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Comparison of PLS and kinetic models for a second-order reaction as monitored using ultraviolet visible and mid-infrared spectroscopy

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Abstract

A second-order reaction between benzophenone and phenylhydrazine to give benzophenone phenylhydrazone was followed using UV/vis and mid-infrared spectroscopic probes. Established kinetic (hard) and partial least squares (soft) modelling chemometrics methods were applied to both datasets in order to compare the information acquired with each probe. To this purpose, an experimental design with 25 samples and a test set with 5 samples were used to build a partial least squares calibration model to predict the concentration profiles of the compounds present in the reaction vessel. In addition, multivariate kinetic modelling was also performed on the spectroscopic data. Using a guess of the rate constant, concentration profiles were estimated. The profiles are then used to calculate the estimated spectroscopic profile, which is compared to the data acquired experimentally. The residual is minimised and the rate constant estimated; this procedure is iterated until convergence. A total of four profiles were obtained for each compound, corresponding to two sets of probes and two sets of models. The results were compared and discussed. It is shown that several different spectroscopic techniques can be used in reaction monitoring, with increasing benefits in terms of information and interpretation of the results. The profiles obtained agreed well which was also demonstrated when comparing the different rate constants obtained.
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1. Introduction

Reaction monitoring using probes that can obtain spectroscopic data on-line as the reaction progresses has an important role to play especially in process chemistry. Over the past decade there has been a major expansion in NIR (near infrared) methods for reaction monitoring [1,2]. Traditionally, partial least squares (PLS) and related multivariate methods have been employed to determine the concentration of individual components from this on-line spectroscopic data, first developing a calibration model and then applying it to the mixture data, in order to estimate change in concentrations of the reactants from the spectroscopic data [3], especially to PLS in reaction monitoring and NIR [4].

However, over the last few years, a new generation of probes in the mid-infrared (MIR), ultraviolet visible (UV/vis) and Raman regions has been developed which promises to revolutionise reaction monitoring [5,6]. Coupled to this are new capabilities in analysis of the spectroscopic data using multivariate kinetic models [7] which has been an especially important growth point. The advantage of kinetic models is that they can incorporate extra information about the reaction that is often known in advance, for example the order of the reaction, and also that they do not require calibration standards. This has the advantage that there is no requirement for calibration using pure compounds: it is sometimes hard to perform calibration especially if the conditions under which a reaction is performed are unstable. Mixing the calibration standards under reaction conditions will lead to mixtures that do not have a long shelf life, for obvious reasons. Because spectra change with pH or temperature or most factors that catalyze a reaction [8], it is not always easy to develop a PLS

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model under reaction conditions. Kinetics models, in contrast, depend on having a good knowledge of the reaction mechanism, often requiring one step reactions without significant intermediates or side products, and if the reaction is more than first order, it is necessary to know the concentration of starting materials. We can show that if some of this information is not accurately known this can result in poor predictions using kinetics methods [9].

We have previously studied the second-order reaction of benzophenone and phenylhydrazine [10,11] but using only kinetics models and a UV/vis probe. In analytical chemistry, it is often important to validate methods using independent approaches. One advance is to be able to monitor a reaction simultaneously using more than one probe, in this paper we report a reaction monitored using both a MIR and a UV/vis probe. Both have their advantages and disadvantages. MIR is a useful approach because compounds often show fairly characteristic spectral peaks that can be identified, but the MIR probe has a lower signal to noise ratio and individual spectra need to be recorded over a longer time period to obtain adequate intensity. Comparing results from both instruments is an important confirmation that our predictions are correct.

PLS models have been used for reaction monitoring [12–17], in some cases to obtain rate constants, but in many cases primarily to obtain reaction profiles, without kinetic information. The problem with PLS models in the context of this paper, is that the reaction is catalyzed by using acid, which also has a significant influence on spectral characteristics. Therefore, PLS calibration sets need to be recorded immediately after the acid is added. For the MIR instrument, because about 5 min are required for recording a spectrum, a small amount of reaction will occur during the calibration. However, the errors introduced by this means are likely to be less than the errors introduced if one performs the calibration in the absence of acid and then applies this model to the reaction which includes acid.

This paper reports the results of four types of analysis, namely two probes (MIR and UV/vis) and two types of data analysis (kinetics and PLS).

2. Theory

2.1. Experimental design for PLS calibration

In order to obtain a suitable calibration set we use systematic experimental designs. Whereas two level designs are valuable for exploratory purposes and can sometimes result in useful models, in many areas of chemistry, such as calibration, it is desirable to have several levels, especially in the case of mixture spectra [18]. A special class of design has been developed for calibration. One of the greatest problems involved [19] in the determination of multicomponent systems is the generation of a suitable training set able to predict any combination of concentrations of the compounds.

If the concentrations of two components in a training set are completely correlated, it is not possible to know whether a change in spectral characteristic results from a change in concentration of one or the other component. In addition, if a future sample arises with a high concentration for the first compound and low concentration for the second, calibration software will give an incorrect answer for the concentration of each component [19]. In mixture experiments [20,21] it is desirable that the compounds be uniformly distributed over the space. Features such as orthogonality are especially important to have a good model.

This paper employs a partial factorial design for five concentration levels ($l = 5$). Mutually orthogonal designs are only possible if the number of concentration levels is a prime number or a power of a prime number. The design requires at least l^2 experiments (25 experiments) to study a mixture [19,21]. After numbering the levels from −2 (lowest) to 2 (highest) the complete design was obtained using what is often described as a cyclic generator (−2, 1, 2, 1, −2), a repeater of 0 and a difference vector (0 2 3 1) [20]. In this type of design, there is no correlation between any concentrations of the compounds; hence, the correlation coefficient is zero.

2.2. Principal component analysis

Principal components analysis (PCA) is a technique used to discover the significant information contained in large amounts of multivariate data, and to accurately represent the data with just a few key components.

The data in this work is presented as a matrix $\boldsymbol{X}$. Each row in the matrix represents the spectrum at one point in time. Each column represents the absorbance at a given wavelength.

The data matrix $\boldsymbol{X}$ (dimensions $I \times J$) can be decomposed [22] into a product of two matrices, as follows:

$$\boldsymbol{X} = \boldsymbol{TP} + \boldsymbol{E} \tag{1}$$

The $\boldsymbol{T}$ matrix contains the scores of I objects on K principal components. The $\boldsymbol{P}$ matrix is a square matrix and contains the loadings of J variables on the K principal components. $\boldsymbol{E}$ is the error matrix.

If the original data matrix is dimension $I \times J$, no more than J principal components can be calculated if $J \leq I$. PC1 represents the direction in the data, containing the largest variation. PC2 is orthogonal to PC1 and represents the direction of the largest residual variation around PC1 and so on. These will contain less and less variation and therefore less information [18]. The first scores vector and the first loadings vector are often called the eigenvectors of the first principal component. Each successive component is characterized by a pair of eigenvectors.

2.3. Partial least squares

There are four steps in the application of PLS:

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