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Sucrose as chiral selector for determining enantiomeric composition of metalaxyl by UV–vis spectroscopy and PLS regression

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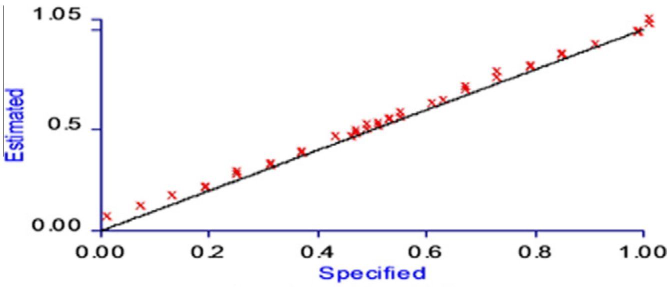
HIGHLIGHTS

- ▶ We use sucrose as a chiral selector to determine the D-met by UV–vis spectral data with PLS models.
- ▶ We develop the model by concentration normalization to eliminate the variations the differences.
- ▶ We introduce a convenient normalization method–RBN to standardize the spectral of all samples.
- ▶ We use the model developed by the medium one to predict the high and low levels and the results are well.

GRAPHICAL ABSTRACT



The prediction of the model after RBN

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ABSTRACT

This study revealed that it was possible to determine the enantiomeric composition of with multivariate regression models of spectral data obtained by ordinary UV–vis spectrophotometry of enantiomeric guest–host complexes. The total 60 samples involving three concentration levels of metalaxyl as low, medium and high were prepared for spectral collecting. Four methods of modeling were subsequently proposed and compared including two common ways and two compensating ways for variations in total analyte concentration. Firstly, without normalization robust modeling was failed to achieve while employing the medium concentration levels as calibration and the other two levels as a validation. The same case occurred when full-cross validation was conducted. Besides, two enhanced methods were developed to account for the systematic variation. One of which normalized the spectra with respect to the total concentration of enantiomeric, along with spectral data, as a variable in the statistical analysis. The other one ignored variations in total concentration, relying on the specific band normalization to sort out any variations due to total concentration differences. The results clearly demonstrated that the spectra according to concentration provided the acceptable predictive ability in determining enantiomeric composition.

Introduction

Chiral analysis is widely focused on in the field of separation science. In chiral notation, R and S refer the orientation in space of the groups around the chiral center of the enantiomer. This orientation is the important factor in determining whether the enantiomer fits the chrial selector. Determination of the enantiomeric composition of chiral substances has been paid much attention in recent years because that chirality is a central factor in biological phenomena.

Enantiomeric forms of many compounds are known to have different physiological and therapeutic effects. In most cases, only one form of an enantiomeric pair is pharmacologically active. The other or others can reverse or otherwise limit the effect of the desired enantiomer [1]. For example, many pesticides, herbicides are

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chiral, one form may persist longer in the environment than the other [2]. In addition, enantiomers often exhibit different effects or toxicity: the ‘‘active’’ enantiomer has the desired effect on a target species, whereas the other enantiomer does not. Optical isomers may also have very different tastes and smells. Therefore, enantiomeric pure products are desirable in pharmaceutical industry and in agriculture especially.

Many separation techniques have been developed for determination of enantiomeric purity over the years, such as gas chromatography [3], liquid chromatography [4] and capillary electrophoresis employing chiral stationary phases [5]. Among all these analytical methods, rapid spectroscopic techniques appear most promising lately, e.g. UV–vis spectroscopy, IR, and fluorescence methods [6–8] have become the most popular methods of studying guest–host interactions for numerous types of chiral substances. However, given our increased understanding of the different roles optical isomers play in complexes, there is a need for rapid, accurate and low-cost methods of determining the enantiomeric composition of chiral molecules by spectroscopic methods.

UV–vis technique is the spectroscopic method that has been used to determine enantiomeric composition coupled with partial least square (PLS) analysis of the spectral data from guest–host mixtures [9–11]. However, the UV absorption spectra vary slightly and are not directly enough to reveal the correlation of the spectra changes and the enantiomeric composition. PLS method is a multivariate regression technique, which is widely used as a means of correlating small changes in spectral data with known compositional changes. This regression model is developed by correlating the known enantiomeric composition with the calibration set of samples using multivariate regression calibration.

As known to us, UV–vis spectra of the enantiomers are the same in nonchiral media. But they may be different in chiral auxiliary due to the dissimilar interactions between enantiomer and chiral medium. One of the most common chiral auxiliary is sucrose. Some researches on the determination of the enantiomeric composition by using UV–vis [12,13] and near-infrared spectrometry [14] combining with multivariate regression with sucrose were reported. As one kind of important chiral selectors, sucrose (Fig. 1) has been shown stereoselectively bind to chiral molecules for their complex and changeable conformations. Therefore, it should be applicable to build a system based on sucrose to determine the enantiomeric composition by UV–vis method. In this study, PLS regression modeling is based on UV–vis spectral data from the metalaxyl embeded sucrose.

Metalaxyl (Fig. 1) poses chiral because it contains a stereogenic centre in the carboxy alkyl moiety. So it consists of a pair of enantiomers, S- and R-enantiomer. Metalaxyl is one of the few marketed pesticides both as a racemic formulation and as a single-enantiomer product, called metalaxyl-M (M-met), which contains only the active (R)-form of the key ingredient. The ultimate goal of this enantiomer-specific determination should be the development of a predictive capability for enantioselectivity.

In this experiment, sucrose was used as a chiral selector to determine the molar fraction of M-met by UV–vis spectral data combining with PLS models. There are three concentration levels low, medium and high. Initially, two means were attempted to develop the model. One of which was to establish a model using the medium level as calibration set and the remaining as validation set. The other way was to calibrate covering the entire range of samples as a full cross-validation. Similarly the SECV of the two methods were not good.

In this paper, two normalization treatments were utilized, one was concentration normalization (CN) and the other was reference band normalization (RBN). Both in CN and RBN, the medium level was set as calibration set in regression while the high and low levels were chosen as the independent validation set. The differences of these normalized spectra were only variations from enantiomeric compositions, with no relation to the variations from total concentrations. In brief, the spectral variations were only caused by the differences in enantiomeric composition.

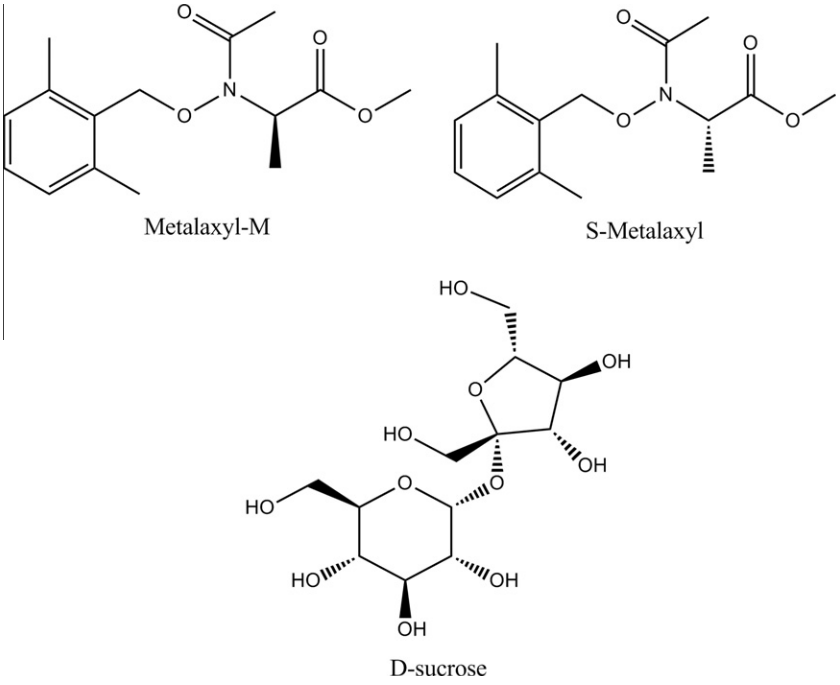

Fig. 1. Structure of the two enantiomers of (a) M-met. (b) S-met and structure of (c) sucrose.