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Resolution enhancement of composite spectra using wavelet-based derivative spectrometry

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Abstract

An approach based on the using of the continuous wavelet transform (CWT) in derivative spectrometry (DS) is considered. Within the framework of the approach we develop a numerical differentiation algorithm with continuous wavelets for improving resolution of composite spectra. The wavelet-based derivative spectrometry (WDS) method results in best contrast in differential curves compared to the conventional derivative spectrometry method. A main advantage is that, as opposed to DS, WDS gives stable estimations of derivative in the wavelet domain without using the regularization. A wavelet shape and the information redundancy are of the greatest importance when the continuous wavelet transform is used. As an appropriate wavelet we offer to utilize the *n*th derivative of a component with a priori known shape. The energy distribution into scales allows one to determine a unique wavelet projection and in that way to avoid the information redundancy. A comparative study of WDS and DS with the statistical regularization method (SRM) is made; in particular, limits of applicability of these are given. Examples of the application of both DS and WDS for improving resolution of synthetic composite bands and real-world composite ones coming from molecular spectroscopy are given.

Keywords: Wavelet transform; Derivative spectrometry; Resolution

1. Introduction

The decomposition of an analytical signal into elementary components is one of important problems in applied spectroscopy when treating and interpreting composite spectra. The knowledge of a number of components, locations and their shapes is necessary for correctly assigning bands in terms of the ordinary least squares (OLS) approximation. Therefore, the preliminary treatment of spectroscopic information plays a key role in further interpretation of molecular (vibrational) spectra.

A large number of methods is currently used to enhance mathematically resolution of composite spectra. More widely used methods are the method of derivative spectrometry (DS) [1–4], the Fourier self-deconvolution method [5,6], regularized algorithms of filtration [1,3,7], procedures based on the spectral estimate of maximum entropy [1], maximum likelihood estimations [8], and neural networks [9,10]. Applying Occam's razor in this situation, the DS method (in a more general case it is the method of fractional derivative spectrometry (FDS) [2,3,11]) is a simple and attractive instrument in analytical spectroscopy for resolving composite spectra. As it is known [1–4], this method represents the linear transform of a spectrum, enhancing its resolution (signal narrowing, background noise suppression), and, therefore, permitting determination of its spectral parameters.

When using the DS method a question about ways to obtain derivatives of experimental data arises inevitably. As it is known [1,3,7], the numerical differentiation of experimental data obtained by both direct and/or inverse methods represents an ill-posed problem, i.e. the acquisition of acceptable results is possible only when a priori information on the required function, e.g. its differentiability, boundedness, monotonicity, etc. is introduced implicitly or explicitly. This information is referred to as a regularization of a solution [7]. In references [1–4] various regularized algorithms for the numerical differentiation of an arbitrary (including fractional) order are analyzed in detail. The algorithm of the numerical differentiation of an arbitrary order on the basis of statistical regularization method (SRM) is set to be highly efficient in contrast to the Savitzky–Golay method, the Kaiser filtration, regularized splines [2,3]. As an

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