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Advancement and Validation of new Derivatives Spectrophotometric Method for Individual and Simultaneous Estimation of Diclofenac Sodium and Nicotinamide

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ABSTRACT

Derivative spectrophotometry, which is primarily based on the first and second derivative spectra of absorption, was applied for individual and simultaneous spectrophotometric determination of diclofenac sodium (DS) and nicotinamide (NAM) in the ultraviolet region. The method depends on 1st and 2nd derivative UV spectrophotometry, with the amplitude of peak-to-base line, peak to peak, the area under peak at selected spectrum intervals and zero-crossing at certain wavelengths for each compound measurement. Under optimal conditions, a linear working range of 5-80 $\mu g.ml^{-1}$ and 10-140 $\mu g.ml^{-1}$ for (DS) and (NAM) with correlation coefficient R^2 between 0.9938-0.9998. The mean % recoveries were found to be in the range of 97.95-102.50 % for two drugs. The proposed technique has been effectively applied to the estimation of (DS) and (NAM) in pharmaceutical formulations.

Keywords: UV-Visible Spectrophotometer, Derivative spectrophotometric method, Simultaneous determination, Diclofenac sodium, Nicotinamide.

INTRODUCTION

Derivative spectrophotometry is a technique of incredible usefulness for separating both qualitative and quantitative information from spectra made of uncertain bands by utilizing the first or higher derivatives of absorbance concerning wavelength[1]. This technique offers different advantages over the customary absorbance methods, for example: the separation of the sharp spectral features over the huge bands and the improvement of the resolution of overlapping spectra[2] what's more, allow the assay of certain analyses from complex mixtures or matrices via mathematical interpretation of the absorption signal[3]. UV-Vis spectroscopic approach for analysis is broadly utilized within the determination of drug in pharmaceutical preparations and for separation studies, which disposes interference from the

formulation of matrix by utilizing zero-crossing techniques[4]. Many reports were found for the analysis in individual form particularly for DS and NAM including spectrophotometric method5-8, chromatographic method[9,10], flow injection[11], voltammetry[12], potentiometric[13], electrochemical method[14], capillary electrophoresis[15,16].

EXPERIMENTAL

Instruments

UV-Visible double beam spectrophotometer with 10 mm quartz cell Shimadzu 1800, a personal computer.

Chemicals and reagents

Pharmaceutical grade DS and NAM powder received in pure form (99.99 %) was provided as an endowment from the State Company for Drug manufacture and Medical Appliances Samara-Iraq (SDI), methanol (99.7 %) provide by (SCR). All chemical substance utilized were of analytical grade.

Preparation of standard stock solution (200 µg. mL^{-1}), Diclofenac sodium and nicotinamide

The standard solution of (DS) and (NAM) were prepared by dissolving accurate weighted 20.0 mg of pure drug in 10.0 ml of methanol and further diluted to 100 ml with distilled water.

Preparation both Diclofenac sodium and nicotinamide from dosage form

The content of 10 Tablets and capsules was grinded and blended well. Take accurately weighted from a specific quantity of the fine powder to give an equivalent to 50 mg for DS Tablets and 20 mg for NAM capsules and dissolve in ten mL of methanol then diluted to the mark with distilled water in a volumetric flask 100 ml. The solution was filtered by utilizing filter paper (Whatman No.41) to evade any undissolved or suspended components before use; also the first part of the solution filtrate was rejected.

Procedures

Individual determination of Diclofenac sodium and nicotinamide

In 10 mL calibrated flask transfer aliquots of (DS) standard solutions containing 50-800 µg (or NAM standard solutions containing 100-1400 µg), and dilute with 10% methanol solution to the mark. The spectrum for each solution was recorded against a 10% methanol solution as blank. Zero order spectrums were then manipulated for each to get its first derivative (D1) and second derivative (D2).

Simultaneous determination of Diclofenac sodium and nicotinamide

(I) The content of a series of 10 mL calibrated flasks containing different amounts (50-800) µg of DS standard solutions and 50 µg of (NAM) solution the mixture was then diluted with 10% methanol solution to the mark. Record the spectrum for each solution against a 10% methanol solution as a blank. The recorded spectra were then manipulated to get D1 and D2.

(II) The content of a series of 10 mL calibrated flasks containing different amounts (100-1400) µg of NAM standard solutions and 100 µg of DS solutionthe mixture was then diluted with 10% methanol solution to the mark. The spectrum for each solution was recorded against a 10% methanol solution as a blank. The recorded spectra were then manipulated to get D1 and D2.

RESULT AND DISCUSSION

Absorption spectra

The absorption spectra were recordof each compounds DS, NAM then their mixtureagainst 10% methanol solution as a blank. Fig. 1 (a) demonstrates the absorption spectrum of DS 10 µg. mL^{-1} with maximum wavelength at 276 nm, (b) demonstrates the absorption spectrum of (NAM) 50 µg. mL^{-1} with two maxima wavelength of absorption at 214 nm and 262 nm. The aggregate spectrum to the mixture is demonstrating in (c) with two λmax 212 and 266 nm.

First derivative mode and 2nd derivative mode

The derivative spectra 1st, 2nd order of DS and NAM and for their blend are appeared within Fig. 2, Fig. 3 respectively. Clearly there is a large overlap in spectra of diclofenac sodium and nicotinamide hence, their determination, making use of the zero order absorption measurements, at the point when present in the same solution it is very difficult when utilizing customary two wavelengths of λmax or the tangential base-line approach strategies[17]. Then again, derivative technique is of a specific utility in finding the concentration of single component in a blends, with a large overlapping in spectrum. Consequently, both first, second order derivative spectrophotometric methods have been applied.

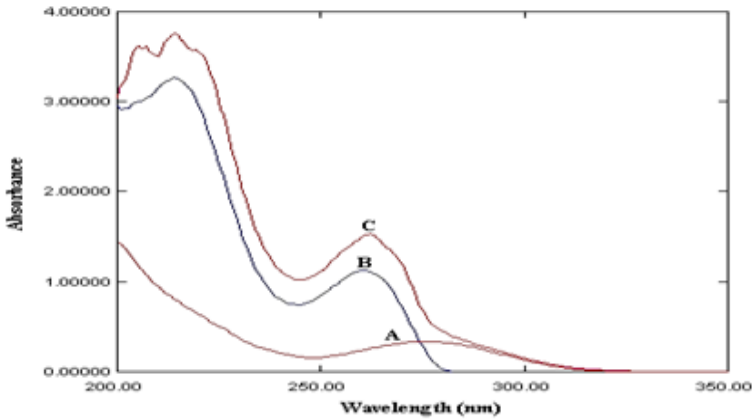

Fig. 1. Absorption spectra of: (A) 10 µg. mL^{-1}(DS),(B) 50 µg. mL^{-1}(NAM) and(C) a mixture of 10 µg. mL^{-1} Diclofenac sodium and50 µg. mL^{-1} nicotinamide

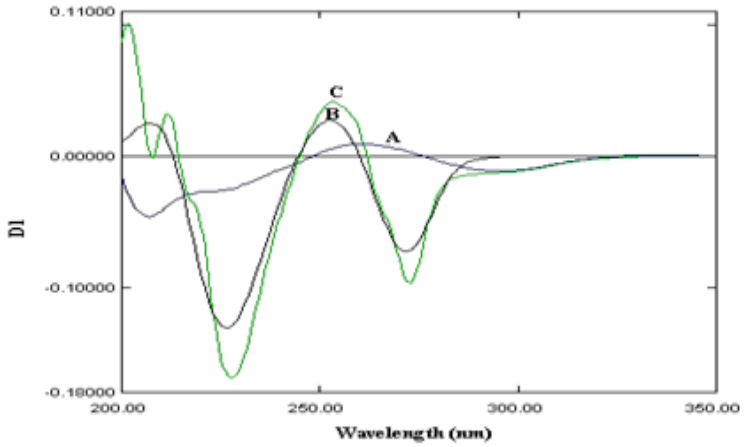

Fig. 2. 1st derivative spectra of (A) 10 µg. mL^{-1} Diclofenac sodium, (B) 50 µg. mL^{-1} nicotinamide and (C) a mixture of 10 µg. mL^{-1} diclofenac sodium and 50 µg. mL^{-1} nicotinamide

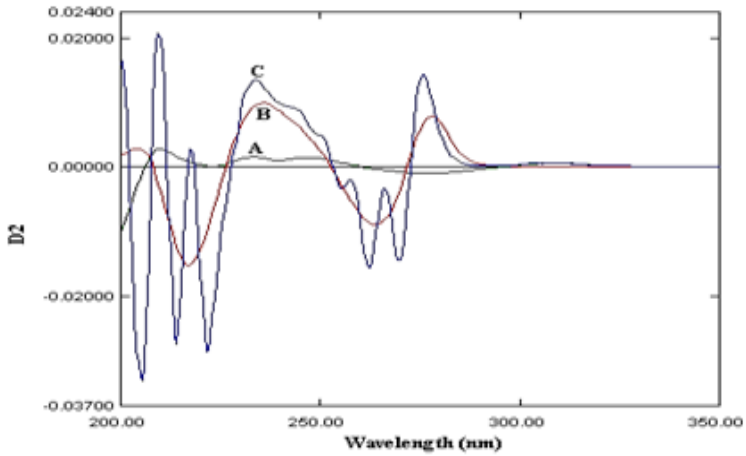

Fig. 3. 2nd derivative spectra of (A) 10 µg. mL^{-1} diclofenac sodium, (B) 50 µg. mL^{-1} nicotinamide and (C) a mixture of 10 µg. mL^{-1} diclofenac sodium and 50 µg. mL^{-1} nicotinamide

In the existing work, graphically peak-to-baseline, peak to peak, zero-crossing technique in addition to peak area were utilized to deal with derivatives spectra to complete the data. Truth be told, Theany one of these techniques in the 1st and 2nd derivative modes indicate good proportion to diclofenac sodium and nicotinamide amounts in their blends.

Figure 4 and Fig. 5 illustrate sets of 1st order spectra of medley containing (5-80) µg.ml^{-1} of diclofenac sodium in the existence of (5 µg.ml^{-1}) nicotinamide and (10-140) µg.ml^{-1} of nicotinamide in the existence of (10 µg.ml^{-1}) diclofenac sodium respectively. Fig. 4 indicate that when the amount of nicotinamide is kept constant and varied the concentration of diclofenac sodium, the peak-to-base line, peak to peak, peak areas and zero crossing of nicotinamide were proportional to the concentration of diclofenac sodium. Moreover, the same features were found for the determination of nicotinamidein Fig. 5, i.e. area under peak, peak-to-baseline, peak to peak and zero crossing of diclofenac sodium were in proportion to the concentration of nicotinamide (Table 1 and 2).

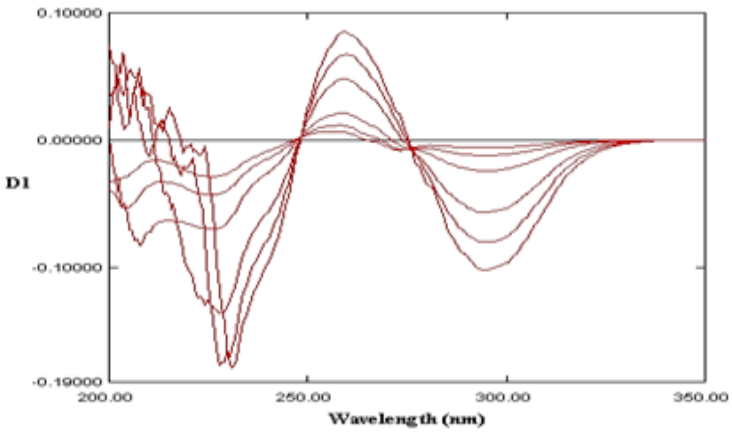

Fig. 4. First derivative spectra of mixture contain (5, 10, 20, 40, 60 and 80 µg. mL^{-1}); diclofenac sodium with (5 µg. mL^{-1}) nicotinamide

Table 1: Statistical analysis for the determination of diclofenac sodium

Drug	Order of derivative	Mode of calculations	λ (nm)	Regression equation	R^2	Slope
Diclofenac sodium	First	Peak to baseline	259	y = 0.0011x + 0.0014	0.9955	0.0011
		Peak to baseline	295	y = -0.0013x + 0.0002	0.9955	-0.0013
		Peak to peak	259-295	y = 0.0024x + 0.0012	0.9955	0.0024
		Area under peak	248.5-276	y = 0.0188x - 0.0095	0.9961	0.0188
		Area under peak	276-334	y = -0.0367x + 0.1702	0.9944	-0.0367
		Zero cross	260	y = 0.0011x + 0.0008	0.9948	0.0011
		Zero cross	296	y = -0.0013x + 0.0001	0.9955	-0.0013
	Second	Peak to baseline	247	y = 0.0002x + 0.0004	0.9965	0.0002
		Peak to baseline	310	y = 7E-05x - 3E-05	0.9961	7E-05
		Area under peak	239-260	y = 0.0017x + 0.0011	0.9988	0.0017
		Area under peak	260-294	y = -0.0027x + 0.0154	0.9961	-0.0027
		Area under peak	294-340	y = 0.0013x - 0.0005	0.9988	0.0013
		Zero cross	252	y = 0.0001x + 0.0002	0.9955	0.0001
		Zero cross	272	y = -0.0001x - 0.0002	0.9938	-0.0001
		Zero cross	310	y = 7E-05x - 3E-05	0.9961	7E-05

Table 2: Statistical analyses for the determination of nicotinamide

Drug	Order of derivative	Mode of calculations	λ (nm)	Regression equation	R^2	Slope
Nicotinamide	First	Peak to baseline	253	y = 0.0007x + 0.0057	0.9994	0.0007
		Peak to baseline	272	y = -0.0021x + 0.0068	0.9998	-0.0021
		Peak to peak	253-272	y = 0.0028x - 0.0011	0.9998	0.0028
		Area under peak	244.5-261	y = 0.0074x + 0.0393	0.9995	0.0074
		Area under peak	261-334	y = -0.0256x - 0.5788	0.999	-0.0256
		Zero cross	248	y = 0.0005x - 0.0009	0.9998	0.0005
		Zero cross	276	y = -0.0014x + 0.0017	0.9997	-0.0014
	Second	Peak to baseline	244	y = 0.0002x + 0.0013	0.9995	0.0002
		Peak to baseline	262	y = -0.0004x + 6E-05	0.9998	-0.0004
		Peak to baseline	270	y = -0.0003x - 0.0006	0.9995	-0.0003
		Peak to baseline	275	y = 0.0003x - 0.0013	0.9996	0.0003
		Peak to peak	270-275	y = 0.0006x - 0.0003	0.9992	0.0006
		Area under peak	272-329	y = 0.0039x + 0.0235	0.9995	0.0039

Table 3: Accuracy and precision of the methods

Drug	Approach of analysis	Wavelengths λ (nm)	Taken (μg.ml^{-1})	Found* (μg.ml^{-1})	RE%	*RSD%
Diclofenac (μg.ml^{-1})	First order (area under peak)	248.5-276	30.00	30.34	1.133	2.130
			60.00	59.57	-0.717	0.499
	Second order (area under peak)	239-260	30.00	29.62	-1.267	0.668
			60.00	60.55	0.917	0.365
nicotinamide	First order (zero cross)	248	50.00	49.70	-0.600	0.748
			100.00	99.45	-0.550	0.235
	Second order (peak to base line)	262	50.00	50.38	0.760	0.878
			100.00	99.67	-0.330	0.277

Table 4: Results for analysis of diclofenac sodium and nicotinamide in four pharmaceutical formulation samples

Pharmaceutical preparation	Method of analysis	λ(nm)	amount (mg) Taken	Found*	Rec.%	*RSD%
Olfen-50 Acion switzerland	First order (area under peak)	248.5-276.0	50	50.41	100.82	0.778
	Second order (area under peak)	239.0-260.0	50	49.68	99.36	0.702
Optifenac-50 M. H. drugs India	First order (area under peak)	248.5-276.0	50	49.54	99.08	0.667
	First order (area under peak)	239.0-260.0	50	49.25	98.5	0.806
Modoplex Caps M. V. C. India	First order (zero cross)	248	20	19.7	98.5	2.005
	Second order (peak to base line)	262	20	20.28	101.4	1.482
P-blex Caps S. D. I. Iraq	First order (zero cross)	248	20	20.5	102.5	0.959
	Second order (peak to base line)	262	20	19.59	97.95	1.244

*Average of three determinations.

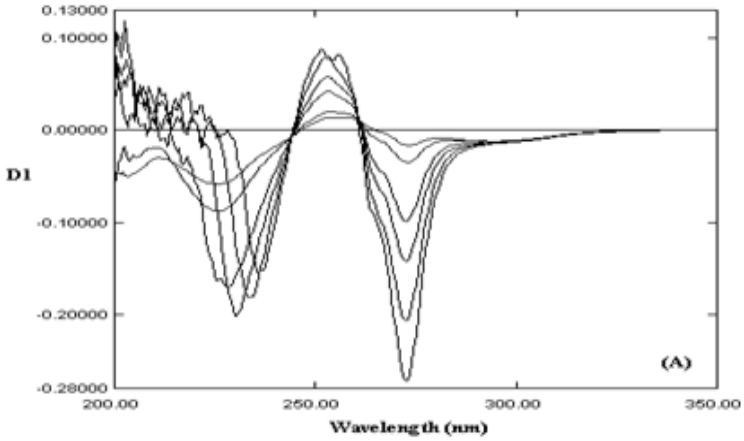

Fig. 5. First derivative spectra of mixture contain (10, 20, 50, 70, 100 and 140 µg. mL^{-1}); nicotinamide with (10 µg. mL^{-1}) diclofenac sodium

In the further sets of 2nd derivative of the same above blend, as illustrated in Fig. 6 and Fig. 7. By applying the same mentioned approached in account peak amplitudes (in millimeter) at peak-to-baseline, peak to peak and at zero crossing point of the other compound, and peak areas at selected wavelengths intervals enable the measurement of diclofenac sodium and nicotinamide respectively (Table 1 and 2).

Calibration graph and statistical analysis

The analytical characteristics and most statistical data for each of the proposed methods are given in (Table 1 and 2). Under optimum conditions, linear calibration curve was obtained in the range of (5-80 µg.ml^{-1}) for DS and (10-140 µg.ml^{-1}) for NAM with correlation coefficient values ranging between (0.9938-0.9998)

Accuracy and precision

Under the optimum conditions, the accuracy and precision of the proposed method (peak to baseline, zero cross and area under the peak for each of first and second order derivative modes) were checked. Table 3 shows the values of relative error percent and relative standard deviation percent for two different level of concentration of diclofenac sodium and nicotinamide with three replicate.

Application in dosage form

The proposed method first and second procedures were successfully applied for direct determination of diclofenac sodium in tablets and nicotinamide in capsules. The results obtained are presented in Table 4, and are in quite agreement with the spiked values. Good recovery 97.95-102.50 % and

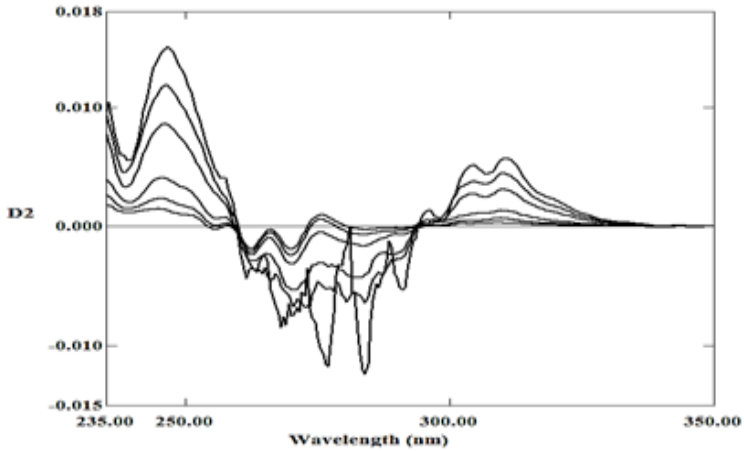

Fig. 6. Second derivative spectra of mixture contain (5, 10, 20, 40, 60 and80 µg. mL^{-1}); diclofenac sodium in existence of (5 µg. mL^{-1}) nicotinamide

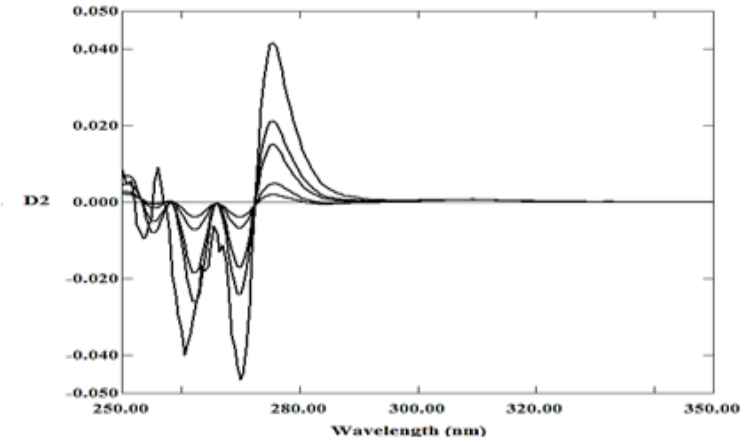

Fig. 7. Second derivative spectra of mixture contain (10, 20, 50, 70, 100 and 140 µg. mL^{-1}); nicotinamide in existence of (10 µg. mL^{-1}) diclofenac sodium

RSD% values 0.667-2.005% indicated the suitability of these methods for routine analysis of diclofenac sodium and nicotinamide.

CONCLUSION

Derivative Spectrophotometric technique was found to be sensitive, simple, rapid, economical, the results indicates that a good accuracy and precision of the proposed method, good recovery from the results applications in dosage form and it can be used in routine analysis of diclofenac sodium and nicotinamide in their pure forms, dosage form without prior separation or treatment.

In this work, 1st and 2nd derivative modes indicate good proportion to diclofenac sodium and nicotinamide amounts in pure form and in their blends, by graphically peak-to-baseline, peak to peak, zero-crossing technique in addition to peak area were utilized to deal with derivatives spectra to complete the data.

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