Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 149 (2015) 201–207

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

Simultaneous determination of binary mixture of amlodipine besylate and atenolol based on dual wavelengths

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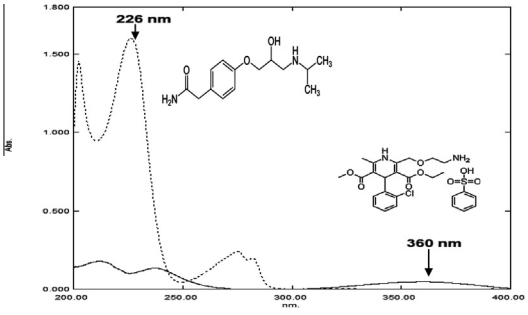
HIGHLIGHTS

- Four spectrophotometric methods for determination of amlodipine and atenolol.
- They can be used for analysis of binary mixtures with severely overlapped spectra.
- They have equal accuracy, precision compared to chromatographic methods.
- Ratio difference does not need fixed wavelengths or any derivative calculation.
- Constant center method predicts the UV spectra of each single drug.

GRAPHICAL ABSTRACT

Absorption spectra of amlodipine 4 μg/ml (___) and atenolol 40 μg/ml (––) using methanol as a blank.



ARTICLE INFO

Article history:
Received 24 January 2015
Received in revised form 19 March 2015
Accepted 24 April 2015
Available online 30 April 2015

Keywords:
Amlodipine
Atenolol
Absorption factor
Ratio difference
Constant center
Mean centering

ABSTRACT

Four, accurate, precise, and sensitive spectrophotometric methods are developed for simultaneous determination of a binary mixture of amlodipine besylate (AM) and atenolol (AT). AM is determined at its λ_{max} 360 nm (^{0}D), while atenolol can be determined by four different methods. Method (A) is absorption factor (AF). Method (B) is the new ratio difference method (RD) which measures the difference in amplitudes between 210 and 226 nm. Method (C) is novel constant center spectrophotometric method (CC). Method (D) is mean centering of the ratio spectra (MCR) at 284 nm. The methods are tested by analyzing synthetic mixtures of the cited drugs and they are applied to their commercial pharmaceutical preparation. The validity of results is assessed by applying standard addition technique. The results obtained are found to agree statistically with those obtained by official methods, showing no significant difference with respect to accuracy and precision.

Introduction

Amlodipine (AM) is 2-[(2-aminoethoxy) methyl]-4-(2-chlorophenyl)-1,4-dihydro-6-methyl-3,5-pyridine carboxylic acid 3-ethyl5-methyl ester [1] (Fig. 1a). It is a dihydropyridine derivative with calcium antagonist activity. It is used in the treatment of hypertension and chronic stable angina pectoris [2]. It inhibits the transmembrane influx of calcium ions into vascular smooth muscle and cardiac muscle [3]. AM is official in British Pharmacopoeia [4] and United State Pharmacopeia [5] where it is determined by reversed phase high performance liquid chromatographic method, Also UV-spectroscopy method [6] is reported.

Atenolol (AT) is chemically 2-[4-{(2RS)-2-hydroxy-3-[(1-methylethyl)amino] propoxy} phenyl] acetamide [1] (Fig. 1b). It is a β-adrenoreceptor blocking agent primarily used for hypertension, angina pectoris and myocardial infarction. It mainly acts

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http://dx.doi.org/10.1016/j.saa.2015.04.077
1386-1425/

by inhibition of renin release, angiotensin -II (AT-II) and aldosterone production [3]. The British [4] and European Pharmacopoeia [7] describe non-aqueous titration method for the assay of atenolol.

Few methods are available for the simultaneous determination of AM and AT in combination; RP-HPLC [8], HPTLC [9] and spectrophotometry [10].

The aim of this work was to develop four, sensitive, accurate, precise, reliable, fast and inexpensive analytical methods for the determination of both drugs without prior separation.

Theory of the proposed methods

Absorption factor method (AF)

AF [11] utilized mathematical calculation that is applied on the absorption spectra in order to cancel the absorbance value of the interfering substance at λ_{max} of the proposed drug. The only requirement is that one of the two drugs should has two absorption points and only one of them overlapped with the other one.

Ratio difference method (RD)

Ratio difference spectrophotometric method [12,13] was recently developed for analyzing a mixture of two drugs *X* and *Y* having overlapped spectra. It depends on the amplitude difference between two chosen wavelengths λ_1 and λ_2 in the ratio spectra where the interfering substance should be contributed at these wavelengths and subtracting the recorded amplitudes at these two points, the constant will be canceled along with any other instrumental error. This can be summarized as the following:

Suppose the amplitudes at the two wavelengths are P_1 and P_2 at λ_1 and λ_2 respectively; by subtracting the two amplitudes the interfering *Y* shows no interference; then:

$P_1 - P_2 = (X/Y')_1 - (X/Y')_2$ where; P_1 is the peak amplitudes of the ratio spectrum at λ_1, P_2 is the peak amplitudes of the ratio spectrum at λ_2. The concentration of *X* is calculated by using the regression equation representing the linear relationship between the differences of the ratio spectra amplitudes at the two selected wavelengths using *Y* as a divisor (*Y*′) to the corresponding concentrations of drug (X). Similarly, *Y* could be determined by the same procedure using a known concentration of *X* as a divisor *X*′.

Constant center method (CC)

The constant center method consists of two steps complementary to each other namely constant calculation via amplitude difference method followed by constant multiplication.

The first step constant calculation via amplitude difference method depends on that, if you have a mixture of two drugs *X* and *Y* having overlapped spectra, you can determine *X* by dividing the spectrum of the mixture by a known concentration of *X* as a divisor (*X*′). The division will give a new curve that represents $\frac{X+Y}{X'}$ i.e. $\frac{X}{X'} + \frac{Y}{X'}$ where $\frac{X}{X'}$ is a constant. On the obtained ratio curve; by selecting 2 wavelengths λ_1 and λ_2 and subtract the value of the ratio amplitudes at these two points, the constant $\frac{X}{X'}$ will be canceled along with any other instrumental error or any interference from the sample matrix [14,15].

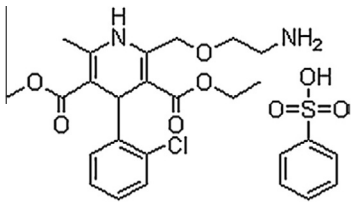

Fig. 1a. Structural formula for amlodipine besylate.

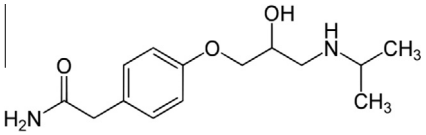

Fig. 1b. Structural formula for atenolol.

Experimental

Instruments

Spectrophotometer: SHIMADZU dual beam UV–visible spectrophotometer (Kyoto/Japan), model UV-1650 PC connected to IBM compatible and a HP1020 laserjet printer. The bundled software, UV-Probe personal spectroscopy software version 2.21(SHIMADZU) was used. Spectral band of 2 nm and scanning speed of 2800 nm/min with 0.1 nm interval.

Software

Matlab® version 7, release 14.

Chemicals and reagents

Pure samples were kindly supplied by Epico Pharmaceutical Industry, Cairo, Egypt. AM purity was found to be 100.56 ± 0.945 by high performance liquid chromatographic method [4] while AT purity was 100.96 ± 1.210 by non aqueous titration method [4].

Pharmaceutical formulations

Amlokind-AT tablet dosage forms; labeled to contain 5 mg (AM)/50 mg (AT); batch number A2AFN160 manufactured by Mankind Pharma, India. They were procured from Indian market.

Methanol: Spectroscopy grade (E. Merck, Darmstadt, Germany).

Standard solutions

AM and AT standard solutions (each, 0.1 mg/ml), were prepared by dissolving 10 mg of AM and AT separately in methanol into two 100-ml volumetric flasks and then completing to volume with the same solvent.

Procedures

Spectral characteristics of AM and AT

The absorption spectra of the two compounds were recorded over the range 200–400 nm using methanol as a blank.

Linearity and construction of calibration curves

Aliquots equivalent to (100–800 μg) and (40–400 μg) of AM and AT, respectively were separately transferred from their standard solutions (0.1 mg/ml, each) into two series of 10-ml volumetric flasks. The volume was completed to the mark with methanol. The spectra of the prepared standard solutions were scanned from 200 to 400 nm and stored in the computer.

(^0D) Direct spectrophotometric method for AM. For the determination of AM for the four proposed methods, the zero order absorption of the stored spectra of AM were measured at its λ_{max} 360 nm (no interference from AT). A linear calibration graph

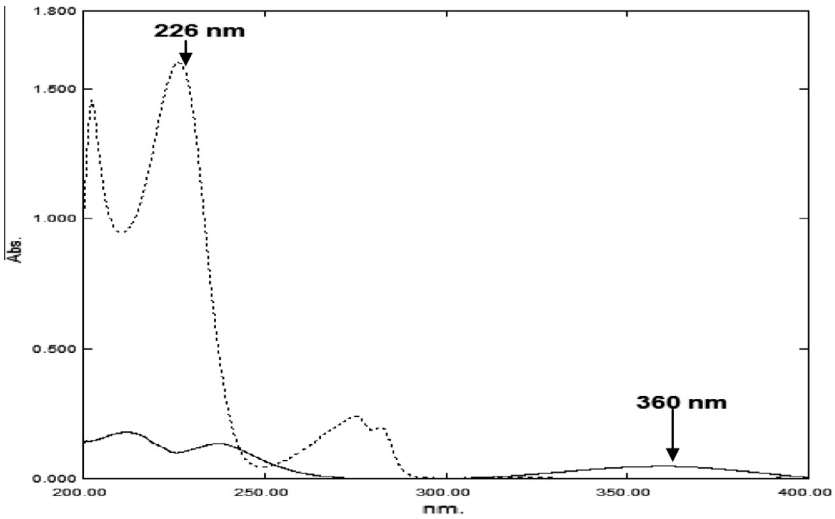

Fig. 2. Absorption spectra of amlodipine 4 μg/ml (___) and atenolol 40 μg/ml (––) using methanol as a blank.

relating the absorbance at 360 nm to the corresponding concentrations of AM was constructed and regression equation was computed.

Absorption factor method (AF). For the determination of AT: the scanned spectra of AM were measured at 226 and 360 nm. The absorption factor (the ratio of the absorbance at these two wavelengths) was calculated. Calibration curve relating the absorbance of the zero order spectra of AT at 226 nm to the corresponding concentrations of AT was constructed and the regression equation was computed.

For ratio difference spectrophotometric method (RD). For the determination of AT: the stored spectra of AT were divided by the spectrum of 24 μg/ml AM. Calibration curves of AT were constructed by plotting the difference between the amplitudes of ratio spectra at 210 and 226 nm, versus its corresponding concentrations and the regression equation was computed.

For constant center method (CC). For the determination of AT: the stored spectra of AM were divided by the spectrum of 24 μg/ml AT′. The obtained ratio spectra were recorded. Calibration curves were constructed by plotting the difference between the peak amplitudes of the obtained ratio spectra at (210 and 226 nm) versus amplitudes at 210 nm of AM ratio spectra and regression equation was computed.

Mean centering of ratio spectra method (MCR). For the determination of AT: the scanned spectra were exported to Matlab for subsequent calculation, then the spectra of AT were divided by the absorption spectrum of standard solution of AM′ (24 μg/ml), the obtained ratio spectra were mean centered. The calibration curve for AT was constructed, by plotting the mean centered values at 284 nm versus corresponding concentrations and the regression equation was computed.

Analysis of laboratory prepared mixtures

Aliquots of AM and AT were accurately transferred from their standard solutions (each, 0.1 mg/ml) into a series of 10-ml volumetric flasks, completed to volume with methanol to prepare mixtures containing different ratios (1:1, 1:1.5, 1:2, 2:1, 3:1, 4:1) of AM and AT; respectively. The spectra of the prepared mixtures were scanned from 200 to 400 nm and stored in the computer.

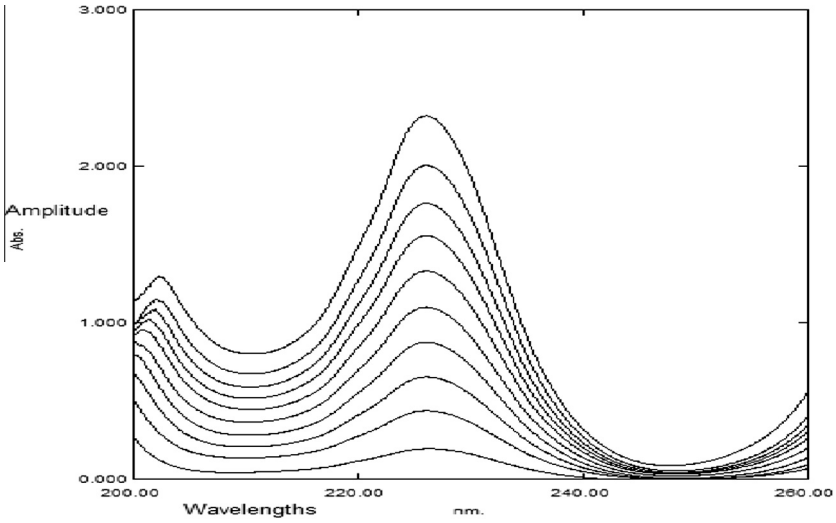

Fig. 3. Ratio spectra of AT (4–40 μg/ml) using 24 μg/ml of AM′ as a divisor.

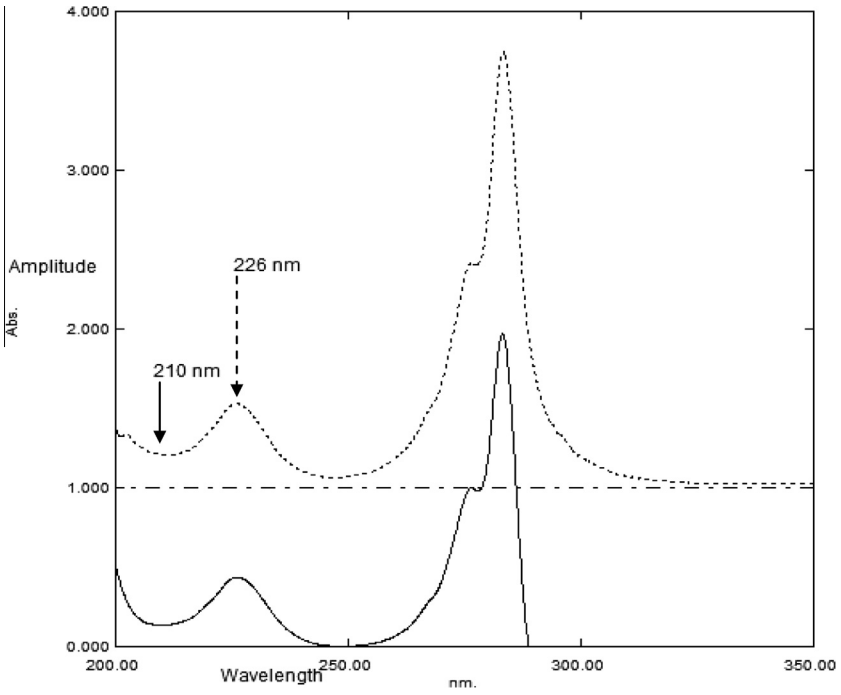

Fig. 4. Ratio spectra of AT 8 μg/ml (___), 24 μg/ml of AM (– – – – –), and laboratory-prepared mixture of both (with the same concentration of each) (. . .) using 24 μg/ml of AM as a divisor showing that the difference of peak amplitudes of ratio spectra at λ_1 and λ_2 is constant for pure AT and the laboratory-prepared mixture containing same concentration.

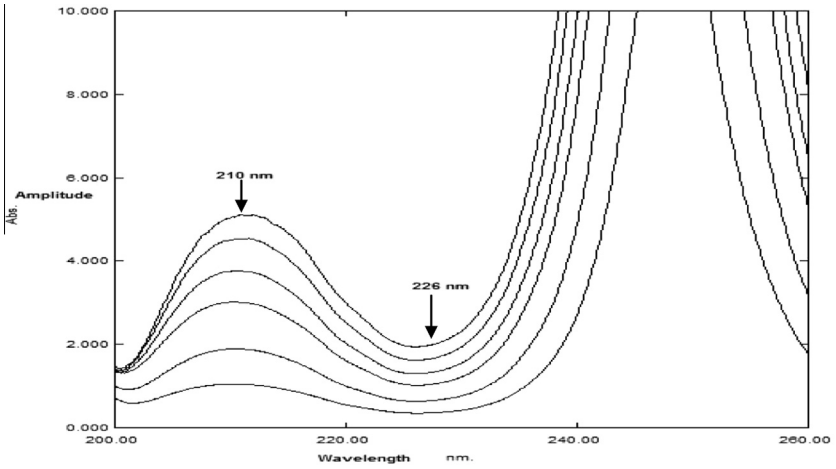

Fig. 5. Ratio spectra of AM (10–60 μg/ml) using 24 μg/ml of AT as a divisor.

For Absorption factor method (AF); into a series of 10-ml volumetric flasks, aliquots equivalent to (40–400 μg) and (300 μg) of AT and AM, respectively were accurately transferred from their standard solutions (0.1 mg/ml; each) then completed to volume with methanol. The absorbance at 226 and 360 nm was recorded. The absorbance of AT at 226 nm after subtraction of AM interference was calculated using the absorption factor equation, then the concentration of AT was calculated from the computed regression equation at 226 nm.

For Ratio difference spectrophotometric method (RD), the stored spectra of different laboratory prepared mixtures were divided separately by the absorption spectra of standard AM′ (24 μg/ml). The ratio spectra were recorded at 210 and 226 nm. The concentrations of AT were calculated from the computed regression equation.

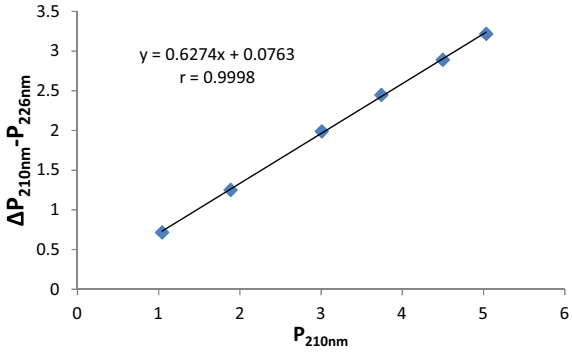

Fig. 6. Linear correlation between amplitude difference ($P_{210nm} - P_{226nm}$) of AM ratio spectra against the amplitude at 210 nm.

For constant center method, the stored spectra of each laboratory prepared mixture was divided separately by the absorption spectrum of standard AT′ (24 μg/ml). The ratio spectra were recorded at 210 and 226 nm, the difference in the amplitudes between 210 and 226 nm was used to calculate the postulated value of the ratio amplitude at 210 nm for each mixture. The constant of each mixture was calculated by subtracting the postulated value from the recorded value of each mixture at 210 nm. The obtained constant values of AM for each mixture were multiplied by the spectra of 24 μg/ml standard AT′, so the original spectra of AT was obtained. The concentration of AT was calculated using its corresponding regression equation.

For Mean Centering Method (MCR), the ratio spectra of the prepared solutions were mean centered then process them via matlab as under the proposed method. The concentration of each drug was calculated using the specified regression equation.

Application to pharmaceutical preparation

Twenty tablets (each tablet labeled to contain 5 mg AM and 50 mg AT) were weighed and finely powdered. A portion of powder equivalent to one tablet was weighed, dissolved in methanol by shaking in ultrasonic bath for about 30 min. The solution was filtered, transferred quantitatively into 100-ml volumetric flask and completed to the mark with methanol (A). 2 ml of this solution was transferred into 10 ml volumetric flask and completed to volume with methanol to determine AM directly. 4 ml of solution (A) was transferred to a 50 ml volumetric flask and completed to volume using methanol for determination of AT. The proposed methods were applied for the analysis of the studied drugs in their pharmaceutical formulation using the procedures mentioned under analysis of laboratory prepared mixtures for each method and the concentrations of the cited drugs were calculated from the corresponding regression equations.

Results and discussion

The main task of this work is to establish new, simple, sensitive and accurate analytical methods for simultaneous determination of AM and AT in their bulk powders and pharmaceutical dosage form with satisfactory accuracy and precision. As well, the ability of the proposed methods to determine both drugs in their pure form, laboratory prepared mixtures and in their pharmaceutical formulations.

By scanning the absorption spectra of AM and AT in methanol, severely overlapped spectral bands are observed in the wavelength region of 200–300 nm which hinders their direct determination (Fig. 2).

Absorption factor method (AF)

The absorption spectra of the standard solutions of the AM with different concentrations were recorded in the wavelength range of 200–400 nm. The value of absorption factor was found to be 2.45 (the ratio between the absorbance of pure AM at 226 and 360 nm) (Fig. 2). Quantitative estimation of AT in mixtures was carried out by subtracting the absorption due to AM at λ_{max} of AT using the following equation:

$$\text{Absorption of AT at 226 nm} = A_{\text{mix }226} - \frac{\text{AAM}226}{\text{AAM}360} \times A_{\text{mix AM }360}$$

Ratio difference spectrophotometric method (RD)

This method comprises two critical steps [12,13]: the first is the choice of the divisor, the selected divisor should compromise between minimal noise and maximum sensitivity. Different concentrations of divisor were used and the divisor concentration 24 μg/ml of AM was found to be the best regarding sensitivity, repeatability, signal to noise ratio and average recovery percent when used for the prediction of AT concentrations, in bulk powder as well as in laboratory prepared mixtures.

The second critical step is the choice of the wavelengths at which measurements were recorded. Any two wavelengths can be chosen provided that they exhibit different amplitudes in the ratio spectrum and good linearity is present at each wavelength individually.

For AT, The absorption spectrum of AT was scanned and divided by the absorption spectrum of 24 μg/ml standard AM, (Fig. 3). The wavelength pair 226–276 could not be used as they showed poor linearity. 210–226 showed the best results. (Fig. 4). Linear correlation was obtained between the differences in peak amplitude at 210–226 nm for AT against its corresponding concentration. The regression equation was found to be:

$$RD_{AT} = 0.4375\,C + 0.0575 \quad r = 0.9997$$

where RD is the amplitude difference, C is concentration (μg/ml) and r is the correlation coefficient.

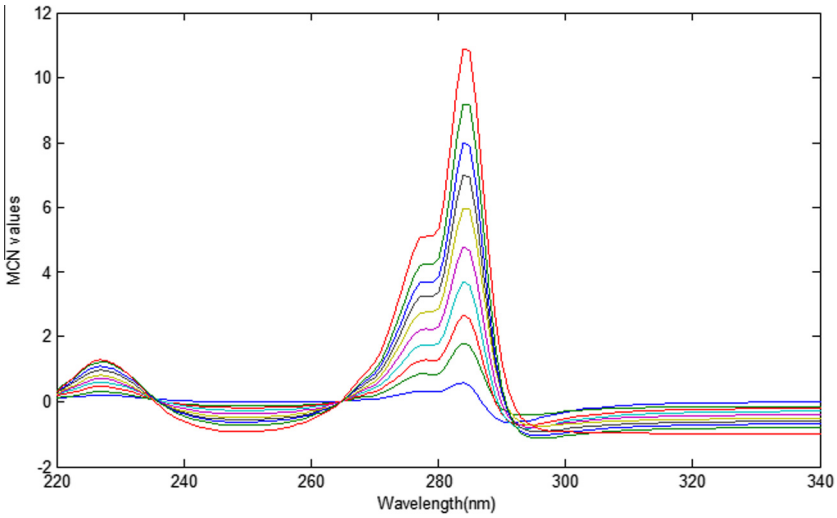

Fig. 7. Mean centered ratio spectra of AT (4–40 μg/ml) using AM (24 μg/ml) as a divisor.

Table 1
Assay validation parameters of the proposed spectrophotometric methods for the determination of pure samples of AM and AT.

Parameter	AM	AT		
	Zero order	^{0}D for AF and CC	RD	MCR
Accuracy (mean ± S.D.)	100.10 ± 0.890	100.07 ± 1.007	100.20 ± 1.287	100.23 ± 1.208
Specificity[a]	99.65 ± 0.923	99.04 ± 0.787	100.55 ± 0.833	100.91 ± 1.133
Precision Repeatability[b]	0.948	1.082	0.992	0.859
Intermediate precision[c]	1.090	1.256	1.220	1.121
Linear range (μg/ml)	10–80	4–40	4–40	4–40
Slope	0.0126	0.0385	0.0375	0.2712
Standard error of the slope	0.0001	0.0001	0.0004	0.0018
Intercept	0.0171	−0.0122	−0.0088	−0.5836
Standard error of the intercept	0.0027	0.0030	0.0088	0.0457
Correlation (r) coefficient	0.9999	0.9999	0.9997	0.9998

[a] Laboratory prepared mixtures.
[b] The intraday (n = 3) relative standard deviations of 10, 20 and 30 μg/ml of AM and AT by the proposed methods.
[c] The interday (n = 3) relative standard deviations of 10, 20 and 30 μg/ml of AM and AT by the proposed methods.

Table 2
Quantitative determination of AM and AT in pharmaceutical formulation by the proposed spectrophotometric methods and results of application of standard addition technique.

Amlokind-AT tablets batch no. A2AFN160 5 mg AM and 50 mg AT	Zero order	AF	RD	CC	MCR
AM found% ± S.D.*	100.04 ± 1.15				
Standard addition	99.86 ± 1.23				
AT found% ± S.D.*		99.05 ± 0.570	100.33 ± 0.91	99.42 ± 0.592	101.80 ± 0.905
Standard addition		99.08 ± 1.115	101.08 ± 1.28	100.55 ± 0.396	99.60 ± 0.852

* Average of three different determinations.

Table 3
Statistical analysis of the results obtained by the proposed spectrophotometric methods and official methods for the determination of AM and AT in pure powder form.

Parameter	AM		AT			
	Official* method [4]	Zero order	Official** method [4]	AF and CC	RD	MCR
Mean	100.56	100.10	100.96	100.07	100.20	100.23
S.D.	0.945	0.890	1.210	1.007	1.287	1.208
Variance	0.893	0.792	1.464	1.014	1.656	1.459
n	6	8	6	10	10	10
Student's t test		0.933 (2.179)		1.589 (2.145)	1.167 (2.145)	1.168 (2.145)
F value		1.128 (3.970)		1.444 (3.480)	1.131 (4.770)	1.003 (3.480)

The values in parenthesis are the corresponding tabulated t and F values at P = 0.05.
* HPLC method octadecylsilyl silica gel (5 μm) (150 mm, 3.9 mm i.d.), mobile phase: 15 ml acetonitrile: 35 ml methanol: 50 ml buffer solution, flow rate: 1 ml/min, UV detection: 237 nm.
** Non aqueous titration method.

Constant center method (CC)

In this work a simple and recently developed method; namely constant center spectrophotometric method was applied for resolving this binary mixture. Ratio spectra of AM was obtained using spectrum of 24 μg/ml standard AT, (Fig. 5).

For the determination of AT in binary mixtures, the ratio spectra of the mixtures was obtained using the absorption spectra of 24 μg/ml AT′ as a divisor {(AM/AT′) + constant}. Ratio difference at two selected wavelength {210 and 226 nm} was calculated $\{(AM/AT')^1 - (AM/AT')^2\}$, where the interfering substance AT was canceled and subsequently showed no interference. The practical ratio amplitude of the mixtures at 210 nm was recorded {(AM/AT′) + (AT/AT′)} for each laboratory prepared mixture, while the postulated ratio amplitude value of (AM/AT′) could be calculated using the equation representing the linear relationship between the difference of ratio spectra at 210 and 226 nm versus the corresponding ratio amplitudes at 210 nm as shown in (Fig. 6).

$$P_1 - P_2 = 0.6274P_1 - 0.0763 \quad r = 0.9998$$

where P_1, P_2 are the ratio amplitudes at 210 and 226 nm of the ratio spectra of different concentrations of AM (10–60 μg/ml) using 24 μg/ml AT′ as a divisor.

The constant value was calculated by monitoring the effect on the amplitude of the ratio spectrum of AM at 210 nm. $\{\Delta P = (P_{recorded} - P_{postulated})\}$, so the constant value is calculated by measuring the difference between the recorded amplitude and postulated amplitude at this wavelength.

$$C \cdot V = [P_{recorded} - P_{postulated}]$$

where C·V is the constant value, $P_{recorded}$ is the recorded amplitude of the ratio spectra of the laboratory prepared mixtures using 24 μg/ml AT′ as a divisor at 210 nm and $P_{postulated}$ is the calculated amplitude using the specified regression equation.

The original spectra of AT in the mixture could be obtained by multiplying the obtained constant (AT/AT′) of the laboratory mixtures by the divisor AT′, which was used for direct determination of AT from the corresponding regression equation (obtained by plotting the absorbance values of the zero order spectra at its λ_{max} 226 nm against the corresponding concentrations of AT).

Mean Centring Method (MCR)

It depends on manipulation of the ratio spectra via Matlab software to cancel the effect of one component of the mixture to determine the other one [16,17]. The ratio spectra of AT were mean centered in the range of (220–360 nm) where the obtained mean centered spectra had peak maximum at 284 nm, (Fig. 7); then the calibration curve was constructed between the concentration of AT and amplitude at 284 nm.

For all the proposed methods, the statistical parameters of the regression equations and the concentration ranges are presented in (Table 1). The selectivity of the proposed procedures was assessed by the analysis of laboratory prepared mixtures containing different ratios of the AM and AT, where satisfactory results were obtained over the calibration ranges as shown in (Table 1).

The proposed spectrophotometric methods were applied for the determination of AM and AT in their combined pharmaceutical formulation (Amlokind tablets). Although the concentration of AM was low in tablet second dilution but there was still great interference in the range 200–250 nm giving satisfactory results. The validity of the methods was assessed by applying the standard addition technique (Table 2). It shows that the developed methods are accurate and specific for determination of the cited drugs in presence of dosage form excipients.

Statistical analysis

Results of the suggested methods were statistically compared with those obtained by applying official methods; (Table 3). The calculated *t*- and *F*-values [18] were found to be less than the corresponding theoretical ones, confirming good accuracy and excellent precision.

Conclusion

In this work smart and recently developed spectrophotometric methods were applied for the simultaneous analysis of binary mixture of AM and AT. The AF utilized simple mathematical calculation in order to cancel the absorbance value of the interfering component at λ_{max} of the other drug. RD does not need critical measurement at fixed wavelengths and by difference between two wavelengths, noise will be canceled. The constant center method has the advantage of getting the zero order absorption spectra of a drug which act as spectral profile of the drug. The mean centering method can be carried in very few steps giving accurate and precise methods.

The developed methods could be used as alternative methods to LC methods. They could be used for routine analysis of AM and AT in their dosage form without any preliminary separation steps.

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