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Derivative UV-vis absorption spectra as an invigorated spectrophotometric method for spectral resolution and quantitative analysis: Theoretical aspects and analytical applications: A review

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ABSTRACT

With the objective of extracting a large amount of analytical information from spectral data comprising of unresolved bands, a number of techniques have been proposed. In context to spectral data analysis, 1st or higher order mathematical derivative treatments of absorbance plots have proven to be a pioneer. Pharmacy, food, cosmetics and environment are some of the areas where derivative spectrophotometry (DS) have contributed significantly. Enhancement of peak signals and resolution of overlapping peaks are some of the important applications of derivative spectrophotometry. This enhanced resolving effect may be attributed to the fact that derivative spectrophotometry can easily differentiate between closely adjacent peaks, and identify weak peaks obscured by sharp peaks. The prime objective of this review is to comprehensively address the instrumental development and analytical applications of derivative UV-vis spectrophotometry in 20th century.

Contents

Abbreviations: AP, Ampicillin; API, Active pharmaceutical ingredient; AMD, Amiloride hydrochloride; BC, Butamirate citrate; BE, Benzaepril hydrochloride; BAR, Barnidipine; CCDs, Charge coupled devices; CMC, Critical micellar concentration; COD, Chemical oxygen demand; DS, Derivative Spectrophotometry; DIA, Diacerein; DYS, Doxylamine succinate; DDRD, Double divisor ratio spectra derivative method; DRSZ, Derivative ratio spectra zero crossing method; FA, Folic acid; FF, Formoterol fumarate; FCV, Famciclovir; FWT, Fourier wavelet transform; GA, Glycyrrhizic acid; GB, Glyburide; GI, Gastrointestinal tract; HCT, Hydrochlorothiazide; HPLC, High performance liquid chromatography; IR, Infra red; LQ, Liquiritin; MF, Metformin Hcl; MS, Montelukast sodium; MCPP, 2-(4-Chloro-2-methylphenoxy) propinoic acid; MLRA, Multi wavelength regression analysis; ODS, Octadecyl silyl; PH, Pyridoxine hydrochloride; PCR, Principal component regression; PEG, Polyethylene glycol; PLS, Partial least square; PLSR, Partial least square regression; RBR, Red K-2G; SB, Sublactum; SC, Sodium cromoglycate; SV, Solenoid valve; SM, Spectrophotometric methods; SIM, Stability indicating methods; TIM, Timolol maleate; TLC, Thin layer chromatography; UV-Vis, Ultraviolet-Visible; WT, Haar wavelet transform; Y2G, Yellow 2 G.

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1. Introduction

Spectrophotometric methods (SM) are the most commonly employed techniques which appear to be striking. Owing to the common availability of instrument, simplicity of procedures, speed, precision and accuracy the SM have gained wide popularity. When compared with other state-of-the-art methods of analysis such as chromatography and electrophoresis, the spectrophotometric techniques are far more economical and offer simplified operations.

A serious predicament is observed while dealing with the analysis of overlapping bands of the analytes and interferences which makes the extraction of qualitative and quantitative data difficult. However, a compelling solution to this problem is provided by derivative spectrophotometry (DS) in the UV-vis region. DS plays an outstanding function in the multi component analysis. The differentiation of normal spectrum is done by applying mathematical transformation, where the spectral curve is transformed into 1st or higher order derivatives. When compared to direct absorption spectra, DS provides many alluring features [1];

(i) Enhanced resolution,
(ii) Detection and enhancement of minor or subtle spectral features,
(iii) Elimination of background or matrix interference,
(iv) Defined fingerprints,
(v) Discrimination against broad band interference,
(vi) Enhancement of sensitivity and specificity in mixture's analysis,
(vii) Higher separation efficiency in sharpened peaks,
(viii) Reagent, time and labour saving.

DS have made tremendous contributions in agriculture, pharmacy and biomedical field. It has been widely used as a tool for quantitative analysis, characterization and quality control. When coupled with other data processing techniques *viz.* zero crossing, least square deconvolution, or Fourier transform, DS becomes a powerful analytical tool and thus, has received enormous attention in single and multi component quantitative analysis, especially in UV-absorbing matrices [1]. The inflections are converted into maxima or minima when the spectral data is derivatized; also the maxima and minima of the original function take zero values respectively. The tiny differences between the original spectra are highlighted, as the derivative curves are far more structured than the original spectra. Owing to its ability to identify, differentiate between closely adjacent peaks and weak peaks obscured by sharp peaks, the peak signals are enhanced and resolved to a much greater extent. This makes DS possess an additional advantage over traditional spectra. DS also provides greater selectivity for simultaneous multi component analysis without prior chemical separation [2].

However, like any other technique DS is accompanied by some limitations. Scanning speed and slit width are some of the instrumental parameters which govern the accuracy and precision of DS. It has also been observed that the shape and intensity of the generated derivatized peak is strongly influenced by the initial instrumental conditions while recording parent zero-order spectrum [2]. Slightly lower reproducibility and sensitivity are the limitations which hampers the usage of DS for routine analytical purpose [1].

2. Theoretical and instrumental aspects

The main objective of DS is to determine two or more active compounds in the same mixture without any preliminary separation. Classical derivative spectrophotometry, Vierdot's method, orthogonal function method, Fourier functions method, dual wavelength spectrophotometry, pH induced differential spectrophotometry, least square method, multi component analysis programme, partial least square regression (PLSR), principal component regression (PCR), H-point standard addition method and multi wavelength regression analysis (MLRA) are some of the other spectrophotometric methods which have been used for resolving overlapping spectra of mixtures. Absorbance ratio spectrum has also been used for the treatment of spectra and generation of signals from the mixture, depending only upon a single analyte. It is also the underlying principle for many analytical procedures *viz.* ratio derivative spectrum method, derivative ratio spectra zero crossing method (DRSZ), double divisor ratio spectra derivative method (DDRD), fourier function ratio spectrum method [1]. Other advancements in derivative spectrophotometry are as follows;

(i) Complexes of Cobalt, nickel and zinc with 1-(2-pyridylazo)2-napthol in micellar media were simultaneously determined by successive derivative ratio spectra [3].
(ii) Afkhami et al. developed a method based upon the mean centring of ratio spectra. The derivative steps are eliminated resulting in enhancement of signal-to-noise ratio [4].
(iii) For analysing ternary mixtures comprising of isoniazid, rifampicin and pyrazinamide in synthetic mixtures, commercial tablets and human urine sample, Youssef et al. devised a new hybrid convolution double divisor ratio spectra method. A combined trigonometric Fourier function is employed for dividing the absorption spectrum of the ternary mixture by a standard spectrum of two or more compounds in the mixture. The concentration of each drug in the mixture is directly related to the magnitude of the Fourier function coefficients either at maximum or minimum points [5].
(iv) Zhang et al. quantified overlapping peaks in capillary electrophoresis using derivative spectrophotometry. It has been deciphered that the derivative method leads to complete resolution of peak baseline [6].

Recent advances in sensitive array detectors, fibre optic wave guides, high speed electronics and powerful software have lead to the development of a new generation of spectrometers. These high tech spectrometers have replaced conventional spectrometers. These spectrometers are equipped with latest technology *viz.* charge coupled devices (CCDs) or a photodiode array which promises to facilitate and deliver a better and efficient detection of the analyte. Starting from UV to near-IR (Infra Red), these spectrometers offer a wide range of application and assure to deliver excellent performance. Owing to their speculative properties like higher sensitivity, high speed, low noise, compactness, low cost, robustness and instantaneous capacity to capture full spectra these detectors have revolutionized the concept of detection [1].

In order to analyze derivative spectra, determination of analytical wavelength becomes prerequisite. According to the principle of derivative additivity, the value of the mixture derivative should be equal to the derivative of second component, when one of the components crosses the zero line. Zero crossing technique and DS, both require the analysis of spectrum at multiple wavelengths especially in case of spectra having high course variation or high order derivative spectra. In present scenario, measuring points are deciphered via ratio spectra derivative method. This may be attributed to the fact that the ratio spectra derivative method is easy and user friendly as compared to the zero crossing technique for reading the derivative value [2]. Zero crossing presents some limitations, ascribed to the selection of suitable signals along slopes of the spectral curve, giving rise to low and accurate and precise results [7].

The application of zero crossing has been depicted by J. Krystek [8] where, two methods *viz.* "The *method of distributing effect*" and "*The method of sixteen solutions*" has been proposed for the