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Spectrochimica Acta Part A 60 (2004) 2125–2133

SPECTROCHIMICA ACTA PART A

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A simple method to extract spectral parameters using fractional derivative spectrometry

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Received 16 June 2003; accepted 10 November 2003

Abstract

The nonlinear fitting method, based on the ordinary least squares approach, is one of several methods that have been applied to fit experimental data into well-known profiles and to estimate their spectral parameters. Besides linearization measurement errors, the main drawback of this approach is the high variance of the spectral parameters to be estimated. This is due to the overlapping of individual components, which leads to ambiguous fitting. In this paper, we propose a simple mathematical tool in terms of a fractional derivative (FD) to determine the overlapping band spectral parameters. This is possible because of several positive effects of FD connected with the behavior of its zero-crossing and maximal amplitude. For acquiring a stable and unbiased FD estimate, we utilize the statistical regularization method and the regularized iterative algorithm when a priori constraints on a sought derivative are available. Along with the well-known distributions such as Lorentzian, Gaussian and their linear combinations, the Tsallis distribution is used as a model to correctly assign overlapping bands. To demonstrate the power of the method, we estimate unresolved band spectral parameters of synthetic and experimental infra-red spectra.

Keywords: Derivative spectrometry; Fractional derivative; Overlapping peaks; Fitting

1. Introduction

The derivative spectrometry (DS) method is a simple and attractive instrument in analytical spectroscopy that provides a score of positive effects such as separating overlapping peaks and background noise suppression, this is made possible due to the considerable increase in contrast of the derivative spectrum compared to the original one. Even small changes of monotonicity in the initial spectrum are clearly recorded by its derivatives. Traditionally, DS have been successfully applied to the determination of a number of completely unresolved peaks and their positions [1–4].

However, the application of integer-order derivatives is not always enough, since shapes of nth and $(n+1)$th differentiation curves are not close to each other in a qualitative sense and, therefore, some information on the data under study can be lost. On the other hand, as the differentiation order increases, a high-frequency color noise amplifies strongly, so that the signal-to-noise ratio (SNR) decreases abruptly. This circumstance negates the use of higher order derivatives for studying spectra. In order to get around these restrictions and to make DS more flexible for processing and interpretation of the data it is necessary to generalize the DS method for non-integer (fractional) orders, this will be referred to as *fractional* derivative spectrometry (FDS). A fractional derivative (FD) provides information "gain" allowing one to follow the smooth variation in the analyzed data [3,5]. This redundancy can be rather useful when studying the behavior of non-simple points, for example, zero-crossing, extreme values, etc.

It is important to note that the numerical differentiation of experimental data obtained by both direct and/or inverse methods represents an ill-posed problem because of inevitable measurement errors. Therefore, a crucial question on how to regularize the differentiation problem arises inevitably to obtain a stable and unbiased derivative estimate. A sense of the regularization is to introduce a priori information on the derivative sought (e.g. boundedness, monotonicity, etc.) and statistical properties of the measurement error implicitly or explicitly, thus, avoiding the computation instability [6].

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doi:10.1016/j.saa.2003.11.013