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Utilization of green analytical chemistry principles for the simultaneous estimation of paracetamol, aceclofenac and thiocolchicoside by UV spectrophotometry

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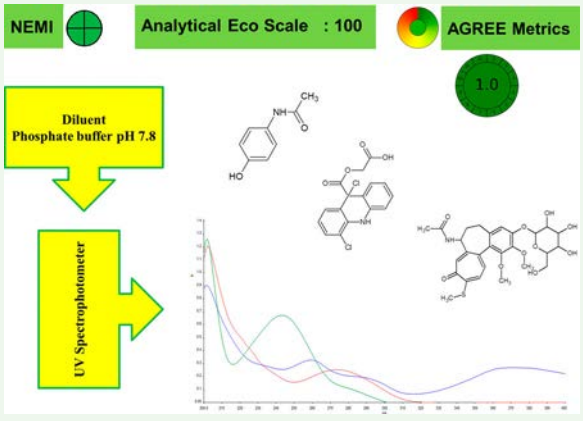
ABSTRACT

The present paper describes multicomponent UV spectrophotometric method for the determination of paracetamol, aceclofenac, and thiocolchicoside based on the fundamentals of green analytical chemistry. Major pharmaceutical companies and research laboratories encompass on green analytical methodologies for developing environmental friendly analytical methods. The present work is based on the principle of simultaneous equation involving additive of absorbances at the selected wavelengths. The linear range was established between 5–15 µg/mL for paracetamol, 1–5 µg/mL for aceclofenac, and 1–5 µg/mL thiocolchicoside. The greenness profile of the developed UV spectrophotometric technique was evaluated using National Environmental Methods Index, Analytical Eco-scale and AGREE metrics which proved the greenness of the method with respect to solvent, chemicals, energy consumed, and waste produced. The proposed method being simple, economical, and eco-friendly could be convenient substitutes for the use of hazardous chemicals in the routine investigation of the selected triple drug combination.



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Green analytical chemistry; National Environmental Methods Index; Analytical eco scale; AGREE metrics; UV simultaneous equation method

1. Introduction

The basic principle of the green analytical chemistry involves the replacement of hazardous solvents and chemicals. The 12 basic ethics of green chemistry recommended by Galuszka et al. aim to replace toxic solvents with greener alternatives which are highly environmental friendly (*1*). The approach to develop green UV spectrophotometric method is to minimize the consumption of organic solvent which in turn reduces the production of organic waste. This can be achieved by replacing solvents such as methanol, acetonitrile, and so on with less hazardous chemicals.

Paracetamol (PCM) (Figure 1a), chemically *N*-(4-hydroxyphenyl) acetamide, is a non-steroidal anti-inflammatory drug (NSAID) with antipyretic and analgesic action (*2*, *3*). It is used in the treatment of reducing the elevated body temperatures. It is listed in Pharmacopoeia's of India, the USA and the UK (*4*–*6*). Aceclofenac (ACE) (Figure 1b), chemically, 2-[2-[2-[(2, 6-dichlorophenyl) amino] phenyl] acetyl] oxyacetic acid, is an NSAID to relieve pain and inflammations (*2*, *3*). It is listed in Pharmacopoeia's

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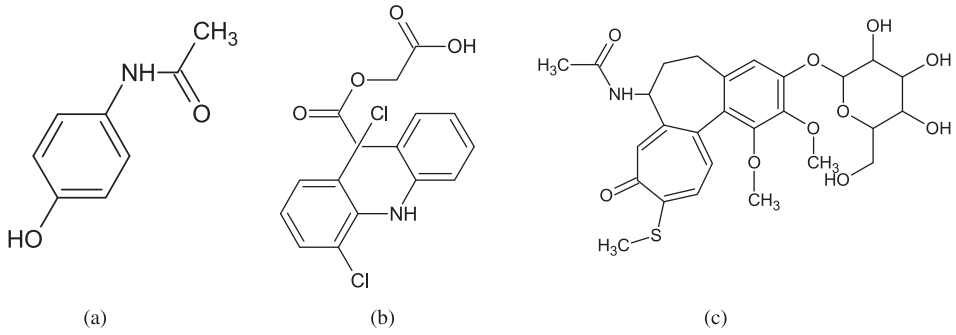


Figure 1. (a) Structure of paracetamol, (b) structure of aceclofenac, (c) structure of thiocolchicoside.

of India and the UK (*4, 6*). Thiocolchicoside (THC) (Figure 1c), chemically, *N*-[(7S)-3-(β-D-Glucopyranosyloxy)-1, 2-dimethoxy-10-(methylsulfanyl)-9-oxo-5, 6, 7, 9-tetra hydrobenzo[a] heptalen-7-yl] ethanamide, is used as a muscle relaxant. It is official in Indian Pharmacopoeia (*4*) and British Pharmacopoeia (*6*). The selected drug combination of PCM, ACE, and THC is not listed in any Pharmacopoeias. The outcome of the literature survey narrowed down that only one UV spectrophotometric (*7*), two HPLC (*8, 9*), and one HPTLC (*10*) methods were reported for the concurrent quantification of PCM, ACE, and THC in tablet dosage form. As the reported UV spectrophotometric method utilizes environmentally hazard methanol as the solvent, an endeavor has been made to develop eco-friendly UV spectrophotometric method employing phosphate buffer pH 7.8 as the diluent.

2. Experimental

2.1. Chemicals and reagents

The active pharmaceutical ingredients PCM, ACE, and THC were supplied by Ideal Analytical and Research Institution, Puducherry, India, and the same was used as the working standard devoid of any additional treatment. The supplier for analytical grade potassium dihydrogen phosphate and sodium hydroxide was M/s Rankem, India. The diluent employed was phosphate buffer pH 7.8.

2.2. Preparation of phosphate buffer pH 7.8

0.2 M sodium hydroxide and 0.2 M potassium dihydrogen phosphate were prepared separately using distilled water and then the respective volumes were measured out, mixed well and made up to the volume in accordance with Indian Pharmacopoeia.

2.3. Marketed formulation

The commercially available Bakflex Plus tablet, labeled to contain 500 mg PCM, 100 mg ACE, and 4 mg THC, manufactured by Intas Pharmaceuticals limited was procured from the local drug store.

2.4. Instrumentation

A Perkin Elmer double beam UV–Visible spectrophotometer (lambda 25) with 1 nm spectral bandwidth and 0.3 nm accuracy of wavelength (with automatic wavelength correction and also with a pair of 1 cm matched quartz cell) was used for all the spectrophotometric measurements. The data was collected in UVWinLab Version 5.1.1. Software.

2.5. Method

2.5.1. Selection of common diluent

After evaluating the solubility and stability of the selected drugs in diverse green chemicals, phosphate buffer pH 7.8 was found to be ideal and economical. Hence, the same was employed as a common diluent.

2.5.2. Preparation of standard stock solution

Standard stock solution of PCM, ACE, and THC (1 mg/mL) was prepared by dissolving accurately 100 mg of every drug in 25 mL of phosphate buffer pH 7.8, sonicated for complete dissolution and made up to 100 mL with phosphate buffer pH 7.8. The operational standard solutions of 10 µg/mL of PCM, ACE, and THC were prepared and scanned in the range of 200–400 nm to identify the absorption maxima. The absorption maxima of PCM, ACE, and THC were at 243, 274, and 259 nm respectively and the overlay spectra obtained is shown in Figure 2.

2.6. Stability of the solution

The diluted mixed standard solutions containing 10 µg/mL of PCM, 3 µg/mL of ACE, and 3 µg/mL of THC were prepared in phosphate buffer pH 7.8. The sample solution was prepared in accordance with the procedure described in Section 2.9. The standard and sample

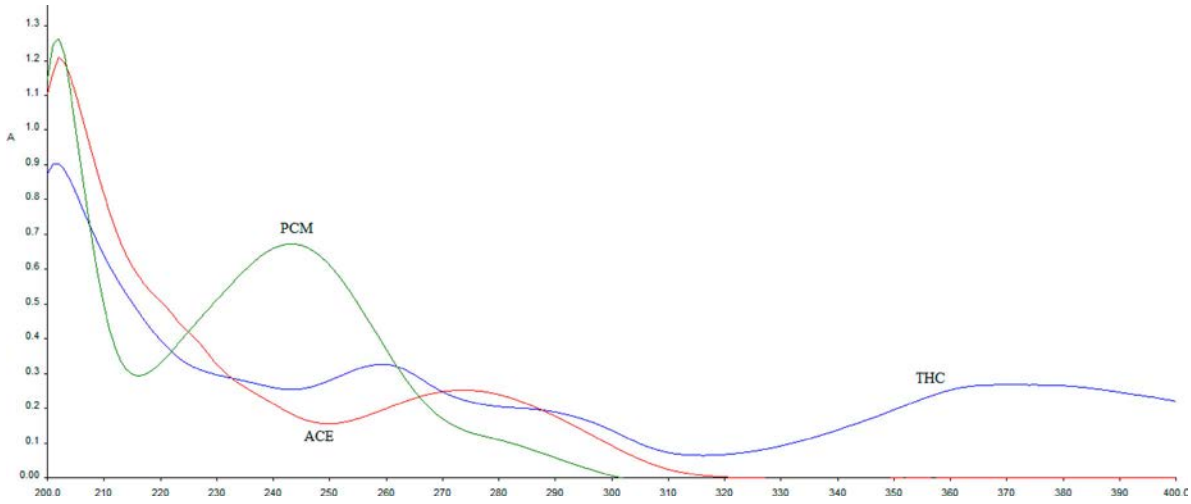


Figure 2. Overlay spectrum of PCM, ACE, and THC (10 µg/mL).

Table 1. Solutions stability studies.

	% RSD of absorbance at wavelength		
Parameter	243 nm	274 nm	259 nm
Standard solution	0.22	0.89	0.52
Sample solution	0.82	0.79	0.69

solutions were kept at room temperature (27±5°C) and their absorbance at the selected wavelengths were measured from 0 to 24 h with a time interval of 6 h. The % RSD of the absorbance was calculated and the results were shown in Table 1.

2.7. Simultaneous equation method

Simultaneous equation method depended on the absorbance of the drugs (PCM, ACE, and THC) at the absorption maximum of each other (*11*). The three wavelengths designated for the progress of the simultaneous equations were 243, 274, and 259 nm, the λ_{max} of selected drugs. The absorbances of PCM, ACE, and THC were determined and the absorptivity values (ε) were calculated at all the three selected wavelengths. These values were a mean of five assessments. The following simultaneous equations can be constructed to calculate the concentration of three drugs (*12*).

where C_{PCM}, C_{ACE}, and C_{THC} are the concentrations of PCM, ACE, and THC respectively in mixture in sample solutions

A_1, A_2, and A_3 – the absorbances of the sample at 243, 274, and 259 nm respectively

ax_1, ax_2, and ax_3 – the absorptivity of PCM at 243, 274, and 259 nm respectively

ay_1, ay_2, and ay_3 – the absorptivity of ACE at 243, 274, and 259 nm respectively

az_1, az_2, and az_3 – the absorptivity of THC at 243, 274, and 259 nm respectively.

2.8. Analytical method validation

In accordance with ICH Q2 (R1) guidelines, the developed UV spectrophotometric method was validated for the parameters like accuracy, precision, and linearity (*13*).

2.8.1. Linearity, limit of detection (LOD) and limit of quantification (LOQ)

The standard stock solutions were diluted with the selected diluent to get a concentration range of 5–15 µg/mL for PCM, 1–5 µg/mL for ACE and THC. The concentration ratio of PCM, ACE, and THC in the mixture is

$$C_{PCM} = \frac{A_1(ay_2az_3 - az_2ay_3) - ay_1(A_2az_3 - az_2A_3) + az_1(A_2ay_3 - ay_2A_3)}{ax_1(ay_2az_3 - az_2ay_3) - ay_1(ax_2az_3 - az_2ax_3) + az_1(ax_2ay_3 - ay_2ax_3)}$$

$$C_{ACE} = \frac{ax_1(A_2az_3 - az_2A_3) - A_1(ax_2az_3 - az_2ax_3) + az_1(ax_2A_3 - A_2ax_3)}{ax_1(ay_2az_3 - az_2ay_3) - ay_1(ax_2az_3 - az_2ax_3) + az_1(ax_2ay_3 - ay_2ax_3)}$$

$$C_{THC} = \frac{ax_1(ay_2A_3 - A_2ay_3) - ay_1(ax_2A_3 - A_2ax_3) + A_1(ax_2ay_3 - ay_2ax_3)}{ax_1(ay_2az_3 - az_2ay_3) - ay_1(ax_2az_3 - az_2ax_3) + az_1(ax_2ay_3 - ay_2ax_3)}$$

Table 2. Concentration ratio of PCM, ACE, and THC in mixed standard.

	Concentration (µg/mL) in mixed standard				
Name of the drug	1	2	3	4	5
PCM	5	7.5	10	12.5	15
ACE	1	2	3	4	5
THC	1	2	3	4	5

depicted as shown in Table 2. Each concentration was analyzed in three replicates. The linear regression analysis was performed on the selected wavelength. The LOD and LOQ were calculated as per ICH guidelines.

2.8.2. Accuracy

To study the accuracy of the established method, recovery tests were accomplished using standard addition method at 80, 100 and 120% levels and the percentage recovery from the spiked solution was determined.

2.8.3. Precision

The reproducibility of the established method was resolved at diverse time intervals on same day (intra-day precision) and on three dissimilar days (inter-day precision). The coefficient of variance, standard deviation for the intra-day and inter-day precision were determined and the decision was made.

2.9. Analysis of marketed formulation

For the quantification of drugs in the marketed formulations, 20 tablets were taken and their average weight was determined. The tablets were crumpled to a fine powder. Weight equivalent to 500 mg of PCM (equivalent to 100 mg of ACE and 4 mg of THC) was weighed accurately and transferred to 50 mL volumetric flask, 96 mg of THC (standard addition technique) was weighed accurately and added in the same flask since the amount of THC in the formulation is less. Thereafter 25 mL of buffer solution was added and sonicated for 20 min and the volume was adjusted with phosphate buffer pH 7.8 to the mark. This solution was filtered using Whatmann filter paper no. 4 and the filtrate was appropriately diluted to get a concentration of 10 µg/mL of PCM, 3 µg/mL of ACE, and 3 µg/mL of TCH within the concentration range of the mixed standards.

3. Results and discussion

The principle goal of this work is to present green chemistry principles for the simultaneous analysis of triple drug combination containing PCM, ACE, and THC with a positive impact to the environment. Further, the established method was validated in accordance with ICH Q2 (R1) guidelines (*11*). The zero order UV absorption spectra showed maximum absorbance at 243 nm, 274 nm, and 259 nm for PCM, ACE, and THC respectively.

3.1. Stability of the solution

The % RSD obtained for the absorbance of the standard and sample solution were less than 1% which indicates that the solutions ensure good stability at room temperature.

3.2. Linearity, LOD, and LOQ

The linearity was established between the concentration range of 5–15 µg/mL for PCM, 1–5 µg/mL for ACE and THC and the regression equations were $y = 0.0087x + 0.0108$ at 243 nm, $y = 0.0035x + 0.0012$ at 274 nm and $y = 0.0063x + 0.0062$ at 259 nm.

The correlation coefficient value (r^2) closer to +1 indicates that the selected concentration range is linear as showcased in Table 3, while the linearity spectrum and plot of calibration curve is depicted in Figures 3 and 4 respectively. The calculated LOD and LOQ values were presented in Table 3.

3.3. Accuracy

The data obtained from the accuracy runs by standard addition method for the three selected concentrations at 80, 100 and 120% were presented in Table 4. The percentage recovery ranged between 99.56 % and 100.99 % w/w, ensuring accuracy of the developed method.

3.4. Precision

The results of intra-day and interday precision studied at 100% concentration level were tabulated in Table 5. The % RSD values were within limit (<2%) which assured a high degree of precision of the developed method.

Table 3. Statistical results of regression analysis.

	Investigated wavelength (nm)		
Description	243	274	259
Regression equation*	$y = 0.0087x + 0.0108$	$y = 0.0035x + 0.0012$	$y = 0.0063x + 0.0062$
Slope	0.0087	0.0035	0.0063
Intercept	0.0108	0.0012	0.0062
R^2	0.9992	0.9974	0.999
LOD (µg/mL)	0.24	0.33	0.32
LOQ (µg/mL)	0.78	1.01	0.95

*Mean of 3 determinations: R^2, Correlation coefficient.

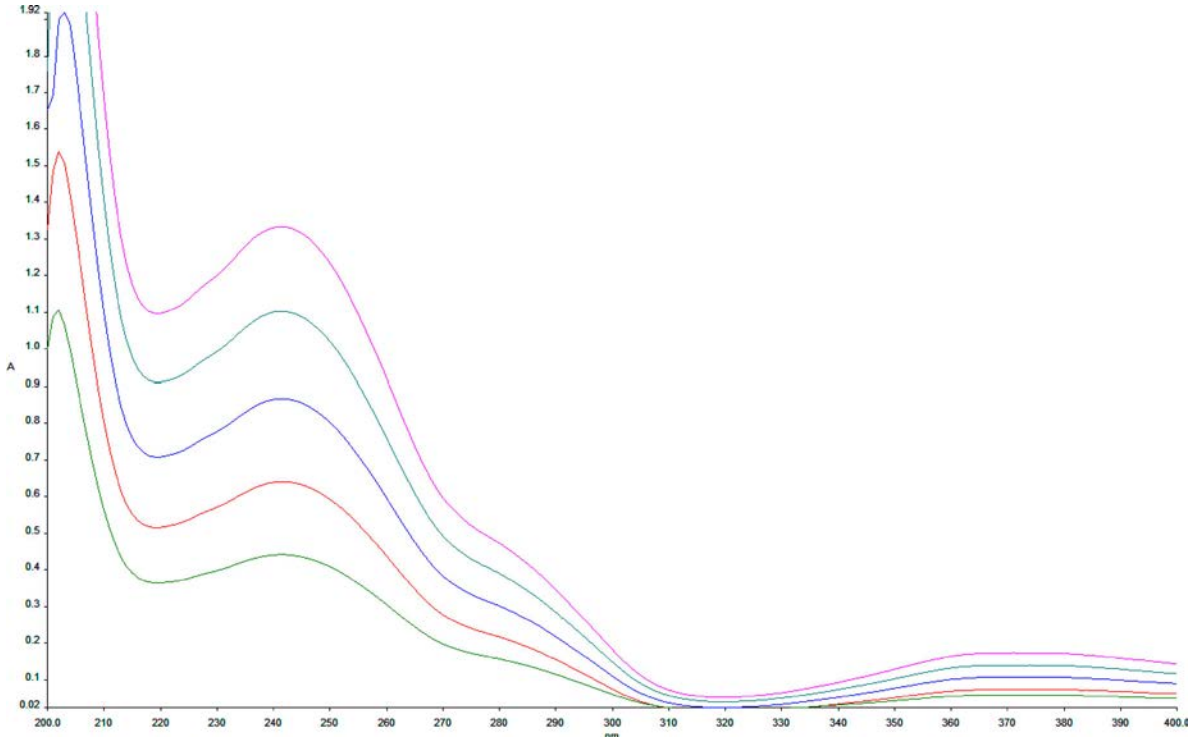


Figure 3. Overlay spectrum of mixed standard.

3.5. Analysis of marketed formulation

The proposed UV spectrophotometric assay of PCM, ACE, and THC in pharmaceutical tablet formulation showed good percentage recovery on assay and is depicted in Figure 5 and the results obtained have been provided in Table 6.

3.6. Evaluation of greenness profile

The U.S. Environmental Agency has rated methanol, the one used in the reported UV spectrophotometric method (*7*) as hazardous solvents (EPA Hazardous listing) in terms of their inherent toxicity and disposal (*14*). Green analytical method tries to accomplish

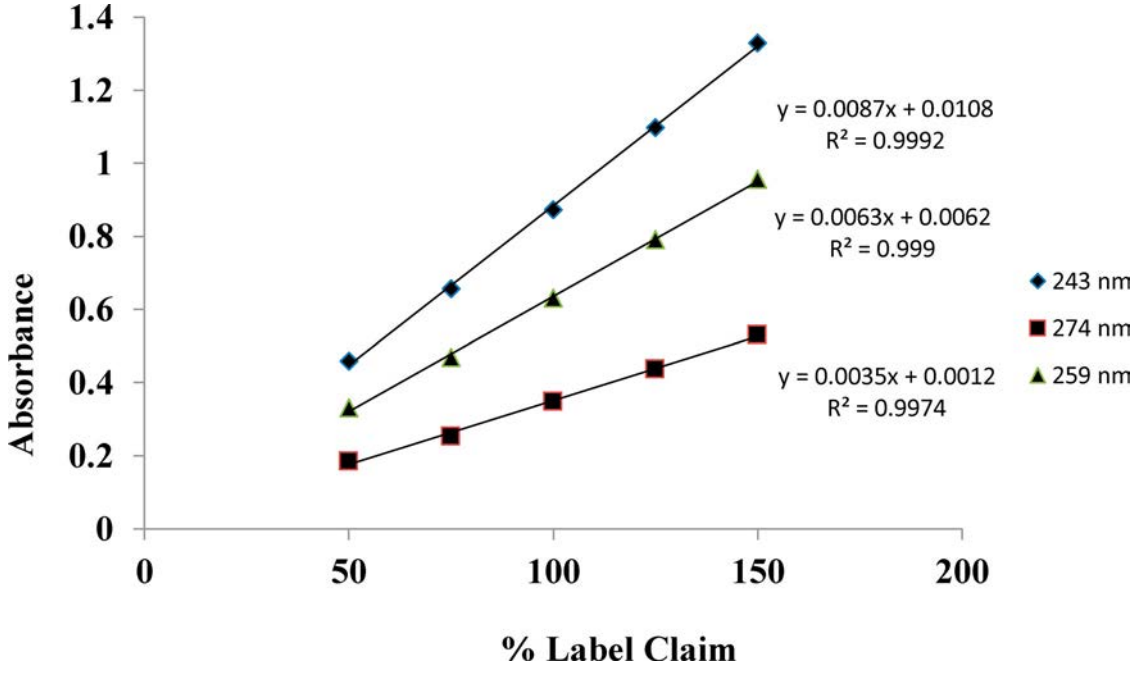


Figure 4. Calibration curve at selected wavelength (50–150% level).

Table 4. Result of the accuracy studies.

	Percentage recovery % w/w ± Standard deviation[#]		
Recovery level assessed	PCM	ACE	THC
80%	99.56 ± 0.06	100.99 ± 0.05	100.19 ± 0.01
100%	100.43 ± 0.07	99.88 ± 0.01	100.06 ± 0.01
120%	99.79 ± 0.07	100.03 ± 0.01	99.99 ± 0.01

[#]Average of three determinations.

greenness by lessening or ruling out possible hazards related with chemical procedures. In the recent years, the assessment of analytical procedures for their greenness profile has become vital which ultimately made way for ranking greenness profile (*15*). To evaluate the greenness profile of the established UV spectrophotometric method, National Environmental Methods Index (NEMI) (*16*, *17*, *18*), Analytical Eco-scale (*18*, *19*), and AGREE – Analytical GREEnness Metric Approach and Software (*20*) which is based on 12 principles of green chemistry were used.

The Methods and Data Comparability Board of United States proposed NEMI, which has four terms, namely PBT (persistent, bio accumulative and toxic), Hazardous, Corrosive and Waste as the criteria for the greenness profile (*16*, *17*). Every single quadrant is colored green or blank depending upon the specific criterion is met or not. Subsequently, the assessment of the overall greenness profile is found easily. Phosphate buffer pH 7.8 which is used in the established technique was neither characterized as PBT nor hazardous by the environmental protection agencies (EPA) toxic release inventory which suggests that the proposed UV spectrophotometric method fulfills the greenness profile as per the four principles of NEMI and is shown in Table 7.

Table 5. Results of intra-day precision and interday precision.

	Intra-day precision*			Interday precision#		
	Investigated wavelength			Investigated wavelength		
Description	243 nm	274 nm	259 nm	243 nm	274 nm	259 nm
Mean of absorbance	0.8637	0.3322	0.6293	0.8655	0.3278	0.6273
Standard deviation	0.012	0.006	0.011	0.0099	0.0055	0.0074
% RSD	1.3456	1.7904	1.7222	1.1432	1.6753	1.1871
SE	0.0047	0.0024	0.0044	0.0040	0.0022	0.0030

*Mean of 6 determinations; [#]Mean of 3 determinations: RSD – Relative Standard Deviation: SE – Standard Error.

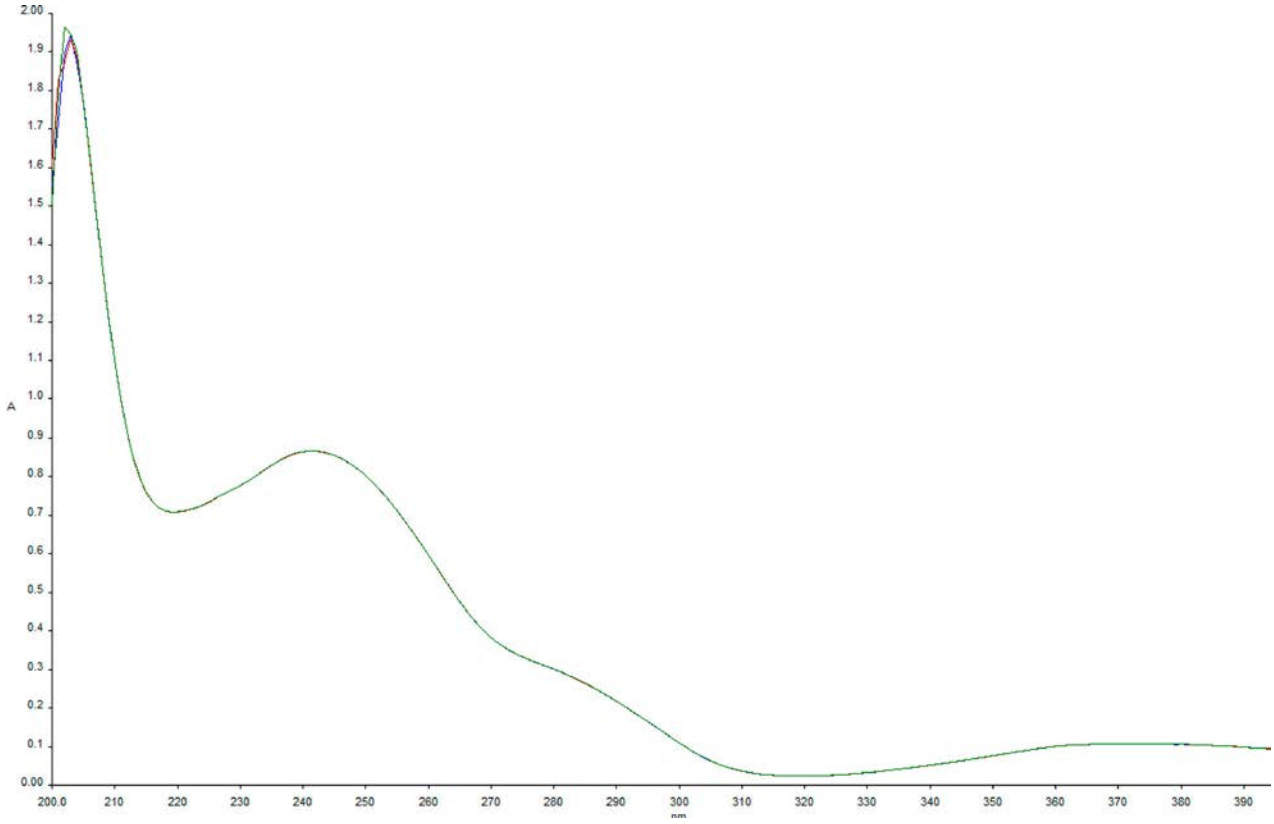


Figure 5. Spectrum of the marketed formulation at 100% concentration level.

Table 6. Assay results of the selected formulation.

Description	PCM	ACE	THC[#]
Label claim (mg)	500	100	4
Amount found (mg)*	502.95	101.90	4.01
% Label claim	100.59	101.90	100.45
S. D	1.1299	1.0271	0.0783
%RSD*	0.2247	1.008	1.9495
S.E.	0.5053	0.4594	0.0350

*Mean of 6 determinations.
[#]Excluding 96 mg of THC (added towards standard addition technique).

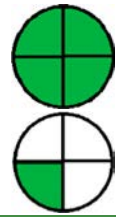
Analytical Eco-scale (*21*), another tool for the assessment of greenness was also enforced the established and reported method (*7*) as presented in Table 8. The penalty points are assigned for each of the selected analytical parameters like the amount of reagent, hazards, energy, and waste generated. The penalty points for the entire procedure are added and combined in the Eco-scale calculation, as indicated by the following formula:

$$\text{Analytical Eco-scale} = 100 - \text{total penalty points}.$$

The value of the Eco-scale adjacent to 100 indicates a greener analytical method. The current proposed method uses phosphate buffer pH 7.8 as the diluent which has a score of 100 indicating the excellent nature of its greenness profile.

The third evaluation technique is based on a novel software tool for assessing the greenness profile is

Table 7. Comparison of the greenness profile between the proposed and reported spectrophotometric method.

Mixture	Method	Diluent	Waste generated	Greenness profile[#]
PCM, ACE and THC	Proposed method	Phosphate buffer pH 7.8	Nontoxic to environment	
PCM, ACE and THC	Reported UV method	Methanol	Toxic to environment	

[#]Four key terms are PBT, hazardous, corrosive, and waste.

Table 8. Analytical eco-score calculation and comparison between the proposed and reported UV spectrophotometric method.

Reported method		Proposed method	
Reagents/parameter	Penalty points	Reagents/parameter	Penalty points
Methanol	6	Phosphate buffer pH 7.8	0
Occupational hazard	3	Occupational hazard	0
Instrument	0	Instrument	0
Total penalty points	09	Total penalty points	0
Analytical eco-scale total score	91	Analytical eco-scale total score	100

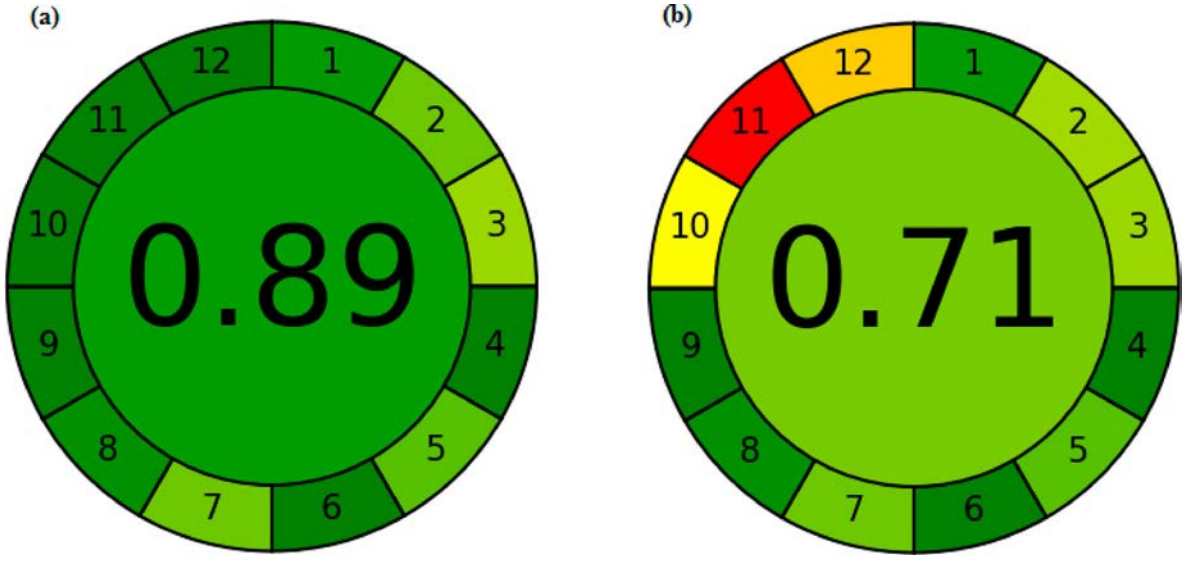


Figure 6. AGREE metrics score: (a) proposed method and (b) reported method.

AGREE (*20*). The output of AGREE software is a clock-wise circular diagram with numbers from 1 to 12 around the edge that indicate 12 ideology of green analytical chemistry. The results of each segment of the 12 principles were given on the aggregate scale from 0 to 1 with the inputs provided along with their weightage. The net outcome of all the 12 principles and the core of the AGREE diagram (Figure 6a) depicts the score. The color range from red–yellow–green is based on the value of results obtained from 0 to 1. The color is dark green when the score values are close to 1 while it is red color if the score values are close to 0. The output score of the AGREE metrics software was 0.89 for the proposed method and 0.71 for the reported spectrophotometric method and is shown in Figure 6(a and b). The score obtained for the proposed method is close to the maximum score of 1 and hence the greenness profile was established. It is evidenced that NEMI, Eco-scale and AGREE metrics assessment tools for greenness profile was satisfied with the established method and hence can be utilized for the regular analysis of the selected drugs with a positive impact for the environment.

4. Conclusion

The proposed green spectrophotometric simultaneous equation method for the analysis of PCM, ACE, and THC was rapid, economical, accurate, and precise for the regular analysis of these drugs in their mixed dosage form without any prior separation. Further the proposed method has least environmental impact as assessed by the assessment tools and hence could be used as a routine alternative for the existing method. The suggested diluent phosphate pH 7.8 employed in this work was demonstrative for employing surrogate chemicals other than methanol which can be used successfully without affecting the UV spectral characteristics of the drugs chosen. It is concluded that the proposed spectrophotometric method will be superior in terms of greenness with the existing spectrophotometric method (*7*). The fact that PCM, ACE, and THC are insoluble in water implies that water cannot be used as a diluent for the estimation of the selected drugs, while phosphate buffer pH 7.8 was found to be suitable as a diluent for developing green spectrophotometric method.

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Disclosure statement

No potential conflict of interest was reported by the author(s).

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Dr. K. S. Lakshmi, is currently the Dean at SRM College of Pharmacy, SRM Institute of Science and Technology (SRMIST), Chennai. She has 32 years of academic experience. She is specialized in the area of Analytical method development and validation of drugs in pharmaceutical formulations and biological fluids. She has more than 300 research papers in various peer reviewed national and international journals of repute with high impact factor. She has guided 60 post graduates and 8 PhD scholars in the area of Pharmaceutical Sciences. She is serving as editorial member and reviewer committee member for more than 15 peer reviewed national and international journals.

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