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Comparative study between recent methods manipulating ratio spectra and classical methods based on two-wavelength selection for the determination of binary mixture of antazoline hydrochloride and tetryzoline hydrochloride

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ABSTRACT

A comparative study was developed between two classical spectrophotometric methods (dual wavelength method and Vierordt's method) and two recent methods manipulating ratio spectra (ratio difference method and first derivative of ratio spectra method) for simultaneous determination of Antazoline hydrochloride (AN) and Tetryzoline hydrochloride (TZ) in their combined pharmaceutical formulation and in the presence of benzalkonium chloride as a preservative without preliminary separation. The dual wavelength method depends on choosing two wavelengths for each drug in a way so that the difference in absorbance at those two wavelengths is zero for the other drug. While Vierordt's method, is based upon measuring the absorbance and the absorptivity values of the two drugs at their λ_{max} (248.0 and 219.0 nm for AN and TZ, respectively), followed by substitution in the corresponding Vierordt's equation. Recent methods manipulating ratio spectra depend on either measuring the difference in amplitudes of ratio spectra between 255.5 and 269.5 nm for AN and 220.0 and 273.0 nm for TZ in case of ratio difference method or computing first derivative of the ratio spectra for each drug then measuring the peak amplitude at 250.0 nm for AN and at 224.0 nm for TZ in case of first derivative of ratio spectrophotometry. The specificity of the developed methods was investigated by analyzing different laboratory prepared mixtures of the two drugs. All methods were applied successfully for the determination of the selected drugs in their combined dosage form proving that the classical spectrophotometric methods can still be used successfully in analysis of binary mixture using minimal data manipulation rather than recent methods which require relatively more steps. Furthermore, validation of the proposed methods was performed according to ICH guidelines; accuracy, precision and repeatability are found to be within the acceptable limits. Statistical studies showed that the methods can be competitively applied in quality control laboratories.

1. Introduction

Antazoline HCl is 4,5-dihydro-N-phenyl-N-(phenylmethyl)-1H-imidazole-2-methanamine hydrochloride (Fig. 1a). [1,2]. Antazoline has antihistaminic and anticholinergic properties used to relieve nasal congestion and is used in eye drops to relieve the symptoms of allergic conjunctivitis [3]. Tetryzoline HCl is a 2-[(1*RS*)-1,2,3,4-Tetrahydronaphthalen-1-yl)-4,5-dihydro-1H-imidazole hydrochloride (Fig. 1b).[1,2]. It is a sympathomimetic drug (alpha agonist) that constricts blood vessels and is used as nasal and conjunctival decongestant [4].

The combination of the two drugs is available in the market as eye drop (Trillerg®) for treatment of allergic-inflammatory affections of the conjunctiva. Literature survey reveals that there are only four analytical reports for simultaneous determination of the selected drugs in their pharmaceutical preparation: three HPLC methods [5–7] and one HPTLC method [8].

No spectrophotometric methods are reported for the simultaneous determination of the selected drugs in their pharmaceutical preparation, this is probably due to the absence of distinctly measurable peak in the absorption spectrum of TZ especially at low concentrations.

Therefore the aim of this paper is to develop, rapid and sensitive spectrophotometric methods for the simultaneous determination of AN and TZ in their binary mixture in the presence of benzalkonium chloride as a preservative without preliminary separation. A comparative study between classical spectrophotometric methods and recent methods manipulating ratio spectra is also performed to highlight the advantages and disadvantages of such methods.

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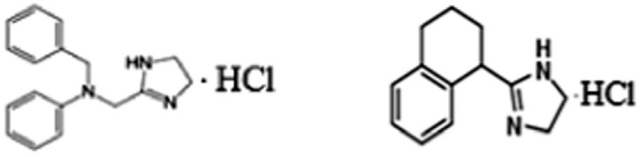

a b

Antazoline HCl **Tetryzoline HCl**

Fig. 1. Chemical structures of AN and TZ.

2. Experimental

2.1. Instruments

Shimadzu UV-2400 PC Series Spectrophotometer (Tokyo–Japan) with two matched 1 cm quartz cells using the following spectral parameters; a single fast scan mode and a fixed slit width (2 nm). Connected to an IBM-PC computer loaded with Shimadzu UVPC software and was equipped with HP desk jet printer and used for all the absorbance measurements and treatment of data.

2.2. Materials and reagents

Pure samples were kindly supplied by Shanghai Yurui Bio-Tech Pharmaceutical Co., Ltd., China. Their purities were found to be 99.78% ± 1.007 and 99.79% ± 1.487 for AN and TZ; respectively according to the reported HPTLC method [8]. Benzalkonium chloride was kindly supplied by Orchidia Pharma, (Cairo, Egypt). Pharmaceutical formulation; Trillerg eye drops Batch No. 0514102 was kindly supplied by Orchidia Pharma, (Cairo, Egypt). Each mL is claimed to contain 0.5 mg of AN, 0.4 mg of TZ and 0.05 mg of benzalkonium chloride. Sodium hydroxide and methanol were of analytical grade and obtained from ADWIC (Cairo, Egypt).

2.3. Standard solutions

Stock standard solutions of AN and TZ (0.1 mg/mL) in 0.1 M methanolic NaOH.

2.4. Laboratory prepared mixtures containing different ratios of AN and TZ

Into a series of 10-mL volumetric flasks, aliquots of AN and TZ were transferred from their corresponding stock standard solutions (0.1 mg/mL) of each, and then the volume was completed with methanolic NaOH. That prepares mixtures containing different ratios of the two drugs including the ratio of their commercial product.

2.5. Procedures

2.5.1. Linearity and construction of calibration curves

Aliquots equivalent to (30–300 μg) and (50–450 μg) of AN and TZ, respectively were separately transferred from their stock standard solutions (0.1 mg/mL) into two series of 10-mL volumetric flasks. Then volumes were made-up to the mark with 0.1 M methanolic NaOH. The spectra of the prepared standard solutions were scanned from 200 to 400 nm, stored in the computer and used for the construction of the proposed methods.

2.5.1.1. For classical spectrophotometric methods (dual wavelength method and Vierordt's method)

2.5.1.1.1. Dual wavelength method. The calibration curves were constructed relating the difference in absorbance of zero order spectra between 262.0 nm and 273.0 nm for AN and the difference between 230.0 nm and 258.6 nm for TZ versus the corresponding concentrations and the two regression equations were computed.

2.5.1.1.2. Vierordt's method. The absorbances of the both drugs were recorded at 248.0 nm and 219.0 nm and the absorptivity values, $E_{(1\%,\ 1\ cm)}$ were calculated by using following formula:

$$E_{(1\%,1\ \ cm)} = A/bC$$

where, A = absorbance b = path length of cell (1 cm) and C = concentration in gm/100 mL.

Calibration curves were constructed relating the absorbance of zero order spectra of AN at 248.0 nm (λ_{max}) and TZ at 219.0 nm (λ_{max}) versus the corresponding concentrations and the two corresponding regression equations were computed.

2.5.1.2. For recent methods manipulating ratio spectra (ratio difference method and first derivative of ratio spectrophotometry). For the determination of AN, the stored spectra of AN were divided by the spectrum of 45 μg/mL TZ, while for the determination of TZ, the stored spectra of TZ were divided by the spectrum of 30 μg/mL AN.

2.5.1.2.1. For ratio difference spectrophotometric method. Calibration curves of AN and TZ were constructed by plotting the difference between the peak amplitudes of ratio spectra at 255.5 & 269.5 nm for AN and 220.0 & 273.0 nm for TZ, versus their the corresponding concentrations then the corresponding regression equations were computed.

2.5.1.2.2. For the first derivative of ratio spectra method. The first derivative of the ratio spectra was obtained using Δλ = 4 and scaling factor 100 for both AN and TZ. Calibration curves of AN and TZ were constructed by plotting the peak amplitudes of the first derivative of the ratio spectra at 250.0 nm for AN and at 224.0 nm for TZ.

2.5.2. Application of the proposed methods for the determination of AN and TZ in laboratory prepared mixtures

2.5.2.1. For dual wavelength, ratio difference and first derivative of ratio spectra methods. For the determination of AN and TZ, the absorption spectra of laboratory prepared mixtures [Section 2.4], were scanned and stored. Then procedures were performed as described in linearity. The concentration of each drug was calculated using the corresponding regression equation.

2.5.2.2. For Vierordt's method. For the determination of AN and TZ, the recorded spectra of the laboratory-prepared mixtures [Section 2.4], were

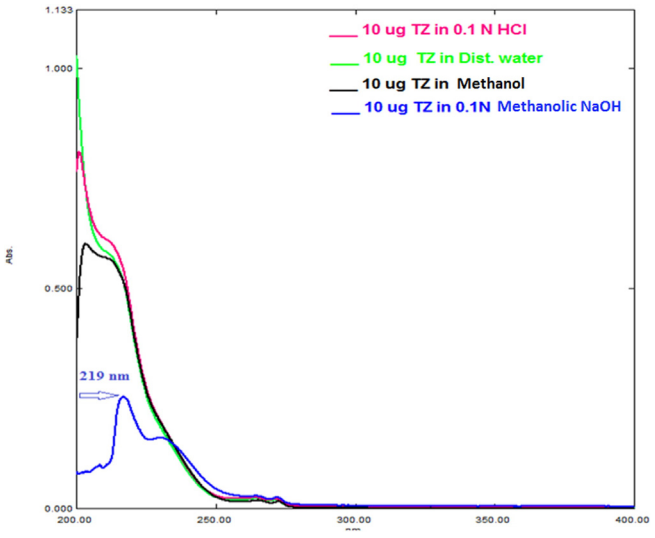

Fig. 2. Zero-order absorption spectra of TZ (10 μg/mL) using different solvents.