

Advanced Spectrophotometric Analysis of Sunset Yellow Dye E110 in Commercial Food Samples

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Received: 27 February 2016 / Accepted: 8 August 2016 / Published online: 5 September 2016
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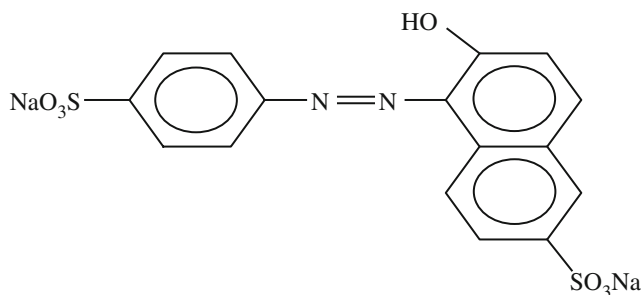
Abstract Sunset Yellow E110 is one of the famous synthetic food dyes, which belongs to the family of azo dyes and widely used in food industry as additives and nutrient sources. Two highly sensitive and simple spectrophotometric methods are developed for determination of Sunset Yellow E110 in some commercial food samples. The first method is based on redox reaction of Sunset Yellow with copper (II) followed by complex formation. Results indicated the formation of 1:1 metal-dye complex at pH 9.0. The second one is based on its oxidation by alkaline KMnO_4 to green manganate species. The two reactions are monitored spectrophotometrically at maximum absorbance 350 and 610 nm for methods I and II, respectively. Variables are carefully studied, and the conditions are optimized. Under the optimized experimental conditions, Beer's Law was obeyed in the concentration ranges 9.05–67.87 and 13.57–72.38 $\mu\text{g ml}^{-1}$ for the two methods, respectively. The apparent molar absorptivities, Sandell's sensitivity, and detection and quantification limits are calculated. Matrix effects are also investigated. The proposed methods are successfully applied for the determination of Sunset Yellow dye in commercial food products. The concentration level of the dye is found to be within the safe recommended limits.

Keywords Sunset Yellow dye · Cu (II) ions · Oxidation by KMnO_4 · Commercial food samples

Introduction

Synthetic dyes are widely used in food industries as they show several advantages compared with natural dyes such as high stability to light, oxygen and pH, color uniformity, low microbiological contamination, and relatively lower production costs. Food additives are incorporated in food products to improve their sensory qualities (Davidek and Janicek 1983). Colorants are very important ingredients in many commercial products such as confectionery products, gelatin desserts, snacks, and beverages. Without colorants, they would be colorless and appear undesirable (Combes 1986). The concentration of these additives must be carefully controlled as they may have various harmful effects at high concentration on human health. Food and Agricultural Organization (FAO) and World Health Organization (WHO) (El-Sheikh and Al-Degs 2013) are concerned with the evaluation of such dyes in various products.

Sunset Yellow E110 colorant dye for example is normally applied in food and pharmaceuticals to impart orange or red color. It is usually used in the production of Swiss roll, soft drink, jellies custard powder, sodas juices candies, ice creams, and jam (Kashanina et al. 2012; Xu et al. 2013; Botelho et al. 2014; Dennis et al. 1997).



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Numerous methods were published for the determination of Sunset Yellow dye E110 in food-stuffs such as paper chromatography TLC, HPLC (Nevado et al. 1998a; Li and Sepu 1990; Ren et al. 1990; Garcia Penalver et al. 1999), spectrophotometric (Capitan et al. 1996; Lau et al. 1995; Capitan-Vallvey 1998; Sayar and Ozdemir 1998; Ni and Gong 1997; Nevado et al. 1998b; Yongnian and Bai 1997), and voltametric (Nevado et al. 1997; Frazier and Benhard 1981) techniques. However, some of these methods are not suitable for routine monitoring as they are time consuming, complicated, and have poor sensitivity.

No spectrophotometric methods based on complexation with copper have been reported for the quantification of Sunset Yellow dye (Nevado et al. 1999). The main target of the present work is to describe the development of simple and rapid spectrophotometric methods for the determination of Sunset Yellow in different food samples. The first method is based on the oxidation of the dye by copper at pH 9.0 followed by complex formation, and the second one is based on oxidation with alkaline KMnO_4 under optimum conditions.

Experimental

Apparatus

An evolution 300 UV-Vis spectrophotometer with 1.0-cm matched cells with vision pro-software of Thermo Electron Corporation (Cambridge, UK) was used for electronic spectral measurements. pH measurements were made with Jenway 3040 ion analyzer-pH meter, equipped with Jenway 924005 combined glass electrode. The pH-meter was calibrated before use with standard buffer solutions of 4.0 ± 0.01 and 7.0 ± 0.01 . All measurements were made at 25 °C.

Chemicals and Reagents

All chemicals used were of analytical reagent grade. Deionized water was used to prepare all solutions. Stock solution of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ($1 \times 10^{-3} \text{ mol L}^{-1}$) was prepared by dissolving the required amount in deionized water and standardized complexmetrically with EDTA (Vogel 1973). The ionic strength of solutions was maintained at a constant value of $I = 0.1 \text{ mol L}^{-1}$ (NaClO_4). All measurements were made at 25 °C. Potassium permanganate solution (Merk, Germany) $1.0 \times 10^{-2} \text{ mol L}^{-1}$ was prepared in deionized water.

Standard Sunset Yellow E110 Solutions

Sunset Yellow E110 was purchased from Alfa Aesar (Germany). Stock solution of Sunset Yellow ($5 \times 10^{-4} \text{ mol L}^{-1}$) was prepared by dissolving the accurately

weighed amount of the pure dye in deionized water (method I) and in 1.0 mol L^{-1} NaOH for (method II). The working solutions were prepared daily by appropriate dilution.

Preparation of Real Food Samples

The real samples (Original Caramel, Custard Powder, Tang Mango, Tang Mango Delights Flavor, Jelly Mango, Jelly Orange, Jelly Apricots) were bought from local supermarket in Assiut City (Egypt). These samples contained many components such as sugar, color caramel (E150), artificial crème caramel flavor, disodium phosphate (E339), artificial colors, carrageenan (E407), Allura red, vitamin C, gum Arabic, salt, pure beef gelatin (halal), Tartrazine(E102), and Sunset Yellow E110.

Each samples were weighed exactly 0.5 g and dissolve in 10 ml of buffer solution (boric acid, NaOH) at pH 9.0, heated to 70 °C for 2 min with stirring, and then cooled, and the solution was centrifuged (10 min, 2000 rpm) to remove the insoluble particles. The filtrate was collected in 100-ml volumetric flask and diluted with deionized water. For determination of Sunset Yellow in the above real samples, 0.2 ml of sample solution was used and analyzed according to (method I). Finally, the Sunset Yellow content in different food samples was determined using the calibration equation and standard addition calibration curves procedure.

General Procedures

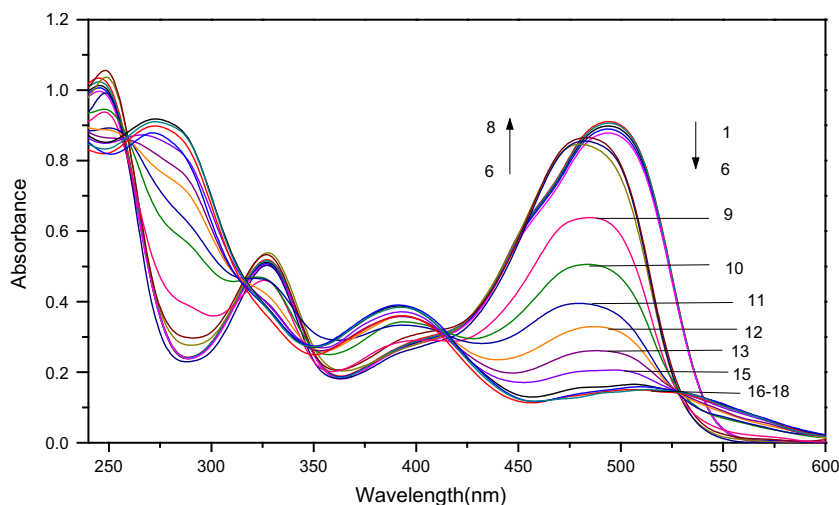
Method I (Complexation Reaction with Copper II)

Into 10-ml volumetric flasks, transfer a suitable aliquot of standard solution in deionized water containing up to 79.166 μg of Sunset Yellow and 1.0 ml of $5 \times 10^{-4} \text{ mol L}^{-1}$ Cu (II) solution and 1 ml of NaClO_4 (1.0 mol L^{-1}). After mixing, the mixture was buffered to pH 9.0 with (boric acid—NaOH) buffer. The resulting solution was made up to volume with deionized water and measures the absorbance at 350 nm by using 1-cm quartz cell against a similarly prepared blank of the same pH. The calibration graph was constructed by plotting absorbance vs. Sunset Yellow dye concentration.

Method II (Oxidation with KMnO_4)

Standard solutions containing 81.428 $\mu\text{g ml}^{-1}$ Sunset Yellow E110 in (1.0 mol L^{-1}) NaOH were transferred into individual 10-ml calibrated flask. 2.5 ml of (1.0 mol L^{-1}) NaOH was added followed by 2.0 ml of ($1.0 \times 10^{-2} \text{ mol L}^{-1}$) KMnO_4 solution, and the solution was diluted to the final volume with deionized water. After 30 min., the absorbance was measured at 610 nm against reagent blank treated similarly.

Fig. 1 Absorption spectra of 0.5 ml (1×10^{-3} mol L $^{-1}$) Sunset Yellow E110 in water at 25 °C at different pH values: (1) 0.52, (2) 2.29, (3) 3.95, (4) 5.19, (5) 6.03, (6) 7.12, (7) 8.78, (8) 10.55, (9) 11.43, (10) 11.85, (11) 12.10, (12) 12.29, (13) 12.54, (14) 12.63, (15) 12.72, (16) 12.79, (17) 12.85, (18) 13.49



Interference

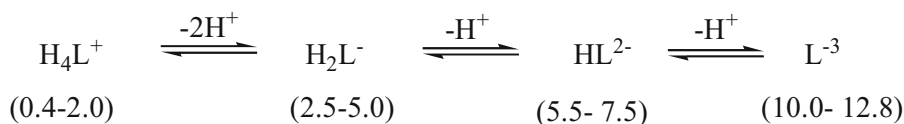
To assess the usefulness of these methods (I, II), the effect of foreign ions which often interfere determinations was studied under optimum conditions. Samples were prepared by mixing 22.619 μg of Sunset Yellow (method I) or (45.238 μg in case of method II) with various amounts of common matrix cations, anions, Tartrazin E102, Ponceau 4R E124, Tropadine 000, L-ascorbic acid, and Allura red Ac.

The procedure was continued as described under general procedures.

Results and Discussion

Acid-Based Equilibria of Sunset Yellow Dye E110

The absorption spectra of 0.5 ml from Sunset Yellow E110 (1×10^{-3} mol L $^{-1}$) in water at $I = 0.1$ mol L $^{-1}$ (NaClO $_4$) 25 °C were recorded at various pH values. The food additive Sunset Yellow displayed three bands within all the pH range of (0.4–12.8) exhibiting the absorption maximum at 335, 390, and 474 nm (Fig. 1). The different acid-based equilibria existing in solution of Sunset Yellow dye could be represented by the following equation:



The protonated acid form H_4L^+ at azo nitrogen ($-\text{N} = \text{N}-$) predominates in strongly acidic medium ($\text{pH} < 2.0$). The corresponding bands at λ_{max} 335, 474 nm disappear at $\text{pH} > 2.0$. The bands at 335, 390, and 474 nm are apparently due to the absorption by the mono-, di-, and tri-anions (HL^-), (HL^{2-}), and (L^{3-}) of Sunset Yellow, respectively.

The electronic spectra of Sunset Yellow at pH (5.5–7.5), it exhibits a double-headed band at λ_{max} (470–490) nm related to tautomeric equilibria of dianionic form of food additive salt (Scheme 1).

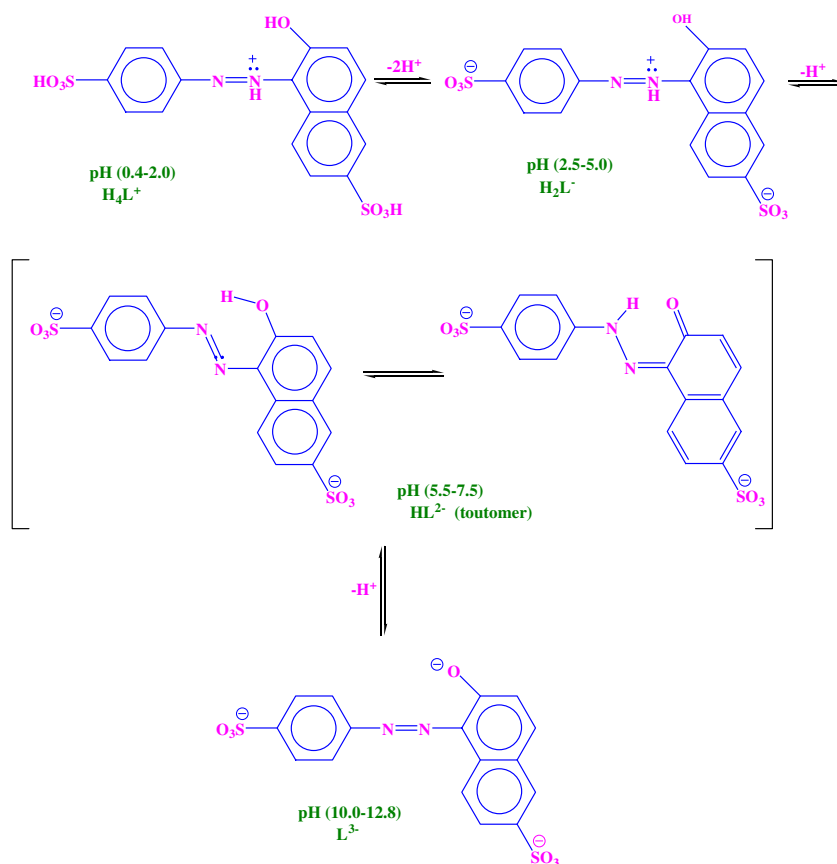
So, by increasing the pH 's in strongly alkaline media ($\text{pH} < 10.6$), the form (HL^{2-}) transferred to tri-anion form (L^{3-}) at λ_{max} 474 nm. The proton dissociation constant of Sunset Yellow dye in aqueous media $I = 0.1$ mol L $^{-1}$ at 25 °C was evaluated from the individual regions of the absorbance-pH curves by graphical analysis. The principles

of the graphical treatment of data have been given elsewhere (ICH Q2 (R1) 2005; Sommer et al. 1970; Rosstti and Rossotti 1961). Under our experimental conditions, the calculated pK_a values of Sunset Yellow dye are 6.1 ± 0.01 and 11.8 ± 0.09 .

Absorption Spectra of Sunset Yellow E110 Reaction Products

The dye Sunset Yellow E110 reacts with Cu (II) in water to produce a complex in the pH range (5.0–9.5). Absorption spectra were recorded over the wavelength range 250–600 nm. (Cu (I)-L) complex shows a sharp band at $\lambda = 350$ nm Fig. 2a. Under the same conditions, the metal ion has no absorbance over the 250–600 nm. All measurements were performed against a reagent blank. Sunset Yellow does not absorb at the given pH 's and wavelengths

Scheme 1 Tautomeric and acid-based equilibrium for Sunset Yellow



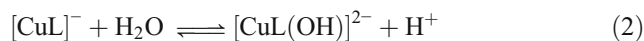
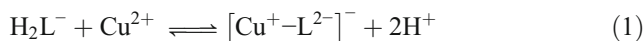
range for complex. Figure 2b shows the spectrum obtained for the alkaline potassium permanganate solution (maximum at 530 nm). With the addition of Sunset Yellow dye, the solution produced a maximum at 610 nm, previously indicative of the green-colored species of Mn(VI). This band may be attributed to the formation of manganate ion as a result of the oxidation of Sunset Yellow dye with $KMnO_4$ in alkaline medium.

Complexation Equilibrium of Sunset Yellow Dye with Cu (II)

The complexation equilibrium of Cu (II) with Sunset Yellow was recorded in aqueous medium in the pH range 4.5–12.8. The absorption spectra of solutions were recorded in the presence of an excess of the metal ion and in equimolar solution. The solution spectra reflected the formation of one complex species with λ_{max} at 350 nm and the existence of one chelate equilibrium in the pH range 4.8–9.5. All the absorbance versus pH graphs exhibit a similarly shaped descending branch above pH 9.5 which is due to the hydrolysis of the complexed ligand (Fig. 3). So, the absorbance versus pH graphs for copper-Sunset Yellow were interpreted using relations derived earlier

by Sommer et al. (1970), Elham et al. (Hashem et al. 2003, 2010; Hashem and Youssef 2013).

By considering the values of the dissociated constants of Sunset Yellow under our experimental conditions, we can assume that the (mono-anionic form H_2L^-) of the dye is the prevalent ligand species in the pH range of complexation, and the complex forming equilibrium which exists at pH 4.8–9.5 probably represents interaction of Cu(II) with Sunset Yellow according to the following equations:



The analysis of the ascending parts of solutions containing an equimolar and excess of metal gives the best fit for equilibrium (1) and the formation of $[CuL]^-$ complex species. The ascending part of the absorbance-pH species for equimolar solutions was analyzed using equation (3).

$$\log \left[\frac{\Delta A}{(\varepsilon_1 C_L - \Delta A)^2} \right] = qpH - \log(\varepsilon_{complex} - \varepsilon_{dye}) + \log K^* \quad (3)$$

Fig. 2 a Absorption spectra of Sunset Yellow-Cu(II), pH = 9, $I = 0.1 \text{ mol L}^{-1} (\text{NaClO}_4)$; 25°C (1) 2 ml Cu(II) $1 \times 10^{-3} \text{ mol L}^{-1}$ (2) 0.5 ml (Sunset Yellow) $5 \times 10^{-4} \text{ mol L}^{-1}$ (3) 1:1SnY-Cu complex; [Sunset Yellow] = [Cu(II)] = $1 \times 10^{-3} \text{ mol L}^{-1}$. **b** Absorption spectra of SunsetYellow-KMnO₄ reaction (in alkaline medium) (1) 1 ml Sunset Yellow (in 1 mol L^{-1} NaOH) ($1 \times 10^{-3} \text{ mol L}^{-1}$) (2) alkaline KMnO₄ ($1 \times 10^{-2} \text{ mol L}^{-1}$) (3) Sunset Yellow-KMnO₄ reaction products [Sunset Yellow] = $1 \times 10^{-3} \text{ mol L}^{-1}$, [KMnO₄] = $1 \times 10^{-2} \text{ mol L}^{-1}$, 3 ml [NaOH] 1 mol L^{-1}

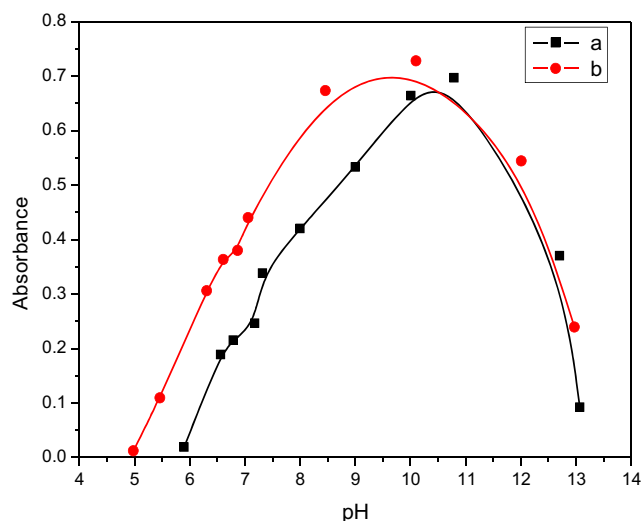
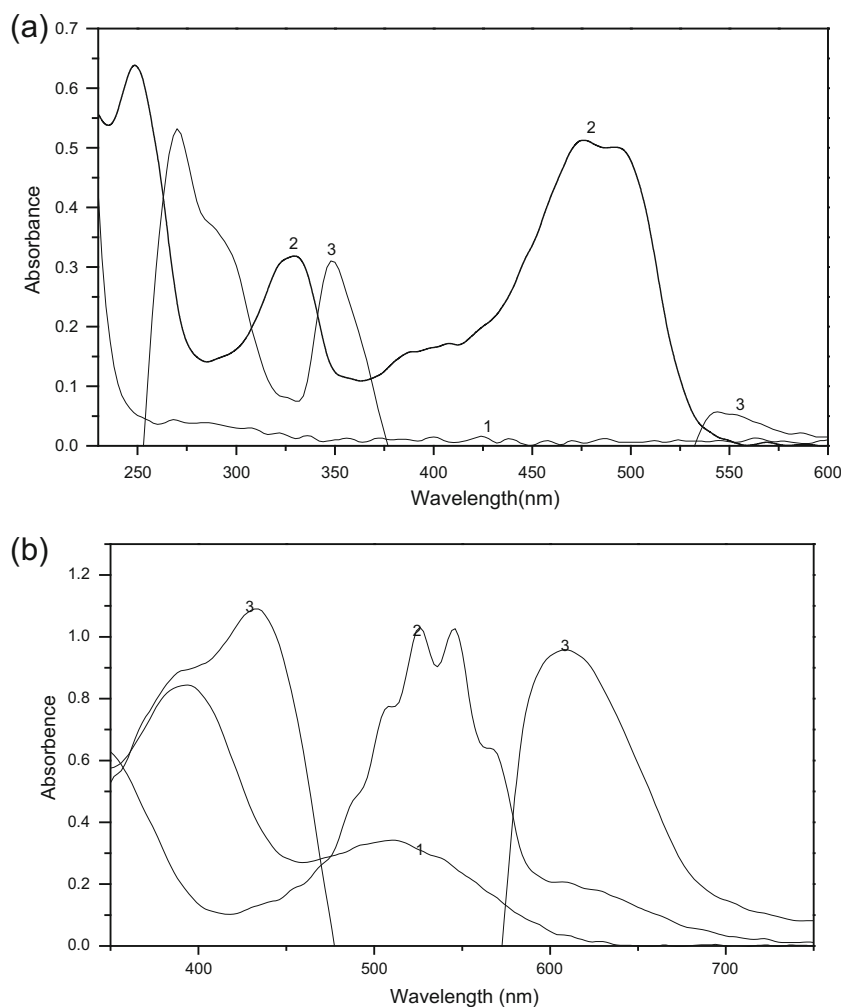


Fig. 3 Absorption versus pH for Cu(II)-SunsetYellow system, $I = 0.1 \text{ mol L}^{-1} (\text{NaClO}_4)$, 25°C . **a** $[C_L] = [C_M] = 1 \times 10^{-4} \text{ mol L}^{-1}$ at $\lambda 350 \text{ nm}$. **b** (2:1), $[C_M] = 2 \times 10^{-4} \text{ mol L}^{-1}$, $[C_L] = 1 \times 10^{-4} \text{ mol L}^{-1}$, at 350 nm

For solutions containing excess of metal ion, the following equation (4) is applied:

$$\log[\Delta A / (\varepsilon_1 C_M - \Delta A)] = qpH + \log C_M + \log K^* \quad (4)$$

The transformations (3) and (4) were found to be linear with a slope $q = 2$, indicating the release of two protons during complexation of copper with Sunset Yellow dye in the pH range of study. The calculated values of equilibrium constant and stability constants of [Cu(II)—Sunset Yellow] complexes are given in Table 1.

Optimization of Reaction Conditions

Method (I) Complexation with Cu(II)

In order to optimize the conditions, we have investigated a number of parameters such as pH, effect of metal ion, and effect of time as shown in Fig. 4.

Table 1 Mean values of equilibrium ($\log K_{\text{eq}}$), stability constants ($\log \beta$), and molar absorptivity (ϵ) of Cu(II)-Sunset Yellow complex, $I = 0.1 \text{ M NaClO}_4$, 25°C

Equilibrium ^a	Constant	Log constant	Molar absorptivity (ϵ) $\text{L mol}^{-1} \text{ Cm}^{-1}$
$[\text{Cu}^{2+}][\text{H}_2\text{L}^-] \rightleftharpoons [\text{CuL}^-][\text{H}^+]^2$	K_{eq}	$(-9.680 \pm 0.01)^{\text{b}}$ $(-9.651 \pm 0.02)^{\text{c}}$	$\epsilon = 1 \times 10^4$
$[\text{CuL}^-] \rightleftharpoons [\text{Cu}^{2+}][\text{L}^-]$	β	$(27.560 \pm 0.01)^{\text{d}}$	

^a Changes are omitted. Values are taken as average for various component concentrations $I = 0.1 \text{ M}$ (NaClO_4), at 25°C

^b From the absorbance versus pH graphs for solutions with equimolar concentrations

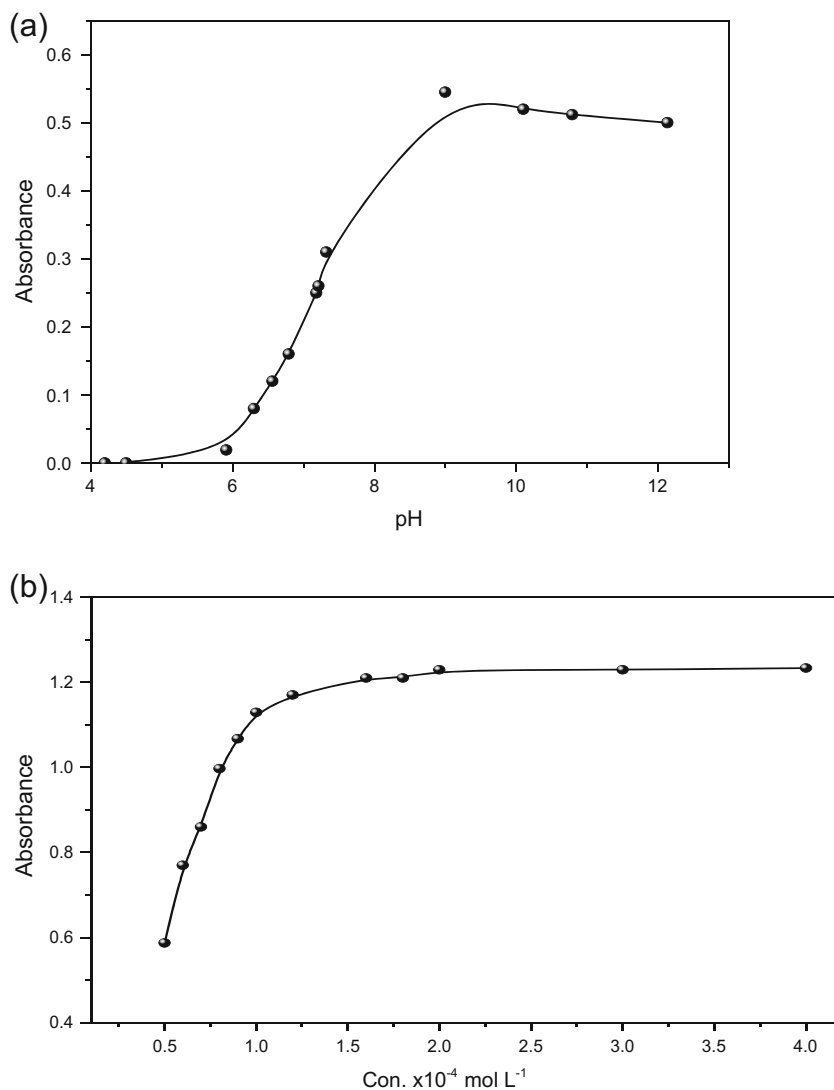
^c From the absorbance versus pH graphs for solutions with excess metal

^d $\log B = \log K^* + \text{pk}_2$

Effect of pH With other conditions fixed the effect of the pH on absorbance of Cu (II)-Sunset Yellow complex at λ_{max} 350 nm investigated from pH range (0.4–12.8). Fig. 4a shows that the optimum pH achieved at 9.0.

Effect of Metal Ion At optimum conditions, the effect of the volume of metal ion Cu(II) $1 \times 10^{-3} \text{ mol L}^{-1}$ on the absorbance of the complex was studied in the range of 0.5–4.0 ml at 25°C . It is clear from Fig. 4b that the absorbance individually increases with the increase of Cu (II) metal ion volume and

Fig. 4 a Absorption versus pH for Cu(II)-Sunset Yellow complexes, $I = 0.1 \text{ mol L}^{-1}$ (NaClO_4), 25°C , pH = (1) 5.90; (2) 6.44; (3) 6.56; (4) 6.79, (5) 7.18; (6) 7.32; (7) 8.00, (8) 9.00; (9) 10.01; (10) 10.7; (11) 11.53; (12) 12.12. **b** Variation of concentration of metal ion Cu(II) $1.0 \times 10^{-4} \text{ mol L}^{-1}$, $I = 0.1 \text{ mol L}^{-1}$, 25°C , $\lambda = 350 \text{ nm}$, pH = (1) 9.0 $[\text{Cu(II)}] = 0.5 \times 10^{-4}$, (2) 0.6×10^{-4} , (3) 0.7×10^{-4} , (4) 0.8×10^{-4} , (5) 0.9×10^{-4} , (6) 1×10^{-4} , (7) 1.2×10^{-4} , (8) 1.6×10^{-4} , (9) 1.8×10^{-4} , (10) 2×10^{-4} , (11) 3×10^{-4} , (12) $4 \times 10^{-4} \text{ mol L}^{-1}$



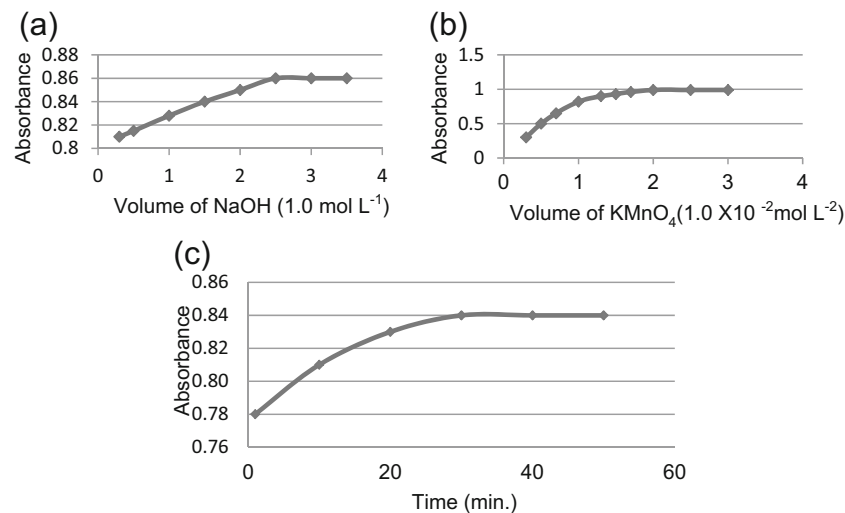


Fig. 5 Reaction conditions for oxidation reaction of Sunset Yellow with alkaline KMnO₄ at 25 °C. **a** Effect of NaOH (1.0 mol L⁻¹) (by volume), [Sunset Yellow] = 45.237 μg ml⁻¹, [KMnO₄] = 2 × 10⁻³ mol L⁻¹ at λ_{max} = 610 nm, t = 30 min. **b** Effect of KMnO₄ (1.0 × 10⁻² mol L⁻¹)

(by volume), [Sunset Yellow] = 45.237 μg ml⁻¹, [NaOH] = 0.25 mol L⁻¹ at λ_{max} = 610 nm, t = 30 min. **c** Effect of time, [Sunset Yellow] = 45.237 μg ml⁻¹, [NaOH] = 0.25 mol L⁻¹, [KMnO₄] = 2 × 10⁻³ mol L⁻¹ at λ_{max} = 610 nm

become constant at 1.5 ml. Further addition of reagents does not change the absorbance.

Effect of Time Under optimum conditions, the reaction time was determined by following the absorbance of the complex at different time intervals. Complete complex formation was attained after 30 min.

Method (II) KMnO₄ Oxidation

Potassium permanganate has been used as a strong oxidizing agent in the determination of many pharmaceutical compounds (Hassan and Belal 2002a; Rahman et al. 2004; Saleh et al. 2015).

Sunset Yellow dye reacts with KMnO₄ in strongly alkaline medium producing green manganite at λ_{max} = 610 nm (Fig. 2b). During the current study, the produced color intensity increased gradually with time to reach maximum after 30 min and was stable for at least 24 h. The factors affecting the formation of manganite ions were optimized.

Effect of NaOH Fig. 5a shows the effect of varying NaOH concentration upon the reaction of the Sunset Yellow dye with KMnO₄. The maximum absorption was attained using 2.0 ml of 1 M NaOH with no significant changes appeared after the volume was increased. Consequently, 2.5 ml of 1 M NaOH was used as an optimum value for the reaction mixture.

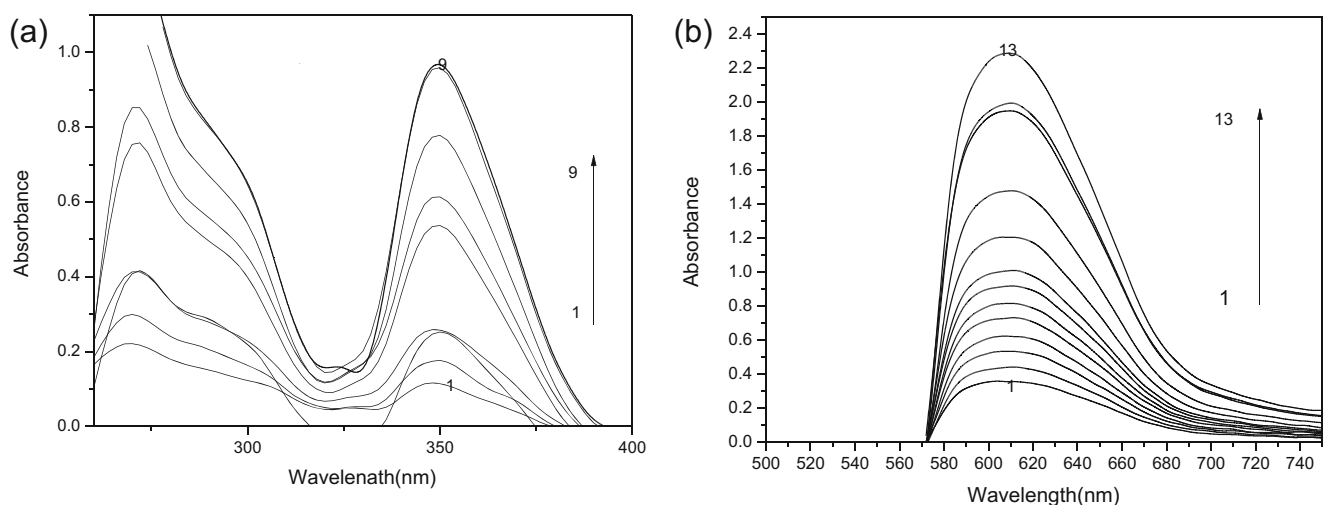


Fig. 6 a Absorption spectra of Sunset Yellow-Cu(II) complex, in water, pH = 8.8, I = 0.1 mol L⁻¹ NaClO₄; Sunset Yellow concentration range (1) 2 × 10⁻⁵ mol L⁻¹ to 15 × 10⁻⁵ mol L⁻¹ (12) with regular successive additions in presence of 1 ml (1 × 10⁻³ mol L⁻¹) CuCl₂·2H₂O at 25 °C.

b Absorption spectra of Sunset Yellow-KMnO₄ oxidation reaction in alkaline medium, Sunset Yellow concentration range 0.3 × 10⁻⁴–2.7 × 10⁻⁴ mol L⁻¹ with regular successive additions in presence of 2 ml (1 × 10⁻² mol L⁻¹) KMnO₄, 2.5 ml (mol L⁻¹) NaOH at 25 °C

Table 2 Summary of optical and regression characteristics of the proposed methods (I) and (II) for determination of Sunset Yellow E110

Method Parameter	Cu (II)	KMnO ₄
Color	–	Green
λ_{\max} , nm	350	610
Beer's low limits ($\mu\text{g ml}^{-1}$)	9.05–67.87	13.57–72.38
Ringbom limits ($\mu\text{g ml}^{-1}$)	15.85–56.23	12.95–61.66
Sandell's sensitivity ($\mu\text{g Cm}^{-2}$)	0.0808	0.0452
Molar absorptivity $\text{L mol}^{-1} \text{Cm}^{-1}$	0.5×10^4	1×10^4
Regression equation $A = a + bc$	$A = 0.01203C - 2.178 \times 10^{-3}$	$A = 0.0212C + 0.0488$
Slope (b)	0.01203	0.0212
Intercept (a)	-0.002.178	0.0488
Correlation coefficient (<i>r</i>)	0.9999	1.0030
Limit of directional (LOD) ($\mu\text{g ml}^{-1}$)	0.4334	0.6176
Limit of quantification (LOQ) ($\mu\text{g ml}^{-1}$)	1.3134	1.8716

Effect of KMnO₄ The effect of varying concentration of potassium permanganate upon the rate of reaction is depicted in Fig. 5b. The results show that maximum absorbance was obtained using 1.5 ml of 1×10^{-2} mol L⁻¹ KMnO₄. Thus, the 2.0 ml 1×10^{-2} mol L⁻¹ KMnO₄ in the final solution was appropriate to achieve maximum color development.

Effect of Time During the current study, the produced color intensity increased gradually with time to reach a maximum after 30 min and was stable for at least 24 h (Fig. 5c).

Stoichiometry of the Reactions in Methods (I) and (II)

The stoichiometry for the reaction of Sunset Yellow with Cu(II) or KMnO₄ was determined using Job's continuous variation method (Hassan and Belal 2002b). In solution having

$C_o = C_M + C_L = 6.0 \times 10^{-4}$ mol L⁻¹ at pH 9.0. The plot of absorbance at 350 and 610 nm versus mole fraction of reagent Cu(II) or KMnO₄ respectively shows a maximum at 0.5 for Cu(II) suggesting the formation of 1:1 (dye: M) complex and a maximum at 0.66 revealing the formation of 1:2 (dye: KMnO₄).

Quantification

Validation of the Proposed Methods

At the optimum conditions, the absorbance of the reaction solution containing varying amounts of additive dye was measured and calibration plots for absorbance versus dye concentration curves for the two proposed methods obey Beer's Law over the concentration ranges of (9.05–67.86) and (13.57–72.38) $\mu\text{g ml}^{-1}$ at λ_{\max} 350 and 610 nm,

Table 3 Evaluation of the accuracy and precision of the proposed methods for determination of Sunset Yellow E110 Dye

Method/Reagent	Amount $\mu\text{g ml}^{-1}$		RSD %	Recovery %	Mean recovery %
	Taken	Found ^a D			
Cu(II)					
Intraday assay	11.31	10.63 ± 0.03	0.28	93.988	102.40
	22.62	23.08 ± 0.08	0.36	102.034	
	33.93	37.75 ± 0.12	0.32	111.258	
Interday assay	11.31	10.49 ± 0.02	0.19	92.750	96.72
	22.62	21.59 ± 0.05	0.23	95.447	
	33.93	34.60 ± 0.09	0.26	101.975	
KMnO ₄					
Intraday assay	22.62	21.18 ± 0.07	0.33	98.05	97.98
	31.67	30.67 ± 0.11	0.36	96.84	
	45.24	44.82 ± 0.13	0.29	99.07	
Interday assay	22.62	21.75 ± 0.04	0.18	96.15	96.99
	31.67	30.43 ± 0.08	0.26	96.08	
	45.24	44.68 ± 0.10	0.22	98.76	

^a Mean for 5 independent analysis

respectively, Fig. 6a, b. The regression equation, correlation coefficients, limit of detection, limit of quantification, and molar absorptivity were also calculated and provided in Table 2.

Accuracy and Precision (Intraday and Interday)

The accuracy and precision of the proposed spectrophotometric methods with (CuCl₂·2H₂O and KMnO₄) were determined at three concentration levels of Sunset Yellow dye by analyzing five replicate samples of each concentrations. The relative standard deviation (RSD %) obtained for the analytical results did not exceed 2 % (Table 3) which proved a high reproducibility of the results and precision of the methods. The good level of precision was suitable for quality control analysis of Sunset Yellow in food samples. Under optimum conditions, the intraday precision assay was carried out for all procedures used through replicate analysis ($n = 5$) for Sunset Yellow corresponding to 10.63, 23.08, and 37.75 $\mu\text{g ml}^{-1}$ for (method I) and 21.18, 30.67, and 44.82 $\mu\text{g ml}^{-1}$ for (method II).

The interday precision was also evaluated through replicate analysis of the pure sample for three consecutive days at the same concentration levels as used in within day precision. The results of these assays are reported in (Table 3). The (RSD %) and recovery values for intraday and interday precision were in the range 0.18–0.36 % and 92.75–111.25 %, respectively.

Analytical Recovery and Interference Liabilities (Specificity)

The accuracy of the proposed methods was also checked by performing recovery experiments using a standard addition method (Job 1928). Known amounts of pure Sunset Yellow

Table 4 Recovery of Sunset Yellow in presence of different matrices and diverse ions

Ions and matrix	Recovery %	
	Cu(II)	KMnO ₄
Diverse ions		
Li ⁺ , Na ⁺ , K ⁺ , NH ₄ ⁺	96.83 ± 0.03	96.69 ± 0.09
Ca ²⁺ , Ba ²⁺ , Mg ²⁺ , Co ²⁺	99.08 ± 0.08	99.38 ± 0.06
Ni ²⁺ , Zn ²⁺ , Sr ²⁺	93.85 ± 0.12	93.95 ± 0.21
SO ₄ ²⁻ , NO ₃ ⁻ , Cl ⁻	97.79 ± 0.06	97.39 ± 0.05
Matrix		
Tartrazine E102	101.905 ± 0.02	101.087 ± 0.09
Ponceau 4R E124	97.58 ± 0.08	97.52 ± 0.06
Tropadine 000	96.84 ± 0.03	96.79 ± 0.09
L-Ascorbic acid	94.94 ± 0.05	94.73 ± 0.08
Allura red Ac	95.43 ± 0.02	95.87 ± 0.03

Table 5 Statistical analysis of results obtained by the proposed method (I) for Sunset Yellow E110 in commercial food samples applying the standard addition technique

Commercial samples	Present $\mu\text{g ml}^{-1}$	Added $\mu\text{g ml}^{-1}$	Found	Recovery %	Mean	RSD %
The original carmelle ^a	0.9047	11.309	11.309	99.20	99.13	0.27
		15.833	16.511	98.65		
		20.874	20.357	99.56		
Custard powder ^a	1.58333	11.309	12.892	99.34	99.56	0.16
		15.833	16.738	96.10		
		20.357	22.619	103.26		
Tang Mango ^b	1.35714	11.309	12.214	69.64	99.39	0.41
		15.833	16.738	97.37		
		20.357	21.619	104.16		
Tang Mango delights flavor ^b	2.7142	11.309	13.571	96.77	98.76	0.44
		15.833	18.095	97.56		
		20.357	23.523	101.96		
Jelly Mango ^b	1.58333	11.309	12.214	94.47	99.45	0.33
		15.833	18.095	103.89		
		20.357	20.357	100.00		
Jelly Orange ^a	2.2619	11.309	13.116	96.63	98.04	0.30
		15.833	17.64	97.50		
		20.357	22.619	100.00		
Jelly Apricot ^b	3.6190	11.309	14.476	96.97	103.06	0.41
		15.833	20.357	104.65		
		20.350	25.785	107.57		

^a Manufactured by Hassani Food Industries P.O. Box: 286, Dubai, United Arab Emirates for Kerry Foods Ltd., Thorpe Lea Manor, Thorpe Lea Road, Egham, Surrey, TW20 8HY, England

^b Made in Egypt for Mondelez Egypt Foods S.A.E. (Formerly Kraft Foods Egypt S.A.E.) First Industrial lane A1 10th of Ramada by Holw El Sham Co. 6th of October. Egypt

dye were added to different matrix and then determined by the recommended procedures. Determination of Sunset Yellow was possible in the presence of cations and anions such as Li⁺, Na⁺, K⁺, NH₄⁺, Ca²⁺, Sr²⁺, Ba²⁺, Mg²⁺, Co²⁺, Ni²⁺, Zn²⁺, SO₄²⁻, NO₃⁻, and Cl⁻. The obtained mean recoveries are ranged between 94.98 and 101.90 %, respectively, as shown in Table 4.

Also, Sunset Yellow was possible determine in the presence of 5.343 μg Tartrazine (E102), 6.044 μg Ponceau 4R (E124), 3.503 μg Tropaeolin 000, 4.964 μg , Allura red Ac, and 1.761 μg L-ascorbic acid. The results in (Table 4) proved the accuracy of the proposed methods in absence of interference from common matrix.

Limit of Detection (LOD) and Limit of Quantification (LOQ)

Limit of detection (LOD) and limit of Quantification (LOQ) define the sensitivity of the method. LOD and LOQ were

calculated (Darwish 2005), according to ICHQ₂ recommendation (Sarka et al. 2010) from the following equations:

$$\text{LOD} = 3.3\delta/\text{slope}$$

$$\text{LOQ} = 10 \delta/\text{slope}$$

where δ is the standard deviation of the intercept of regression line and the slope of calibration. LOD was found to be 0.4334, 0.6176 $\mu\text{g ml}^{-1}$, while LOQ was found to be 1.313, 1.871 $\mu\text{g ml}^{-1}$ for the two methods, respectively. The small values of LOD and LOQ indicated high sensitivity Table 2.

Application to Commercial Food Samples

To confirm the usefulness of the proposed two methods, Sunset Yellow has been determined in seven different kinds of commercial food samples (the original carmelle, tange mango, mango delights flavor, Jelly mange, Jelly orange, Jelly apricot, and custard powder). The two proposed spectrophotometric methods were successfully tested without any interference from different matrix in commercial food samples. The standard addition method was applied for our proposed methods. Known amounts of the standard Sunset Yellow were added to reanalyzed additive dye containing foods samples and determined by the recommended procedure. The concentration of additive dye was calculated from the corresponding regression equation, and the recoveries were found to be higher than 95 % (Table 5).

Conclusion

The work evidenced that the proposed spectrophotometric methods were found to be simple, selective, economical, rapid, and sensitive compared with other available spectrophotometric methods for the analysis of the additive dye Sunset Yellow. The statistical parameters and recovery study data clearly indicated the reproducibility and accuracy of the proposed methods in the range of the determination. Analysis of the different seven confectionery food samples containing Sunset Yellow E110 dye showed no interference from the common matrix. Hence, the present work seemed to be very suitable for the analysis of Sunset Yellow E110 dye in commercial food samples within the safe recommended limits.

Compliance with Ethical Standards

Funding Assuit University, Faculty of Science

Conflict Interest Elham Y. Hashem declares that she has no conflict of interest. Magda S. Saleh declares that she has no conflict of interest. Najat O. A. Al-Salahi declares that she has no conflict of interest. Ahmed K. Youssef declares that he has no conflict of interest.

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