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Computation of geometric representation of novel spectrophotometric methods used for the analysis of minor components in pharmaceutical preparations

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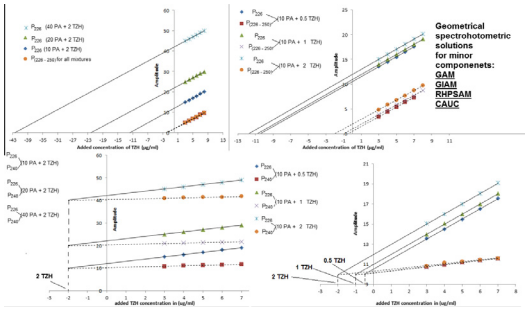
HIGHLIGHTS

- Minor component represents a challenge for spectrophotometric analysis.
- Novel geometrical spectrophotometric solutions for minor components.
- Geometrical relation by standard addition or subtraction GAM, GIAM, RHPSAM, CAUC.
- Minor component tetryzoline with ofloxacin and prednisolone in ratio (1:7.5:5).
- Minor component tetryzoline with sodium cromoglicate in ratio (1:80).

GRAPHICAL ABSTRACT



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ABSTRACT

Novel spectrophotometric methods were applied for the determination of the minor component tetryzoline HCl (TZH) in its ternary mixture with ofloxacin (OFX) and prednisolone acetate (PA) in the ratio of (1:5:7.5), and in its binary mixture with sodium cromoglicate (SCG) in the ratio of (1:80). The novel spectrophotometric methods determined the minor component (TZH) successfully in the two selected mixtures by computing the geometrical relationship of either standard addition or subtraction. The novel spectrophotometric methods are: geometrical amplitude modulation (GAM), geometrical induced amplitude modulation (GIAM), ratio H-point standard addition method (RHPSAM) and compensated area under the curve (CAUC). The proposed methods were successfully applied for the determination of the minor component TZH below its concentration range. The methods were validated as per ICH guidelines where accuracy, repeatability, inter-day precision and robustness were found to be within the acceptable limits. The results obtained from the proposed methods were statistically compared with official ones where no significant difference was observed. No difference was observed between the obtained results when compared to the reported HPLC method, which proved that the developed methods could be alternative to HPLC techniques in quality control laboratories.

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1. Introduction

The minor component is the component of a mixture which is present in very low concentration either in dosage forms or biological fluids. The analysis of minor component always represents a challenge for analytical chemists as it requires sensitive and specific methods for its analysis such as GC and LC–MS . . .etc. The problem rises upon applying spectrophotometric techniques due to the problem of interference of the spectrum of the major ones leading to hindering its accurate determination by conventional spectrophotometric techniques. Another problem with the minor component is the deviation from Beer's law which occurs in case of low concentrations, when transmittance values are close to 100% where incident light approaches transmitted light [1]. Therefore, special approaches were developed to eliminate those problems based on either standard addition [2–5] or blank subtraction [6–8].

The selected minor component for this work is tetryzoline HCl (TZH) with a chemical formula of 4,5-dihydro-2-(1,2,3,4-tetrahydro-1-naphthalenyl)-1*H*-imidazole hydrochloride. It is a sympathomimetic agent with marked alpha adrenergic activity exhibiting a vasoconstrictor effect, so it is used as conjunctive and nasal decongestant. Tetryzoline HCl (TZH) is combined together with antibiotics, corticosteroids and anti-histamines to formulate anti-infective eye preparations to treat acute and sub-acute conjunctivitis, keratitis and corneal ulcers [9]. Different analytical techniques were reported for TZH determination in pharmaceutical preparations and in biological fluids such as: colorimetric determination [10], spectrophotometry [11–14], high performance thin layer chromatographic method (HPTLC) [15], high performance liquid chromatographic method (HPLC) [16–21] and gas chromatography [22]. Two ophthalmic combinations were selected for the analysis of the minor component TZH; the first one is mixture (A): Ofloxacin (OFX), prednisolone acetate (PA) and TZH in the ratio of (7.5:5:1) respectively, while the second one is mixture (B): sodium cromoglicate (SCG) and TZH in the ratio of (80:1) respectively. The structural formulae of the components of interest are shown in Fig. 1. The UV absorption spectra of both mixtures are shown in Fig. 2.

Different spectroscopic and liquid chromatographic methods have been previously reported for the determination of the cited drugs: OFX [23–27], PRD [28–32], SCG [33–36] and TZH [15,16]. For mixture (A), HPLC methods [37,38] and spectrophotometric methods [39] were reported for its analysis, where the later used standard TZH addition to the dosage form and then the claimed concentration of TZH in the preparation was calculated after subtraction of the added concentration; Meanwhile, no methods have been reported for the analysis of mixture (B).

This work presented four novel spectrophotometric methods for the determination of the minor component (TZH) in the two selected mixtures based on computing the geometrical relationship of either standard addition, such as: geometrical amplitude modulation (GAM), geometrical induced amplitude modulation (GIAM) and ratio H-point standard addition method (RHPSAM); or blank subtraction such as compensated area under the curve (CAUC). The four methods were applied to the synthetic mixtures and pharmaceutical dosage forms of the drugs of interest where the minor component (TZH) was accurately estimated in addition to the major components present. The determination of each component concentration was done with no interference of the added excipients. The obtained results from the spectrophotometric methods were compared to each other to ensure their accuracy and precision.

2. Theory

2.1. Geometrical amplitude modulation method (GAM)

A new approach is introduced to determine the concentration of the minor component X in the presence of the major component Y. It is based on the geometric representation of the effect of standard addition of X on the response of the binary mixture of (X and Y), and the interpretation of this result as a regression equation. The method is a novel ratio spectrum manipulating method using normalized spectrum of the divisor obtained by dividing certain spectrum of Y′ component by its concentration.

2.1.1. In case of Y is more extended than X

By using the normalized spectrum of Y′ as a divisor, two points were selected in the overlapped region of the ratio spectra of X and Y (P_1 and P_2), where the amplitudes were calculated as follow:

$$P_1 = [a_{X1}.C_{X(added)}]/a_Y + [a_{X1}.C_{X(minor)}]/a_Y + \dot{C}_Y \quad (1)$$

$$P_2 = [a_{X2}.C_{X(added)}]/a_Y + [a_{X2}.C_{X(minor)}]/a_Y + \dot{C}_Y \quad (2)$$

By calculating the difference ΔP (P1 − P2)

$$\Delta P = [a_{X1}.C_{X(added)}]/a_Y + [a_{X1}.C_{X(minor)}]/a_Y - [a_{X2}.C_{X(added)}]/a_Y + [a_{X2}.C_{X(minor)}]/a_Y \quad (3)$$

This can be rearranged as follows:

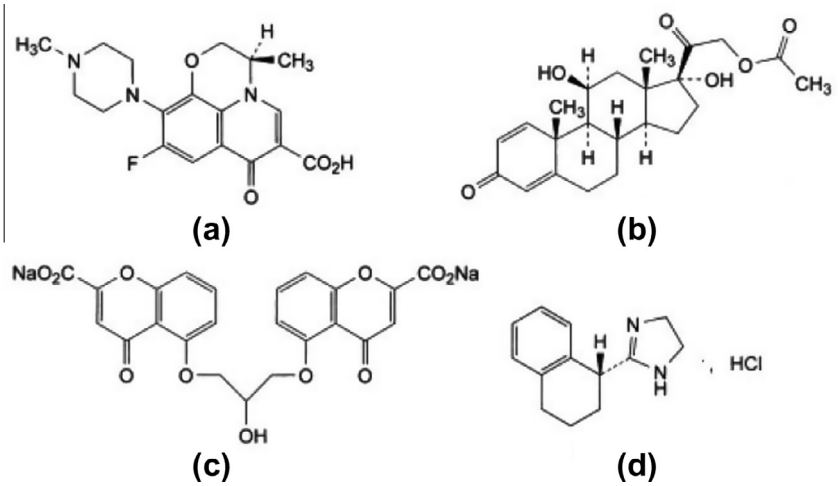

Fig. 1. The structural formulae of (a) ofloxacin (OFX), (b) prednisolone acetate (PA), (c) sodium cromoglicate (SCG) and (d) tetryzoline hydrochloride (TZH).