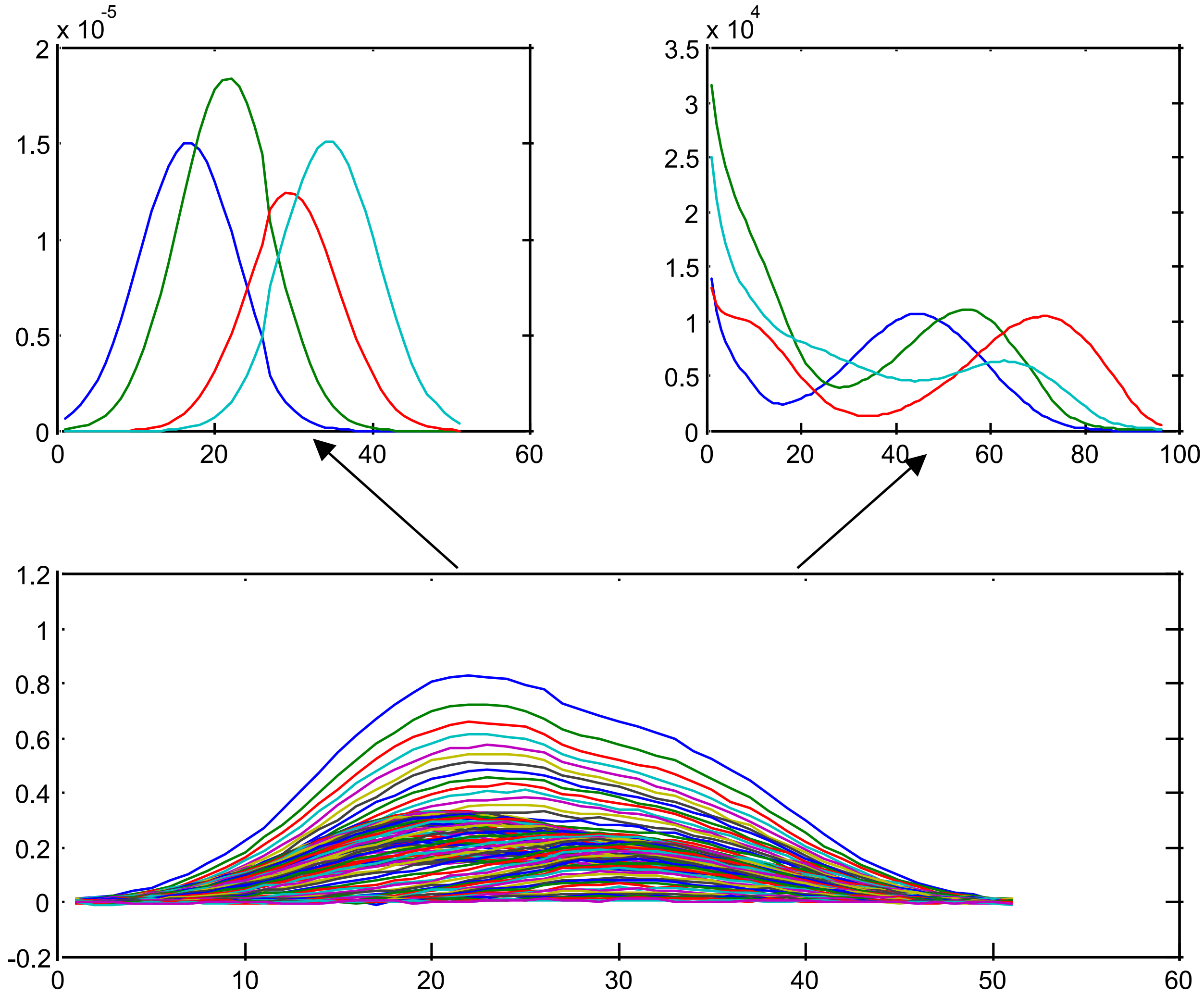
Outline

- Introduction
  - multivariate curve resolution
  - ambiguities and feasible bands
- Calculation of feasible bands
  - method of optimization
- Examples of application

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.

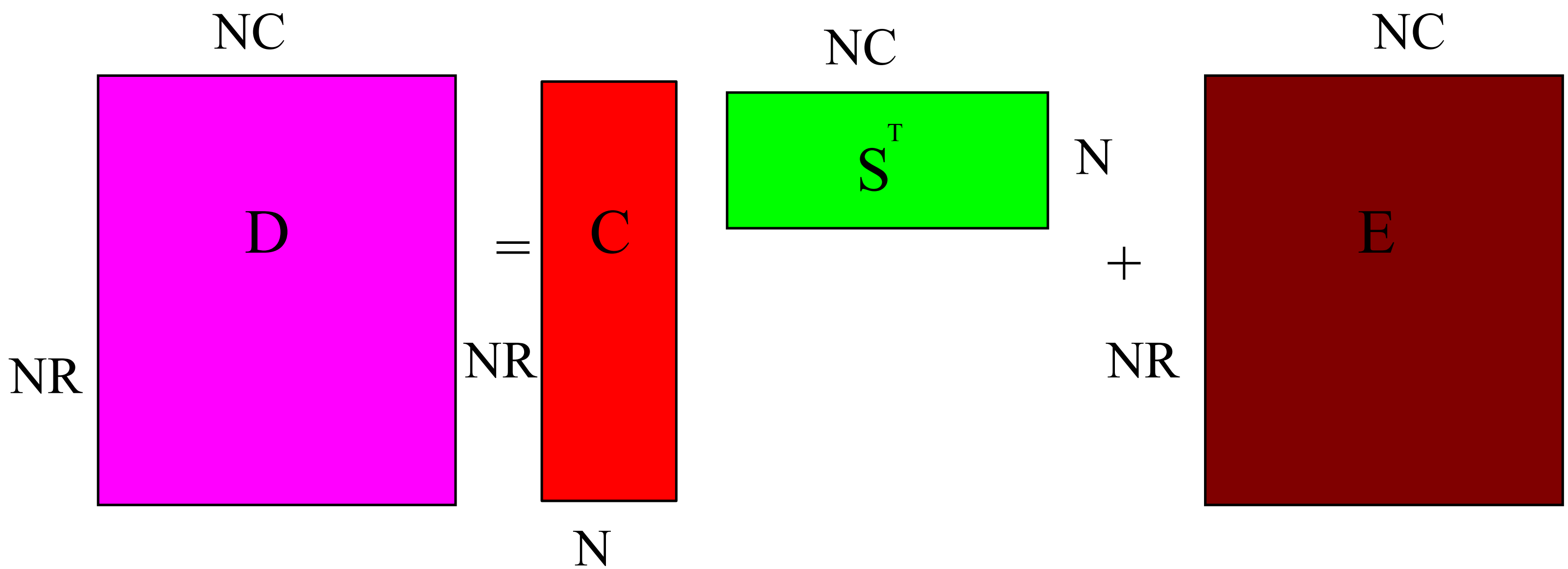
Multivariate Curve Resolution



Multivariate Curve Resolution (MCR)

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

Bilinearity!



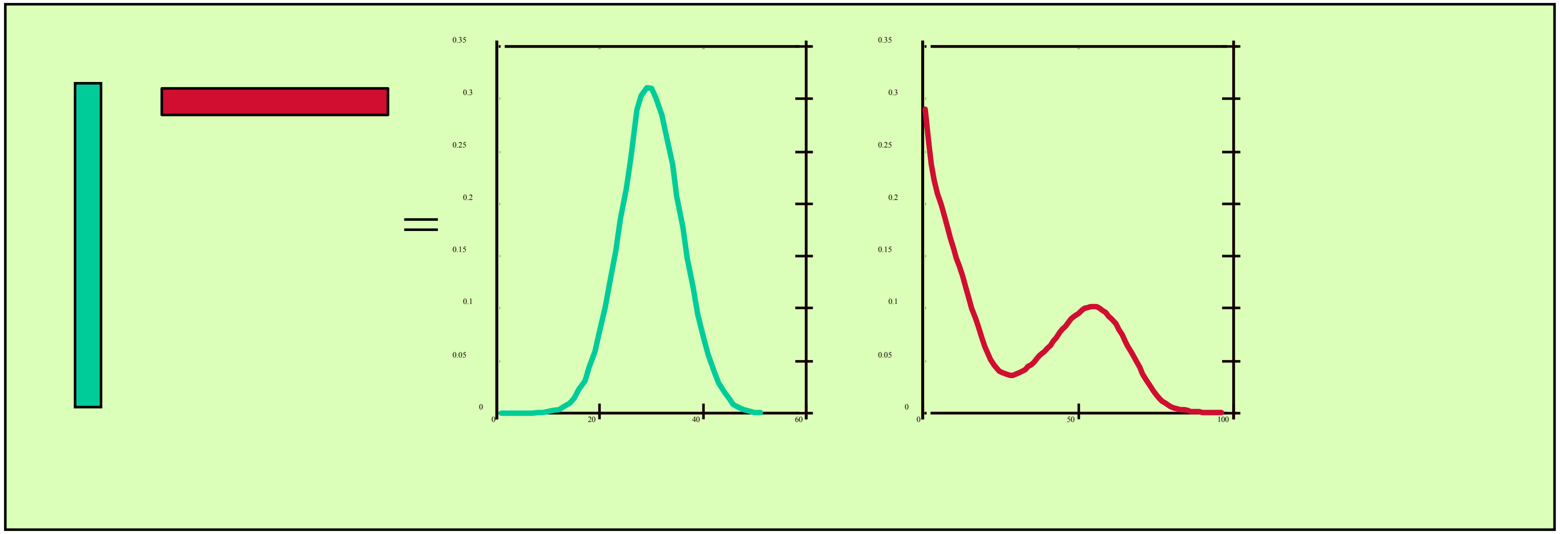
D(NR,NC) experimental data matrix

C(NR,N) row (concentration) profiles matrix

S(NC,N) column (spectra) profiles matrix

E(NR,NC) residual (noise, error) matrix

GOALS OF MCR



•Recovery of the responses of every component (chemical species) in the different orders of measurement: qualitative information, identification)

•Is it possible to recover quantitative information?

Rotational Ambiguities

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

$$\mathbf{S}^T_{new} = \mathbf{T}\,\mathbf{S}^T$$

(N,NC) *(N,N)* *(N,NC)*

$$\mathbf{C}_{new} = \mathbf{C}\,\mathbf{T}^{-1}$$

(NR,N) *(NR,N)* *(N,N)*

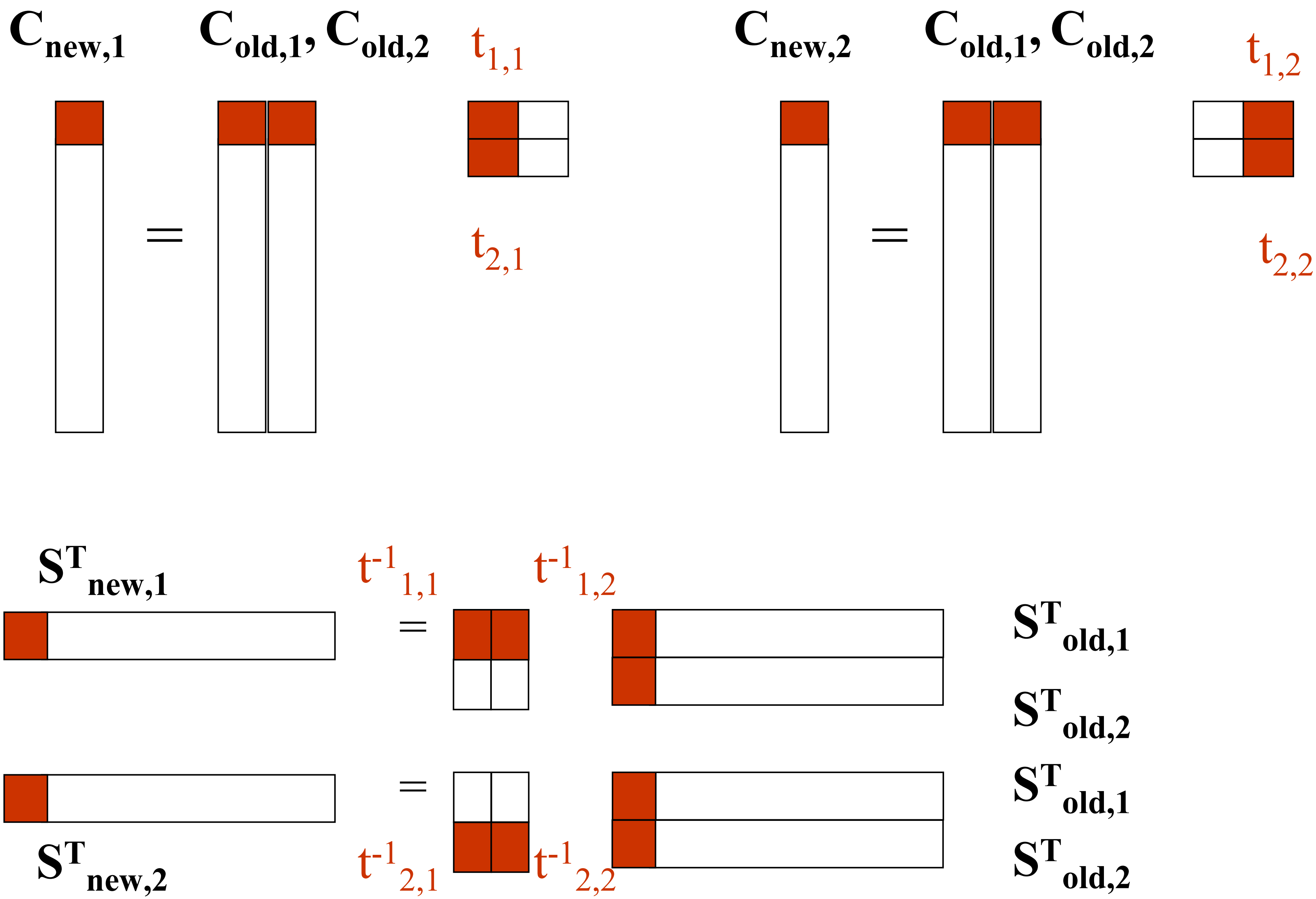
$$\mathbf{D}^* = \mathbf{C}\,\mathbf{S}^T = \mathbf{C}_{new}\mathbf{S}^T_{new}$$

Matrix decomposition is not unique!

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

Rotational freedom for any **T**

Rotational ambiguities and T(N,N)



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

1) By using selective variables and/or by using local rank information
2) By using natural constraints (*non-negativity, unimodality, closure, shape*,...)
3) **By matrix augmentation (three-way data analysis)**

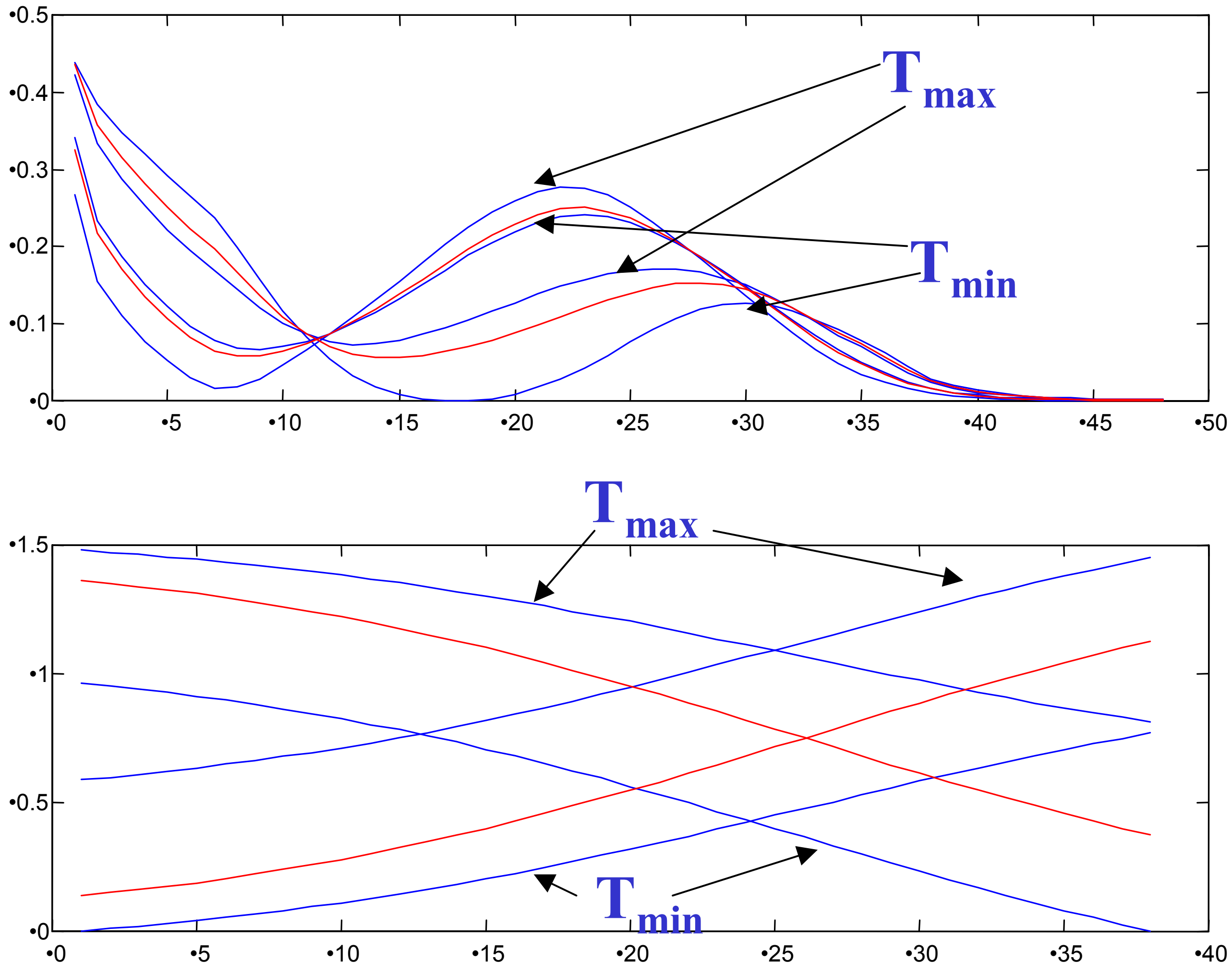
How to define feasible ranges/bands ?

- Feasible bands may be defined by rotation matrices **T** giving the maximum/outer and minimum/inner bounds of the feasible bands under a set of constraints

$$\mathbf{D}^* = \mathbf{C}_{inic}\,\mathbf{S}^T_{inic} =$$
$$= \mathbf{C}_{inic}\,\mathbf{T}_{min}\,\mathbf{T}^{-1}_{min}\,\mathbf{S}^T_{inic} = \mathbf{C}_{min}\mathbf{S}^T_{min} =$$
$$= \mathbf{C}_{inic}\mathbf{T}_{max}\,\mathbf{T}^{-1}_{max}\,\mathbf{S}^T_{inic} = \mathbf{C}_{max}\mathbf{S}^T_{max}$$

where: $\mathbf{D}$(NR,NC), $\mathbf{C}$(NR,N), $\mathbf{S}^T$(N,NC), $\mathbf{T}$(N,N)

T_{max} and T_{min} define maximum and minimum feasible ranges/bands



FACTOR ANALYSIS AMBIGUITIES

Scale (intensity) ambiguities:

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

How to break intensity ambiguities?

In the analysis of a single data matrix intensity ambiguities can only be solved providing external Information, by closure or by normalization.

In the simultaneous analysis of a set of correlated data matrices, intensity ambiguities are solved in relative terms: Recovery of quantitative information is possible!

Evaluation of feasible bands: previous studies

- W.H.Lawton and E.A.Sylvestre, Technometrics, 1971, 13, 617-633
  - *resolution of mixtures of two component systems*
  - *boundary regions for two component systems*
  - *non-negativity, normalization and selectivity constraints*

- O.S.Borgen and B.R.Kowalski, Anal. Chim. Acta, 1985, 174, 1-26
  - *extension to three components*
  - *boundary regions were obtained using a simplex rotation algorithm*

- R.C.Henry and B.M.Kim (Chemomet. And Intell. Lab. Syst., 1990, 8, 205-216)
  - *outer and inner boundaries were obtained using a linear programming method*
  - *constraints were expressed as linear inequalities in the space defined by the eigenvectors of the matrix*
- P.D.Wentzell, J-H. Wang, L.F.Loucks and K.M.Miller (Can.J.Chem. 76, 1144-1155 (1998))
  - *permissible bands are obtained using a non-linear simplex optimization procedure including a penalty function and a weighthing factor to constrain appropriately the function to optimize*
- P. Gemperline (Analytical Chemistry, 1999, in press)
  - *feasible bands are calculated using a non-linear constrained optimization algorithm (constr.m function in MATLAB Optimization Toolbox)*
  - *non-negativity and selectivity constraints*

General Optimization Problem:

$$\underset{\mathbf{X}}{\text{minimize}}\ f(\mathbf{X}) \quad \text{subject to} \quad g_e(\mathbf{X}) = 0 \quad \text{and to} \quad g_i(\mathbf{X}) \leq 0$$

where **X** is the matrix of variables, f(**X**) is a non-linear scalar function of **X** and **g(X)** is the vector of constraints (non-linear function of **X**)

Constrained Non-Linear Optimization Problem (NCP)

MATLAB Optimization Toolbox functions for non-linear constrained optimization:

constr.m and nlconst.m Find the constrained minimum of a non-linear scalar function of several variables

qp.m Solves a QP Quadratic programming subproblem: X=QP(H,f,A,b)

min 1/2*x'Hx + f'x
x
subject to: Ax <= b

Optimization Method

Sequential Quadratic Programming with a mixed quadratic and cubic line search:

- SQP methods represent the state-of-art in non-linear programming optimization methods
- At each major iteration, an approximation is made of the Hessian of the Lagrangian function using a quasi-Newton updating method
- A Quadratic Programming (QP) sub-problem is iteratively generated whose solution is used to form a search direction for a line search procedure

Practical Optimization, P.E.Gill, W.Murray and M.H.Wright, Academic Press, 1981; MATLAB Optimization Toolbox

Implementation of the optimization algorithm:

1) What are the **X** variables of the problem?
2) What is the objective function to optimize?
3) What are the constraints of the problem?. Are they equality or inequality constraints?
4) What are the initial values of the variables and of the parameters of the optimization?

1) What are the variables of the problem?

$\mathbf{X} = \mathbf{T}$ (rotation matrix), $\mathbf{D} = \mathbf{C}\,\mathbf{T}\,\mathbf{T}^{-1}\,\mathbf{S}^{T}$

2) What is the objective function f(T) to be optimized?

For each species i = 1,..,ns

$$f(\mathbf{T}) = \frac{\left\| \mathbf{c}_i \mathbf{s}_i \right\|}{\left\| \mathbf{c}\ \mathbf{s} \right\|} \quad \text{or} \quad f(\mathbf{T}) = \frac{\sum_{j} c_{ij} s_{ij}}{\sum_{i,j} c_{ij} s_{ij}}$$

f(T) is scalar value between 0 and 1!

3) What are the constraints g(T)?

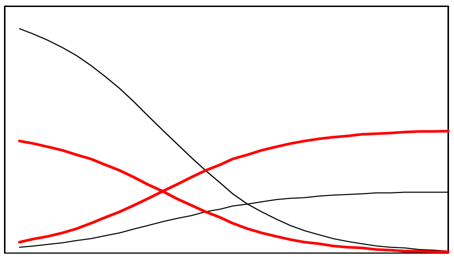
The following constraints are considered:

normalization/closure	g_{norm}/g_{clos}
non-negativity	g_{cneg}/g_{sneg}
known values/selectivity	g_{known}/g_{sel}
unimodality	g_{unim}
trilinearity	g_{tril}

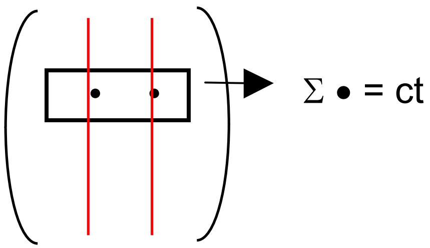
Are they equality or inequality constraints?

$\mathbf{g_{norm}}$ normalization/closure constraints

- spectra normalization
  - $||(\mathbf{s(T)})|| = 1$
  - $\mathbf{g_{norm}}(\mathbf{T}) = 1 - ||(\mathbf{s(T)})|| = 0$
  - N equality constraints
- closure
  - $\Sigma c_i(\mathbf{T}) = \mathrm{TOT}$
  - $\mathbf{g_{clos}}(\mathbf{T}) = \mathrm{TOT} - \Sigma c_i(\mathbf{T}) = 0$
  - N x NR equality constraints



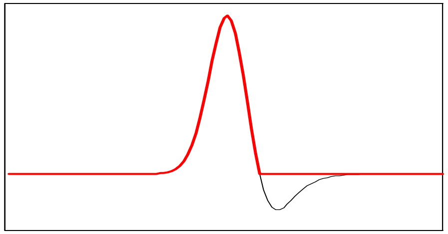
closure



g_{neg} non-negativity constraints

- concentration non-negativity
  - **$c(T) \geq 0$**
  - **$g_{cneg}(T)$ = $-c(T)$** ≤ 0
  - N x NR inequality constraints
- spectra non-negativity
  - **$s(T) \geq 0$**
  - **$g_{sneg}(T)$ = $-s(T)$** $\leq$ 0
  - N x NC inequality constraints

non-negativity



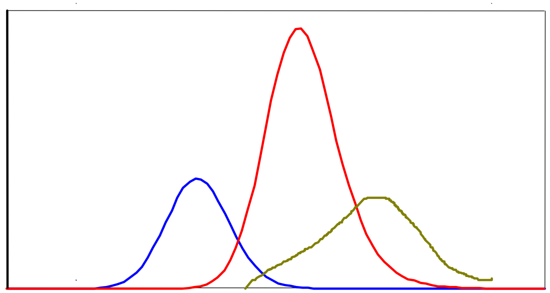
g_{known} (known values) and g_{sel} (selectivity) constraints

- known values of **c** and **s** ($\mathbf{c}_{known}$, $\mathbf{s}_{known}$)
  - $\mathbf{c}(T) = \mathbf{c}_{known}$, $\mathbf{s}(T) = \mathbf{s}_{known}$
  - $\mathbf{g}_{cknown}(T) = \mathbf{c}(T) - \mathbf{c}_{known} = 0$
  - $\mathbf{g}_{sknown}(T) = \mathbf{s}(T) - \mathbf{s}_{known} = 0$
  - equality constraints
- selectivity/zero local rank values ($\mathbf{c}_{sel}$, $\mathbf{s}_{sel}$)
  - $\mathbf{c}(T) \leq \mathbf{c}_{sel}$ $\mathbf{s}(T) \leq \mathbf{s}_{sel}$;
  - $\mathbf{g}_{csel}(T) = \mathbf{c}(T) - \mathbf{c}_{sel} \leq 0$
  - $\mathbf{g}_{ssel}(T) = \mathbf{s}(T) - \mathbf{s}_{sel} \leq 0$
  - inequality constraints

Resolution based on local rank information (*resolution theorems, R.Manne, Chemolab, 1995, 27, 89-94*)

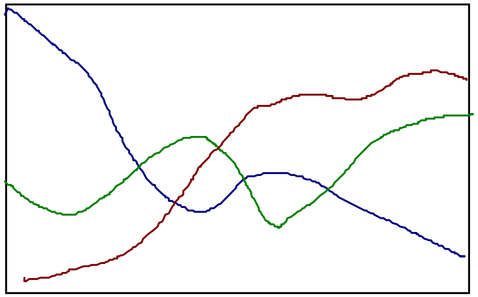
- **The true concentration profile of a component in a multicomponent mixture can be recovered without ambiguity when all the other components in the mixture inside its concentration window are also present outside.**
- **The true spectrum profile of a component in a multicomponent mixture can be recovered without ambiguities if its concentration window is not completely embedded inside the concentration window of a different component of the mixture**

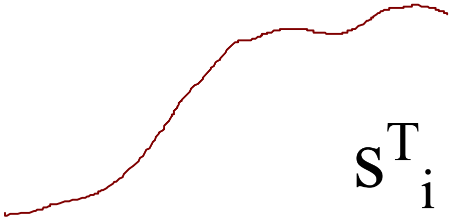
Selectivity/ local rank constraints



$$\mathbf{C} = \begin{pmatrix} \mathbf{x} & 0 & 0 \\ \mathbf{x} & \mathbf{x} & 0 \\ \mathbf{x} & \mathbf{x} & \mathbf{x} \\ .. & .. & .. \\ \mathbf{x} & \mathbf{x} & \mathbf{x} \\ 0 & \mathbf{x} & \mathbf{x} \\ 0 & \mathbf{x} & \mathbf{x} \end{pmatrix}$$

Known values/profiles



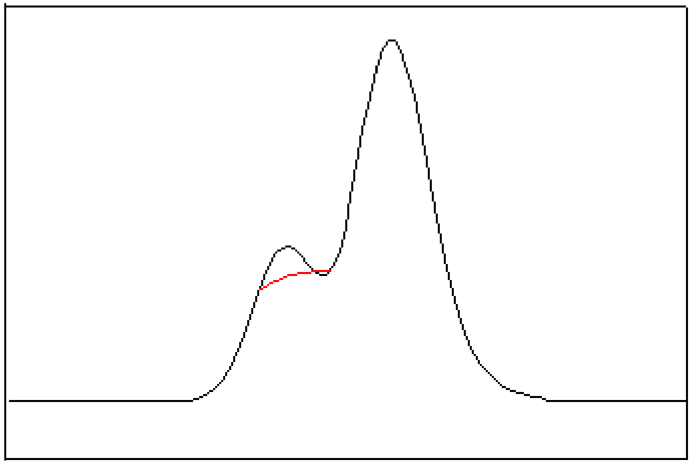


$\mathrm{S}^{\mathrm{T}}{}_{\mathrm{i}}$

known spectrum

g_{unimod} unimodality constraints

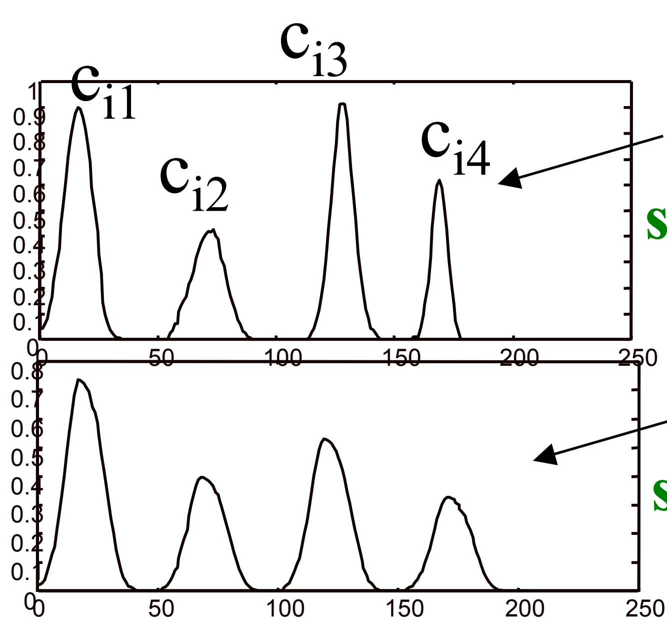
- Find values in C which are non unimodal:
  - find c(non-unimodal)
  - $\mathbf{g_{unimod}(T)} = |\mathbf{c}\text{ (non-unimodal)-}\mathbf{c}\text{ (last unimodal)}| \leq 0$
  - implemented as inequality constraints



g_{tril} trilinearity constraints (for three-way data)

- For each species i=1,..N :
  - calculate ratio(T) = sv(2)/sv(1) from $\mathbf{C}_{i,aug}$ matrix
  - $\mathbf{g}_{tril}(\mathbf{T}) = \text{ratio}(\mathbf{T}) - 0.001 \leq 0$
  - N inequality constraints

$$\mathbf{C}_{i,aug} = [c_{i1}(\mathbf{T});c_{i2}(\mathbf{T});....;c_{ik}(\mathbf{T})]$$



Profiles with different shape: sv(2)/sv(1) ≥ 0.001

Profiles with equal shape sv(2)/sv(1) < 0.001

4) What are the initial estimates of C, S^T?

C and $\mathbf{S^T}$ are obtained by MCR-ALS

(*solving iteratively the two LS equations*):

$$\min_{\hat{C}} \left\| \hat{D}_{PCA} - \hat{C}\hat{S}^T \right\|$$

$$\min_{S^T} \left\| \hat{D}_{PCA} - \hat{C}\hat{S}^T \right\|$$

- Optional constraints (*non-negativity, unimodality, closure, selectivity,...)* are applied at each iteration
- Initial estimates of C or S are obtained from EFA or from pure variable detection methods.
- *R.Tauler, A.Smilde and B.R.Kowalski J.of Chemometrics, 1995,9,31-58*

4) What are the initial values of T?

NCP depends on initial estimates of **T**! (local minima, convergence, speed …)

$$\mathbf{T} = \mathbf{eye(N)} = \begin{pmatrix} 1 & 0 & \dots & 0 \\ 0 & 1 & \dots & 0 \\ \dots & \dots & \dots & \dots \\ 0 & 0 & \dots & 1 \end{pmatrix}$$

For N = 2, **T**(2,2)
N = 3 **T**(3,3)
N = 4 **T**(4,4)
………………

What are the initial optimization parameters?

- termination tolerance for t values; e.g 1e-4
- termination tolerance for f(t) values; e.g 1e-4
- termination criterion on constraint violation, e.g. 1e-5
- maximum number of iterations is 100*number of t values; for N=2, 100 * 2+2 = 400;
- minimum change in variables for finite difference gradients; e.g 0.001
- maximum change in variables for finite difference gradients; e.g. 0.1
- initial step length = 1

Optimization algorithm

Initial estimations of $\mathbf{C}_{ALS}$ and $\mathbf{S}_{ALS}$ profiles are obtained by MCR-ALS

$\mathbf{T}$=eye(number of species)

For each species define objective function

$f(\mathbf{T})=\mathrm{norm}(\mathbf{c}(\mathbf{T})\mathbf{s}(\mathbf{T}))=\mathrm{norm}(\mathbf{c}_{ALS}\ \mathbf{T}\ \mathbf{s}_{ALS}\ /\ \mathbf{T})$

Select constraints $g(\mathbf{T})$:

equality g_e: normalization/closure, known values,

inequality g_i: non-negartivity, selectivity, unimodality, trilinearity,

Find T_{min} which gives a minimum of $f(\mathbf{T})$ under constraints $g_i(\mathbf{T})<0$, $g_e(\mathbf{T})=0$

Find T_{max} which gives a maximum of $f(\mathbf{T})$ under constraints $g_i(\mathbf{T})<0$. $g_e(\mathbf{T})=0$

Built minimum band

$\mathbf{c}_{min} = \mathbf{c}_{ALS}\ /\ \mathbf{T}_{min}$

$\mathbf{s}_{min} = \mathbf{s}_{ALS}\ /\ \mathbf{T}_{min}$

Built maximum band

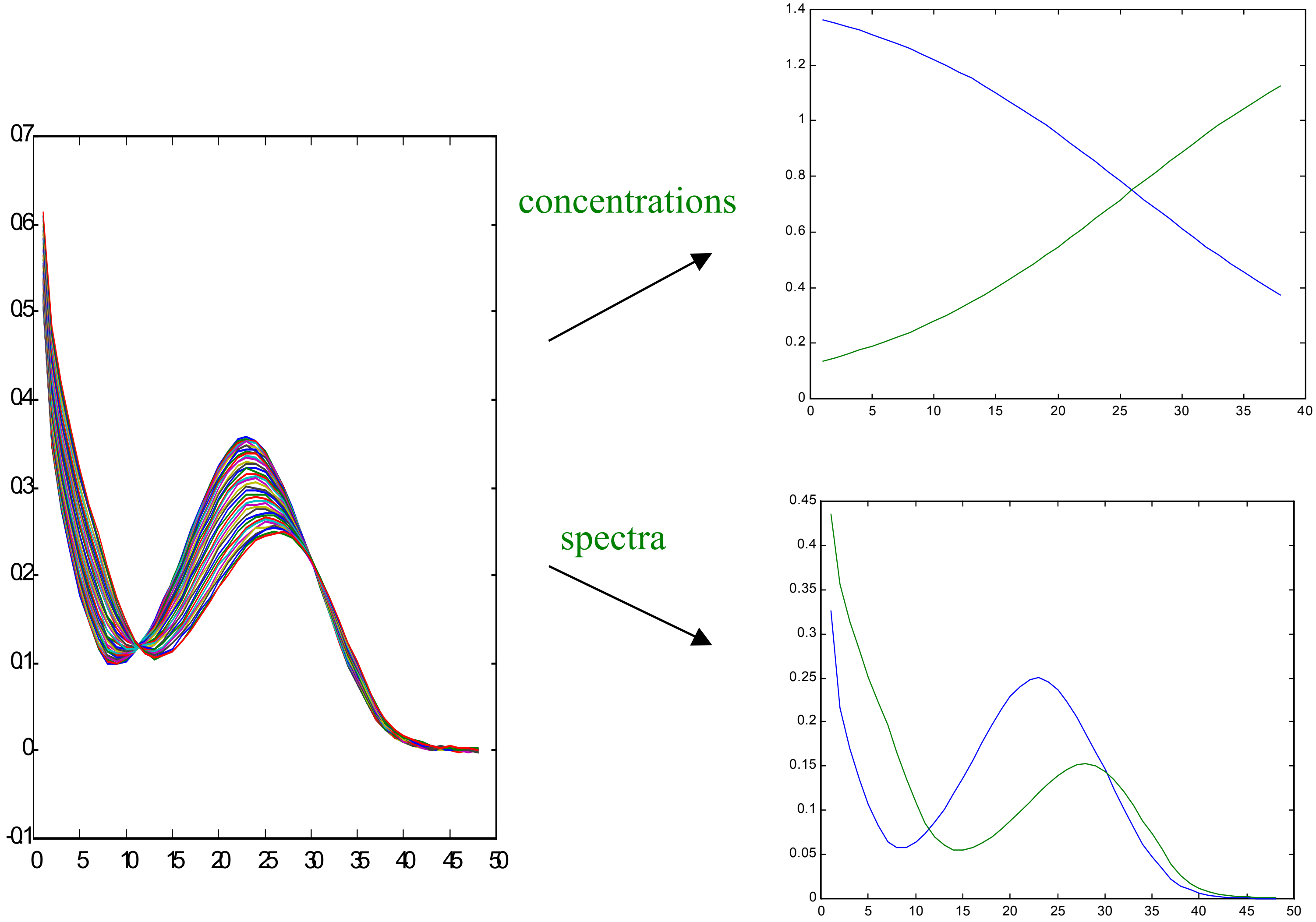
$\mathbf{c}_{max} = \mathbf{c}_{ALS}\ /\ \mathbf{T}_{max}$

$\mathbf{s}_{max}=\mathbf{s}_{ALS}\ /\ \mathbf{T}_{max}$

Examples of application

- Mixture of two reacting components
- Mixture of three LC coeluting components
- Three-way data (non-trilinear/trilinear)
- Real data: UV spectrometric study of Cu(II)-chloride system

Example 1: Mixture of two reacting components

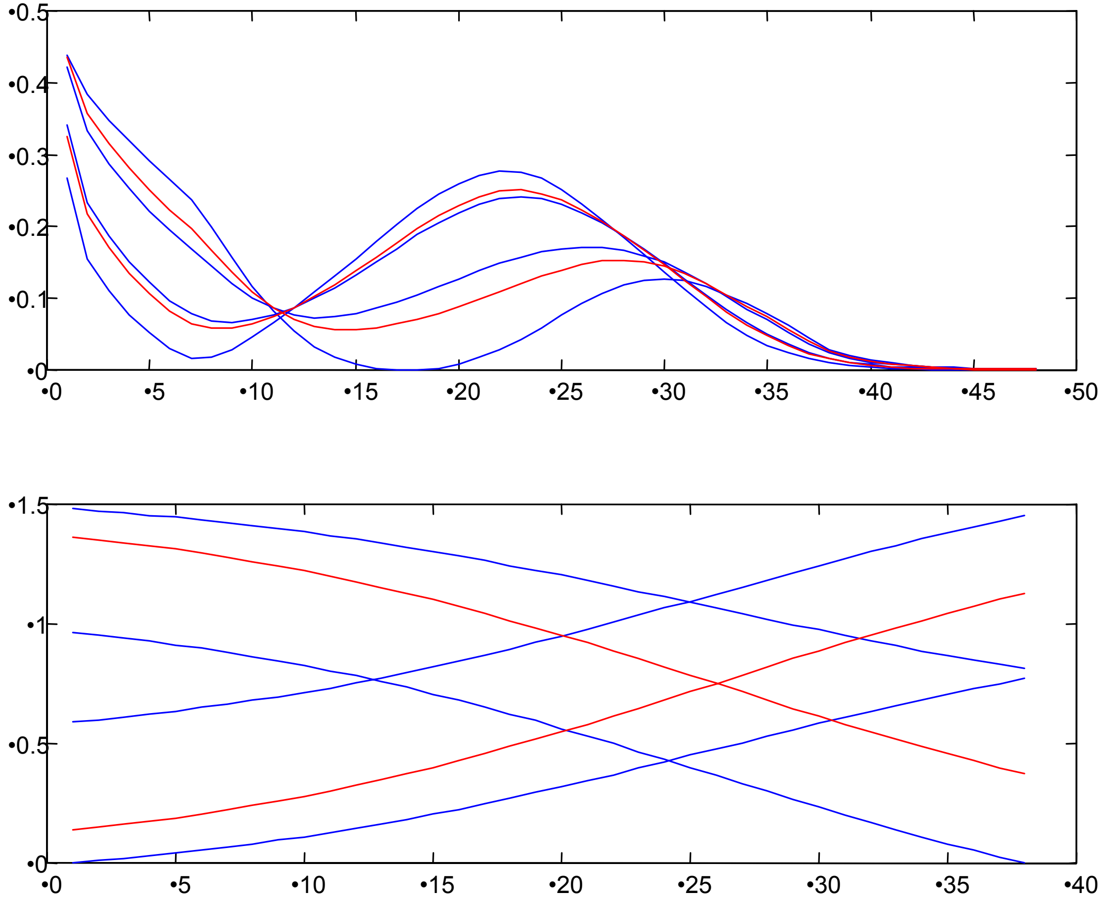


Example 1

- Mixture of two reacting components
  - No selectivity in spectra
  - Possible selectivity in one concentration profile
  - Calculation of feasible bands. Study of effects:
    - Non-negativity and spectra normalization constraints
    - Initial estimates (from simulation or from EFA-ALS)
    - Effect of closure constraint
    - Effect of selectivity constraint

Feasible bands: non-negativity and normalization constraints

(initial estimates from simulation)



Optimal values
(non-negativity and normalization constraints)

- **Optimal t values for max band**

1st species		*2nd species*	
0.9219	0.0922	1.2595	-0.3321
-0.4885	1.3696	0.2569	0.7759

- **Optimal t values for minimum band**

1st species		*2nd species*	
1.2595	-0.3321	0.9219	0.0922
0.2569	0.7759	-0.4885	1.3696

- **Optimal values for f(t)**

f(T) in the maximum band and number of iterations in ( )

0.4303 (21)   0.2892 (26)

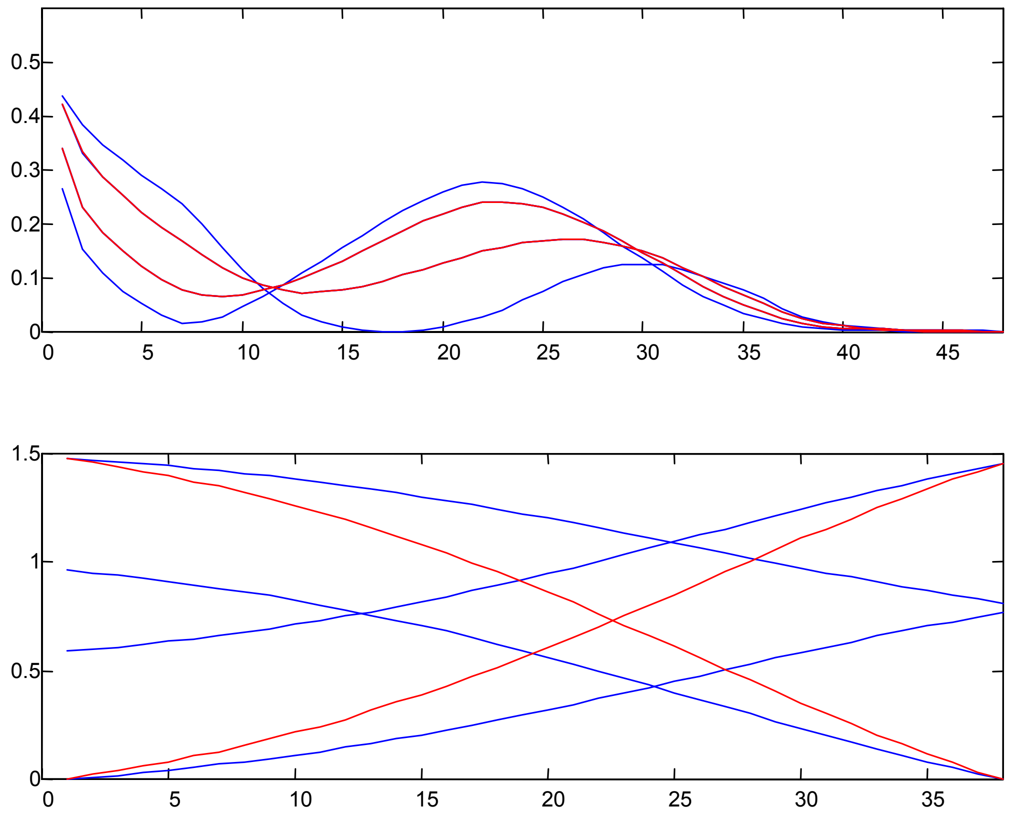
f(T) in the minimum band and number of iterations in ( )

-0.8365 (26)   -0.6989 (21)

- **Lack of fit, lof = 0.466**

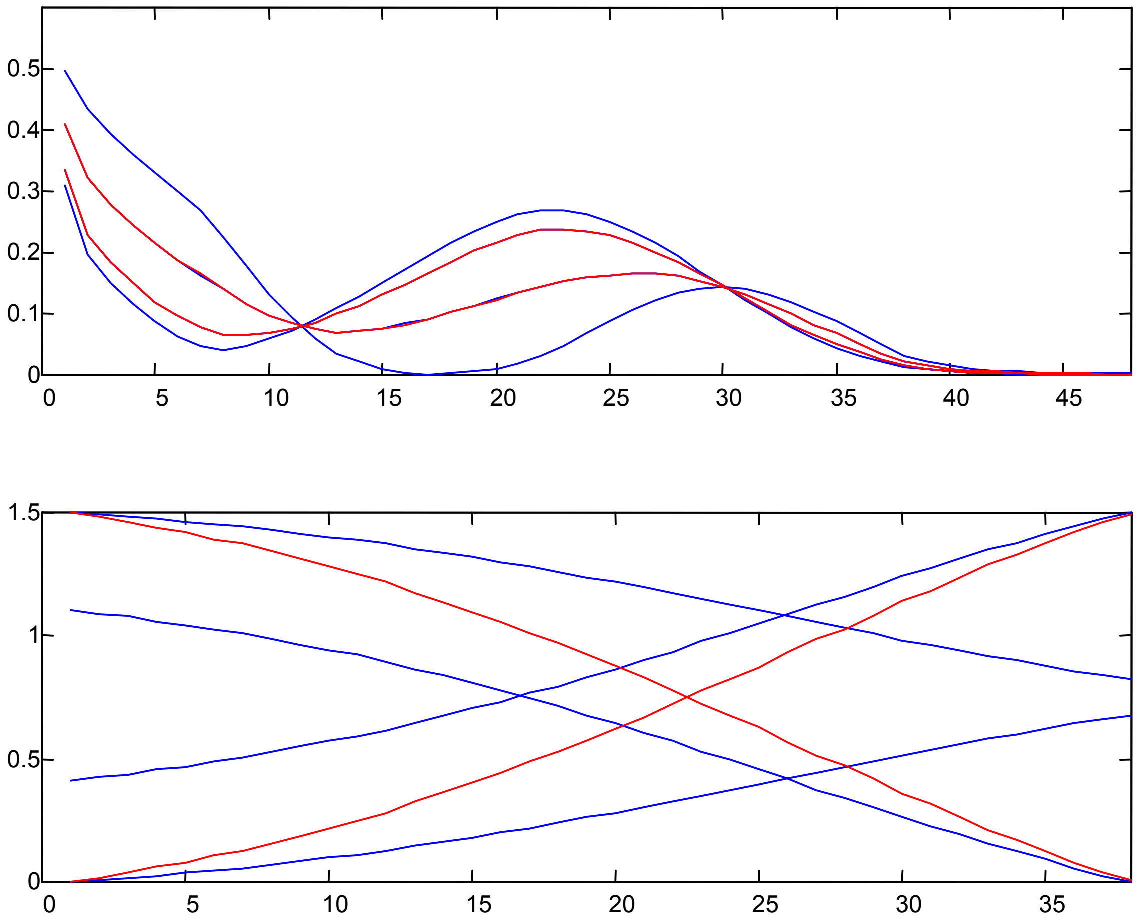
Feasible bands: non-negativity and normalization constraints

(initial estimates from EFA-ALS)



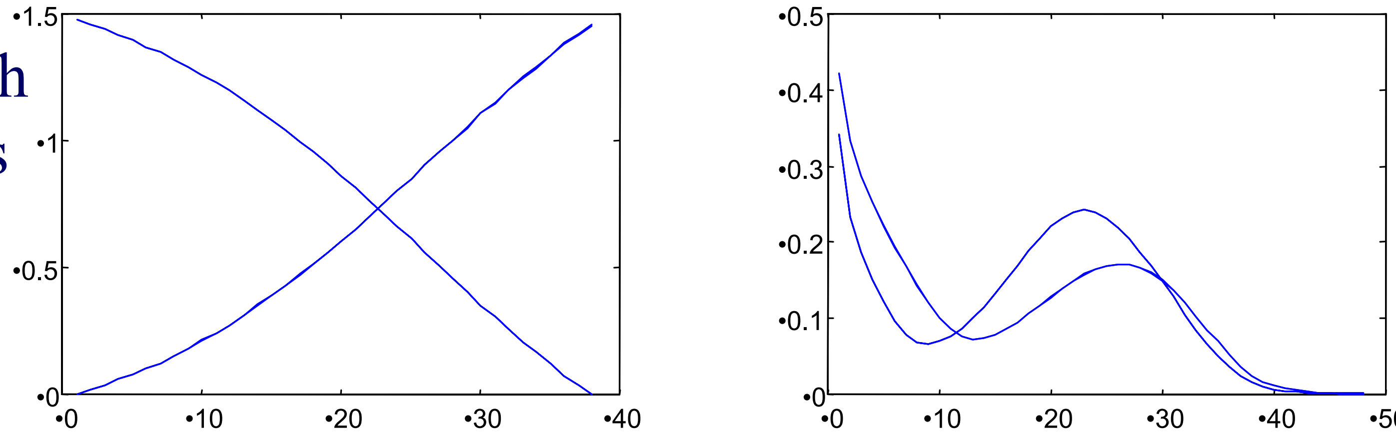
Starting with different initial estimates give the same bands

Feasible bands: ***closure and non-negativity constraints***

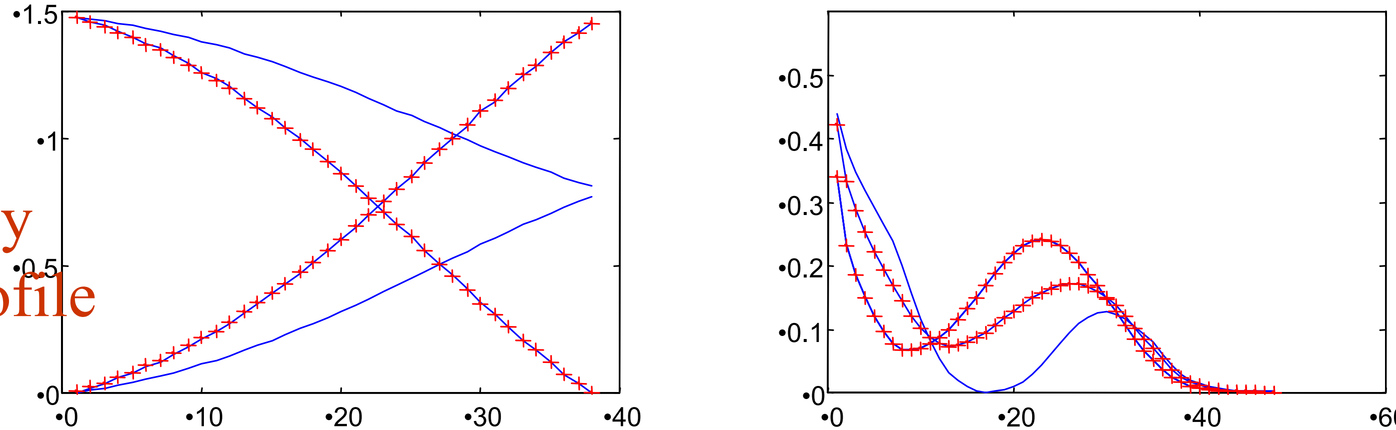


Feasible bands: *selectivity and non-negativity constraints*

Selectivity is applied to both concn profiles



Selectivity is applied to only one concn profile



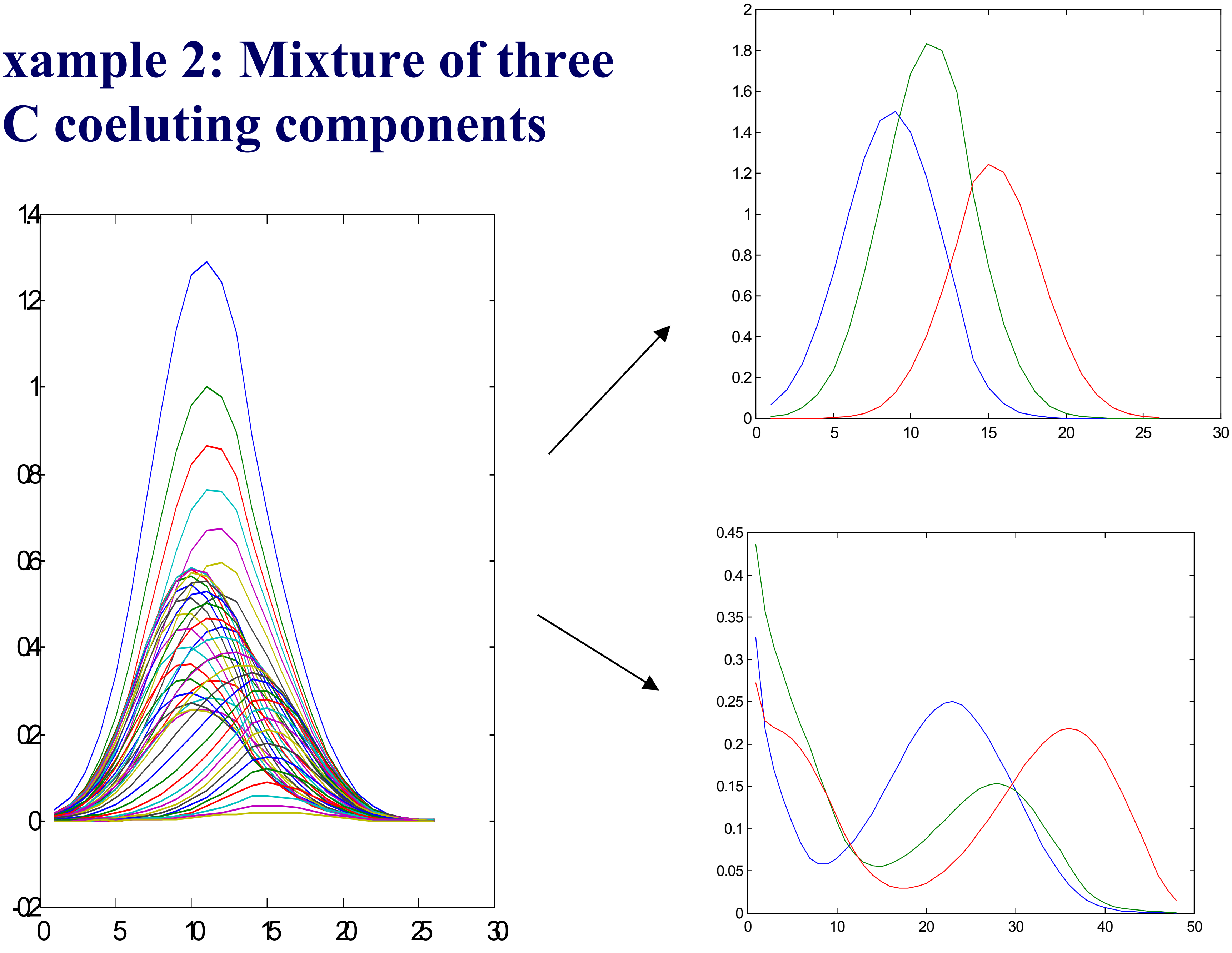
Conclusions: effect of constraints

- non-negativity
  - reduce the set of possible solutions to a smaller subset; rotational ambiguities are only partly solved
  - the set of solutions have physical meaning
- normalization
  - the set of feasible solutions differ only in the shape, not in the intensity; scale-intensity ambiguities are solved
- closure
  - reduce intensity and rotational ambiguities

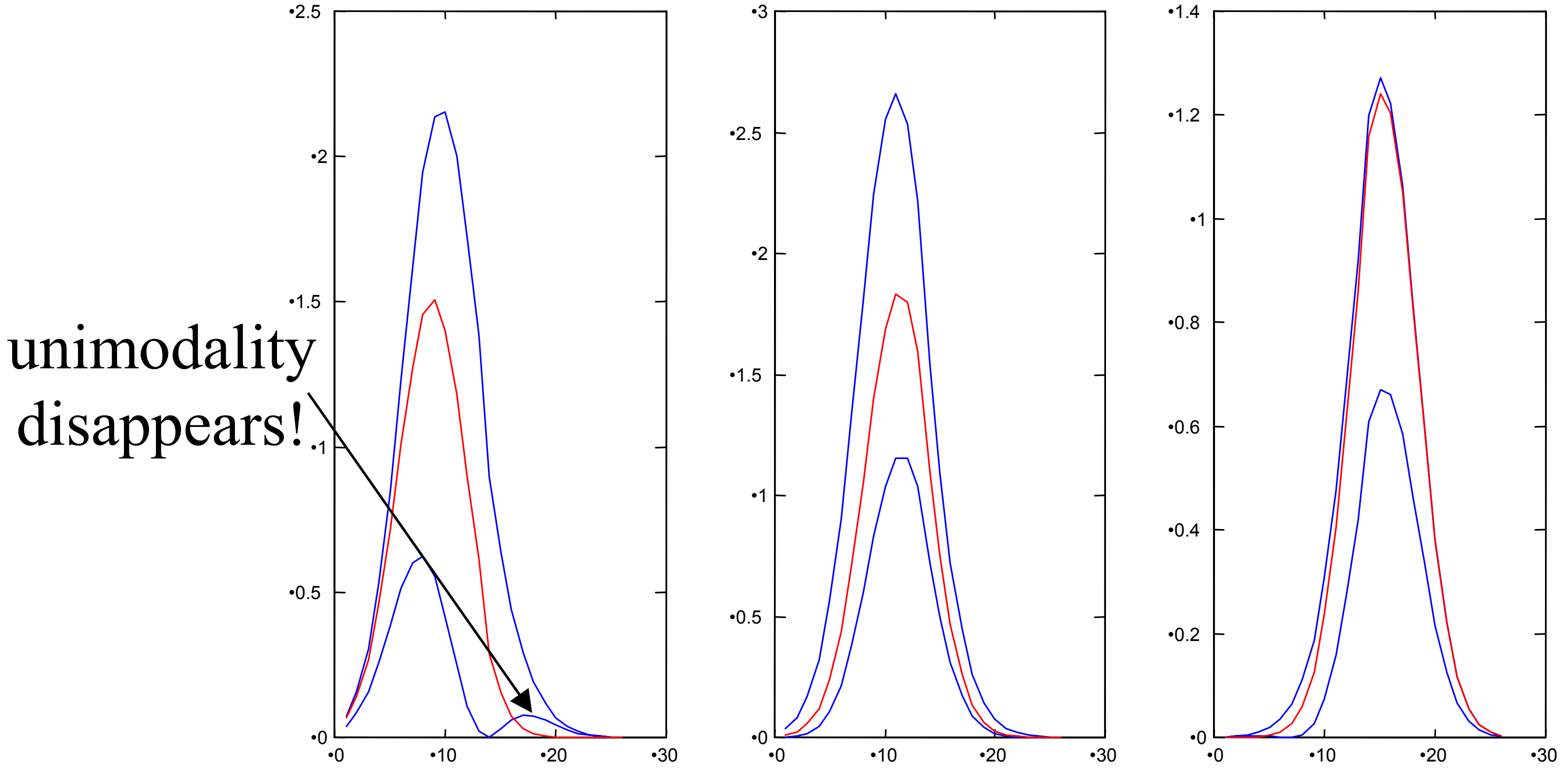
Example 2

- Mixture of three coeluting chromatographic components (chromatographic coelution)
  - Local rank resolution conditions
  - Calculation of feasible bands. Study of possible effects:
    - Effect of non-negativity and spectra normalization constraints
    - Effect of local rank/selectivity constraints
    - Effect of unimodality constraint
    - Initial estimates (from simulation and from EFA-ALS)

Example 2: Mixture of three LC coeluting components

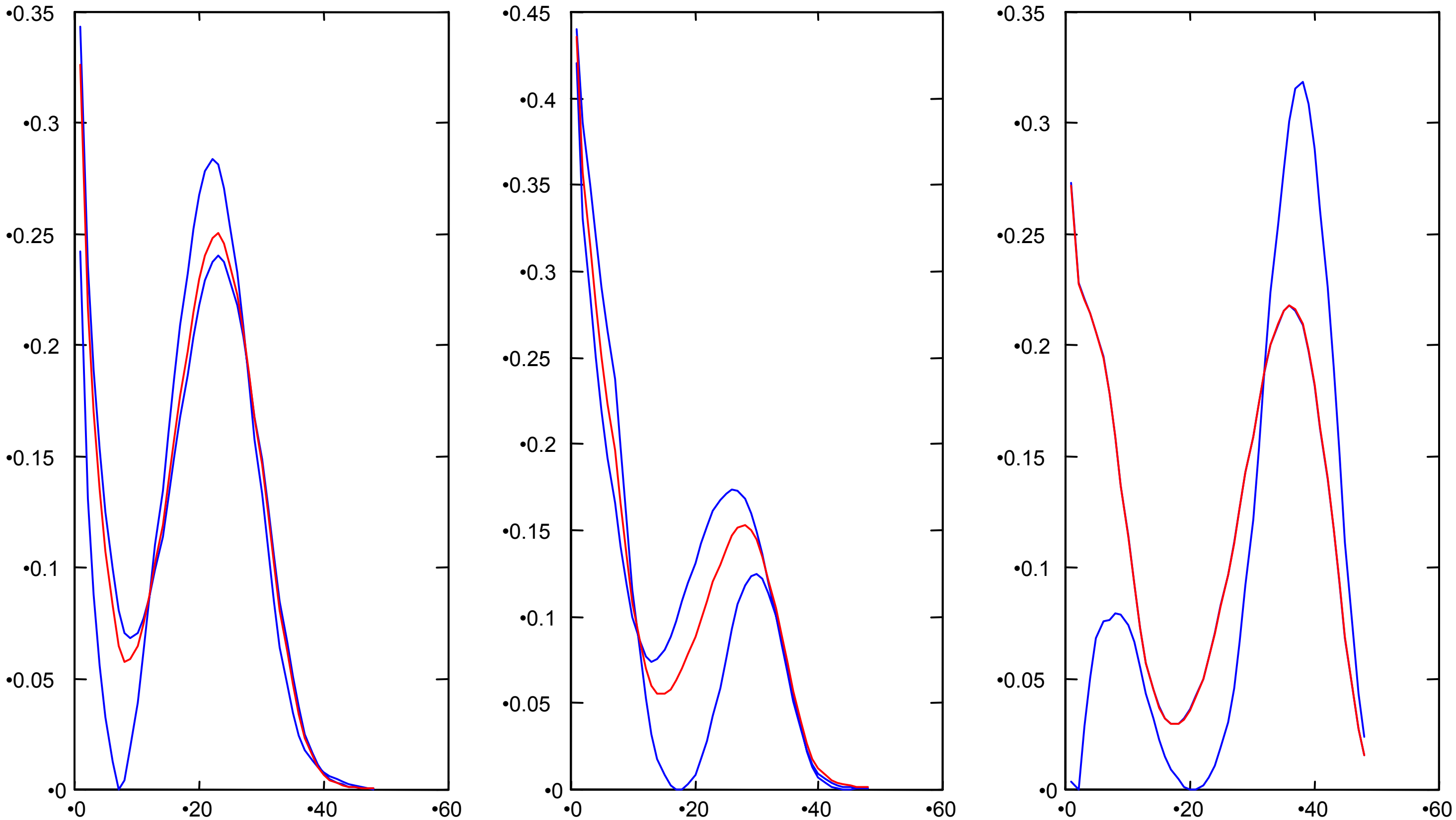


Feasible bands for concentration profiles: non-negativity and normalization constraints
(initial estimates from simulation)



Feasible bands for spectra profiles: non-negativity and normalization constraints

(initial estimates from simulation)



Optimal values

(Initial estimation from simulation, non-negativity and normalization constraints)

- **Optimal t values for max band**

1st species			*2nd species*			*3rd species*		
0.9072	0.1090	0.0030	1.3378	-0.4477	0.0078	1.0013	0.0081	-0.0129
-0.4861	1.3575	0.0122	0.2806	0.7612	-0.0088	0.0092	1.0172	-0.0397
-0.1560	-0.0139	1.1013	-0.1397	-0.0730	1.1374	0.0001	0.0044	0.9964

- **Optimal t values for minimum band**

1st species			*2nd species*			*3rd species*		
1.3405	-0.4637	0.0244	0.9080	0.1091	-0.0011	0.9076	0.1201	-0.0150
0.3438	0.7159	-0.0258	-0.4956	1.4045	-0.0359	-0.2031	1.0786	0.0996
-0.1780	0.0662	1.0511	-0.0016	0.0042	0.9976	0.1923	-1.1702	1.6539

Optimal values for f(t)

f(T) in the maximum band and number of iterations in ( )

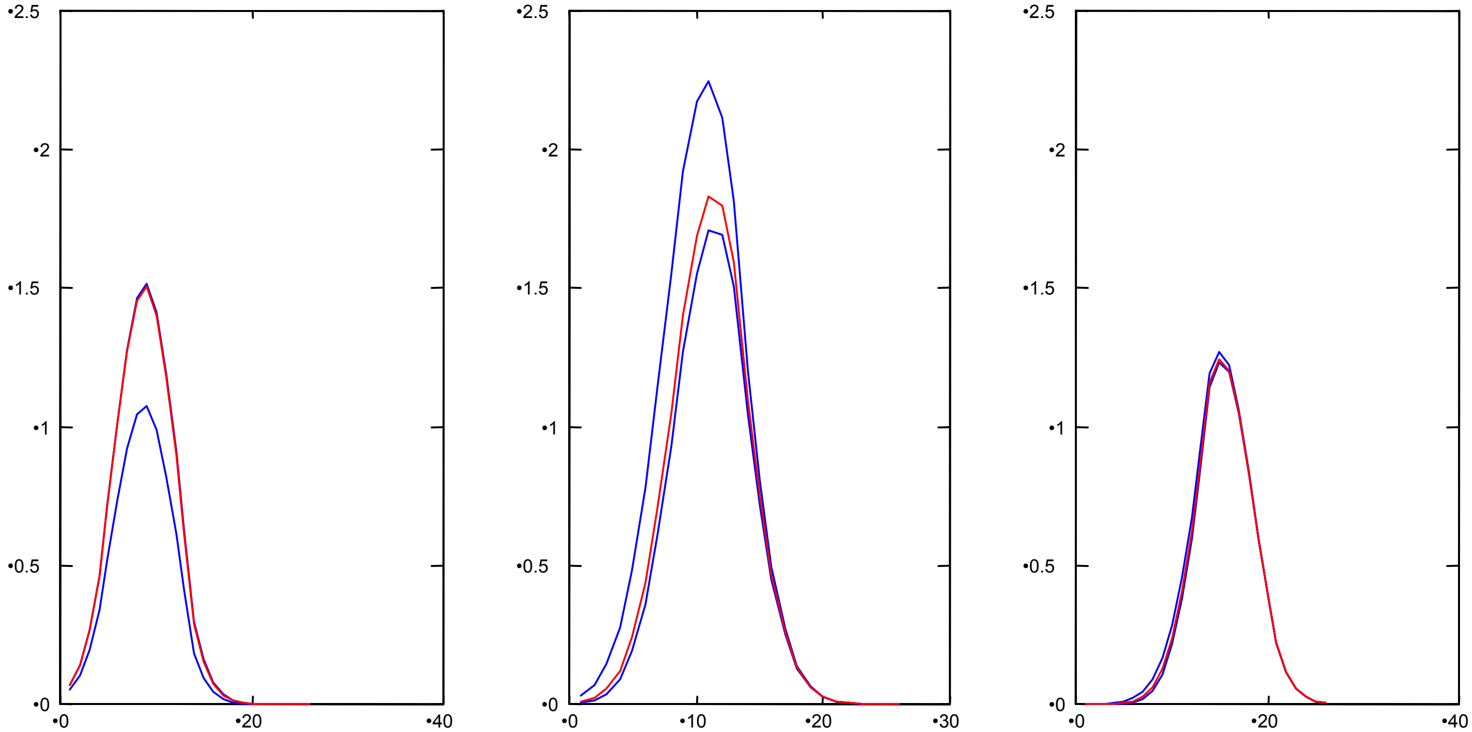
0.1166 (71) 0.1947 (51) 0.1222 (81)

f(T) in the minimum band and number of iterations in ( )

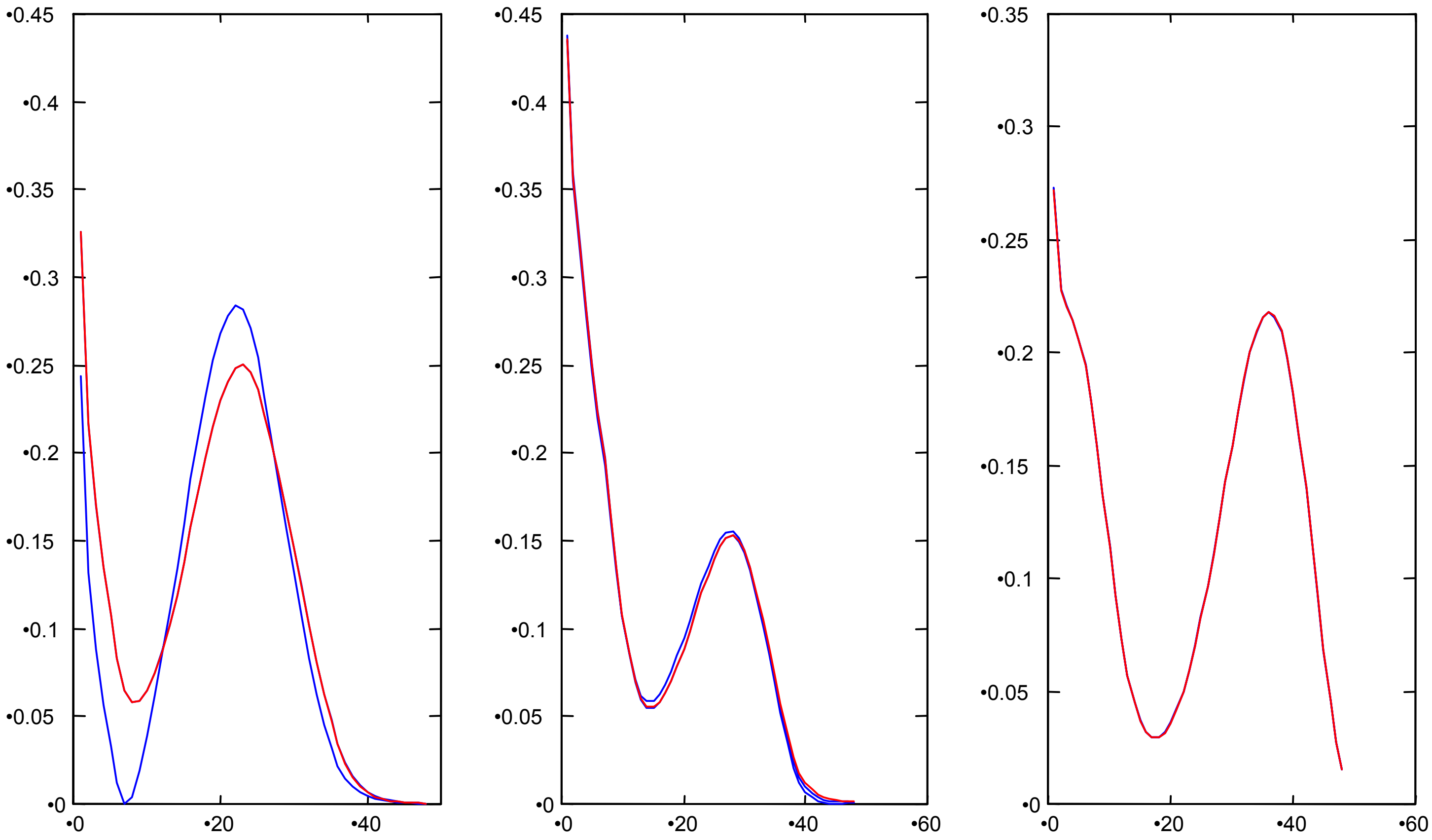
-0.5461 (71) -0.6229 (81) -0.3107(113)

Lack of fit, lof = 0.3854 %

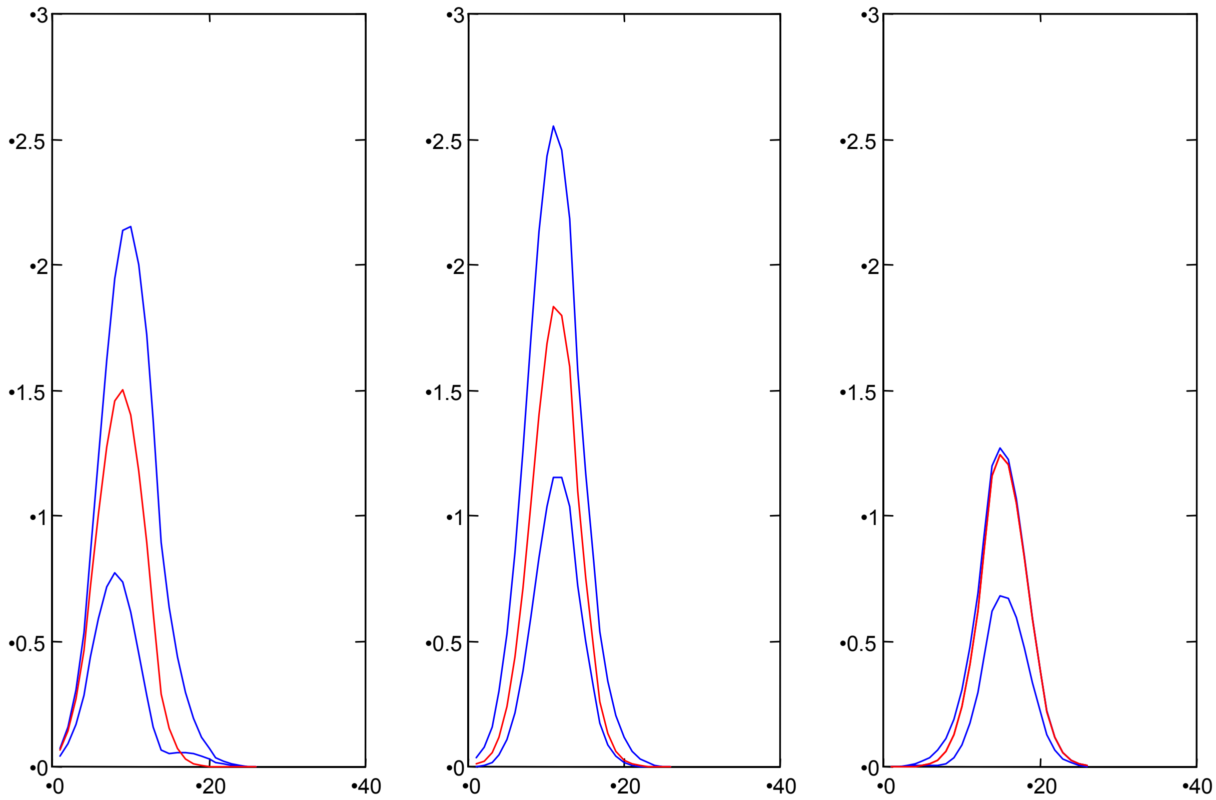
Feasible bands for concentration profiles: local rank, non-negativity and normalization constraints



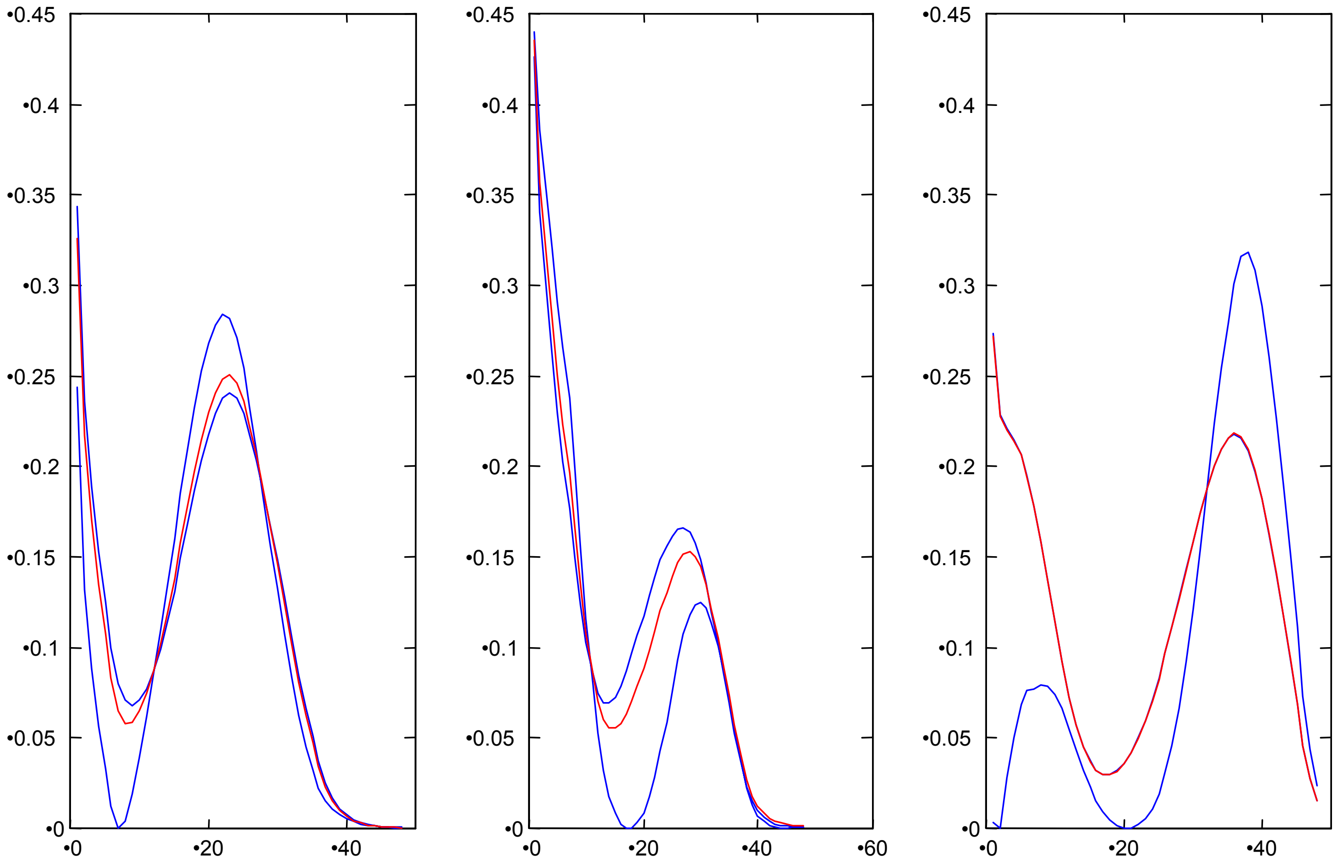
Feasible bands for spectra profiles: local rank, non-negativity and normalization constraints



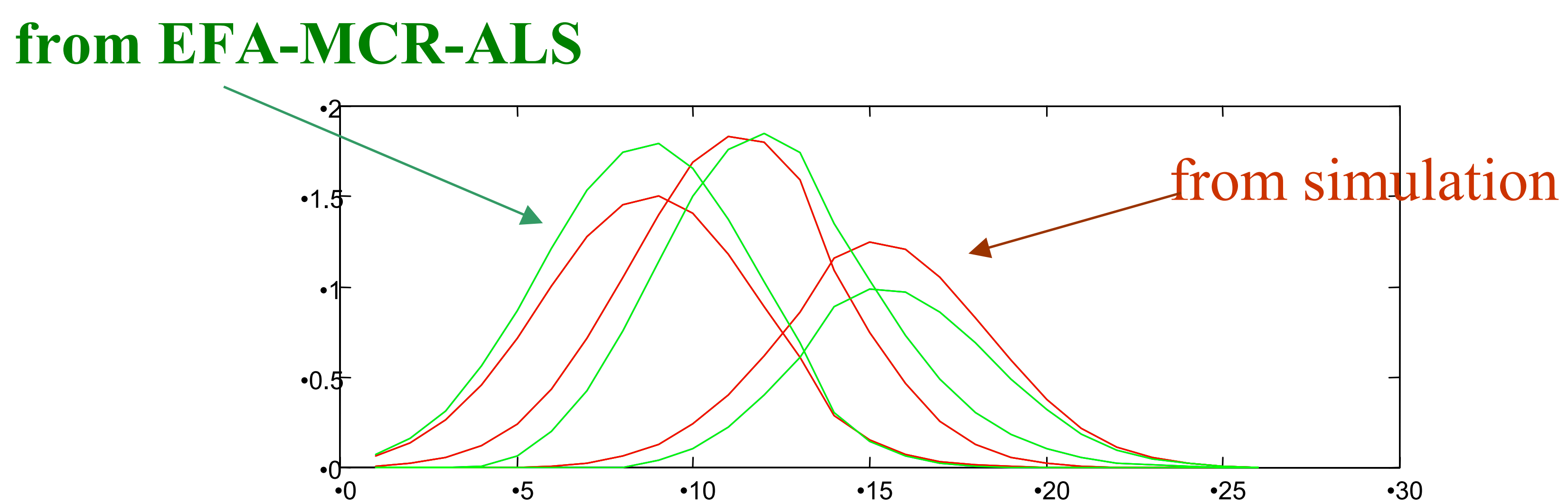
Feasible bands for concentration profiles: unimodality, non-negativity and normalization constraints

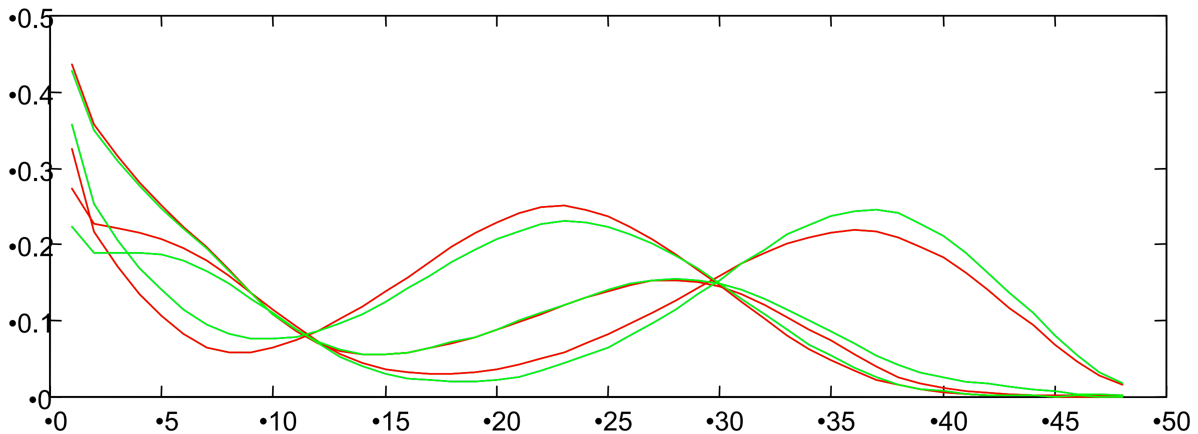


Feasible bands for spectra profiles: unimodality, non-negativity and normalization constraints



Effect of initial estimates: comparison of species profiles from EFA-MCR-ALS and from simulation

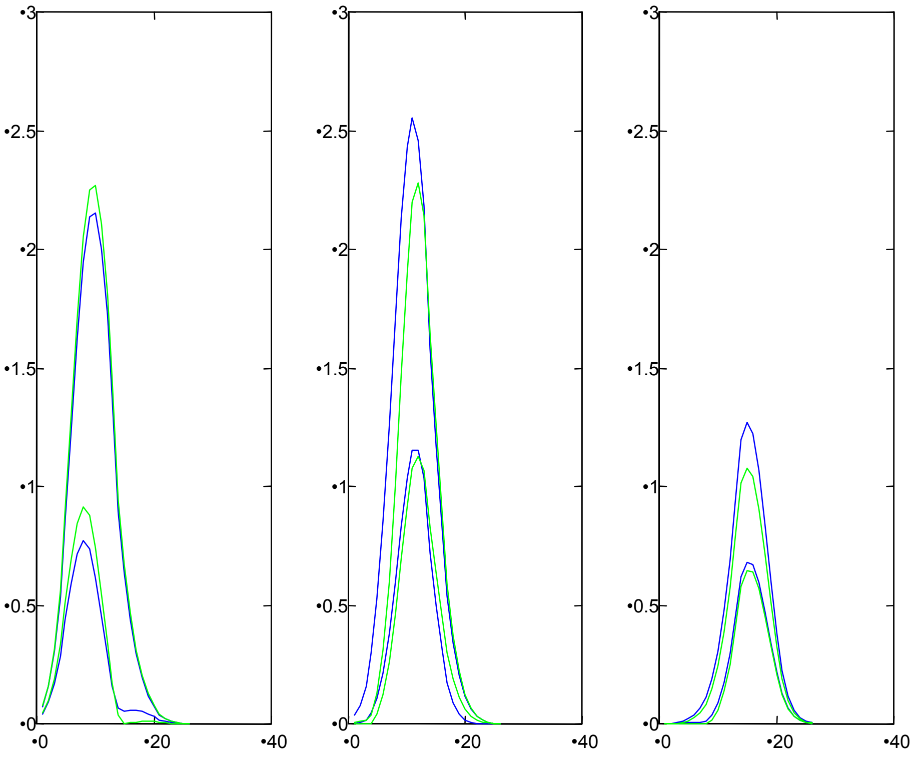




Effect of initial estimates. Calculation of feasible concentration bands:

blue =feasible bands from simulation (lof 0.3854)

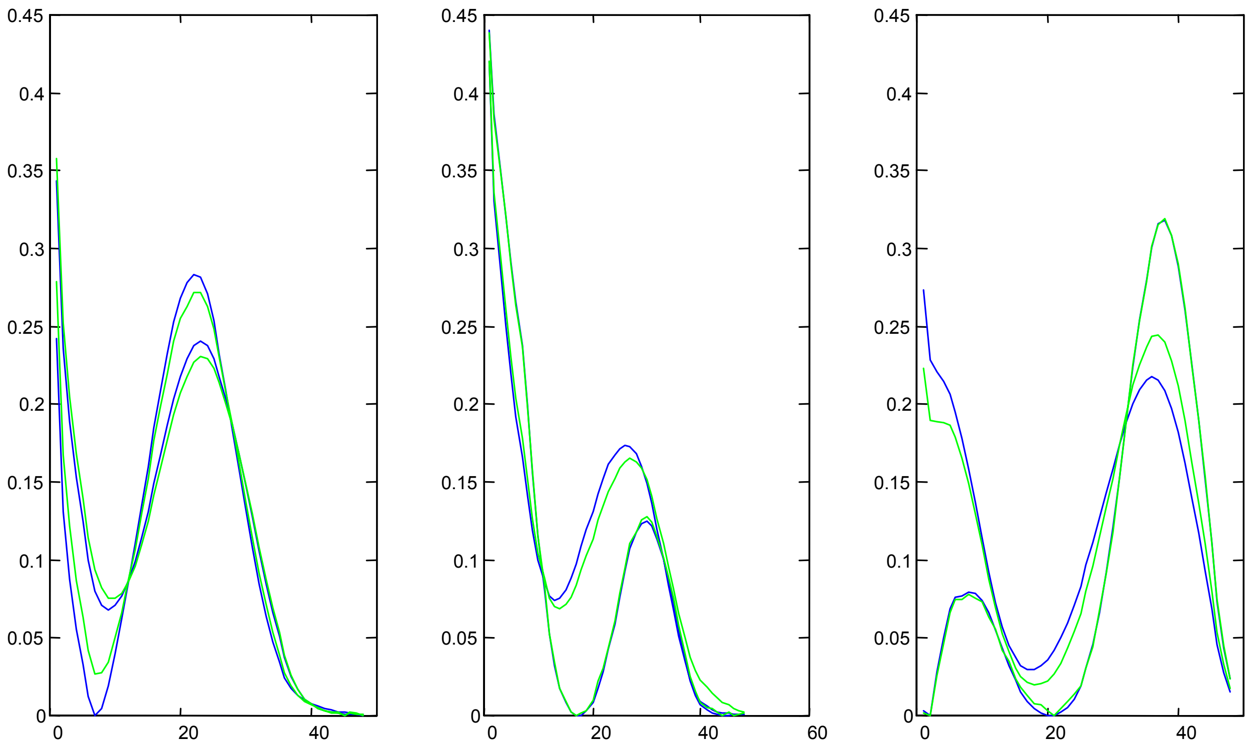
green =feasible bands from EFA-MCR-ALS (lof 0.3765)



Effect of initial estimates. Calculation of feasible spectral bands:

blue =feasible bands from simulation (lof 0.3854%)

green =feasible bands from EFA-MCR-ALS (lof 0.3765%)



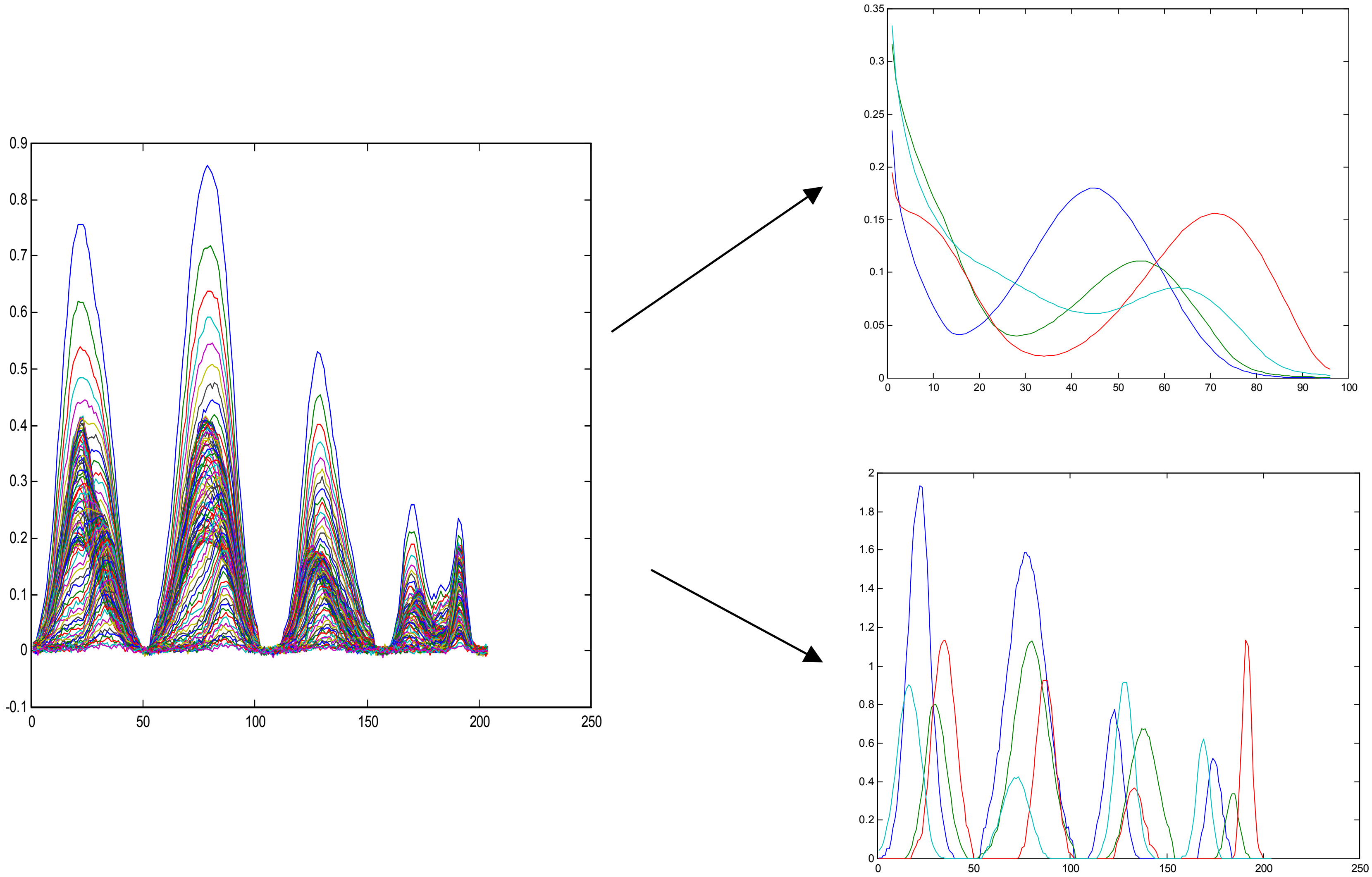
Conclusions: effect of constraints

- Effect of local rank and selectivity
  - Feasible bands are considerably reduced; unique solutions can be found in some cases depending on selective regions
- Effect of unimodality
  - Feasible bands were slightly modified to fulfill unimodality
  - Unimodality constraint is usually not needed when local rank/selectivity constraints are applied
- Effect of initial estimates
  - Practically equal feasible bands are obtained independently of different initial estimations

Example 3

- Four different mixtures of four coeluting chromatographic components
- Three-way data: non-trilinear and trilinear
  - Calculation of feasible bands. Study of possible effects:
    - Effect of local rank/selectivity constraints
    - Effect of trilinieratity

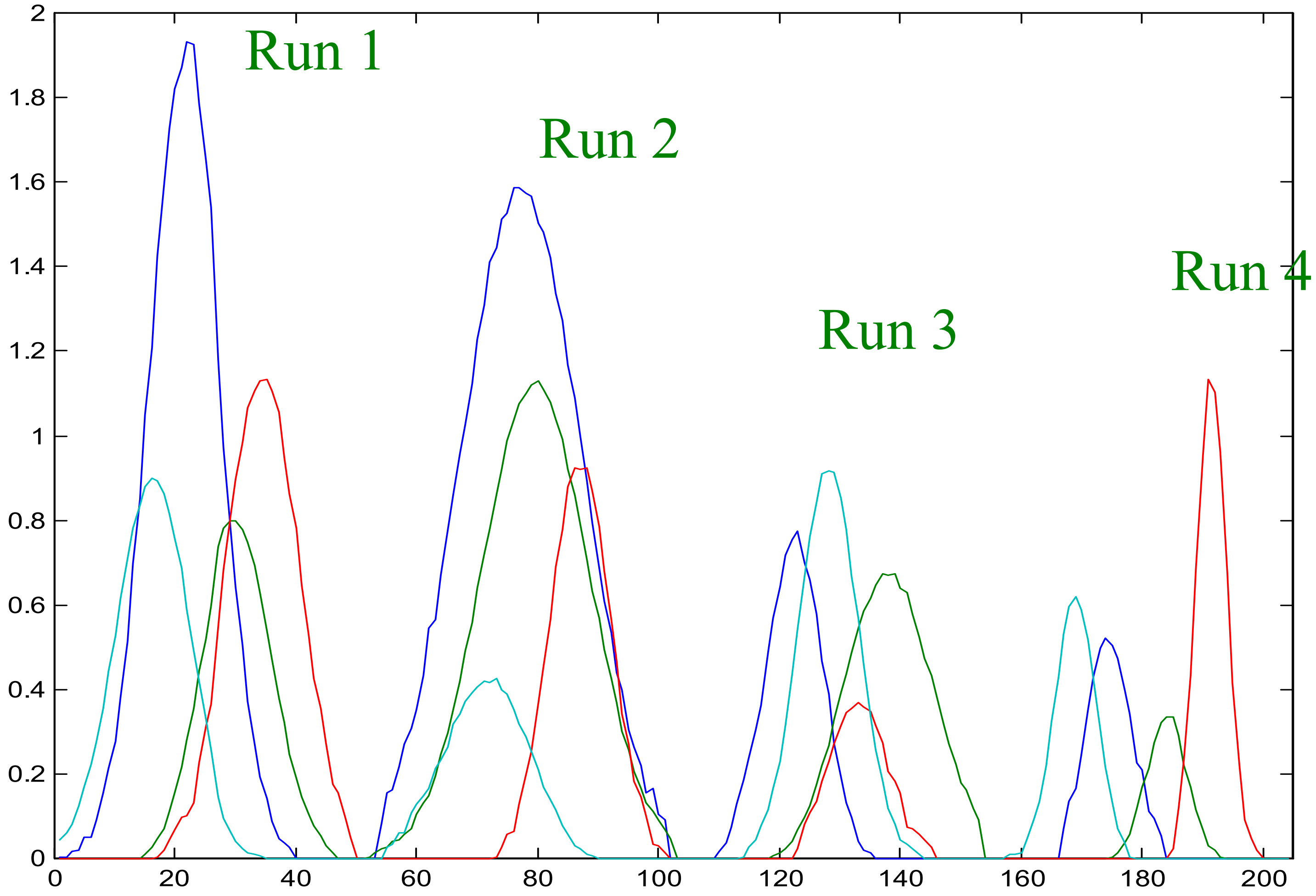
Example 3 : 4 chromatographic runs of 4 coeluting components



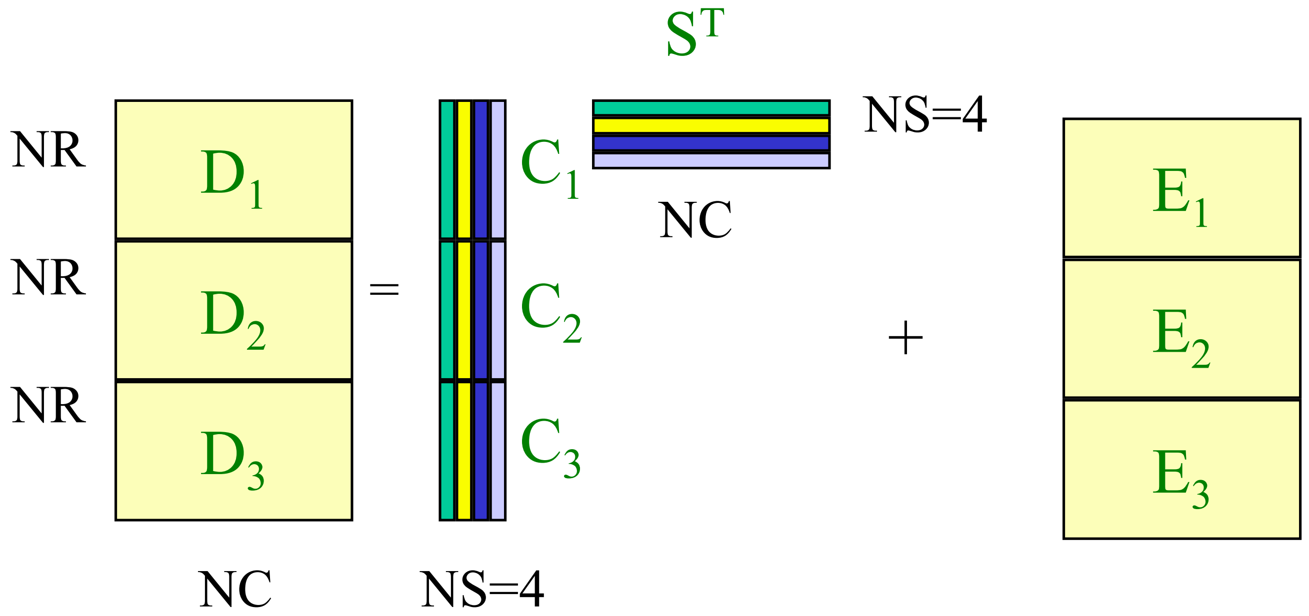
Concentration (elution) profiles: non-trilinear data

It is very difficult to resolve each chromatographic run individually!

Local rank conditions are only clearly present in run 4



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

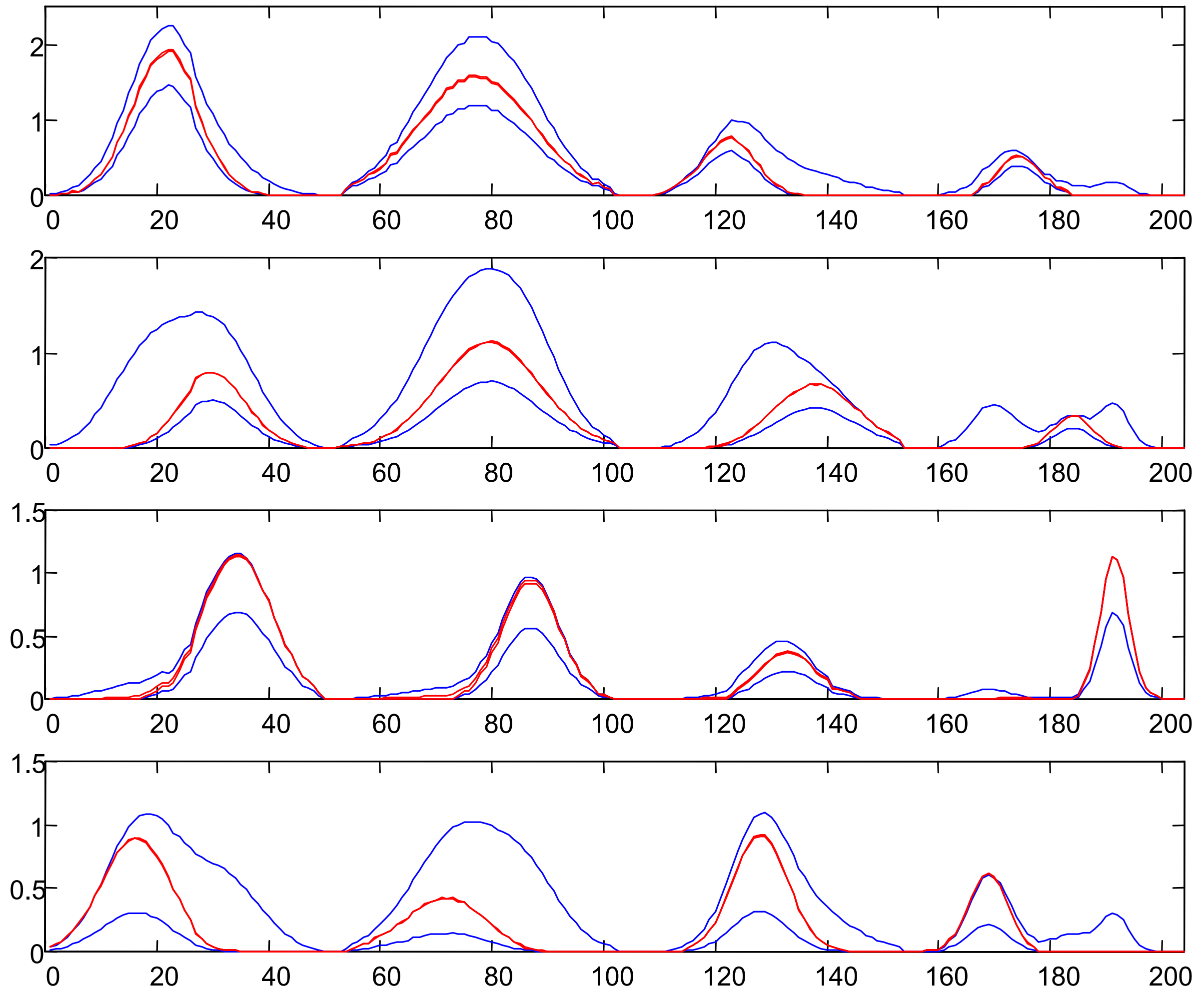


Column-wise Data Matrix Augmentation

Elution feasible bands: matrix augmentation, non-negative, spectra normalization and selectivity constraints

blue = no selectivity (feasible bands no-unimodal)

red = selectivity (unique solutions)

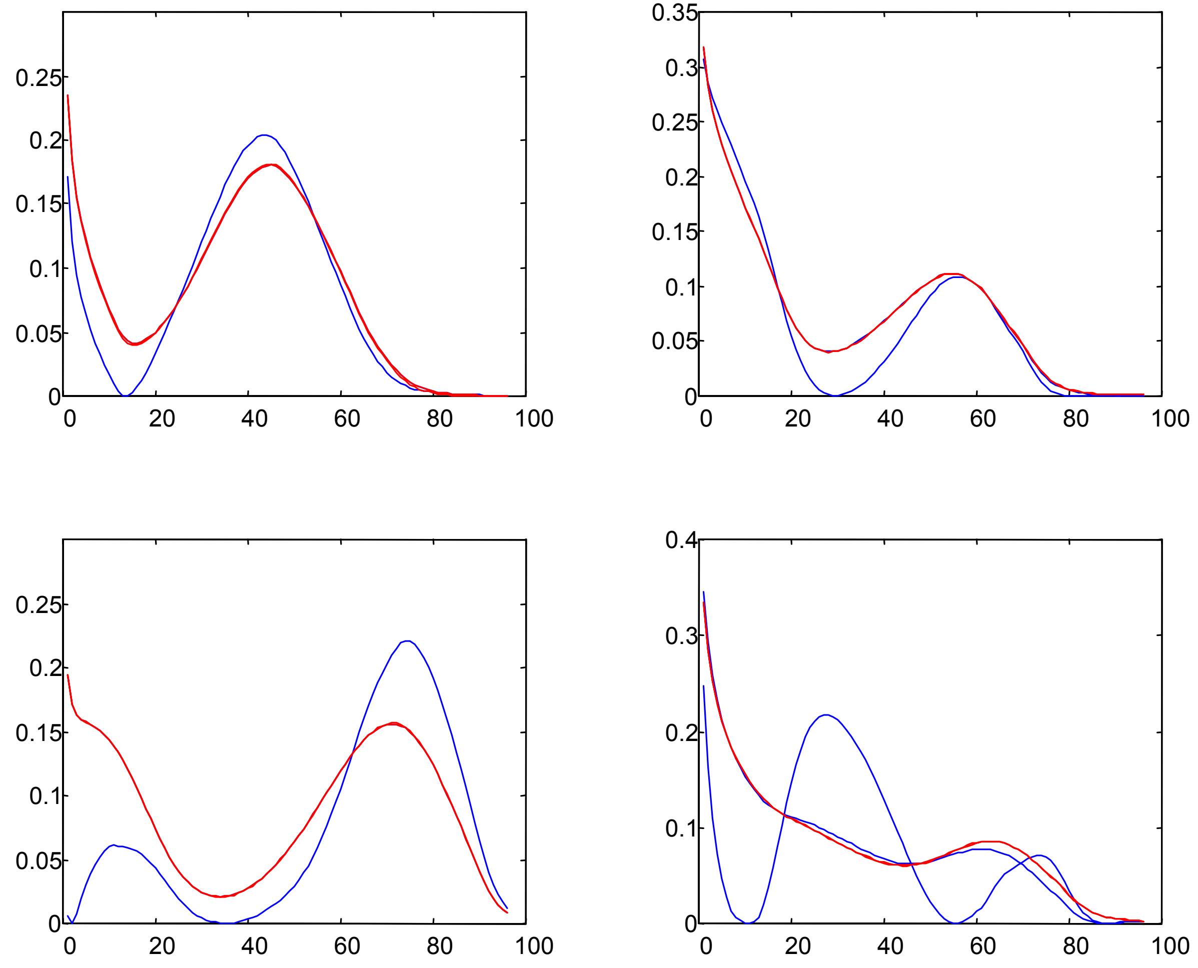


Spectra feasible bands: matrix augmentation, non-negative, spectra normalization and selectivity constraints

blue = no selectivity (feasible bands)

red = selectivity (unique solutions)

one of the bounds of feasible bands (no selectivity) is equal to the real solution



Conclusions: effect of data matrix augmentation and selectivity constraints

- Matrix augmentation
  – decreases a little the breadth of feasible bands

- local rank/selectivity constraints
  - highly decrease rotational ambiguities; eventually givE unique solutions

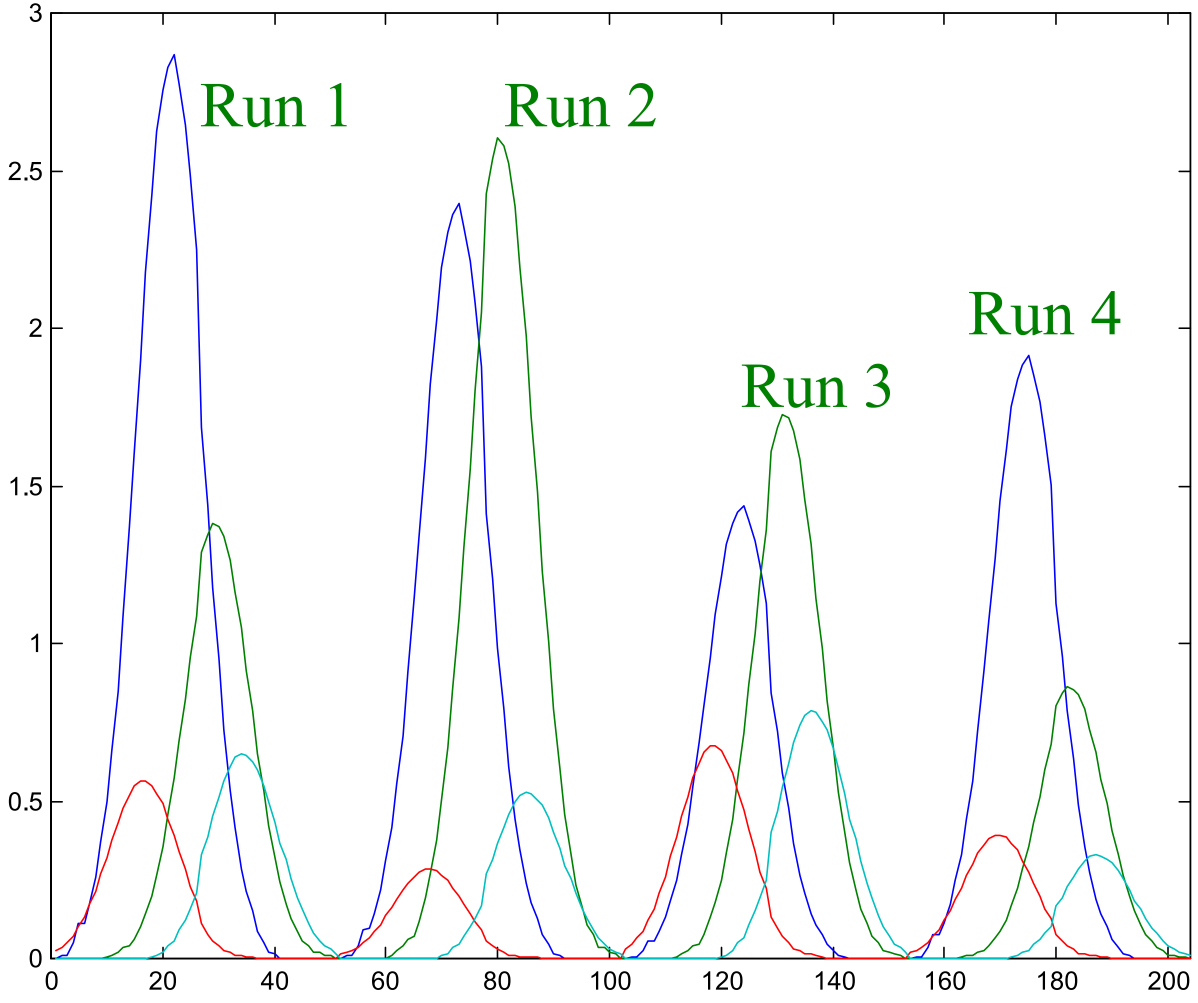
Local rank resolution theorems can be extended to augmented data matrices!

- Resolution local rank conditions are more easily achieved for three-way non-trilinear data (designed augmented column-wise matrices)
- When resolution conditions are achieved for some species present in one of the matrices, the resolution is also achieved for the same species in the rest of matrices
- Resolution (no rotational ambiguities) can be achieved for three-way non-trilinear systems

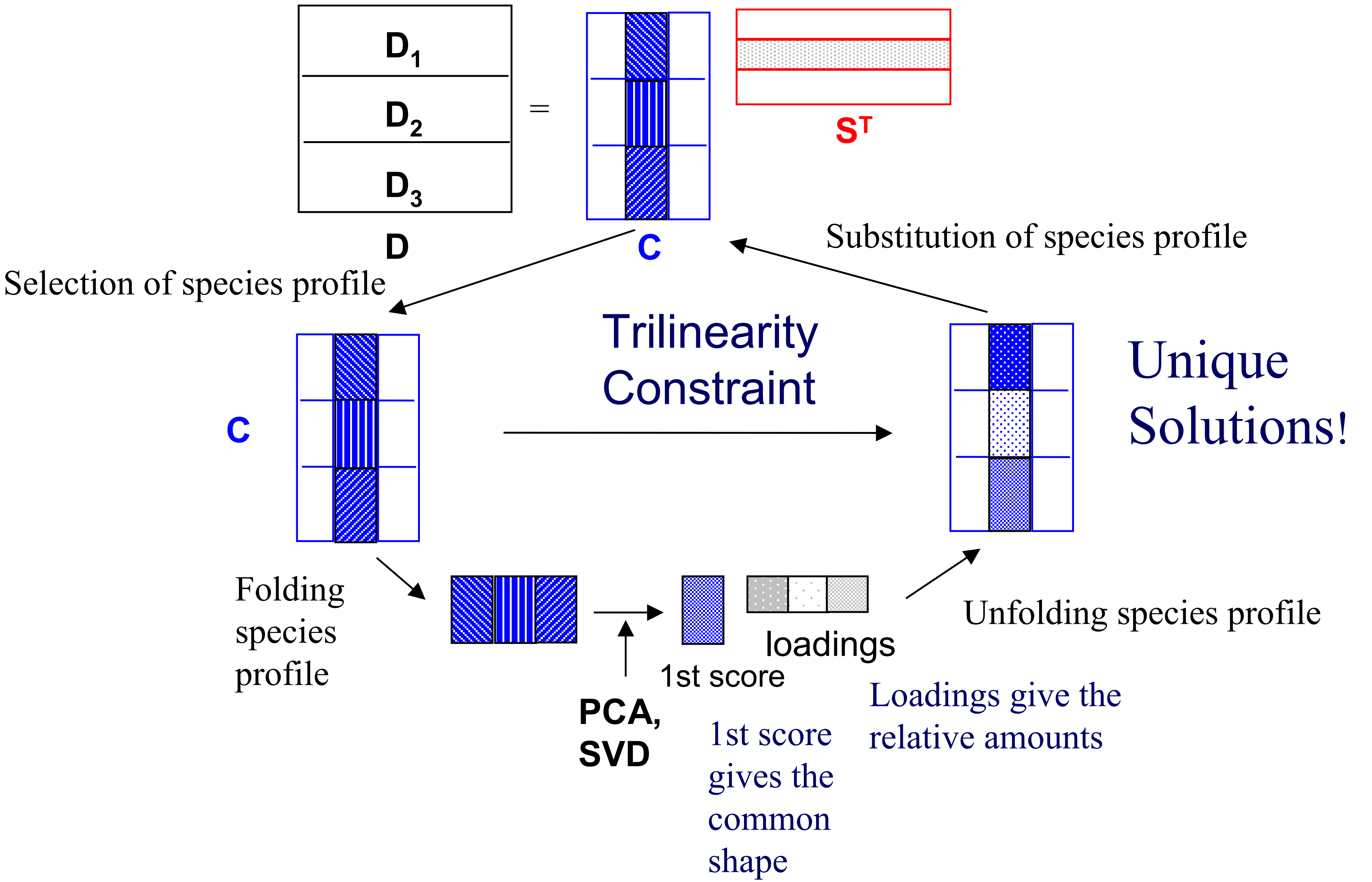
Concentration (elution) profiles: trilinear data

It is very difficult to resolve each chromatographic run individually!

Local rank conditions are not present in any run

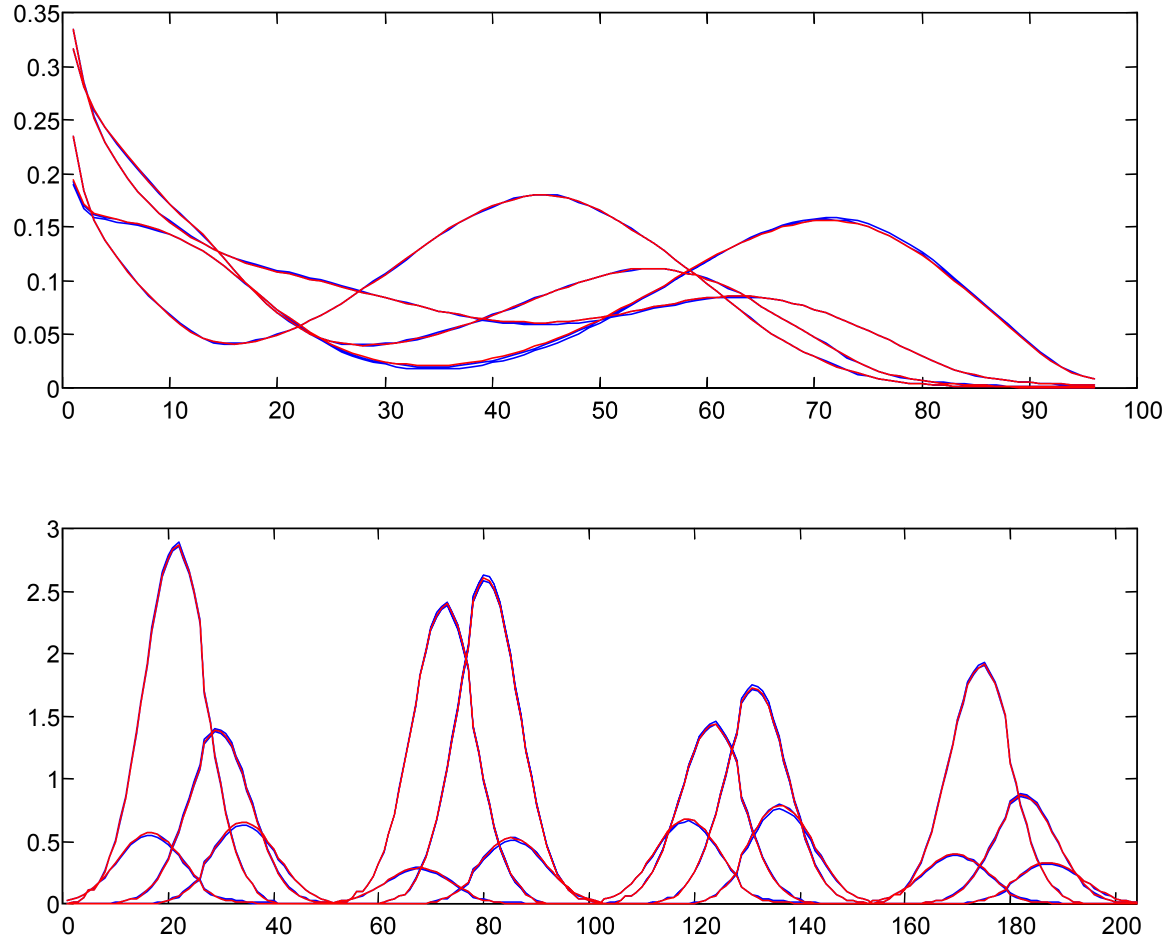


Trilinearity can be implemented independently for each species in MCR-ALS!



Feasible bands: matrix augmentation, non-negative, spectra normalization and trilinearity constraints

Trilinearity gives unique solutions!



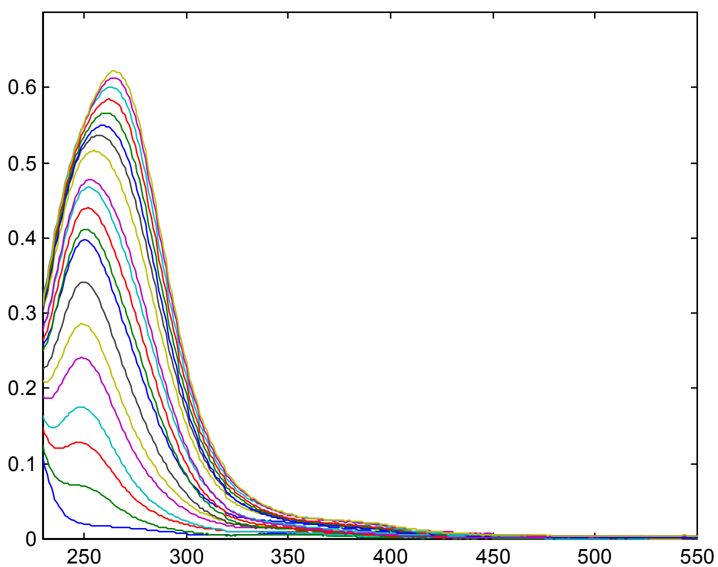
Conclusions : effect of trilinearity constraint

- Effect of trilinearity constraint
  - collapse feasible bands to give unique solutions
- Resolution conditions for three-way data:
  - for non-trilinear data: local rank/local selectivity constraints (if present in data)
  - trilinearity constraints for trilinear data

4rth Example

- Formation of Cu(II)-chloride complexes studied by UV spectrometric titrations ([Cl^-] 0-5.0 M, T 25-80^{o}C)
  - Successive evolving equilibria; species with highly overlapped UV spectra
  - Possible constraints: non-negativity (concn. and spectra), closure and selectivity
  - Strategy:
    - find a feasible solution by constrained MCR-ALS
    - calculation of the feasible bands using the same constraints

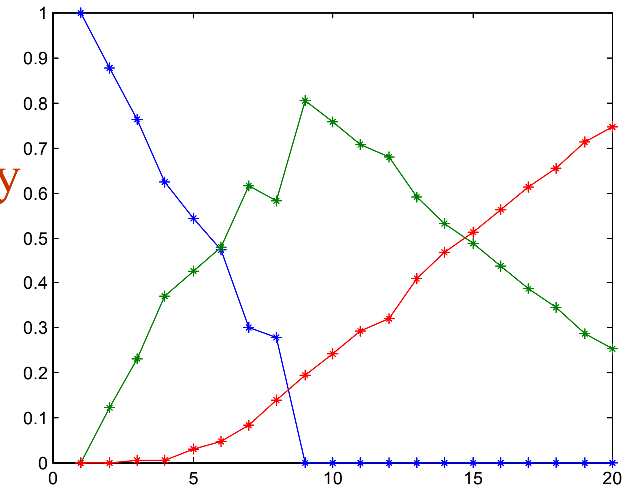
Formation of Cu(II)-chloride complexes studied by UV spectrometric titration ([Cl^-] 0-5.0 M, T 25ºC)

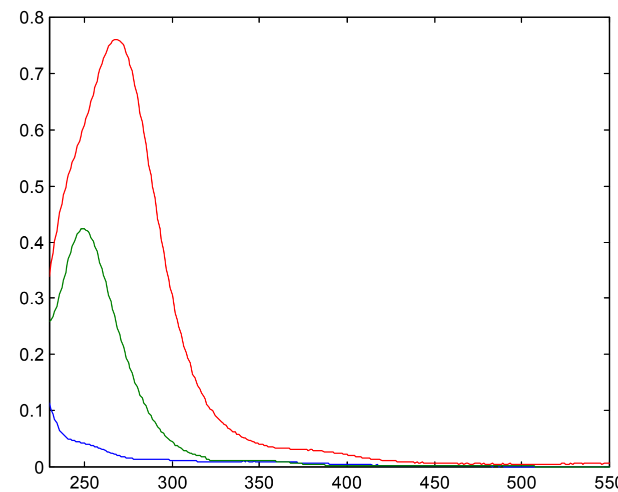


Constrained MCR-ALS

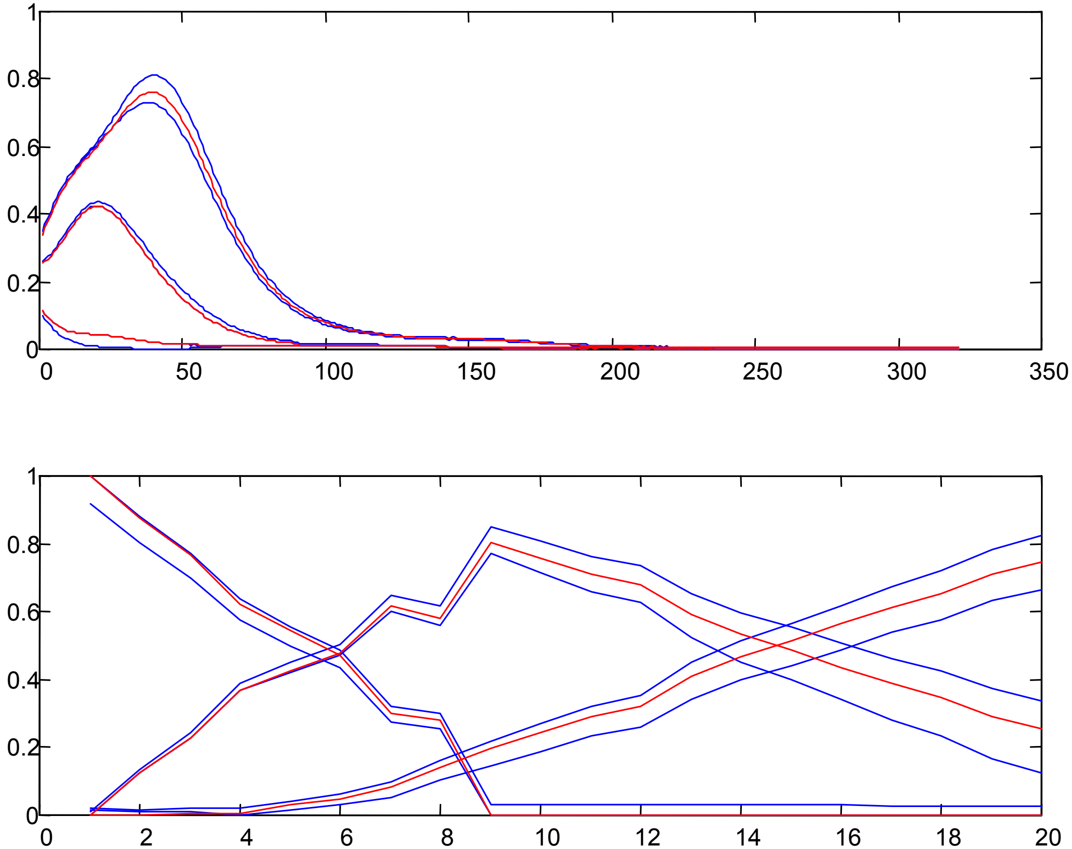
Applied constraints:

Non-negativity, closure and selectivity



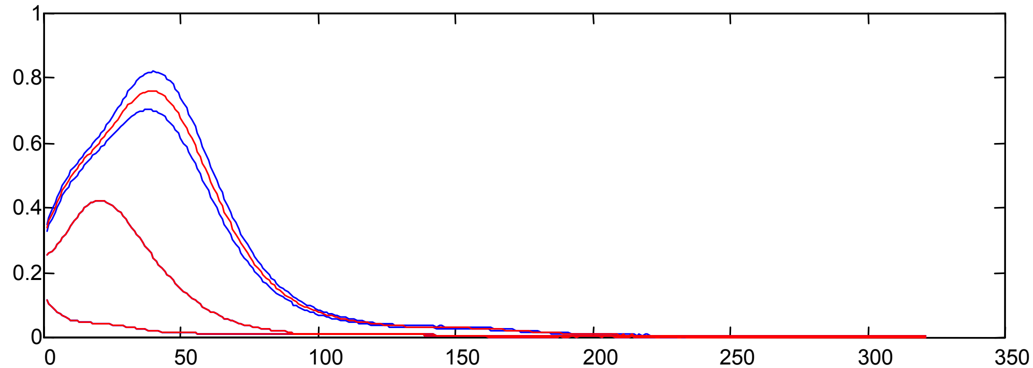


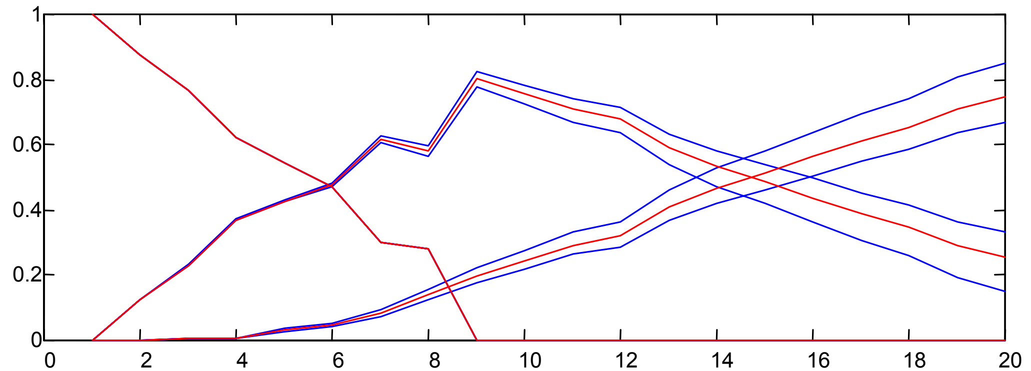
Feasible bands for concentration and spectra profiles: non-negativity and closure constraints



Feasible bands for concentration profiles: non-negativity, closure and selectivity constraints

selectivity is applied for the first species at the **beginning** of the experiment (only Cu(II) is present) and at the end of the experiment (Cu(II) is not present



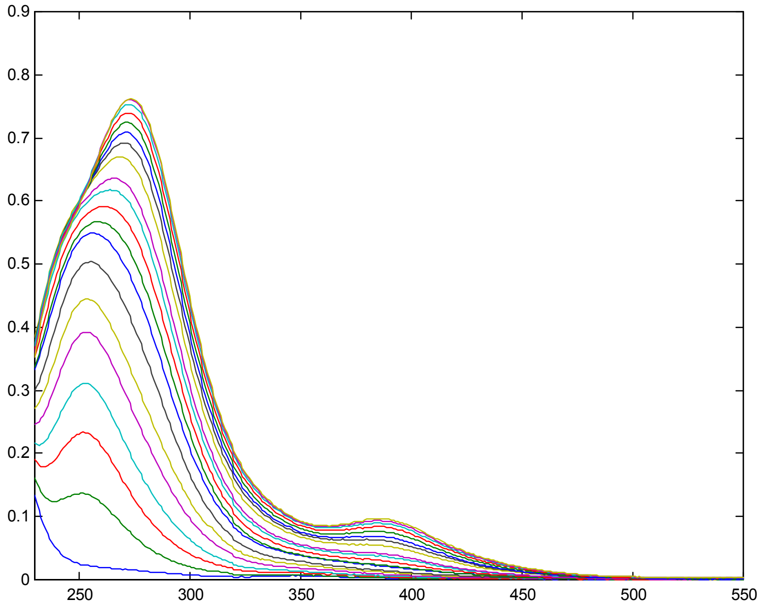


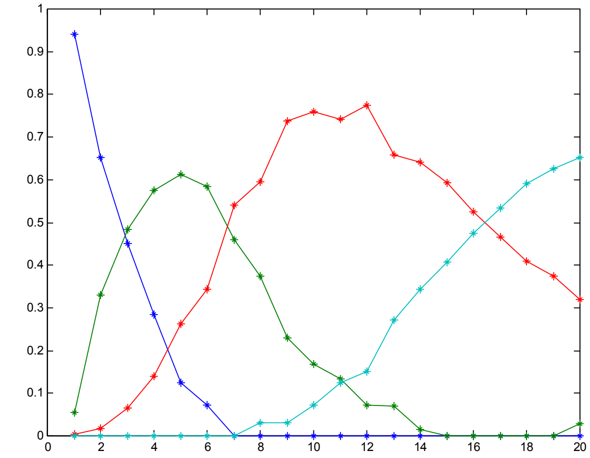
Formation of Cu(II)-chloride complexes studied by UV spectrometric titration ([Cl$^-$] 0-5.0 M. T 80^{o}C)

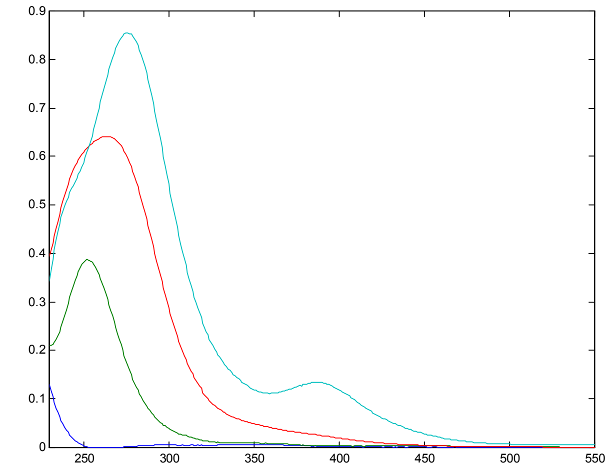
Constrained MCR-ALS

Applied constraints:

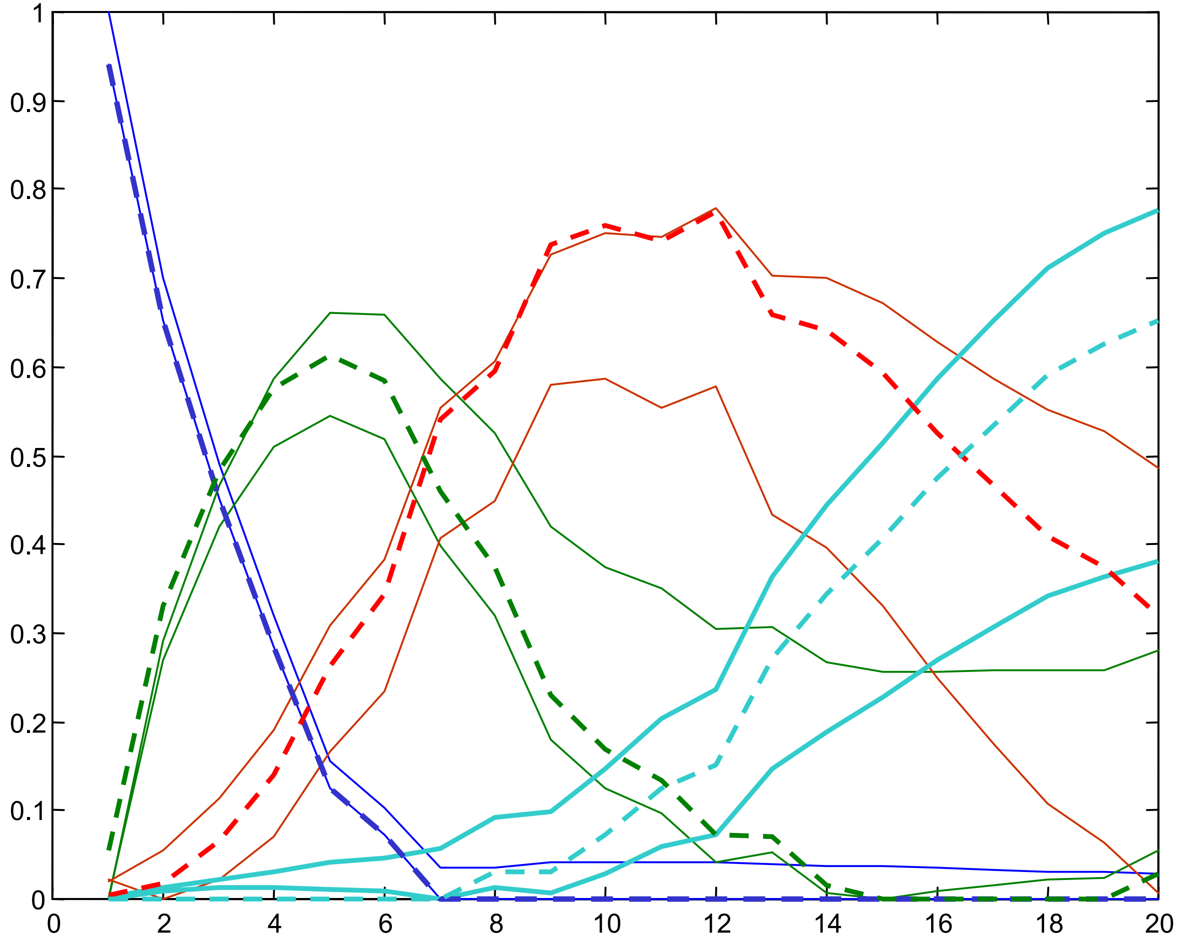
Non-negativity and closure



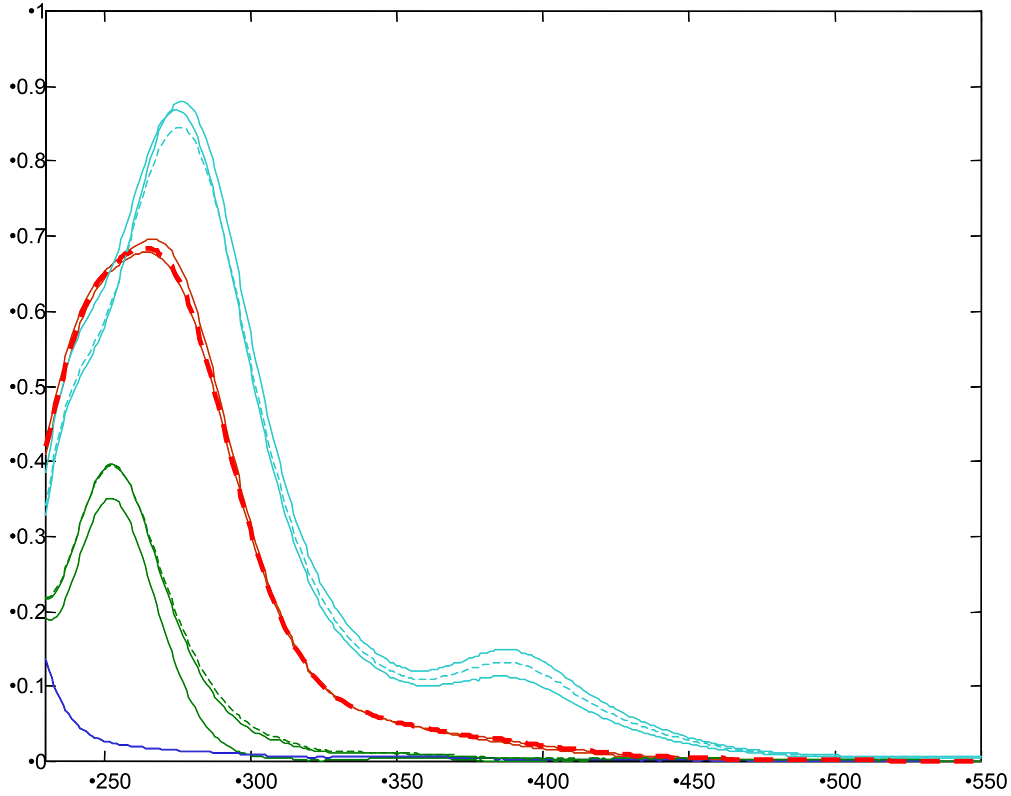




Feasible bands for concentration profiles: non-negativity and closure constraints

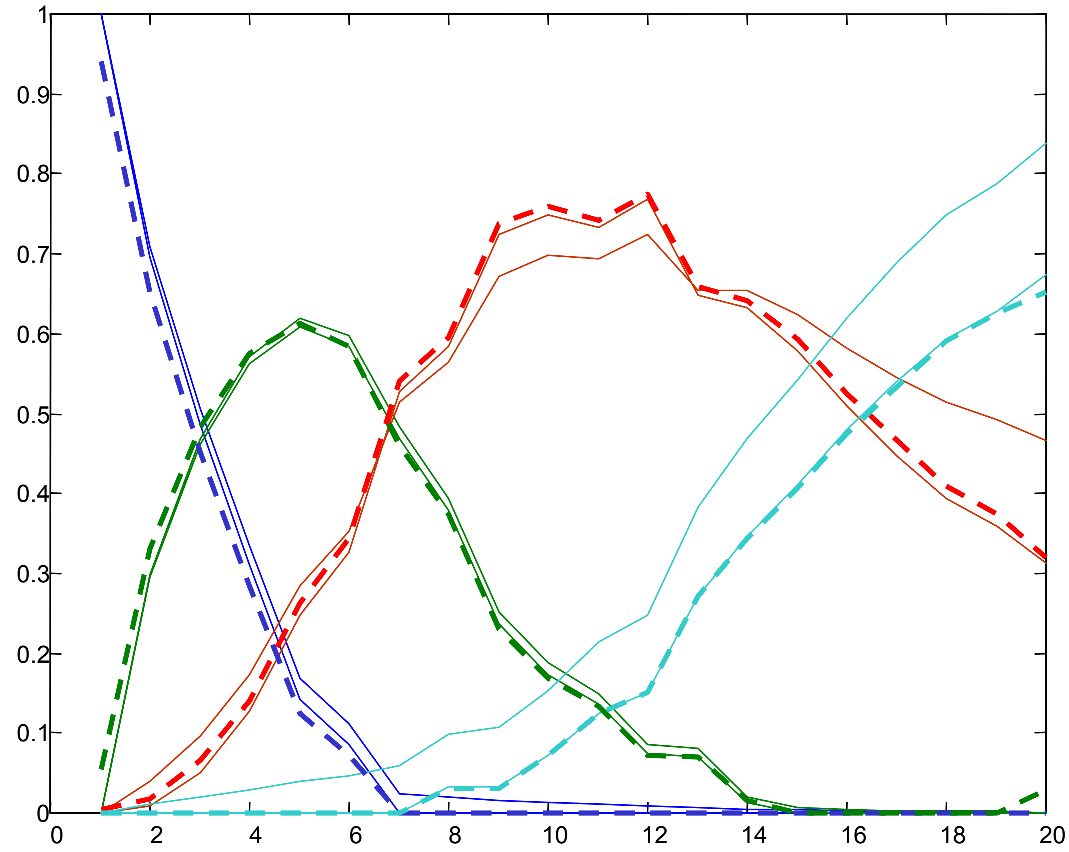


Feasible bands for spectra profiles: non-negativity, closure and selectivity constraints



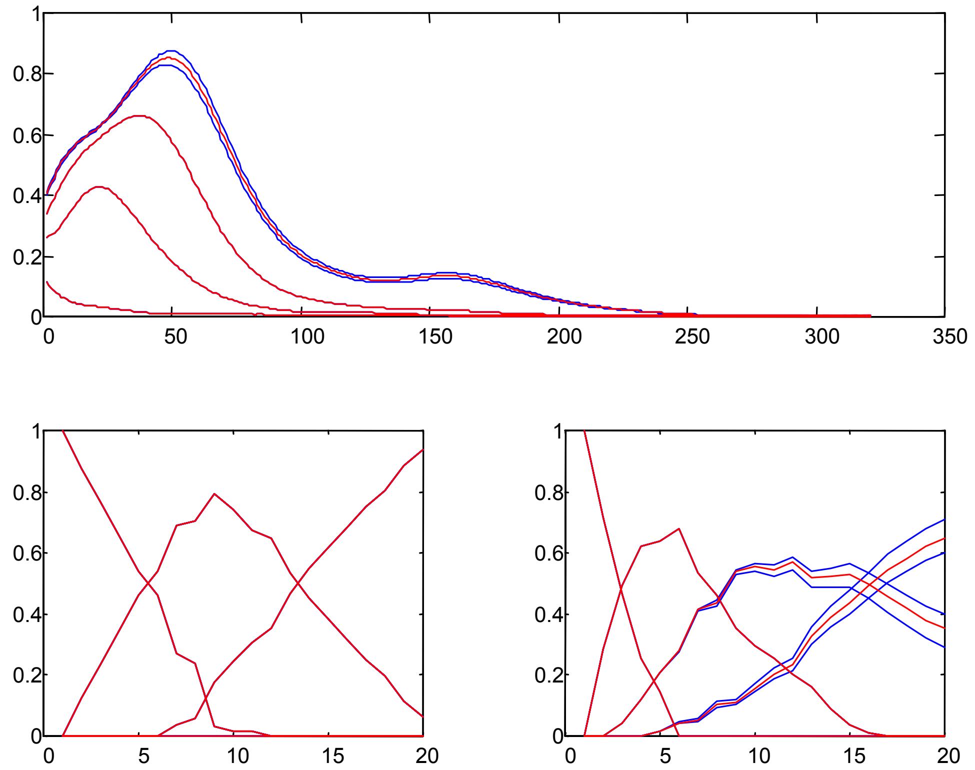
Feasible bands for concentration profiles: non-negativity, closure and selectivity constraints

Selectivity at the beginning of the experiment and at the end of the experiment (1st and 2nd species are absent)

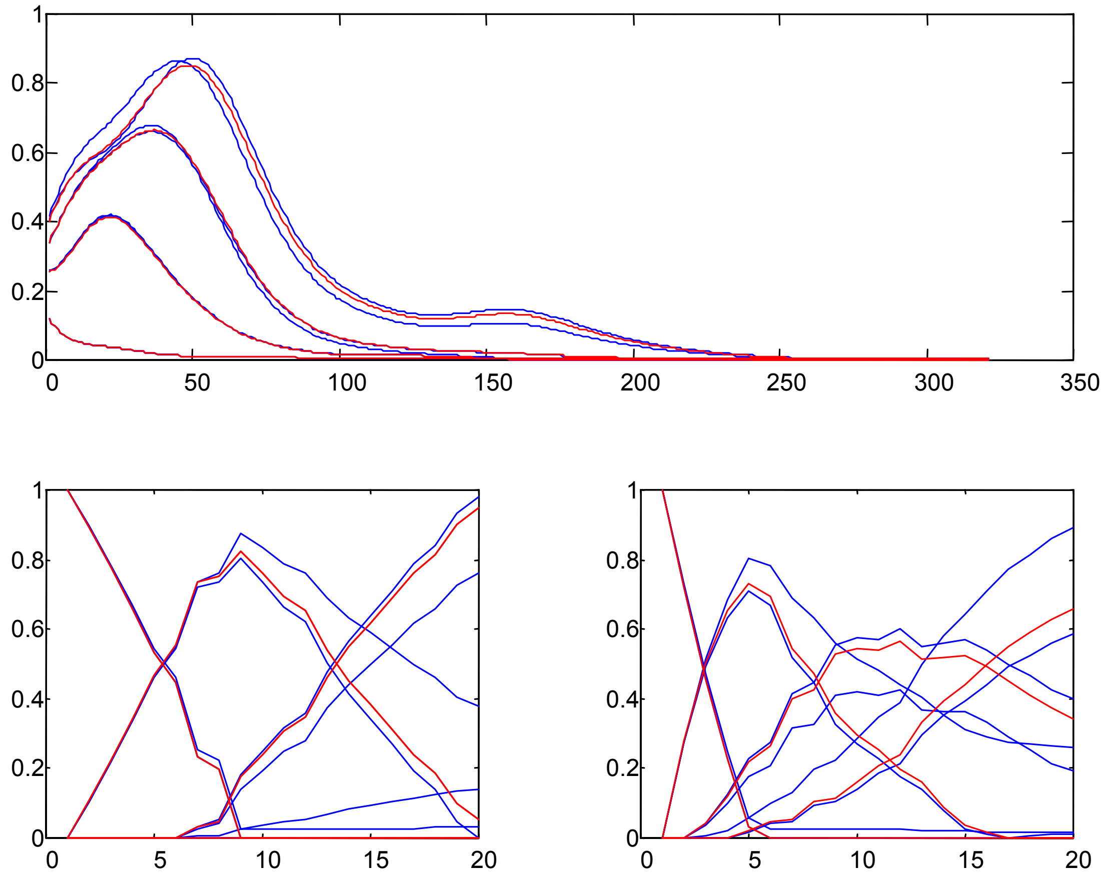


Feasible bands for concentration and spectra profiles: non-negativity, closure, selectivity and data augmentation constraints

Solutions improve considerable and they are close to unique!



Feasible bands for concentration and spectra profiles: non-negativity, closure and data augmentation constraints



Conclusions:

• Calculation of feasible bands for simulated and experimental data is possible using the proposed procedure

• Usual constraints used in soft modeling such as non-negativity, selectivity, unimodality or closure allow a large diminution of rotational and intensity ambiguities

• Solutions obtained by a constrained MCR-ALS method are in most of the cases satisfactory

• Matrix augmentation (three-way data analysis) allows unique solutions