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The Simultaneous Determination of Quinoline Yellow (E-104) and Sunset Yellow (E-110) in Syrups and Tablets by Second Derivative Spectrophotometry

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A very simple spectrophotometric method using measurements at zero-crossing wavelength is described for resolving binary mixtures of the food dyes, Sunset Yellow (E-110) and Quinoline Yellow (E-104). Calibration graphs are linear up to 15.0 μgml^{-1} of Sunset Yellow (r = 0.9998), and Quinoline Yellow (r = 0.9999). The assay procedure for E-110 and E-104 in pharmaceutical products involves the extraction of the dyes with AcOH/NaOAc buffer solution (pH = 4.5), filtration, and measurement of the second derivative absorbance values at 410.0 nm for E-104 and 533.1 nm for E-110. This method was used for determining synthetic mixtures of these dyes in different ratios and it was successfully applied to two commercial products without a previous separation step.

Key Words: Dyes, derivative spectrophotometry, pharmaceutical products, Sunset Yellow, Quinoline Yellow

Introduction

Sunset Yellow (E-110) and Quinoline Yellow (E-104) are synthetic dyes present in pharmaceutical products. Over 50 synthetic dyes are used in food, cosmetic, and pharmaceutical products all over the world. Synthetic dyes are used under governmental regulations and the kinds and numbers of permitted dyes vary from country to country. In Turkey, among the synthetic dyes permitted are Sunset Yellow (E-110), Ponceau 4R (E-124), Tartrazine (E-102), Indigotine (E-132), Erythrosine (E-127), Amaranth (E-123), Carmoisine (E-122), Quinoline Yellow (E-104), and Riboflavin (E-101).

Chromatographic methods have been used for dye analysis in food, cosmetic and pharmaceutical products. These methods are very suitable when the samples contain several dyes[1−3]. Differential pulse polarography[4] and adsorptive stripping voltammetry[6,7] have also been applied by the authors in different commercial products.

In recent years, derivative spectrophotometry and the partial least squares (PLS) method have been widely used for the determination of dyes in food products and satisfactory results were reported[5−10].

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Derivative spectrophotometry and PLS methods have been developed by us in order to resolve binary and ternary mixtures[11,12]. These methods were successfully applied to commercial food products.

For the simultaneous determination of Sunset Yellow (SY) and Quinoline Yellow (QY) in foods, the PLS[13] method has been reported in the literature. No method has been published for the simultaneous determination of Sunset Yellow and Quinoline Yellow in the pharmacopoeias (USP and BP)[14,15] or AOAC[16].

In order to resolve this binary mixture we have described a simple spectrophotometric method based on zero-crossing measurements using the second derivative spectrum.

Experimental

Apparatus

A Philips Model PU 8740 UV-Visible scanning spectrophotometer was used for all measurements and treatment of data. The derivative spectra were automatically obtained from the spectrophotometer. All spectra were recorded from 350 nm to 550 nm with 2 nm slit width, 500 nmmin^{-1} scan speed and very high smoothing. The pH values were measured with a Metrohm 632 digital pH-meter.

Chemicals

Pharmaceutical grade QY, SY and Kuiflex tablets were kindly supplied by Abdi İbrahim İlaç Sanayi A.Ş., İstanbul. Vicks Vapo syrup was supplied by Eczacıbaşı İlaç Sanayi ve Ticaret A.Ş. Analytical grade sodium acetate (NaOAc) and glacial acetic acid (HOAc) were purchased from Merck, Darmstad. Distilled water was used throughout the work.

Pharmaceuticals and Solutions

Kuiflex tablets: Their declared content was as follows: Phenprobamat (200 mg), Paracetamol (200 mg), Sunset Yellow (E-110), Quinoline Yellow (E-104), and sugar.

Vicks Vapo Syrup: This product contains water, guaifenesin, sodium benzoate, sugar, Sunset Yellow (E-110), Quinoline Yellow (E-104) and ethanol.

Acetic acid/sodium acetate (pH = 4.5) buffer solution: 5.4 g sodium acetate was dissolved in 50 ml of water, and pH was adjusted to 4.5 with glacial acetic acid and was diluted with distilled water to 100 ml.

Stock solutions of Quinoline Yellow (QY) and Sunset Yellow (SY): QY and SY stock solutions with a concentration of 200 μg ml^{-1} were prepared. Acetic acid/sodium acetate (pH = 4.5) was used as buffer solution. These solutions were diluted with HOAc/NaOAc buffer solution to obtain standard solutions for the preparation of a calibration graph in the concentration range of 3.0-15.0 μg ml^{-1}.

Diluted aqueous solutions of QY and SY were stable for at least one month.

Procedure

Procedure for calibration graphs

The absorbance and second derivative spectra of the standard solutions were recorded between 350 and 550 nm against acetate buffer solution (pH = 4.5). The peak amplitudes (^{2}D values) were measured at 410.0 nm and 533.1 nm for the determination of QY and SY, respectively.

Procedure for synthetic mixtures

In order to test validity, the proposed method was applied over one set of five synthetic mixtures containing 3.0-15.0 μg ml^{-1} QY and SY. The absorption spectra of the samples thus prepared were recorded between 350 nm and 550 nm against a blank of buffer solution.

Procedure for commercial pharmaceutical products

The proposed method was also applied to the following commercial pharmaceutical preparations.

Kuiflex tablet: Sixty tablets were weighed and powdered. An accurately weighed amount of the powder (0.7 g) was transferred into a 50 ml volumetric flask. Then 25 ml acetate buffer solution (pH = 4.5) was added and agitated for 15 min. After, the flask was filled up with buffer solution and filtered.

Vicks Vapo Syrup: The product was agitated for 5 min and a 1 ml sample was diluted to 10 ml with acetate buffer solution. The spectra of the commercial samples prepared were recorded against a blank of acetate buffer solution. The second derivative absorbance values of the spectra at 410.0 nm and 533.1 nm were measured for the determination of QY and SY, respectively.

Results and Discussion

In Figure 1a the zero-order spectra of QY and SY and their mixture in the 350-550 nm wavelength ranges are shown. As can be seen, the order of existing overlapping bands inhibits the determination of QY, but it permits the determination of SY from direct measurements of absorbance from 482.4 nm. But in a turbid sample such as syrup, SY cannot be determined from direct measurements of absorbance. In order to resolve this binary mixture we applied the proposed method, based on zero-crossing measurement in the second derivative spectra. In Figure 1b the second derivative spectra of samples containing 10 μg ml^{-1} of QY, 10 μg ml^{-1} of SY and their mixture are shown. The shape of second derivative spectra permits the determination of QY in the presence of SY. Sunset Yellow's second derivative absorbance at 410.0 nm ($^2D_{410}$ nm) may be observed to be zero. Thus, QY content of the mixture was determined by measuring the second derivative absorbance at this wavelength, i.e., $^2D_{410}$ without any effect of SY. On the other hand, the value at 533.1 nm of the same spectrum, i.e., $^2D_{533.1}$ was utilized for SY assay. At these wavelengths the analytical signals of the mixture and the dyes to be determined coincide. We used the term $^2D_\lambda$ to indicate the signal of measurement at appropriate wavelength (λ) in the second derivative spectrum (^2D).

The main instrumental parameters that usually affect the shape of derivative spectra are the scan speed, the wavelength increment ($\Delta\lambda$) and the degree of smoothing. These parameters need to be optimized to give well resolved length of peak, good selectivity and larger sensitivity in the determination.

In order to optimize the scan speed, several scan rates were tested: 125, 250, 500, and 1000 nm/min. As an optimum, an intermediate value (500 nm/min) was chosen for each dye, resulting in similar analytical signals concerning the shape of the spectrum.

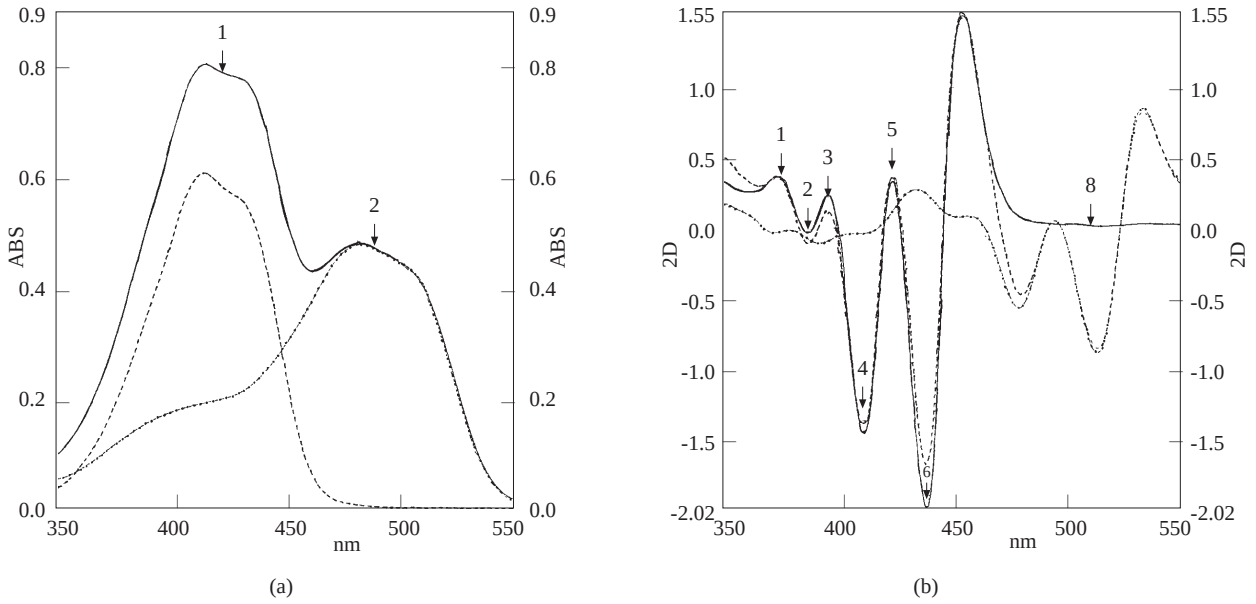


Figure 1. a) Absorption spectra for solutions of 10 μg ml^{-1} of QY (- - - -), SY (-.-.-.-.) and their mixture (——), recorded against a blank of acetate buffer (pH = 4.5)

b) Second derivative spectra for solutions of 10 μg ml^{-1} of QY (——), SY (-.-.-.-.) and their mixture (- - - -), recorded against a blank of acetate buffer (pH = 4.5)

The optimum value of $\Delta\lambda$ should be determined by taking into account the noise level, the resolution of the spectrum and the sample concentration. Some values of $\Delta\lambda$ were tested and 2 nm was found optimum in order to give a satisfactory signal to noise ratio. Due to the extent of noise levels, a very high smoothing function was used.

Using these experimental conditions, calibration graphs for SY and QY on the second derivative spectra were obtained at the appropriate wavelengths (410.0 nm for QY and 533.1 nm for SY) with straight lines between 3.0 and 15.0 μg ml^{-1}. The standard calibration curves for QY and SY are shown in Figure 2. In Table 1 the characteristic statistical data of the calibration graph for each dye are summarized. In all cases, good correlation coefficients were obtained.

Table 1. Statistical parameters of calibration graphs for each dye

Equations	Regression coefficient	Linearity ranged (μg ml^{-1})
$^2D_{410.0} = 1.63\ 10^{-3}+0.1391C_q$	r = 0.9997	3.0-15.0
$^2D_{533.1} = 0.0068+0.0776C_s$	r = 0.9999	3.0-15.0

C_q, QY concentration μg ml^{-1}; C_s, SY concentration μg ml^{-1}

The proposed method was applied over one set of five synthetic mixtures containing 3.0 and 15.0 μg ml^{-1} SY and QY. The composition of these mixtures and the recoveries obtained by this method are summarized in Table 2. Results obtained are good for QY and SY determination in all proposed ratios.

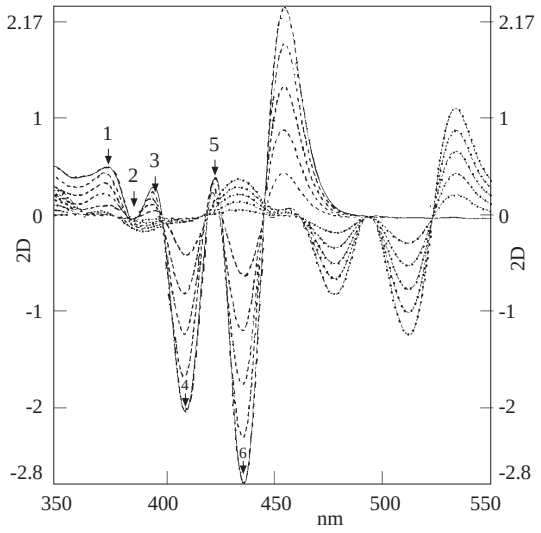


Figure 2. Second derivative spectra of standard solutions of Quinoline Yellow (- - - -) and Sunset Yellow (-.-.-.-.)

Table 2. Found recoveries for SY and QY in synthetic mixtures by second derivative spectrophotometric method

Composition mixtures (μg ml^{-1})		Sunset Yellow (SY) $^2D_{533.1}$ % recov^a	Quinoline Yellow (QY) $^2D_{410}$ % recov^a
SY	QY		
15	3	95.06	106.3
12	6	97.00	103.2
9	9	102.00	104.9
6	12	98.00	105.7
3	15	104.00	102.8
Statistical parameters			
$\overline{X}$		99.33	104.6
SD		3.69	1.53
RSD		3.70	1.46

^{a}means of three determinations

The proposed method was applied to calculate the contents of the two dyes in pharmaceutical products (Vicks Vapo Syrup and Kuiflex tablets). As can be seen from the absorption and second derivative absorption spectra of tablets (Figure 3), Kuiflex tablets only contain QY, and not SY. We found that the last commercial product did not contain E-110 but another dye called E-104. This point has been confirmed by the enterprise Abdi Abrahim A.Ş.

Recovery studies were also performed on synthetic mixtures prepared by addition to accurately weighed amounts of tablets. The obtained results are summarized in Table 3 together with the nominal content found by us.

The proposed second derivative method was also applied to a syrup sample. In Figure 4, the absorption and second derivative absorption spectra of syrup sample are presented. The syrup sample contains both QY and SY. When the Vis-spectrophotometric method was applied to the determination of SY, higher values were found due to the turbidity. This makes the derivative method particularly useful for quantitative determination in the presence of turbidity or when the background absorbance is high or not very well detailed. The second derivative method was applied to overcome this difficulty. The results obtained by the proposed derivative method using ten syrup samples are shown in Table 4.

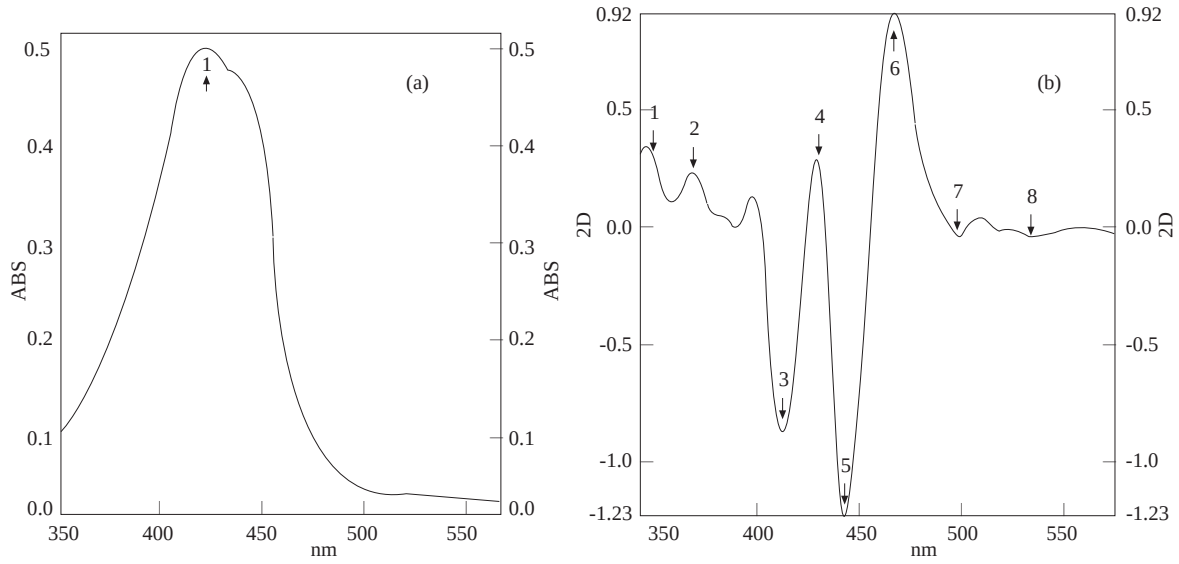


Figure 3. Absorption (a) and second derivative absorption (b) spectra of Kuiflex tablets

Table 3. Determination of the recovery for QY and SY in Kuiflex tablet solution

Present μg ml^{-1} QY ($^2D_{410}$)	Quinoline Yellow $^2D_{410}$			Sunset Yellow $^2D_{533.1}$		
6.84***	Added μ g ml^{-1}	Found** μ g ml^{-1}	Recovery %	Added μ g ml^{-1}	Found** μ g ml^{-1}	Recovery %
6.84	4.00	3.92	98.09	6.00	5.70	94.90
6.84	8.00	7.91	98.92	10.00	10.42	104.2
6.84	12.00	11.98	99.81	14.00	13.70	97.86
	98.91 ± 0.5*			98.99 ± 4.6*		

* Standard deviation of the mean

** Mean values of three determinations

*** Mean values of ten determinations

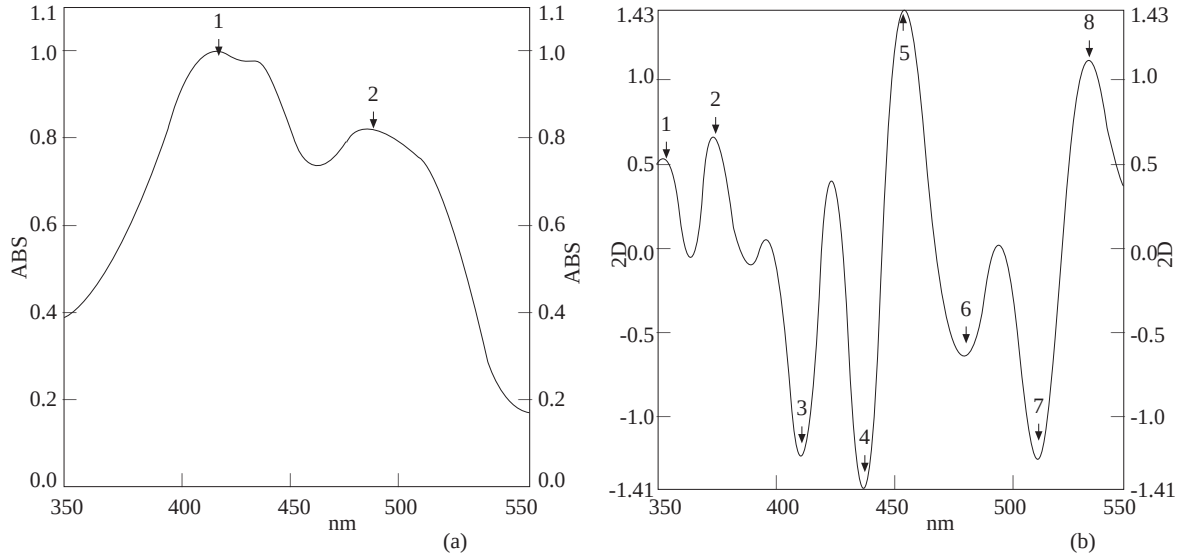


Figure 4. Absorption (a) and second derivative absorption spectra (b) of Vicks Vapo Syrup

Table 4. Determination of the recovery for QY and SY in Vicks Vapo Syrup

Present μg ml^{-1}		Quinoline Yellow $^2D_{410}$			Sunset Yellow $^2D_{533.1}$		
QY ($^2D_{410}$)	SY ($^2D_{533.1}$)	Added μ g ml^{-1}	Found** μ g ml^{-1}	Recovery %	Added μ g ml^{-1}	Found** μ g ml^{-1}	Recovery %
3.92	10.62	6	9.82	99.00	6	16.40	98.71
3.92	10.62	8	11.67	98.00	8	18.48	99.27
3.92	10.62	10	13.70	98.40	10	20.12	97.57
3.92±0***	10.62±0***	98.50 ± 1.3*			98.52 ± 2.2*		

* Standard deviation of the mean

** Mean values of three determinations

*** Mean values of ten determinations

Recovery studies were also performed on the synthetic mixtures prepared by addition to 1 ml syrup sample. Table 4 also contains these results.

The developed spectrophotometric method can be recommended due to its simplicity, the inexpensive instrumentation it uses and the satisfactory results reached in the analysis of synthetic mixtures and in the analysis of commercial pharmaceutical products. The procedure does not require any separation step, expensive solvents or solving equations. It can be confidently used for the rapid, precise and sensitive quantitation of SY and QY mixtures in syrups and tablets, especially for routine quality control analyses.

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