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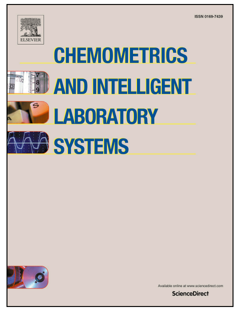

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Robust analysis of spectra with strong background signals by First-Derivative Indirect Hard Modeling (FD-IHM)

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ABSTRACT

Spectral analysis of mixtures often faces challenges due to nonlinear effects such as peak shifts or strong background signals. Nonlinear mixture effects can be effectively treated by the Indirect Hard Modeling (IHM) Method. In IHM, mixture effects are captured by adapting hard models of pure component spectra when fitting a mixture model. However, IHM requires a suitable background treatment, which can become laborious. Background signals do not arise from the components of interest but often superimpose their spectra.

In statistical methods for spectral analysis, background treatment is often conducted by derivatives of a spectrum. Derivatives effectively damp broad background signals. Standard IHM is not applicable to derivatives of spectra as the negative parts of a derivative spectrum cannot be modeled by pseudo-Voigt peaks which are always positive. In this work, we propose First-Derivative Indirect Hard Modeling (FD-IHM). FD-IHM uses the analytical derivatives of the peak functions. The analytical derivatives are fitted to numerical derivatives of the spectra. Thereby, we combine background treatment by first derivatives with the IHM method to treat nonlinear effects.

The presented FD-IHM is validated using Raman spectra of ethanol/acetone mixtures. To introduce a variety of background signals, we used fluorescence dye, scattering bodies (yeast) and various background light sources. Classical IHM allows us to predict the test sets with a root-mean-square error of prediction (RMSEP) ranging from 0.60 wt% to 2.06 wt%, but careful manual background treatment had to be applied. With FD-IHM, we reduce the RMSEP error by 21% to 73% without any background treatment. Thus, FD-IHM allows for both, efficient and accurate analysis of spectra with large background signals.

Keywords: Indirect Hard Modeling; Process analytical technology; Raman spectroscopy; Background treatment; Chemometrics

1. INTRODUCTION

Spectroscopy provides unique insights into complex phenomena in multicomponent systems. In many spectroscopic methods, the spectrum of a multicomponent system is essentially a weighted sum of pure component spectra of its constituting components (e.g., Raman, Mid-Infrared). However, molecular interactions of different components in the mixture induce nonlinear effects such as peak deformations and peak shifts. These nonlinear effects are challenging for statistical methods that are based on linear algebra [1, 2]. To handle these nonlinear effects, Indirect Hard Modeling (IHM) has been designed [3-7]. IHM