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Short communication

A new second-derivative spectrophotometric method for the determination of permethrin in shampoo

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Abstract

Permethrin, a highly effective insecticide agent, has been widely used for the pest control in agriculture and the treatment of lice in human. A fast and reliable method for the determination of permethrin was highly desirable to support formulation screening and quality control. A second-derivative UV spectroscopic method was developed for the determination of permethrin in the shampoo dosage form after extraction. The second-derivative spectrum recorded between 250 and 310 nm, and a zero-crossing technique for second-derivative measurement at 279 nm was selected. It is found that the selectivity and sensitivity of the method to be in desirable range. In comparison with the direct UV method, second-derivative UV spectroscopy eliminates the interference from UV absorbing excipients. This method is also fast and economical in comparison with the more time-consuming GC method regularly used for formulation screening and quality control and can be used routinely by any laboratory possessing a spectrophotometer with a derivative accessory. The linear concentration ranges were 0.25–1.5 ppm ($D2 = 0.00042\text{Conc.} + 0.0018$, $r = 0.9972$, $n = 10$). Between day of CV% ≤ 2.81, within day of CV% ≤ 3.50, and an analytical recovery close to 95–100% shows the suitability of the method for determination in quality control.

Keywords: Permethrin; Second-derivative spectrophotometry; Shampoo

1. Introduction

Spectrophotometric methods of analysis have experienced a high evolution in the last 25 years [1] and widely used as a tool for quantitative analysis, characterization, and quality control in agricultural, pharmaceutical, and biomedical fields [2]. Derivative UV spectroscopy which is based on mathematical transformation of spectral curve into derivative spectra eliminates the influence of background or matrix and usually provides much better fingerprints than the traditional absorbency spectra [3–7].

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Synthetic pyrethroids such as permethrin are important insecticides used in agriculture, forestry, horticulture, public health, and house [8,9]. These compounds which act on the nervous systems by interacting with sodium channels [10] are considered to be safe for human use [11,12]. Determination of permethrin is usually done using GC (in fruits and vegetables [13,14], and in urine and plasma [15,16]), as well as HPLC and first-derivative spectrophotometry (in drug formulations [17]). Considering the profits given by the application of mathematical approach into chemical analysis [18,19] and easy access to analytical apparatus, the authors examined the usefulness of the above-mentioned method in permethrin analysis. The usual method for the determination of permethrin in its pharmaceutical dosage forms is GC that is very expensive and time consuming. The aim of this work was to develop an easy UV spectrophotometric method, using mathematical transformation to eliminate the interference due to matrix material for the determination of permethrin in shampoo.

2. Experimental

2.1. Apparatus

The study used a Shimadzu, 2100, UV–Vis Spectrophotometer, with a 1.00 cm quartz cells. The optimized operating conditions for recording the second-derivative spectra were: scan speed, fast; spectral slit width, 2 nm; $\Delta\lambda$, 10 nm; and an ordinate maximum–minimum of ± 0.1. Measurements were carried out using the second derivative of the absorbance spectra, measuring the height of the trough at 279 nm.

2.2. Materials

Permethrin was kindly donated by Fouman Shimi Co., Iran; *n*-heptane, Merck, Darmstadt, Germany; shampoo matrix (containing α-tochoferol, betaine, sodium lauryl ether sulfate, methyl paraben, and propyl paraben) was kindly donated by Farayand Nik Co., Iran; permethrin shampoo from different manufacturers.

2.3. Procedure

2.3.1. Selection of proper solvent and order of derivation

Permethrin was dissolved at a concentration of 100 ppm in various solvents (polar solvents such as ethanol to nonpolar solvents as *n*-heptane) and their zero- to fourth-derivative spectra was obtained. Because of lipophilic nature of permethrin, and solvent availability, *n*-heptane was chosen as a solvent for permethrin and extraction of it from shampoo matrix. Shampoo matrix has some ingredients such as α-tochoferol, betaine, sodium lauryl ether sulfate, methyl paraben, and propyl paraben that have significant absorbances in normal spectrum in the range that permethrin have maximum absorbency. Because of complex interference of some ingredients with permethrin, spectra of permethrin shampoo matrix as a blank and permethrin shampoo as a real sample was also obtained. The standard solutions of permethrin were prepared by dissolving 10 mg of permethrin in *n*-heptane directly. Working solutions (0.25–1.50 ppm) were prepared by the proper dilutions of the stock standard solution with *n*-heptane.

2.3.2. Standard solution preparation

Standard solutions in shampoo base were obtained by adding appropriate amount of permethrin into shampoo matrix. Concentrations prepared were (0.25–1.50 ppm). The standard solutions of permethrin in shampoo were prepared as follows: 0.25, 0.50, 0.75, 1.00, 1.25, and 1.50 g of permethrin shampoo from pertaining concentrations were transferred into 10 ml volumetric flasks and diluted to volume with *n*-heptane. In some cases, salt was also added before adding *n*-heptane. Finally, the flasks were sonicated (with medium intensity in 15 min) and centrifuged (5000 rpm, 10 min) to separate the layers. The *n*-heptane phase was transferred to quartz cell. The blank solution was also prepared in the same manner but without the addition of permethrin. Obtained aliquots of extract were analyzed at second derivation spectrum at maximum wavelength of 279 nm.

2.3.3. Preparation of permethrin alkali-induced degradation products

A 1% solution of permethrin with ethanolic 0.1 N sodium hydroxide solution was prepared and stirred for about 24 h and analyzed for its permethrin content remained or interfering degradation products with permethrin analysis.

2.3.4. Optimization of extraction conditions

n-Heptane was used as a solvent for the extraction of permethrin from its shampoo matrix. For this purpose, conditions such as sonication time and addition of salt to permethrin shampoo were studied and its effects on recovery of permethrin were evaluated.

2.3.5. Precision assays

Permethrin standard solutions were prepared and analyzed six times within the same day to obtain the repeatability and six times over different days to obtain the reproducibility. Each assay was carried out on a different extraction of permethrin from the shampoo. The percentage relative standard deviation (RSD%) of the data obtained was calculated.

2.3.6. Accuracy

Known amounts of permethrin were added to shampoo matrix in order to obtain three different levels of addition. The samples were analyzed and the mean recovery as well as the repeatability was calculated on six assays for each concentration added.

2.3.7. Linearity of the method

Linearity of second-derivative spectra of permethrin concentration was established by preparing one series of permethrin solution ranging from 0.25 to 1.50 ppm which corresponds to 25–150% of method concentration (1.00 ppm). The second-derivative spectra were recorded using the diluents as a blank. All solutions were measured for absorbency from 250 to 310 nm.

2.3.8. Limit of detection (LOD) and limit of quantitation (LOQ)

LOD determined by measuring the D2 absorbances at 279 nm of at least 25 separate base shampoo samples. Average and S.D. of blank responses were calculated, LOD and LOQ were estimated by calculating of 3S.D. and 10S.D. of blanks, respectively.

2.3.9. Assay of permethrin in commercial shampoo

The proper amount of permethrin shampoo was transferred to volumetric flask. *n*-Heptane was added to volume. The mixture was sonicated and centrifuged (with above-mentioned conditions). Organic layer was transferred into a quartz cell. The spectrophotometric measurements were done at second derivation spectrum at the maximum wavelength of 279 nm.

3. Results and discussion

The zero-, first-, second-, third-, and fourth-derivative spectra for all investigated ingredients of the shampoo were recorded in the wavelength range 250–310 nm. The zero, D1, and D2 spectra of permethrin, permethrin shampoo matrix, and permethrin shampoo in the wavelength of 250–310 nm are shown in Figs. 1–3. Permethrin exhibits an absorbency maximum at 272 nm as shown in Fig. 1. Determination of permethrin in its shampoo dosage form using direct UV measurement was attempted.

However, under most circumstances, pronounced interference from other excipients was observed. A typical UV spectrum of a placebo shampoo is also shown in Fig. 1, which indicates a significant UV response with absorption maximum at 270 nm. Based upon the direct UV spectroscopic data, there is no wavelength where permethrin can be accurately quantified without substantial background interference. This problem also exists in the first-derivative spectra of above-mentioned materials (Fig. 2).

However, the difference does exist between the second-derivative UV spectra of permethrin and the excipients in placebo shampoo, which indicates the feasibility of a derivative UV method. The excipients in placebo shampoo were measured. As demonstrated in Fig. 3, permethrin can be measured at 279 nm with little interference in the second-derivative mode.

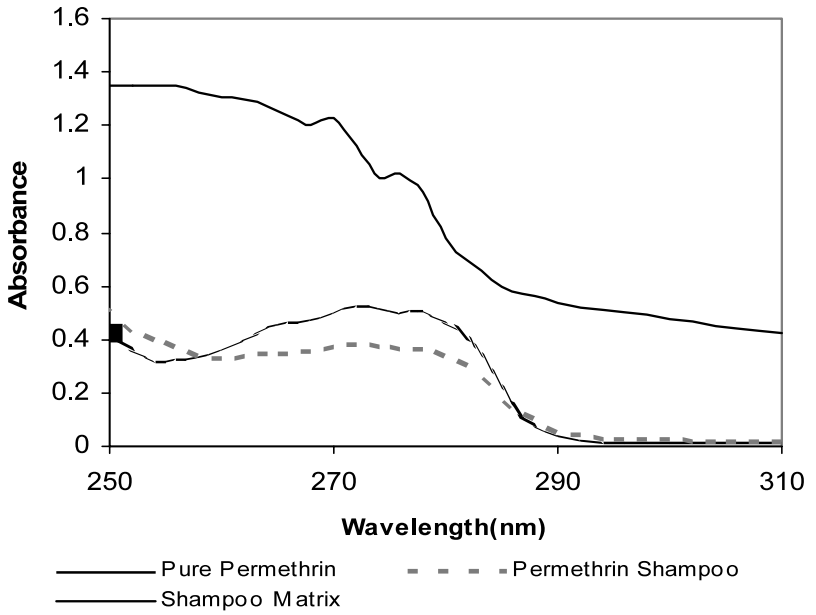

Fig. 1. Spectra of shampoo matrix, pure permethrin, and permethrin shampoo.

3.1. Validation of method

Using regression analysis, the following equation was obtained for standard calibration curve of permethrin:

$$D2 = 0.00042\text{Conc.} + 0.0018,$$

where D2 is the absolute value of the second derivative of permethrin absorbency at 279 nm and Conc. is the concentration of permethrin (ppm). The method was linear in the range 50–150% of target concentration ($r = 0.9972$). The calibration curve was in agreement with beer's law. The regression equations for the permethrin were calculated including the standard error of the slope, standard error of the intercept, correlation coefficient (r), P-value of the correlation coefficient were taken in Table 1.

The validation parameters (linearity, selectivity, recovery, precision, limit of detection, and limit of

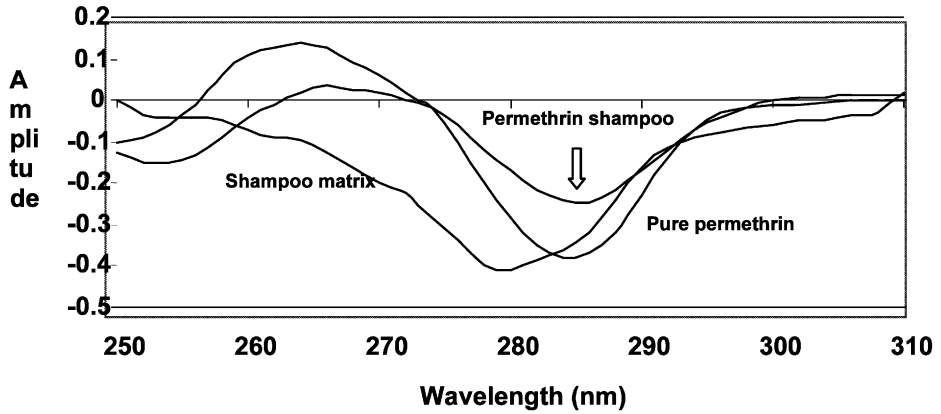

Fig. 2. First-derivative spectra of shampoo matrix, pure permethrin, and permethrin shampoo.

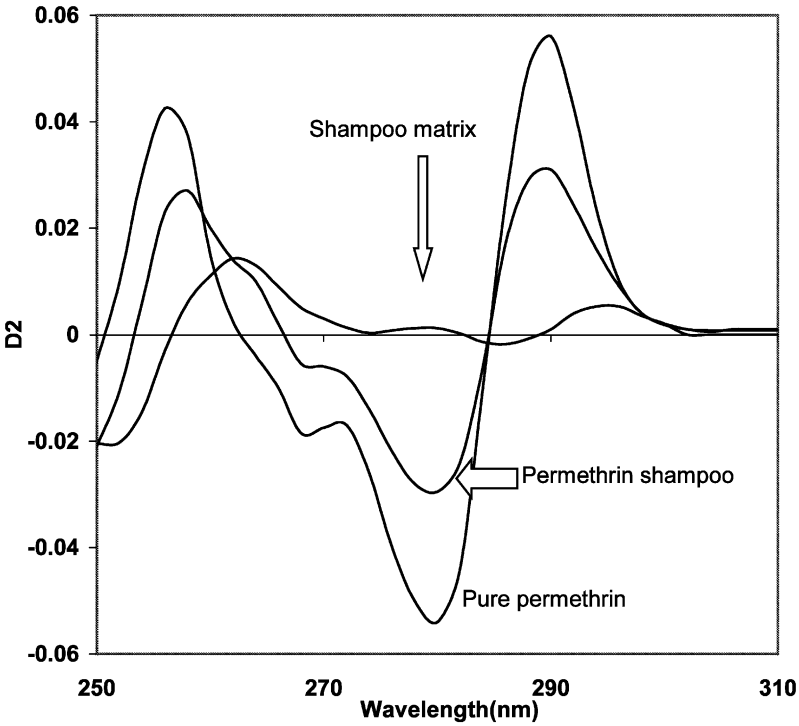

Fig. 3. Second-derivative spectra of pure permethrin, permethrin shampoo, and shampoo matrix.

Table 1
Second-derivative spectrophotometric determination of permethrin shampoo

Parameters	Permethrin ($\lambda = 279$ nm)
Concentration range (ppm)	0.25–1.50
$Y = aX + b$	D2 = 0.00042 + 0.0018
Correlation coefficient	0.9972
Standard error of the slope	0.002
Standard error of the intercept	0.002
P-value for correlation coefficient	0.0001
Within day CV%	3.50
Between day CV%	2.81
Limit of detection (ppm)	2.23
Limit of quantitation (ppm)	7.43
Permethrin shampoo (labeled) (%)	1.00
Permethrin shampoo (found) (%)	0.95–1.02
Recovery (%)	95–100

quantitation) were also determined (Table 1). The derivative spectrophotometric method is selective because the excipients did not interfere during the determination of permethrin. In addition, permethrin was degraded to its acid and alcohol precursors in alkaline media and degradation products of permethrin have not any interference with permethrin in its second-derivative spectrum and therefore the method can be used in stability study of permethrin shampoo. Relatively small amount of CV% (2.81 and 3.5%) confirms a precision of the method, and recovery (greater than 95%) show good accuracy. As demonstrated, extensive interferences exist between shampoo matrix and permethrin. Therefore, zero- and first-derivative spectra cannot be used for quantitation of the drug (in contrast to studies reported by Irj et al. [10]). Meanwhile, the D2 spectrum displayed a trough at 279 nm without any interference. Stability of samples prepared in n-heptane was studied. Results showed that samples are stable at least for 1 month, and changes during sample preparation and time of reading are found to be negligible.

For quantitative analysis of the permethrin shampoo, three solutions were prepared. The

amount of permethrin was calculated by the method of standard. Results (95–102% of label claimed) show that all the formulations are in the acceptable ranges (90–110% of label claimed).

4. Conclusion

The second-derivative order of the spectra of the permethrin was found to be suitable for the determination of the permethrin in shampoo. The obtained results are accurate and precise and confirmed by statistical parameters. There was no interference of the excipients in the shampoo. The described second-derivative spectrophotometric method is a simple, rapid, selective, accurate, and precise method for the determination of the permethrin in shampoo or a corresponding mixture.

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