

Application of MCR-ALS and correlation constrain for determination of compounds in biodiesel blends using NIR and visible spectroscopy.

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Introduction

Biodiesel production has been increased mainly because the environmental concern about fossil fuels consumptions and the consequent increase of greenhouse gas emissions. Biodiesel can partially or completely replace diesel from petroleum and is used blended with diesel to power vehicles engines. It consists of a mixture of alkyl esters of long chain fatty acids susceptible to oxidation. Different analytical methodologies have been proposed for analysis of several biodiesel parameters to overcome this expansion and the quality control necessities.¹⁻⁴ This study describes two applications of a variant of the multivariate curve resolution alternating least squares (MCR-ALS) method with a correlation constraint.⁵⁻⁷ The first application describes the use of MCR-ALS for the determination of biodiesel concentrations in biodiesel blends using near infrared (NIR) spectroscopic data. In the second application, the proposed method allowed the determination of the synthetic antioxidant N,N'-Di-sec-butyl-p-phenylenediamine (PDA) present in biodiesel mixtures from different vegetable sources using visible spectroscopy. Well established multivariate regression algorithm, partial least squares (PLS),^{8,9} were calculated for comparison of the quantification performance in the models developed in both applications.

Results and Discussion

The correlation constraint has been adapted to handle the presence of batch-to-batch matrix effects due to ageing effects, which might occur when different groups of samples were used to build a calibration model in the first application. Different data set configurations and diverse modes of application of the correlation constraint are explored and guidelines are given to cope with different type of analytical problems, such as the correction of matrix effects among biodiesel samples, where MCR-ALS outperformed PLS reducing the relative error of prediction RE(%) from 9.82 % to 4.85 % in the first application, or the determination of minor compound with overlapped weak spectroscopic signals, where MCR-ALS gave slightly higher

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(RE(%) = 3.16 %) for prediction of PDA compared to PLS (RE(%) = 1.99 %), but with the advantage of recovering the related pure spectral profile of analytes and interferences.

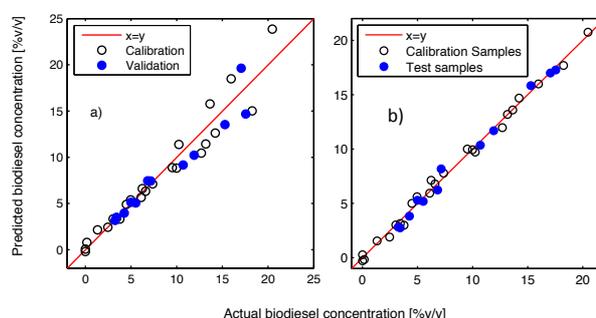


Figure 1 Sample matrix effect correction. a) before, b) after.

Conclusion

The obtained results show the potential of the MCR-ALS method to be adapted to diverse data set configurations and analytical problems related to the determination of biodiesel mixtures and added compounds therein.

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