

Modern Kinetics Part 1:

Global Analysis of Multiwavelength Kinetic Data

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Traditional kinetics involves the detection of the time dependence of a signal that is related to the progress of the reaction. A classical, yet today irrelevant, example is the recording of the small volume changes of a reacting solution. While this approach involves no electronic instrumentation it requires virtually perfect thermostating. The modern equivalent in terms of information content is the recording of the absorption at one single wavelength as a function of the reaction time. For the determination of the rate constant of a very simple and known reaction such data are adequate.

The recording of complete spectra as a function of reaction time brings about tremendous advantages if the mechanism of the reaction is more complex or if the kinetic investigation includes the determination of the mechanism itself together with the determination of the corresponding rate constants.

The goal of this application note is to introduce the concept of multiwavelength data, to touch on the mathematical methods used to deal with and to analyse such data, and mainly to demonstrate the advantages stemming from using such data.

The Data, Beer-Lambert's Law

Consider an absorption spectrum of a reaction solution of three components, **X**, **Y** and **Z** acquired at time *t*. Beer-Lambert's law states that the absorption of this solution at and wavelength λ is:

$$\text{abs}(t, \lambda) = [X](t) \times \epsilon_X(\lambda) + [Y](t) \times \epsilon_Y(\lambda) + [Z](t) \times \epsilon_Z(\lambda)$$

An equivalent equation can be written for each absorption at each wavelength and time. Very quickly we have to deal with very many equations. Fortunately, Beer-Lambert's law is compatible with the rules of matrix algebra. While not essential, the usage of matrix notation

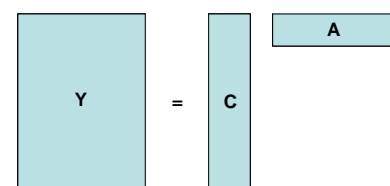
simplifies the equations dramatically. It is possible to write this collection of equations in one matrix equation:

$$Y = CA$$

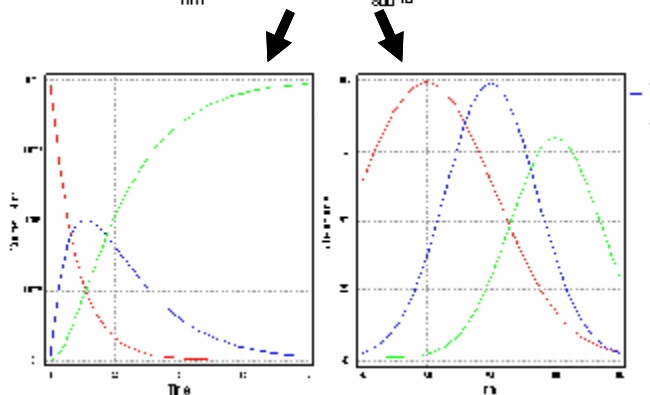
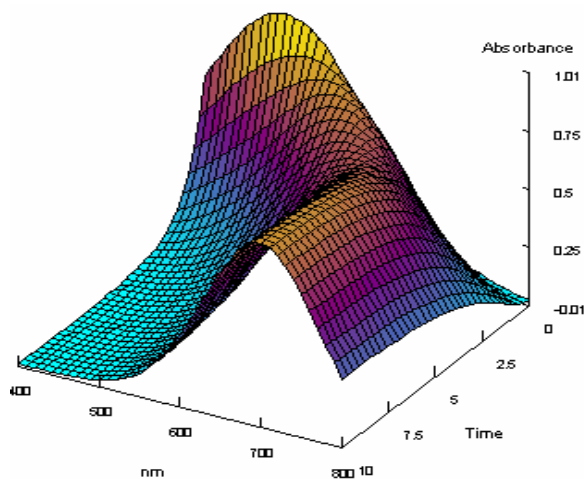
where the rows of the matrix **Y** are the measured spectra, the columns of **C** are the concentration profiles of the reacting species and the rows of **A** are formed by the molar absorptivities. It is useful to represent the equation graphically.

Analysis of the Data

The decomposition of the data matrix **Y** into the product of the matrices **C** and **A** is the goal of the analysis.



The data presented below are computer generated and



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represent the example reaction $X \xrightarrow{k_1} Y \xrightarrow{k_2} Z$ which we will discuss later. The two rate constants are $k_1=1 \text{ sec}^{-1}$ and $k_2=0.5 \text{ sec}^{-1}$ resulting in the concentration profiles on the left. The spectra are shown on the lower right.

The description of the numerical methods and algorithms which perform this decomposition is beyond the scope of this note. For the moment there are a few important aspects: The mechanism of the reaction together with the rate constants and the initial concentration for all reacting species fully describes the concentration profiles of all components, or in other words, the matrix **C**. The computation is explicit for a relatively small number of simple reaction schemes, for any other more complex reaction the computations involve numerical integration. We will describe important features of those in a subsequent Application Note. The task of the non-linear fitting is to find the best set of rate constants for a given mechanism. The matrix **A** of absorbance spectra is effectively a side-product of the fitting, the spectra do not need to be computed independently. This might be surprising, however, the user of state-of-the-art software will agree.

Establishing the correct mechanism is much more difficult and requires the experience researcher with solid chemical knowledge of the system under investigation. There is no generally useful algorithm for the determination of the correct mechanism. In Application Note 3, we will describe experimental tools which support the determination of the correct reaction mechanism.

The Advantages of Multiwavelength Data

There are several advantages in measuring and analysing multiwavelength data. The more prominent include: (a) there is no need to determine a good wavelength; (b) the availability of resulting absorption spectra which allow interpretation and identification of unknown intermediates; (c) the model and the fitted parameters are better defined; and most importantly (d) there are no disadvantages. Thus, even if single wavelength data might suffice, it does not harm to acquire multiwavelength data.

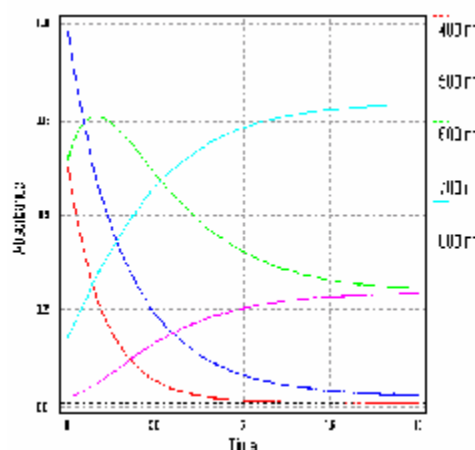
We will substantiate these claims in the following examples. The first one is the reaction scheme with two

consecutive first order reactions which we introduced before.

Example 1: $X \xrightarrow{k_1} Y \xrightarrow{k_2} Z$

(a) there is no need to determine a good wavelength. The figures below represent a few kinetic traces acquired at different wavelengths:

Most of the traces do not clearly define the two reaction steps. In fact, only the traces at 600 and 800nm feature the typical and familiar behaviour for that scheme. It is of course not possible to select the optimal wavelength if the system under investigation is still unknown.



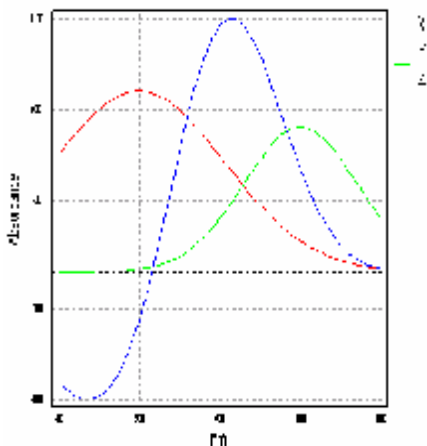
(b) the availability of resulting absorption spectra which allow interpretation and identification of unknown intermediates. As demonstrated in the figure on the previous page, the spectrum of the intermediate **Y** is delivered by the analysis. Such spectra allow structural assignment of an unknown intermediate and can confirm the viability of a given mechanism. This can be invaluable information in a yet unknown system. Single wavelength data deliver at most the molar absorptivity of the intermediate at the particular wavelength.

(c) the model and the fitted parameters are better defined. The reaction scheme $X \xrightarrow{k_1} Y \xrightarrow{k_2} Z$ comprises an interesting and widely discussed ambiguity: it is not possible to assign uniquely the two rate constants k_1 and k_2 to the two steps in the reaction scheme. The quality of the two fits with the two possible arrangements are identical, the only difference between them is the spectrum of the intermediate **Y**. In some instances, depending on the rate constants and the spectra of all components, one of the two options results

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in a spectrum that is physically impossible (negative absorbencies at some wavelengths) or it may contradict independent chemical spectroscopic knowledge about the species. It is much more likely that the wrong assignment is not noticed by single wavelength data, e.g. data in the range 500 to 800 nm will not allow a clear-cut conclusion.

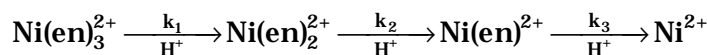


It is straightforward to comprehend that the rate constants are better defined for multiwavelength data. To some extent this is the result of having more data altogether, but more importantly it results from the fact that while one parameter might be well defined in one particular range of wavelengths, the other parameter might be well defined in another independent range. Analysis in the first range will deliver good definition of the first parameter but not the second, vice versa. Analysing both ranges globally results in good definition of both.

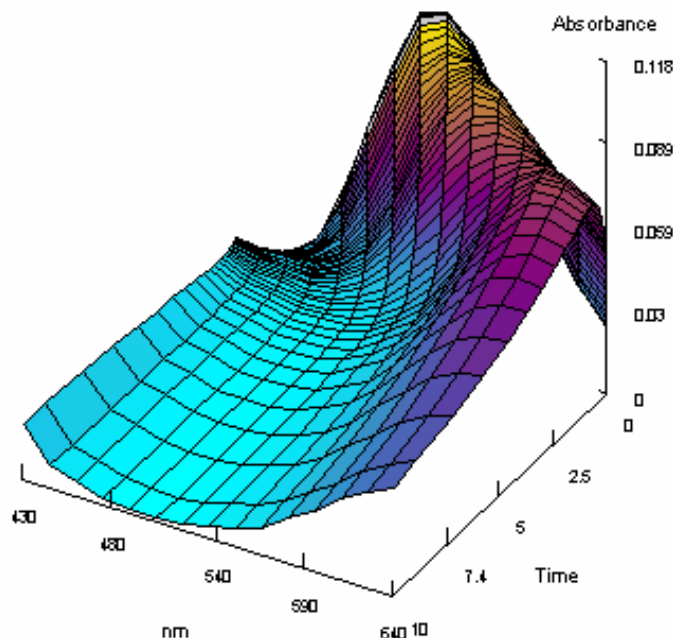
wavelength	$k_1(\text{sec}^{-1})$	$k_2(\text{sec}^{-1})$
global	1.0026 ± 0.0009	0.4998 ± 0.0003
400nm	1.04 ± 0.07	0.7 ± 0.2
500nm	1.00 ± 0.05	0.50 ± 0.01
600nm	1.01 ± 0.01	0.498 ± 0.005
700nm	0.96 ± 0.06	0.505 ± 0.009
800nm	0.99 ± 0.04	0.50 ± 0.01

(d) there are no disadvantages. This is a bold statement. Naturally, the computations are more complex and demanding. However, state-of-the art analysis software, such as ProKII, delivers the results with minimum effort and the user will not notice any difference in the behaviour nor the speed of the execution. For the examples given above computation is essentially instantaneous.

Example 2:



The complex Ni(en)_3^{2+} undergoes hydrolysis in acidic aqueous solution in three irreversible consecutive steps. The observed intermediates are Ni(en)_2^{2+} and Ni(en)^{2+} with the final product Ni^{2+} and protonated ethylenediamine. This reaction is an example which exhibits the advantages of multiwavelength kinetics. The reaction scheme is complex enough to prevent successful analysis at any single wavelength.



The above real data were acquired at 15 wavelengths between 430 and 640 nm. 333 Spectra were acquired on a logarithmic timescale between 2msec and 10 sec. The initial concentration of the Ni(en)_3^{2+} complex was 0.0197M and the proton concentration 0.56 M. Under these conditions protonation of the ligand is complete and all three reaction steps are irreversible.

The fitted rate constants for this particular measurement are $99.0 \pm 0.3 \text{ sec}^{-1}$, $4.100 \pm 0.008 \text{ sec}^{-1}$ and $0.183 \pm 0.001 \text{ sec}^{-1}$. The resulting concentration profiles are shown in

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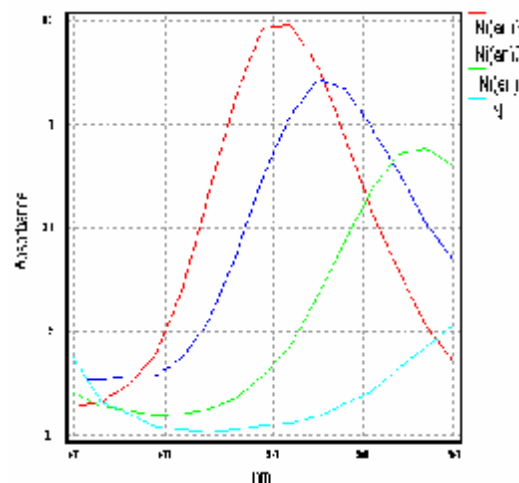
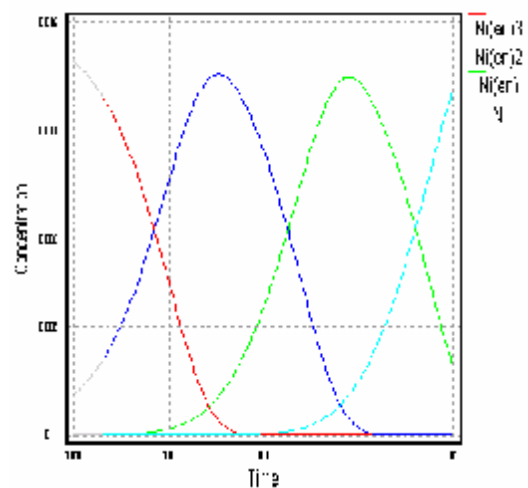
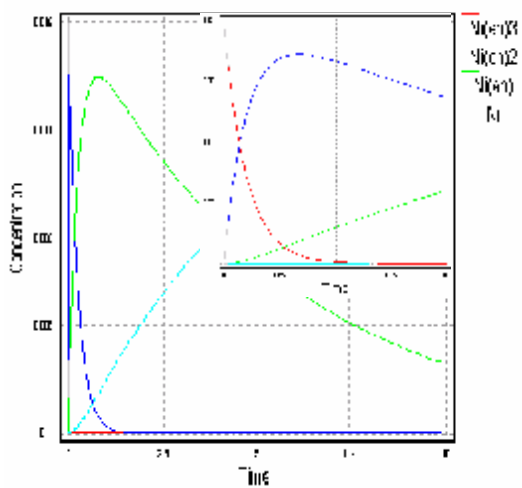
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the next two figures. First on a linear timescale, with an inset for a reduced time scale to 0.1 sec.

The plot underneath uses a logarithmic time scale which beautifully displays the stepwise hydrolysis of the ethylenediamine ligands.

The last figure displays the absorption spectra for all the differently complexed Ni-species. Because of the lability of these complexes, the spectra of the intermediates cannot be measured directly. It is encouraging to know that the computed spectra are confirmed by equivalent spectra resulting from the analysis of spectrophotometric titrations.



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