Estimating rate constants of chemical reactions using spectroscopy
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Appendix

A. Short summary of the datasets

Dataset 1
Dataset 1 contains SW-NIR spectra taken in time of the two-step consecutive epoxidation of 2,5-di-tert-butyl-1,4-benzoquinone using tert-butyl hydroperoxide and Triton B catalyst. The reaction consists of the following two steps:

\[ U + V \xrightarrow{k_s} W + Z \]
\[ W + V \xrightarrow{k_b} Y + Z \]

with second order reaction rate constants \( k_s \) and \( k_b \) both in M\(^{-1}\)min\(^{-1}\). If species \( V \) is present in large excess, the first and second reaction step become both pseudo-first order reactions with pseudo-first order reaction rate constants \( k_1 (\text{min}^{-1}) \) and \( k_3 (\text{min}^{-1}) \), respectively. Species \( U \), \( W \), and \( Y \) are spectroscopically active. The experiment was repeated eight times under identical pseudo-first order conditions.

Dataset 2
Dataset 2 contains UV-Vis spectra of the two-step consecutive reaction of 3-chlorophenylhydrazonopropane dinitrile with 2-mercaptoethanol. The reaction consists of the following two steps:

\[ U + V \xrightarrow{k_s} W \]
\[ W \xrightarrow{k_i} Y + Z \]

with second order reaction rate constant \( k_s (\text{M}^{-1}\text{min}^{-1}) \) and first order reaction rate constant \( k_i (\text{min}^{-1}) \). If species \( V \) is present in large excess the first step of the reaction becomes pseudo-first order with pseudo-first order reaction rate constant \( k_1 (\text{min}^{-1}) \). Species \( U \), \( W \), and \( Y \) are spectroscopically active. The experiment was repeated ten times under identical pseudo-first order conditions at a pH of 5.4.

Dataset 3
Dataset 3 contains spectra taken in time of the same reaction as in case of dataset 2. However, in case of dataset 3 the experiment was repeated 32 times under identical pseudo-first order conditions at a pH of 5.2.
Dataset 4

Dataset 4 contains spectra taken in time of the same reaction as in case of dataset 2. However, in case of dataset 4, the first reaction is performed under second order conditions. A pH of 5.2 was used, the same pH that is valid for dataset 3. In case of dataset 4, the second order experiment was repeated six times for three different initial concentrations of both reactants (species U and species V). The ratio’s $C_{i,0} / C_{i,0}$ were chosen equal to 1:4, 1:5 and 1:6. Hence, for a ratio of $C_{i,0} / C_{i,0}$ equal to 1:4, six experiments were fulfilled. In total 18 second order experiments were performed.

B. The proof for a unique solution of the curve resolution model

*Imposing a kinetic model on the data*

In this Section, a proof is given that a unique solution of the curve resolution model is obtained in case of imposing a kinetic model in the curve resolution algorithm. Consider matrix $F$ from Equation (1), Section 2.2. Chapter 2. Consider also Equation (6)-(8) from the same Section which describe the concentration profiles of species $U$, $W$ and $Y$ of the chemical reaction from Section 2.2 of Chapter 2. Matrix $F$ has a fixed structure, given the kinetic model, and depends only on $k_1$ and $k_2$. This will be indicated as $F(k_1, k_2)$. A simple basis $B$ for the concentration profiles $F$ in Equation (1) can be found by defining $B$ (Equation (51)) and $C$ (Equation (52)):

$$B = \begin{bmatrix} 1 & e^{-k_2t} \end{bmatrix}$$  \hspace{1cm} (51)

$$C = \begin{bmatrix} 0 & 0 \\ 1 & 1 \\ k_1 & k_1 \\ k_2 - k_1 & k_2 - k_1 \\ -k_1 & -k_1 \\ k_2 - k_1 & k_2 - k_1 \end{bmatrix}$$  \hspace{1cm} (52)

where it can be checked that $F = BC$. The notation $e^{+k_2t}$ is shorthand for the vector $[e^{-k_1t_1}, \ldots, e^{-k_1t_N}]$ where the time points $t_1, \ldots, t_N$ are the sampling points. The structure of $B$ and $C$ are fixed. The elements of these matrices depend only on $k_1$ and

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1 This Section is based on the following paper:

- Smilde AK, Hoesloot HCJ, Bijlsma S, Boelens HFM. ‘Sufficient conditions for unique solutions within a certain class of curve resolution models’. submitted.
Appendix

This will be indicated by $B (k_1, k_2)$ and $C (k_1, k_2)$. $B$ is of full rank three (see later), $C$ is also of full rank (see Equation (52)), hence $F$ is of full rank three. Therefore, the columns of $B$ are a basis for the column space of $F$.

If rotational freedom is present, then a $(3 \times 3)$ nonsingular $Q$ exists such that $FQ = F^*$ still has the structure of the kinetic model. This means that a $k_1*$ and $k_2*$ should exist such that $F^* = F (k_1^*, k_2^*)$. Hence, $FQ = F^* = F (k_1^*, k_2^*)$. Also, $F^* = B^*C^*$, where $B^* = B (k_1^*, k_2^*)$ and $C^* = C (k_1^*, k_2^*)$.

The transformation $FQ$ leaves the column-space of $F$ intact, because $Q$ is nonsingular. Now, $B$ is a basis for the column-space of $F$, and likewise, $B^*$ is a basis for the column-space of $F^* = FQ$. Therefore, $B$ should also be a basis for the column-space of $F^*$. Hence, it should be possible to write all columns of $B^*$ as linear combinations of the columns of $B$. Consider the columns $e^{ki*}$ and $e^{j*}$ of $B^*$. Later it is shown that $[1 \ e^{ki*} \ldots \ e^{kj*}]$ forms a linear independent set for $k_1 \neq k_2 \neq \ldots \neq k_J$ and all $k_i > 0$. Hence, the only solutions are: $k_1 = k_1^*$, $k_2 = k_2^*$ or $k_1 = k_2^*$, $k_2 = k_1^*$. The first solution means that there is no rotation possible, and the second solution is simply a relabeling of the reaction constants. The latter can always be checked by associating the constant related to the first profile in $F$ to the first reaction. Hence, in essence, rotational ambiguity is not present anymore.

The proof given above can be used for any kinetic model imposed on the data where the matrix $F$ is of full column-rank and each column of $F$ can be written as a linear combination of a basis $[e^{-k_1t} \ e^{-k_2t} \ldots \ e^{-k_Jt}]$. Of course, by extending $F$ with more columns, there are more labeling permutations possible, but these can be resolved as commented above.

The intensity problem is trivially solved by imposing the kinetic model, because all relative concentrations are imposed by the kinetic model. Providing the algorithm with the correct starting concentrations gives then the unique intensities.

A linear independent set of exponential functions

It is shown that the exponential functions $e^{-k_jt}$ ($j = 1, \ldots, J; t \geq 0$) form a linear independent set provided that $k_1 \neq k_2 \neq \ldots \neq k_J$ and $k_j \geq 0$ for all $j$. In the following the $k_1, \ldots, k_J$ will be ordered, without loss of generality, such that $k_J > k_{J-1} > \ldots > k_1 \geq 0$. Consider the linear combination:

$$a_1 \cdot e^{-k_1t} + a_2 \cdot e^{-k_2t} + \ldots + a_J \cdot e^{-k_Jt} = 0; t \geq 0 \quad (53)$$

then it should follow that necessarily $a_1 = a_2 = \ldots = a_j = 0$. From Equation (54) follows

$$\int_0^\infty \left( a_1 e^{-k_1 t} + a_2 e^{-k_2 t} + \ldots + a_j e^{-k_j t} \right) f(t) dt = 0$$

(54)

which should hold for all functions $f(t)$. By using $f(t) = e^{k't} \delta(t - \infty)$, where $\delta(t - \infty)$ is the Dirac delta function,\footnote{The Dirac delta function $\delta(t - a)$ is defined as $\infty$ for $t = a$, and $0$ otherwise. Moreover,} it holds that

$$\int_0^\infty \left( a_1 e^{-k_1 t} + a_2 e^{-k_2 t} + \ldots + a_j e^{-k_j t} \right) e^{k't} \delta(t - \infty) dt = 0 \Rightarrow$$

$$\int_0^\infty \left( a_1 e^{(k_1 - k') t} + a_2 e^{(k_2 - k') t} + \ldots + a_j e^{(k_j - k') t} \right) \delta(t - \infty) dt = 0 \Rightarrow$$

$$a_1 = 0$$

where the last step is true because if $t$ approaches infinity, all terms in the summation within the integral sign disappear except $a_1$, which is a constant. Multiplied by $\delta(t - \infty)$ the integral can only be zero if $a_1 = 0$.

After having found that $a_1 = 0$, the whole procedure can be repeated with $f(t) = e^{k't} \delta(t - \infty)$ and following the same reasoning as in Equation (55). This results in $a_2 = 0$. This procedure can be repeated for all terms in the linear combination of Equation (53). Hence, all $a_i$ are necessarily zero and thus the functions powers of $e^{-k_i t}$ are linearly independent.

If the functions $e^{-k_i t}$ are sampled in time, this will result in vectors

$$[e^{-k_{1,t}} \ldots e^{-k_{J,t}}]'$$

with shorthand notation $e^{-k_{j,t}}$. If the number of time points $N$ is large enough (that is, $N \geq J$), then the resulting vectors $e^{-k_{j,t}} (j = 1, \ldots, J)$ are linearly independent.