Spectral Validation of Rank Deficient Kinetic Models

Fall Meeting of the Swiss Chemical Society (SCS)
EPF Lausanne, September 4th 2009

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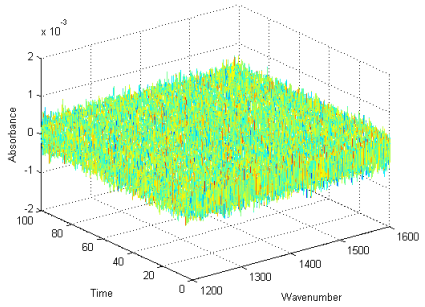
ETH
Eidgenössische Technische Hochschule Zürich
Swiss Federal Institute of Technology Zurich

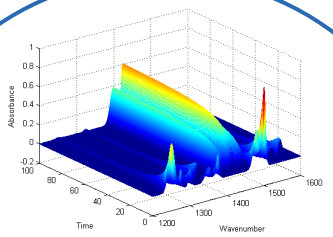
Safety and Environmental Technology Group

Spectroscopic fitting by modelling concentrations



Least square optimisation

$$\min_{k} \left\| \mathbf{Y} - \mathbf{C}_k \mathbf{A} \right\|^2$$

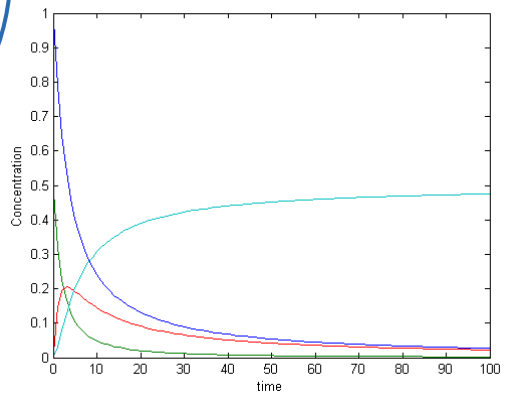


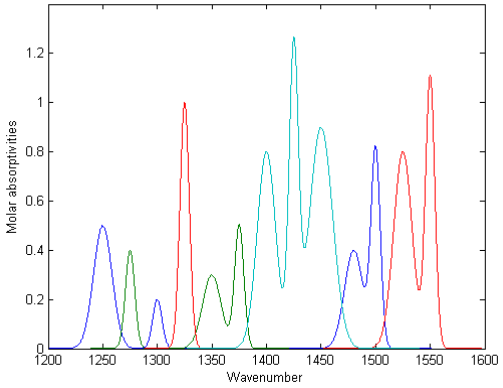
Beer's Law

$$\mathbf{Y} = \mathbf{C}\,\mathbf{A} + \mathbf{R}$$

Numerical integration of the rate law

$\mathbf{C}_k$





Implicit calibration

$$\mathbf{A} = \mathbf{C}_k^{+}\mathbf{Y}$$

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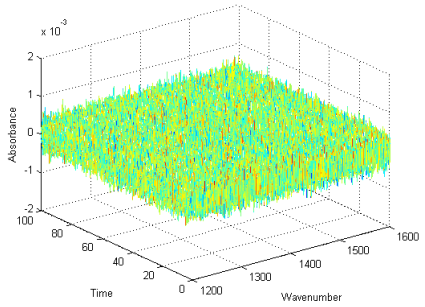

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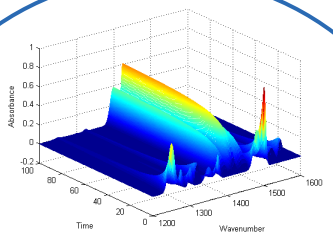

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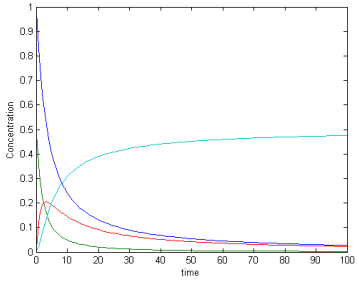

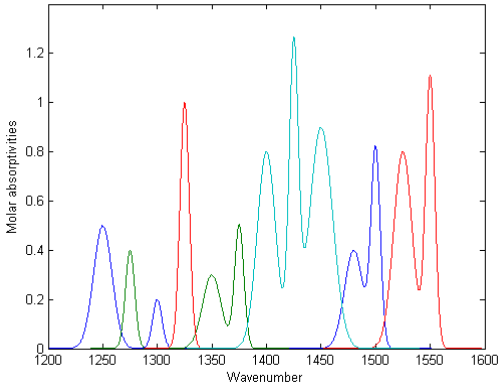

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Explicit calibration

$\mathbf{A}$

Rank deficiency in the concentration matrix C

Rank deficiency occurs when the number of observable species is less than the real number of reactive species, e.g. when two species are consumed or generated at the same rate

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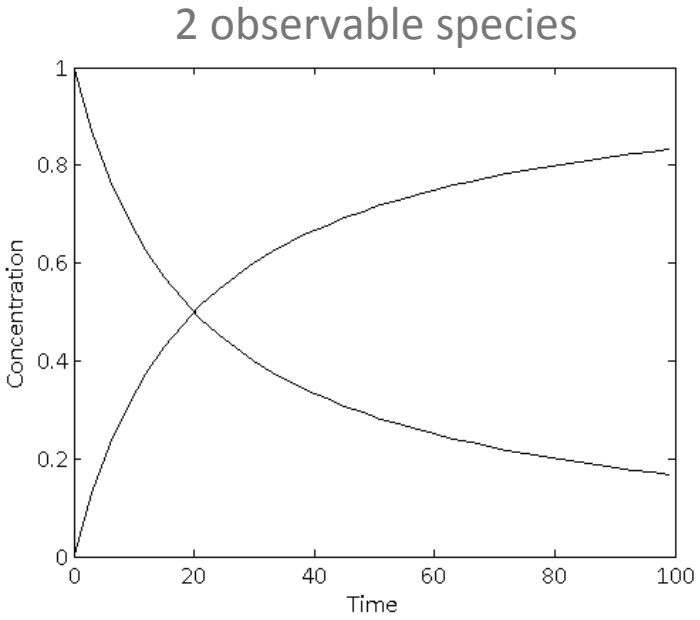

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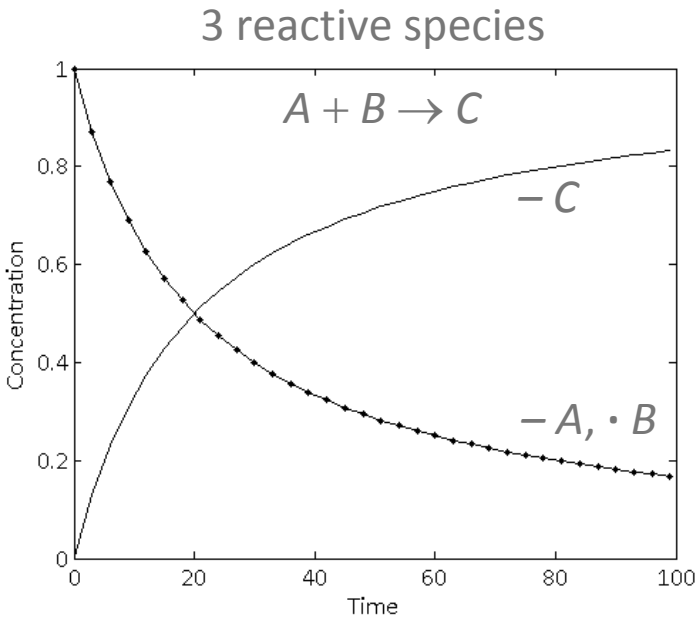

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When rank deficiency occurs, one or more concentration profiles (columns of matrix **C**) are linear combinations of each other

Consequence:

Matrix **C** is singular

$\Downarrow$

$\mathbf{C}^{+}$ cannot be computed

$\Downarrow$

Pure component spectra A cannot be calculated

Strategies for the treatment of rank deficiency

Strategies exist to treat **C** in case of rank deficiency (e.g. dosing, varying initial concentrations…) so that component spectra can be computed

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"Wrong" fitted component spectra

→ Wrong postulated kinetic model (the rate law)

or

→ Linear combinations of true pure component spectra

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2. **Predict** the linear combinations **Δ** in the fitted component spectra, using a spectral balance:

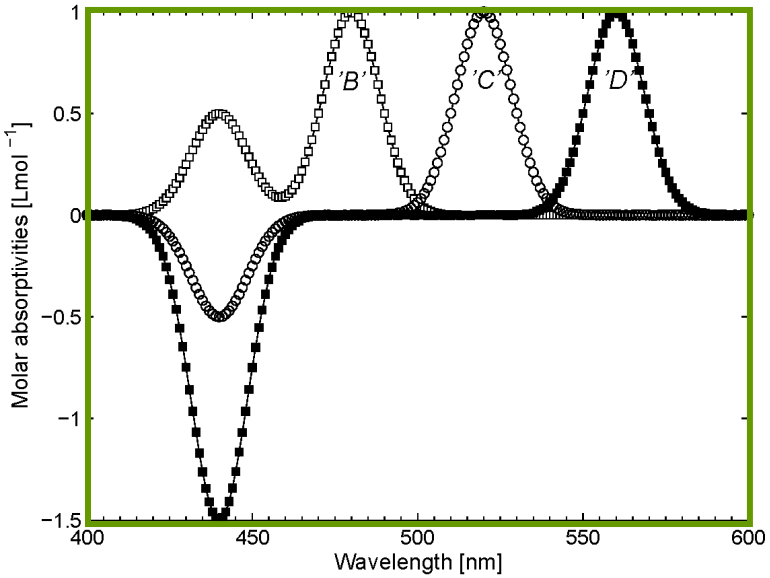
   Solution of the spectral balance: $\mathbf{A_c = \Delta\, A}$

3. **Compare** the linear combinations of (independently measured) true pure component spectra **Δ A** with the fitted spectra $\mathbf{A_c}$

Example of spectral validation

$$A + B \xrightarrow{k_1} C$$
$$A + C \xrightarrow{k_2} D$$

3 Fitted component spectra $\mathbf{A}_c$



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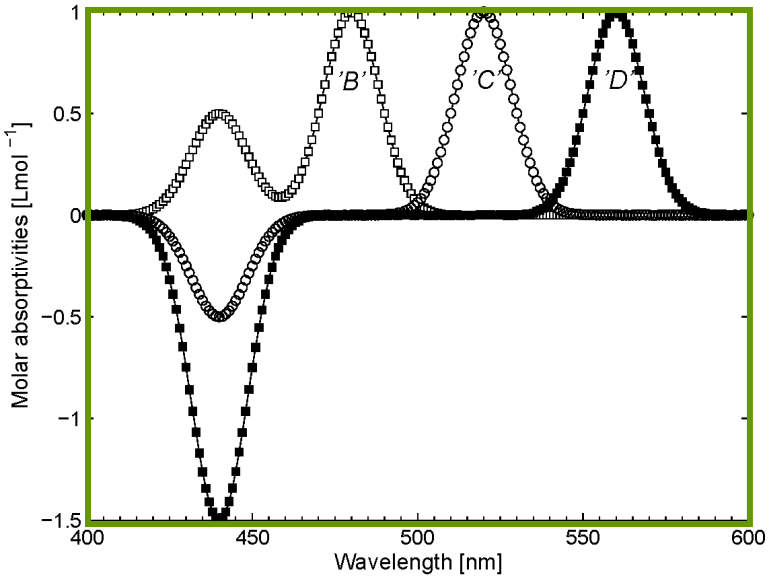
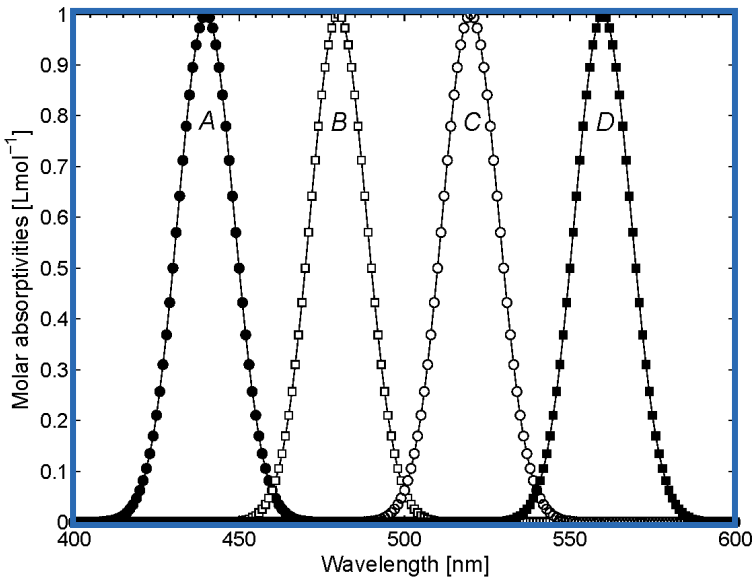


4 True pure component spectra $\mathbf{A}$



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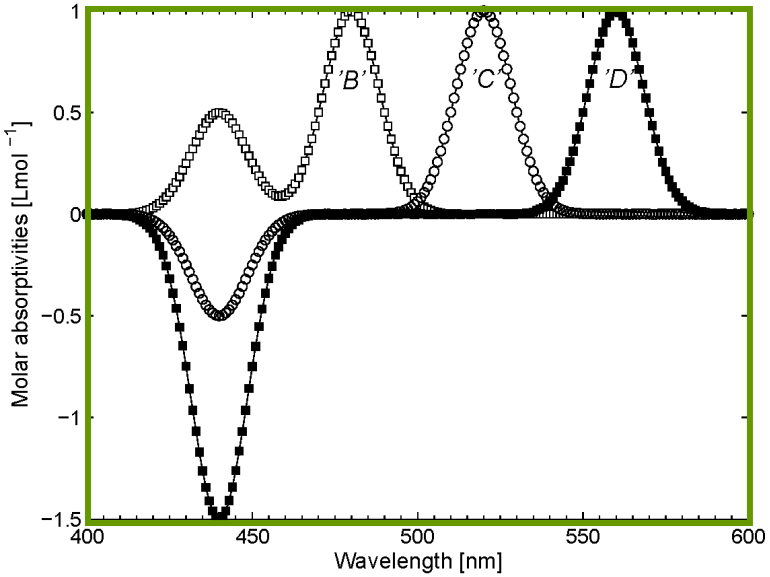

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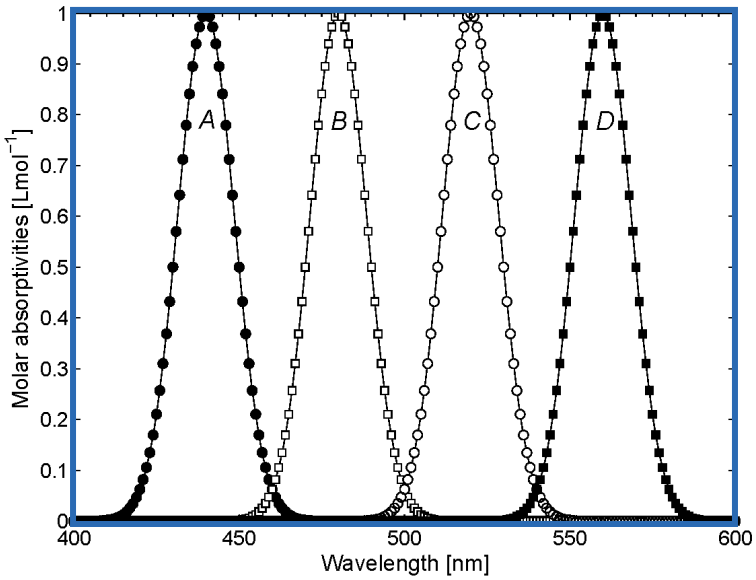
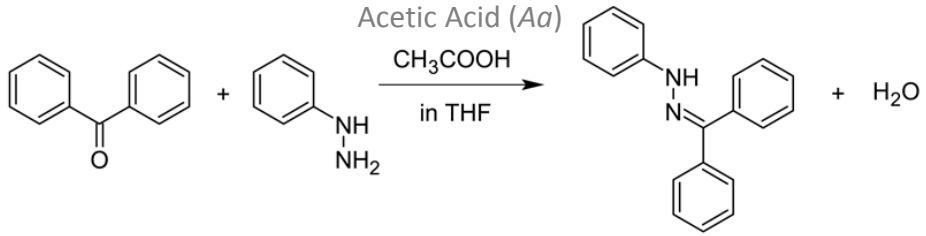


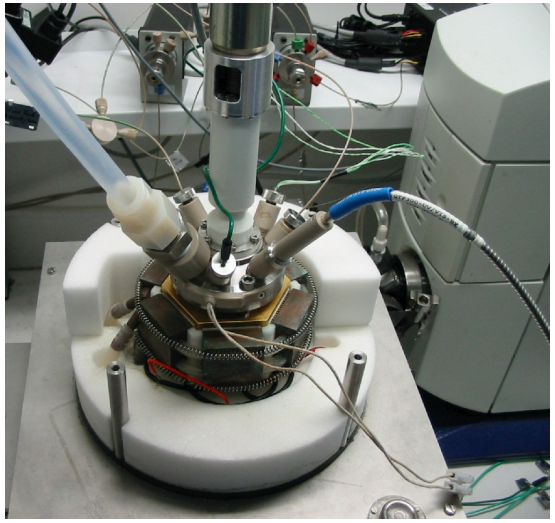
$$\mathbf{A_c} = \begin{bmatrix} \mathbf{a}_{c\,'B',:} \\ \mathbf{a}_{c\,'C',:} \\ \mathbf{a}_{c\,'D',:} \end{bmatrix} = \mathbf{\Delta}\,\mathbf{A} = \begin{bmatrix} 0.5 & 1 & 0 & 0 \\ -0.5 & 0 & 1 & 0 \\ -1.5 & 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} \mathbf{a}_{A,:} \\ \mathbf{a}_{B,:} \\ \mathbf{a}_{C,:} \\ \mathbf{a}_{D,:} \end{bmatrix} = \begin{bmatrix} 0.5 \\ -0.5 \\ -1.5 \end{bmatrix} \mathbf{a}_{A,:} + \begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix} \mathbf{a}_{B,:} + \begin{bmatrix} 0 \\ 1 \\ 0 \end{bmatrix} \mathbf{a}_{C,:} + \begin{bmatrix} 0 \\ 0 \\ 1 \end{bmatrix} \mathbf{a}_{D,:}$$

An experimental case study

Overall reaction



Benzophenone (*B*) | Phenylhydrazine (*P*) | Benzophenone-Phenylhydrazone (*BP*)



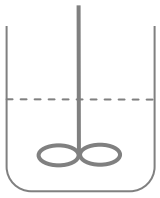
Reactor: CRC.v4 with FT-IR and UV-vis

Kinetic mechanism

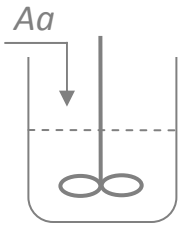
$$B + P + Aa \xrightarrow{k} BP + Aa$$

Experimental conditions

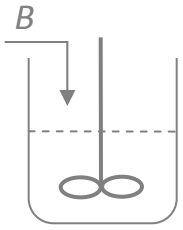
25°C, mid-IR (1200–1650 cm^{-1}), UV-vis (240–400 nm)



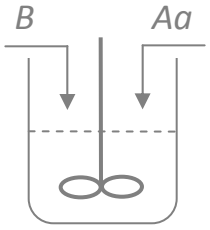
Batch conditions



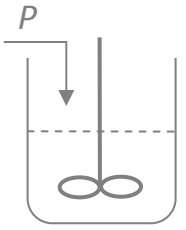
Dosing *Aa*



Dosing *B*



Dosing *B* + *Aa*

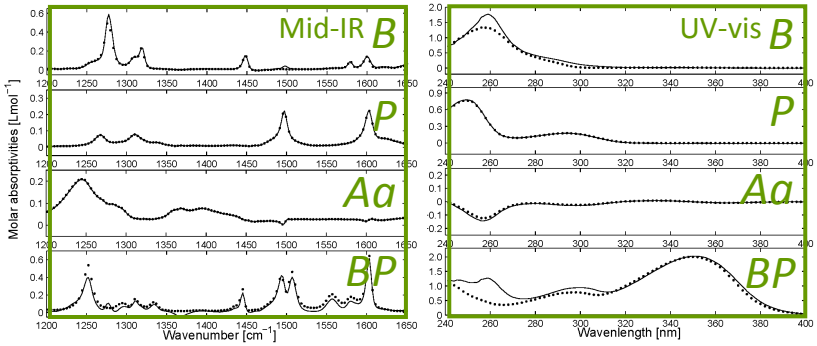


Dosing *P*

Spectral validation

$$B + P + Aa \xrightarrow{k_1} BP + Aa$$

Strategy (3): dosing



Species *B* and *Aa* dosed

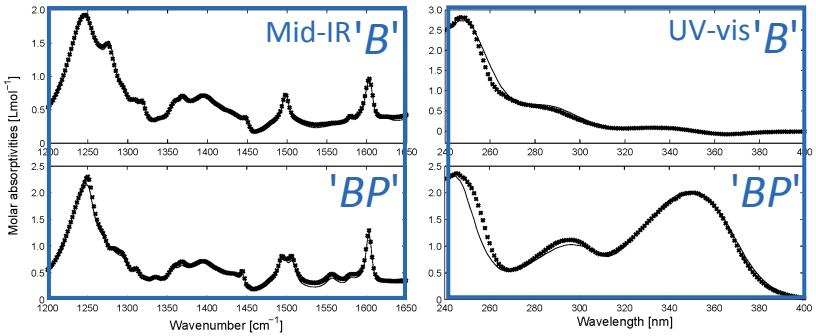
Full spectral resolution

—— Fitted spectra ●●● Measured spectra **XXX** Predicted spectra

Spectral validation

$$B + P + Aa \xrightarrow{k_1} BP + Aa$$

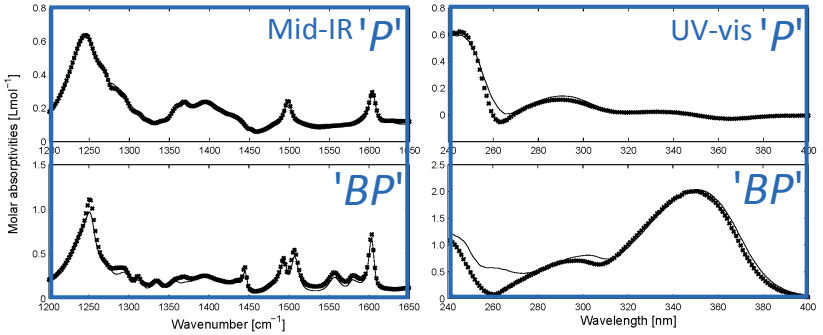
Strategy (1): uncoloured species



Species *P* and *Aa* set uncoloured

Partial spectral resolution

Strategy (1)+(2): provided known spectrum



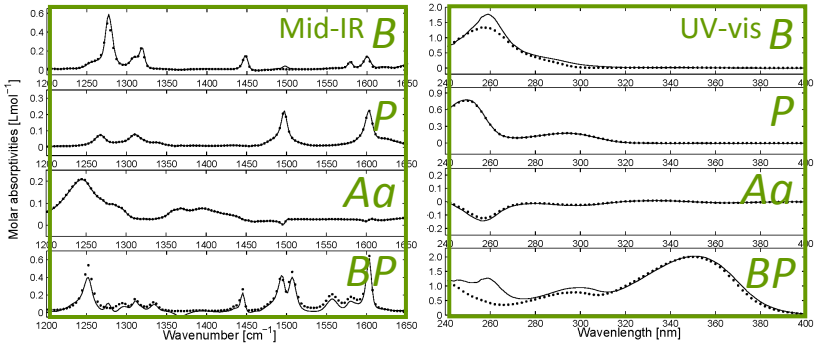
Pure spectrum of *B* provided

Aa set uncoloured

Partial spectral resolution

The model can now be validated **without** and **with** rank deficiency!

Strategy (3): dosing



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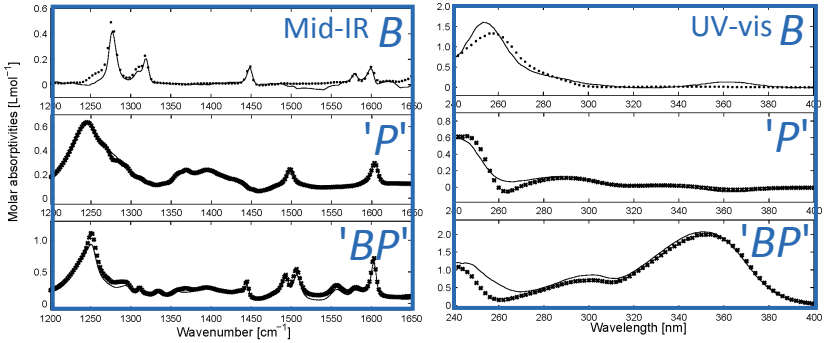
Full spectral resolution

Strategy (1)+(4): second order global analysis



Initial concentration of *B* varied, *Aa* set uncoloured

Partial spectral resolution

—— Fitted spectra ●●● Measured spectra **XXX** Predicted spectra

Conclusion

Rank deficiency

Rank deficiency in spectroscopic data can be treated by different Strategies

Fitted component spectra

These Strategies sometimes lead to fitted component spectra $\mathbf{A}_c$ that are linear combinations of the true ones $\mathbf{A}$

Spectral balance

Linear combinations, observed in the fitted component spectra, can be explained by a spectral balance: $\mathbf{A}_c = \mathbf{\Delta}\ \mathbf{A}$

Conclusion

Rank deficiency — Rank deficiency in spectroscopic data can be treated by different Strategies

Fitted component spectra — These Strategies sometimes lead to fitted component spectra $\mathbf{A}_c$ that are linear combinations of the true ones **A**

Spectral balance — Linear combinations, observed in the fitted component spectra, can be explained by a spectral balance: $\mathbf{A}_c = \mathbf{\Delta}\ \mathbf{A}$

This spectral balance allows the spectral validation of the kinetic model for rank deficient spectroscopic data by comparing linear combinations of true pure spectra $\mathbf{\Delta}\ \mathbf{A}$ with the fitted component spectra $\mathbf{A}_c$

Thank you for your attention

Publications

Systematic prediction of linear dependencies in the concentration profiles and implications on the kinetic hard-modelling of spectroscopic data
Billeter et al, Chemom. Intell. Lab. Syst., 95 (2009), 170 – 187

Kinetic hard-modelling and spectral validation of rank-deficient spectroscopic data: a case study
Billeter et al, Chemom. Intell. Lab. Syst., 2009, in press