Assignment 2 Fitting and Multivariate Curve Resolution

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1 Introduction

In the last assignment, we looked into calculated concentrations in time based on a kinetic model. The drawback of this method is that we need to know the kinetic rates beforehand.

only modelled

2 Background

2.1 Fitting

In order to obtain accurate parameters, we only fit our model to measured date. The bigger the data set used, to more accurate the parameters will be. For example when we want to determine molar absorbtivities, based on the Lambert-beer law:

$$A = \epsilon c l \tag{1}$$

we can in principle use a single measurement to determine ϵ. However it will be more accurate (and less prone to artifacts) if we measure absorbances for a range of concentrations (c) or pathlenghts (l), or in the best case, we vary both. We will now outline how - mathematically the operation of fitting is preformed. We want our model's prediction to be as close as possible to the data. Let's say we have measure A as a function of c. Then we can minimize the following quantity:

$$R(c) = A_{measured}(c) - A_{modelled}(c) \tag{2}$$

$$R(c) = A_{measured}(c) - \epsilon c l \tag{3}$$

however this will cause problems: R(c) can be negative, and therefore minimization does just make $A_{modelled}$ as high as possible. A common solution to this problem is instead of minimizing $A_{measured}(c) - A_{modelled}(c)$, we minimize the sum of its square instead, as that is always positive:

$$SS = \sum_c \left((A_{measured}(c) - A_{modelled}(c))^2 \right) \tag{4}$$

$$SS = \sum_c \left((A_{measured}(c) - \epsilon c l)^2 \right) \tag{5}$$

Note the we first take the difference, then the square and then the sum over all our data points (in this case the concentrations).

2.2 Least-Squares

The method of minimizing equation 4 is called *The Method of Least-Squares* and is very common in science. In this case it will be used to calculate molar absorbtivities from data.

2.3 Multivariate Curve Resolution

Another application of the least-squares method can be found in multivariate curve resolution (MCR). A full description of this method is highly mathematical and therefor only a small outline will be given here. If you are interested I recommend reading[1].

This method can be used to analyse kinetic data (spectral data in time) to help guide towards a chemical mechanism for the data. The method was originally designed for UV-Vis absorption spectroscopy (the first widely used technique) but it nowadays has been applied to many different spectroscopic techniques for instance IR-, Raman- and NMR specotrocopy.

The main assumption of the method is that the concentration of each component in the system has a linear effect towards the signal measured. For example, if we have three molecules in the system that can absorbed 355 nm light, then the measured absorbance should be:

$$A_{355\text{ nm}} = A(1)_{355\text{ nm}} + A(2)_{355\text{ nm}} + A(3)_{355\text{ nm}}$$

$$= \epsilon_{355\text{ nm}}(1)c(1)l + \epsilon_{355\text{ nm}}(2)c(2)l + \epsilon_{355\text{ nm}}(3)c(3)l$$

In words: when a components has double the concentration then the signal corresponding to that component also has to double. This is true for most spectroscopies except when saturation occurs. That is when a signal is so high that the spectrometer cannot distinguish signal anymore. For example in UV-VIS absorption spectroscopy, an absorbance above 1 is not usable anymore for quantification.

Mathematically the method fits the data using a set number of spectral components (i.e. types of molecules in the system). The shape of the spectra and the concentrations in time are then optimized (using a method analogous to the method of least squares above, i.e. to minimize the squared sum of errors) to fit all data at the different time points. Since multiple parameter have to be optimized, this is called multivariate technique. The optimization can be tricky to achieve so the starting points have to be considered carefully.

References

[1] Anna De Juan, Joaquim Jaumot, and Romà Tauler. Multivariate curve resolution (mcr). solving the mixture analysis problem. *Analytical Methods*, 6(14):4964–4976, 2014.