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Different signal processing techniques of ratio spectra for spectrophotometric resolution of binary mixture of bisoprolol and hydrochlorothiazide; a comparative study

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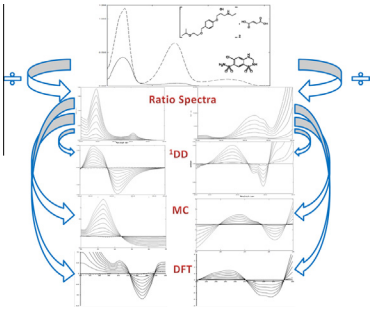
HIGHLIGHTS

- Savitsky–Golay filter and Wavelet Transform as approaches for derivative calculation.
- Fourier Transform and Mean Centering versus traditional derivative algorithms.
- Simple, accurate selective and precise spectrophotometric methods for binary mixtures.
- Methods validated as per ICH guidelines, parameters found to be within the limits.

GRAPHICAL ABSTRACT



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ABSTRACT

Five signal processing techniques were applied to ratio spectra for quantitative determination of bisoprolol (BIS) and hydrochlorothiazide (HCT) in their binary mixture. The proposed techniques are Numerical Differentiation of Ratio Spectra (ND-RS), Savitsky–Golay of Ratio Spectra (SG-RS), Continuous Wavelet Transform of Ratio Spectra (CWT-RS), Mean Centering of Ratio Spectra (MC-RS) and Discrete Fourier Transform of Ratio Spectra (DFT-RS). The linearity of the proposed methods was investigated in the range of 2–40 and 1–22 μg/mL for BIS and HCT, respectively. The proposed methods were applied successfully for the determination of the drugs in laboratory prepared mixtures and in commercial pharmaceutical preparations and standard deviation was less than 1.5. The five signal processing techniques were compared to each other and validated according to the ICH guidelines and accuracy, precision, repeatability and robustness were found to be within the acceptable limit.

Introduction

UV–VIS absorption spectroscopy is a well established technique for rapid and accurate determination of analytes without prior separation, if the interferences can be eliminated. Manipulation of ratio spectra has been the basis of some analytical procedures to eliminate the interference between the spectra of different components.

The ratio spectra were firstly used by Blanco et al. [1,2] for the spectral analysis. After that many signal processing techniques were combined with the ratio spectra for the spectrophotometric resolution of overlapped spectra. Salinas et al. [3] modified the original equations of Blanco and developed the first derivative of ratio spectra method for analysis of binary mixtures and ternary mixtures [3,4], then Dinç and Onur [5] introduced the double divisor of ratio spectra derivative spectrophotometry that was used

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successfully for the analysis of ternary mixtures. Wahbi et al. [6,7] used Glenn's orthogonal functions [8] and Fourier functions [9] in processing ratio spectra for analysis of binary mixtures, and then Youssef et al. [10] extended the use of Fourier functions to analysis of ternary mixtures. Dinç and Baleanu [11,12] proposed the Continuous Wavelet Transform of Ratio Spectra for analysis of binary and ternary mixtures. Also Mean Centering was introduced by Afkhami and Bahram [13] as a processing technique for ratio spectra that was applied for the analysis of binary and ternary mixtures.

Several mathematical methods were also applied to ratio spectra for the analysis of different mixtures. Erk [14] proposed the absorbance ratio equation that was used for analysis of binary mixtures. El-Bardicy et al. [15] developed the ratio subtraction method for analysis of binary mixtures, that was then extended to the resolution of ternary mixtures [16–18]. Recently, Elzanfaly et al. [19,20] introduced the ratio difference method for analysis of binary mixtures. Falcó et al. [21] introduced the H-point standard addition method originally for the analysis of binary mixtures, and then Andrés et al. [22] applied the method on ratio spectra for analysis of ternary mixtures.

Bisoprolol hemifumarate (BIS) is 1-[4-[[2-(1-methylethoxy)ethoxy]methyl]phenoxy]-3-[(1-methylethyl)amino]-2-propanol fumarate (2:1), Fig. 1a [23]. BIS is a highly selective β_1 receptor antagonist. It is approved for the treatment of hypertension and heart failure in combination with ACE inhibitors and diuretics [24]. Hydrochlorothiazide (HCT) is 6-chloro-3,4-dihydro-2H-1,2,4-benzothiadiazine-7-sulfonamide 1,1-dioxide, Fig. 1b [23]. HCT is a benzothiadiazine diuretic which is widely used in antihypertensive pharmaceutical formulations, alone or in combination with other drugs [24]. Concor® Plus tablets contain both BIS and HCT for the treatment of high blood pressure.

Literature survey revealed that BIS and HCT are official in British Pharmacopoeia [25] and United States Pharmacopoeia [26]. There are reported methods for the determination of BIS or HCT in different dosage forms [27–31] and in their binary mixtures [32–38].

In this work, five signal processing techniques manipulating ratio spectra were applied for the simultaneous determination of bisoprolol and hydrochlorothiazide in their binary mixture. The methods are Numerical Differentiation of Ratio Spectra (ND-RS), Savitsky–Golay of Ratio Spectra (SG-RS), Continuous Wavelet Transform of Ratio Spectra (CWT-RS), Mean Centering of Ratio Spectra (MC-RS) and Discrete Fourier Transform of Ratio Spectra (DFT-RS). Also, the mathematical background of the procedures was illustrated.

Theory

If there is no interaction among the compounds and Beer's law is obeyed for each compound, the absorption curve of a mixture M, of two components *A* and *B*, can be written as follows:

$$A_{Mi} = \alpha_{Ai}C_A + \beta_{Bi}C_B \quad (1)$$

where A_{Mi} is the absorbance of the mixture at wavelength *i*; α_{Ai} and β_{Bi} are the absorbtivities of *A* and *B* at wavelength *i*; and C_A and C_B are the concentrations of *A* and *B*.

Dividing Eq. (1) by the spectrum of a carefully chosen concentration of standard *B* (B' = divisor), the following equation can be written as:

$$\frac{A_{Mi}}{\beta_{Bi}C_{B'}} = \frac{\alpha_{Ai}C_A}{\beta_{Bi}C_{B'}} + \frac{C_B}{C_{B'}}$$

and rewritten as:

$$\frac{A_{Mi}}{\beta_{Bi}C_{B'}} = \frac{\alpha_{Ai}C_A}{\beta_{Bi}C_{B'}} + \text{constant} \quad (2)$$

All signal processing and mathematical methods are invented to eliminate the constant term, to produce a signal dependent only on one component (*A*).

First derivative of ratio spectra (^{1}DD) [3]

By applying the first derivative of Eq. (2), Eq. (3) is obtained:

$$\frac{d}{d\lambda}\left(\frac{A_{Mi}}{\beta_{Bi}C_{B'}}\right) = \left(\frac{C_A}{C_{B'}}\right)\frac{d}{d\lambda}\left(\frac{\alpha_{Ai}}{\beta_{Bi}}\right) \quad (3)$$

In Eq. (3), the constant term is eliminated, so the derivative ratio spectrum of the mixture is dependent only on the values of C_A, and $C_{B'}$ and is independent on the value of C_B, in the mixture. So, determination of *A* in the presence of *B* is feasible.

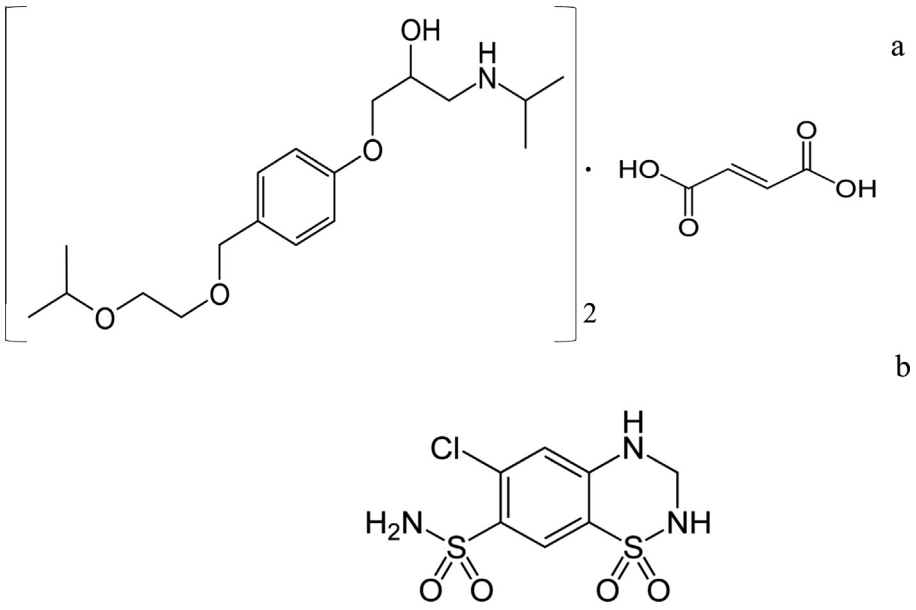

Fig. 1. Structural formulae for (a) bisoprolol hemifumarate and (b) hydrochlorothiazide.