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A sensitive procedure for the rapid electrochemical determination of Eosin-Y dye using voltammetric techniques onto a mercury electrode surface

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Abstract

A sensitive adsorptive stripping procedure (square wave adsorptive stripping voltammetry), was developed to study the adsorption property of Eosin-Y dye on a working electrode (HMDE) and its determination in selected samples. In addition, differential pulse polarographic and cyclic voltammetric methods were used to evaluate the electrochemical preliminary studies of Eosin-Y dye. By means of using the adsorptive stripping voltammetric method, a sensitive approach for the quantitative electro-analysis of this dye was achieved. A well-developed voltammetric peak probably related to the cathodic reduction of carbonyl group was obtained in pH (5) acetate buffer at -550 mV. An irreversibility nature of the reduction process was confirmed by use cyclic voltammetric technique. The adsorptive stripping current was evaluated with respect to various experimental conditions and the optimal values estimated at electrolyte (acetate buffer), pH (5), 30 s accumulation time, 0.0 V accumulation potential, 400 mVs^{-1} scan rate, 80 mV pulse amplitude and 60 Hz square wave frequency. Adsorptive stripping voltammetric peak showed a linear response for Eosin-Y in the concentration range from 5.0×10^{-8} to 5.0×10^{-7} mol L^{-1} (r = 0.99). A limit of detection of 8.73×10^{-10} mol L^{-1} (0.566 ppb) with 0.64 RSD% and average recovery of 107%±1.6 SD; were achieved. Possible interferences with several dyes such as food additive azo dyes (E110, E102) and amaranth, and some metals such as Cu^{+2} and Zn^{+2} were also examined. The developed electrochemical procedure was successfully used for the recovery of Eosin-Y dye in commercially available dirt remover and sea water.

Keywords: Hanging mercury drop electrode, Adsorptive stripping voltammetry, square wave voltammetry, Eosin-Y dye.

1. Introduction

Differential pulse polarography (DDP) is an useful technique for determination of trace levels of organic and inorganic species. In the polarographic technique, fixed magnitude pulses are applied to the working electrode at a time just before the end of the drop. The greater sensitivity of DDP can be attributed to two sources. The first is an enhancement of the faradic current; the second is a decrease in the nonfaradic charging current. On the other hand, the cyclic voltammetric (CV) method is the most widely used for obtaining a qualitative information about electrochemical reactions. The power of cyclic voltammetric results from its ability to rapidly provide considerable information on the thermodynamics of redox processes and the kinetics of heterogeneous electron transfer reactions, and on coupled chemical reactions or adsorption processes[1,2].

Square wave adsorptive stripping voltammetric technique (SW-AdSV) has been considered higher sensitive than other electrochemical methods since half a century ago. This electrochemical technique was applied to develop the sensitivity and the selectivity for analytical measurements of ultratrace determinations of organic and inorganic compounds. The advantages of square wave adsorptive stripping voltammetry are appeared at enhancement of detection, speed of analysis and freedom from sensitivity of dissolved oxygen in the analysed materials compared to other voltammetric techniques [3-5].

The quantitative determination at trace levels of synthetic dyes used as a fibres stained is currently an important analytical task, because of the need to eliminate possible exposure of consumers to over-dosage. Similarly, the potential carcinogenic effects of dye compounds and products of their decomposition create an intense need for a systematic examination of these samples. Hence, a variety of analytical methods for dyes determination have been reported [6,7]. Although dyes most often analysed by spectrophotometric and/or chromatographic methods, however, there are many references to electrochemical monitoring of these species. In fact, Fogg and his colleagues have reviewed the utilization of stripping voltammetric techniques for the determination of several synthetic dyes [8, 9]. In addition, the stripping voltammetric properties of several food additive dyes such as Sunset Yellow (E-110) [10], Tartrazine (E-100) [11], Quinoline Yellow (E-104) [12], Amaranth (E-123) [13] Ponceau 4R (E-124) and Carmoisine (E-122) [14] were also investigated. Eosin is considered a fluorescent red dye which resulted from the action of bromine on flourescin. It can be used to stain cytoplasm, collagen and muscle fibers for examination under the microscope. IUPAC name of Eosin-Y is [2-(2,4,5,7-tetrabromo-6-oxido-3-oxo-3H-xanthen-9-yl)benzoate]. It has molecular structure $C_{20}H_8Br_4O_5$; 647.891 g/mol as shown in scheme 1[15].

Eosin-Y dye was determined in most researches that involved HPLC and HPLC-fluorescence [16,17], spectrophotometry spectral analysis and fluorescence method [18-21]. Due to the low content of these synthetic dyes in some commercial samples and sea water, a powerful electrochemical method was applied to improve the sensitivity and selectivity as needed. In comparison to other analytical procedures, the proposed stripping voltammetric method reduced the length of real time of determination since no pre-treatment steps were requested. Another advantage of this electroanalytical approach is its suitability to analysis very diluted samples, a simple and quick strategy to avoid matrix effect in dyes analysis. Yet no published researches were reported for the analysis of this dye using square-wave adsorptive stripping voltammetric method (SW-AdSV); as in the literature. Considering the above remarks, this work was devoted to a detailed study of the SW-AdSV behavior of this artificial coloring agent, in order to develop this electroanalytical technique for the determination of Eosin-Y in commercial product (varnish) and sea water sample.

2. Materials and methods

2.1. Materials

In 25 ml volumetric flask, a 1×10^{-2} mol L^{-1} Eosin-Y dye as stock solution; was prepared by dissolving of this dye in distilled water to be ready for further preparations. Supporting electrolytes such as Britton-Robinson buffer (pH ≈ 3) which containing boric acid, glacial acetic acid and phosphoric acid, phosphate supporting buffer (NaH_2PO_4 and H_3PO_4), acetate supporting buffer (sodium acetate and acetic acid) and carbonate buffer which containing sodium carbonate and sodium hydrogen carbonate; were prepared by dissolving them contents in 1000 ml distilled water [22].

2.2. Procedure

The general procedure was adopted for obtaining all voltammograms: a 10 ml of acetate supporting buffer at desired pH; was pipetted in a clean and dry voltammetric cell then the required standard solutions of Eosin-Y dye were added. The studied solutions were purged by nitrogen gas for 300 seconds with stirring. The applied accumulation potential was 0.0 V vs. Ag/AgCl reference electrode and Pt auxiliary electrode into surface of a new mercury drop as working electrode. Cathodic voltammetric scans were monitored over the range 0.0 to – 1200 mV and all electrochemical studies were done at 25^{o}C.

In order to apply the developed SW-AdSV method for the recovery of Eosin-Y in detergent sample (Varnish) and sea water. The of $3x10^{-3}$ mol L^{-1} of studied dye was diluted by 2 ml of samples to obtain $1x10^{-4}$ mol L^{-1} dye concentration. Then, a 2 $x10^{-7}$ mol L^{-1} of Eosin-Y was recovered after it has been spiked into a vanish sample and sea water in 10 ml acetate buffer pH 5, which was placed into the voltammetric cell and deoxygenated for 300 seconds. It was also measured five times by use $1.5x10^{-7}$ mol L^{-1} standard dye four times.

2.3. Methods

The differential pulse polarographic, cyclic voltammetric and SW-AdSV measurements were procedure by use 797 VA instrument (Swiss made) with Dell computer and controlled by computrace 2.0 software. The 797 VA mode includes three electrodes; the hanging mercury drop electrode (HMDE), silver/silver chloride reference electrode and platinum assistant electrode. The pH was controlled by the hanna instrument pH211(Romania manufactured) .

3. Results and Discussion

3.1. The electroanalytical properties of Eosin-Y dye

The DPP response of 1×10^{-5} molL^{-1} of Eosin-Y was investigated in pH = 5 acetate buffer, so a well cathodic signal at - 550 mV with noticeably intense peak current (254 nA) was observed as shown in figure 1. This voltammetric reduction peak is probably resulted from the cathodic reduction of the carbonyl electroactive group of the studied synthetic dye. It is well known that the cathodic reduction process of dye compounds containing electro-donating groups such as the carbonyl group (which is the case for Eosin-Y dye) is accompanied by a split of the C=O bond and the figuration of the corresponding alcohol, in acidic media[23] (see scheme 1).

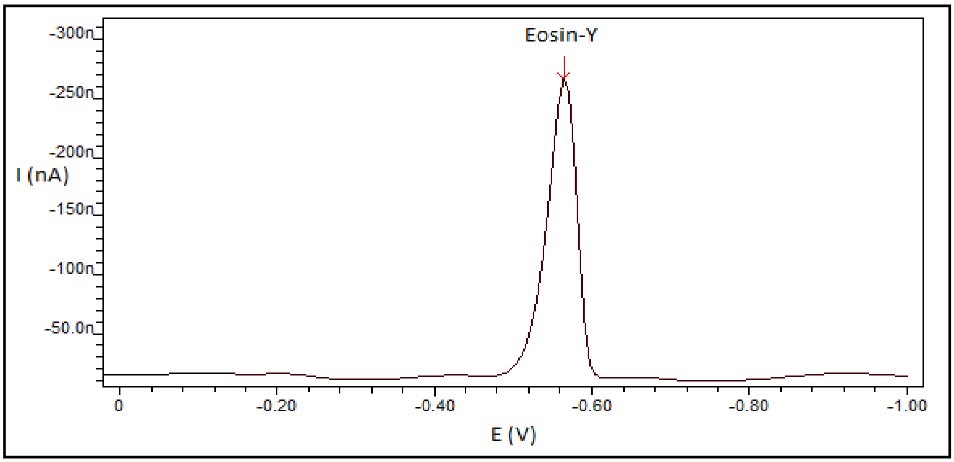
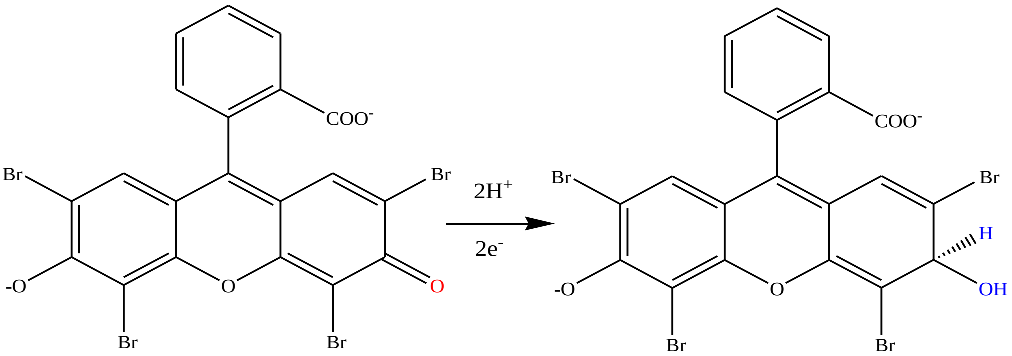


Figure 1. DPP signal of 1×10^{-5} mol L^{-1} Eosin-Y dye at acetate buffer pH = 5



Scheme1. The structure and the proposed mechanism of electrochemical reduction for Eosin-Y dye

The cyclic voltammetry approach was confirmed an irreversible reductive propriety for Eosin-Y dye. The anodic current wasn't observe as informed in CV figure 2 and as suggested in the electrochemical reduction mechanism.

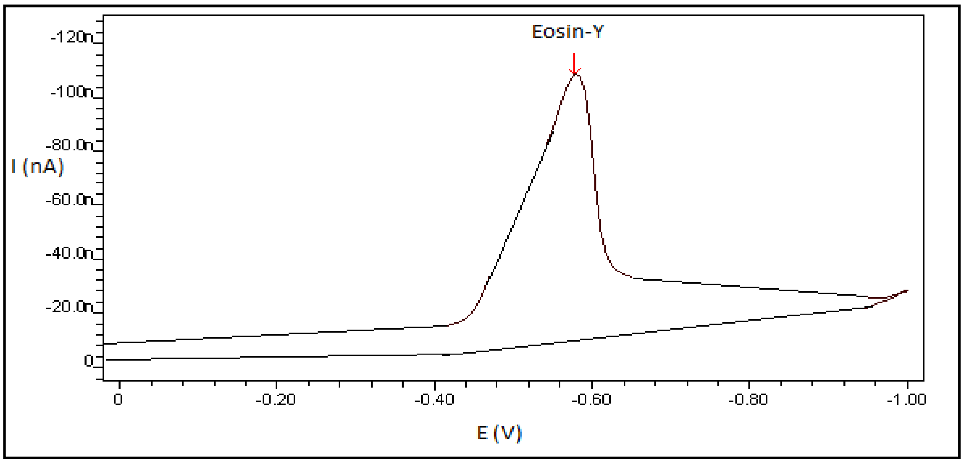


Figure 2. CV property of 1×10^{-5} mol L^{-1} Eosin-Y dye at acetate buffer pH=5

A 5×10^{-7} molL^{-1} Eosin-Y solution was monitored by SW-AdSV technique in pH=5 acetate buffer after a preconcentration step of 30 sec at 0.0 V, a well stripping voltammetric signal was obtained at -550 mV with 1160 nA peak current. Figure 3 represents a typical SW-AdSV voltammogram of Eosin-Y dye.

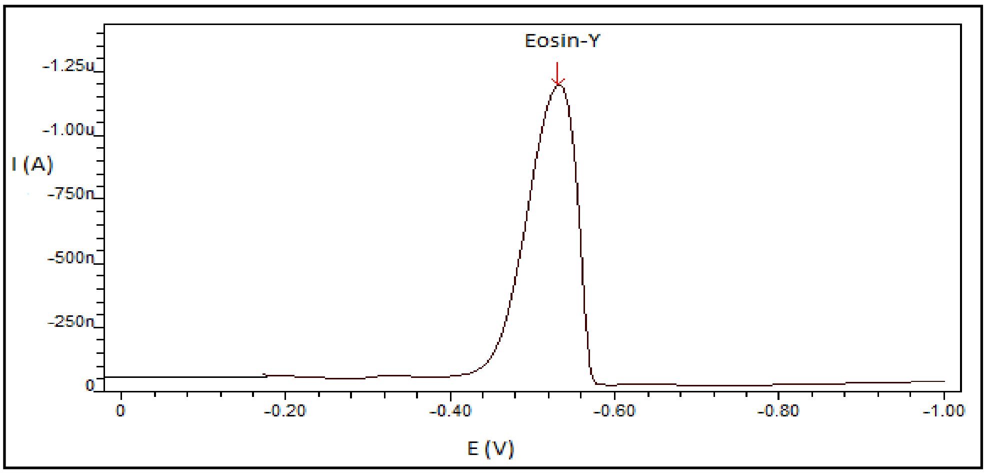


Figure 3. SWAdSV property of 5×10^{-7} mol L^{-1} of Eosin-Y at acetate buffer, pH=5, t_{acc}30 s, E_{acc} 0.0 V and 400 mV s^{-1}

3.2. Optimisation of experimental parameters

3.2.1. Buffer and pH Effects

There are many parameters which used for enhancement of sensitivity and selectivity for determination of Eosin-Y using voltammetric methods onto the surface of mercury electrodes. Several buffer solutions such as B-R, phosphate, acetate and carbonate were tested for obtaining high and sharp of voltammetric signals. According to the study of supporting electrolytes, the best electroanalytical signal in terms of voltammetric current value and shape of peak, was obtained by acetate buffer**.** So, The acetate buffer was selected as a optimized buffer for the further studies.

Generally, the SWAdSV response depends on the pH parameter, so in this study, the monitored voltammetric signal was observed only at acidic media. During measuring the stripping voltammetric peak current as a function of pH over the range 2.0 − 5.5 (figure 4), a steady increase of the peak current was observed, with a maximum at pH value of 5, then it decreased at higher pH values. This value (pH = 5) was selected as optimum pH choice for further investigation. On the other hand, it was observed that the potential of voltammetric peak potential of this dye shifted to lower potential values by nearly 100 mV when pH was varied from 2.0 to 6.5. According to the plot of Ep vs pH, slope value of 26 mV/pH was recorded, that is approximately close to the expected theoretical value of 30 mV/pH. Interestingly, this value indicates that E_p is pH dependent as expected for the reduction approach consuming two protons are involved in the process [24]. This result was supported the proposed mechanism of the electrochemical reduction of Eosin-Y as shown at scheme 1.

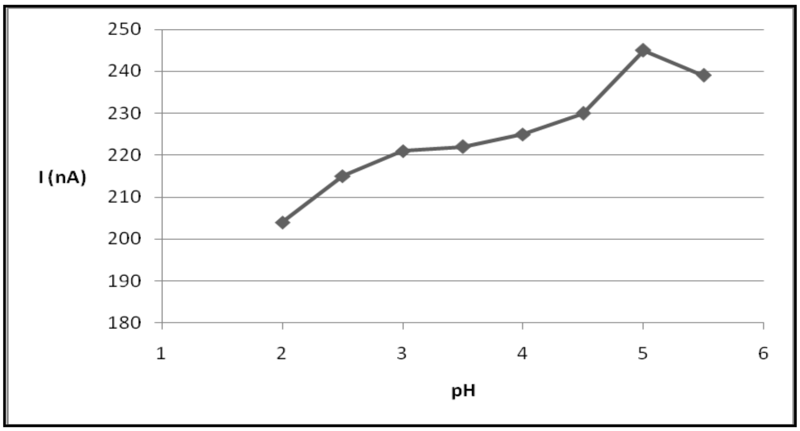


Figure 4. pH Effect on the voltammetric current of 5×10^{-7} mol L^{-1} of Eosin-Y at acetate buffer

3.2.2. Effect of accumulation factors

The deposition of Eosin-Y on the mercury electrode surface depends on many experimental conditions, worth of additional realizations to enclose high sensitive detection for this dye. Therefore, the effect of accumulation time on the voltammetric current of the collection of 5×10^{-7} mol L^{-1} Eosin-Y was evaluated in the range of 0.0-180 s. The resulting peak current-accumulation time ($Ip\text{-}T_{acc}$) profile is depicted in Figure 5, a steadily enhancement of intensity in the peak current was observed over the range 0.0-30 s, followed by an increase upto 40 s, however, the shape of peak became broad and not be suitable. So, 30 s t_{acc} was selected for all the future experiments. Furthermore, variation of the accumulation potential (E_{acc}) over the range from -800 to + 200 mV at 30 s t_{acc}, revealed that a preconcentration potential of 0.0 V was the ideal choice for optimal sensitivity. The voltammetric current was increased after this value followed by a change in the broadness and peak's shape.

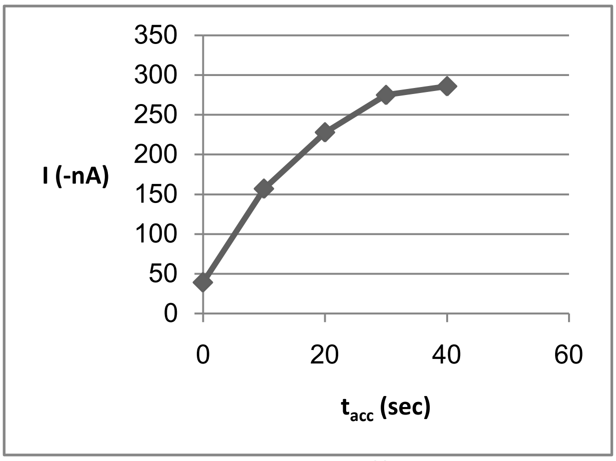


Figure 5. Accumulation time effect on the stripping voltammetric current of 5×10^{-7} mol L^{-1} Eosin-Y at acetate buffer; pH = 5

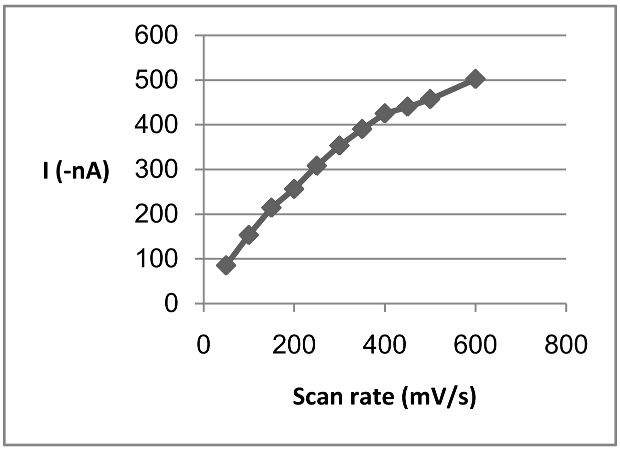


Figure 6. Scan rate Effect on the stripping voltammetric current of 5×10^{-7} mol L^{-1} Eosin-Y at acetate buffer; pH = 5, 30 sec t_{acc} and 0.0V E_{acc}

3.2.3. Effect of potential sweep parameters

The relationship between the measured current and scan rate was studied over 50-600 mV s^{-1} as illustrated in figure 6. Yielding, when scan rates faster than 400 mV s^{-1} were employed, the current was been overlap and became not suitable for voltammetric analysis. Consequently, 400 mV/s would be adequate optimum for the following studies.

In addition, the effect of pulse amplitude on the voltammetric current intensity was also evaluated. It was studied over the range 10-100 mV, yielded, the voltammetric current was gone up to maximum value with 80 mV. This pulse amplitude value was chosen and fixed for the operational conditions. Concerning the effect of square wave frequency's values on the measured voltammetric signal; the variation of this parameter over the range 10-100 Hz, resulting the voltammetric peak particularly over the range 10-60 Hz was had high current, while the increase up this range would led to a split of the peak and to its unsuitability for our studies. So, a 60 Hz SW frequency was selected for the future work.

3.2.4. Effect of other instrumental variables

The influence of other operating parameters such as the drop size of the working electrode (HMDE) and the convection rate on the voltammetric response for the studied dye (Eosin-Y) was additionally checked. As expected, a linear enhancement for the electrochemical peak intensity was observed when the surface area of HMDE was increased over the range 0.15-0.6 mm^2 as shown in figure 7. On the other hand, the SW-AdSV signal can be maximized further by increasing the stirring rate of the rotating rod over the range 0.0-3000 round per minute. Accordingly, 0.6 mm^2 drop size and 3000 rpm stirring speed were selected for future measurements.

In conclusion, for electroanalytical studies, the experimental factors for stripping voltammetric measurements of Eosin-Y were optimised at 30 s with 0.0 V deposition potential and 3000 rpm; stirring rate. These voltammetric studies were carried out in acetate buffer pH 5 and the applied potential was scanned at 400 mV/s with 60 Hz SW frequency and 80 mV.

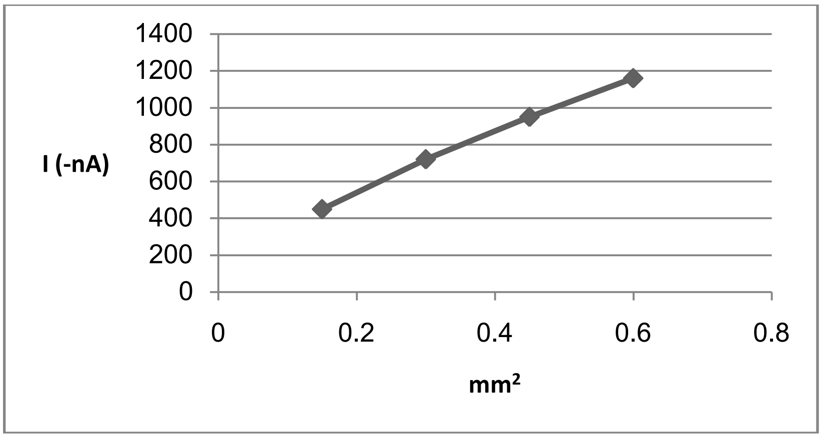


Figure 7. Effect of surface area of electrode on the stripping voltammetric current of 5×10^{-7} mol L^{-1} Eosin-Y at acetate buffer; pH = 5, 30 sec t_{acc}, 0.0V E_{acc}, 400mV/s, 0.08V and 60 Hz

3.3 Analytical performance

3.3.1. Calibration curve and detection limit

Some analytical characteristics of the proposed voltammetric method for determination of Eosin-Y were evaluated under the optimised parameters. In this study, a linear relationship between the voltammetric intensities and the dye concentrations was reported over the range 5.0×10^{-8} – 5.0×10^{-7} mol L^{-1} (see figure 8). The calibration equation was calculated by use a least square relation as it written at the following form:

$$i_p\ (\text{nA}) = 151.5 + 2.2\times10^{9}\ C\ (\text{mol } L^{-1}) \qquad r^2 = 0.99, \quad n = 5$$

where i_p is the voltammetric current in Nano amperes, C is Eosin-Y concentration and r^2 is the correlation coefficient.

The detection limit is defined the signal to noise ratio; (S/N=3) was of 8.73×10^{-10} mol L^{-1} (0.566 ppb). So, the obtained detection limit for this voltammetric measurements was significantly lower compared to UV/Vis spectrophotometer (0.5 ppm) which currently used for determination of Eosin-Y.

3.3.2. Precision, accuracy and stability

The reproducibility of the developed voltammetric method was concluded from 8 repeated voltammetric measurements for 5×10^{-7} mol L^{-1} of Eosin-Y solution with relative standard deviation (RSD%) which recorded 0.64% under optimised conditions. The recovery of the electrochemical measurements was applied for evaluating of the technique accuracy. It is checked for (2.0×10^{-7} mol L^{-1}) of Eosin-Y spiked in acetate buffer solution; pH5. The fifth voltammetric measurements was obtained by standard addition method, which given a recovery mean of 107% with standard deviation (SD) of ± 1.6%. On the other hand, the voltammetric signal of 5×10^{-7} mol L^{-1} of Eosin-Y solution was monitored every 10 minutes, it was found to nearly stable for a analysis period of 60 min at least.

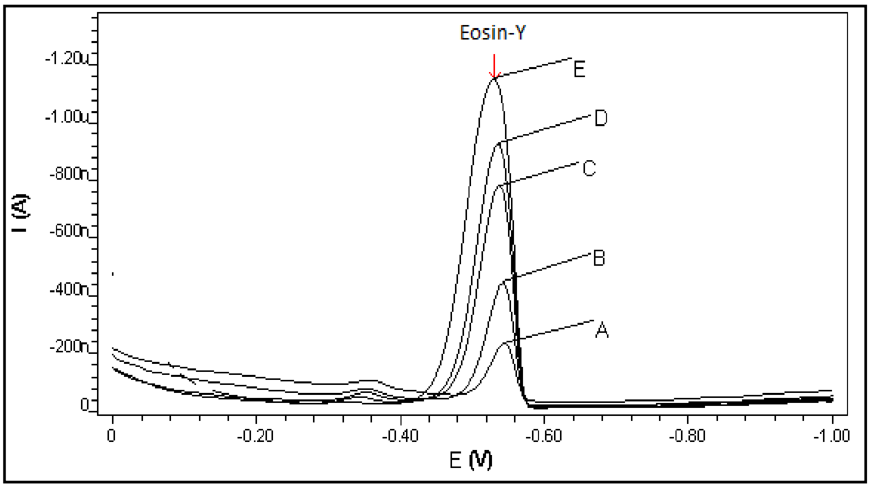


Figure 8. Voltammograms of Eosin-Y dye at acetate buffer pH=5, 30 sec t_{acc}, 0.0V E_{acc}, 400mV/s scan rate, 0.08V pulse amplitude, 60 Hz, 0.6 mm^2 and 3000 rpm; Eosin-Y concentrations: (A) 5.0×10^{-8}, (B) 1.0×10^{-7}, (C) 2.0×10^{-7}, (D) 3.0×10^{-7} and (E) 5.0×10^{-7} mol L^{-1}

3.3.3. Interferences

Taking into account the way this colorant was pre-concentrated onto the working electrode prior to its actual voltammetric measurements, the following types of interference may be expected; amongst them, interferences caused by surface-active materials competing with Eosin-Y for adsorption sites on the HMDE. Other possible source for interference might be associated with the presence of some compounds related to this dye and if these compounds were electro-active they can interfere via an overlapping response with the analyte signal and/or competitive co-adsorption. For these investigations, the interfering species were added at different concentrations (one, 5-fold and 25-fold) higher than the concentration of Eosin-Y (5×10^{-7} mol L^{-1}). Possible interferences from associated azo colorant matters and some metals were evaluated. The effect of other azo dyes was modulated by the additions of Sunset Yellow (E110) and Tartrazine (E102) azo dyes. The presence of Sunset Yellow and tartrazine azo dyes at 25-fold excess of Eosin-Y caused nearly 7.44%, 1.0% respectively, with an enhancement in the monitored AdSV peak current. The addition 25-fold of amaranth dye to Eosin-Y solution caused negative effect by nearly 2.0%. Finally, additions of 25-fold of Cu^{+2} and Zn^{+2} metals decreased the peak current of Eosin-Y by 12.6 and 11%, respectively. These negative results were observed due to the competitive co-adsorption of these added coloring agents and metals on the adsorption sites of HMDE.

3.4. Analytical application

To estimate the validity of the proposed electrochemical method which described above, it was applied for recovery of Eosin-Y in commercial real sample and sea water. The Eosin-Y content of these samples was determined via the optimized SW-AdSV technique. $2x10^{-7}$ mol L^{-1} Eosin-Y dye inside 2 ml sample was added in a 10 ml acetate buffer; pH5, which placed in the voltammetric cell and deoxygenated for 300 seconds. The electrochemical measurements were done by the standard addition method in order to minimize matrix effects. Table 1 summarizes the analytical results which obtained by the SW-AdSV method. The applied method was also used to the recovery of $2x10^{-7}$ mol L^{-1} Eosin-Y spiked in Varnish (Vanish Oxi Action Gel, S.C. Johnson-USA) and sea water (Red Sea, Yanbu-Saudi Arabia) samples. The results obtained by this recovery test for Eosin-Y have a recovery means of 92.25% and 84.5% with standard deviations(SD) of ± 1.71% and 1.3%, respectively.

Table 1: comparative recovery of Eosin-Y dye in varnish and sea water samples by the proposed SW-AdSV method

	Varnish	Sea water
	Found (recovery%)	Found (recovery%)
Recovered concentration of Eosin Y ($2x10^{-7}$ M)	93	85
	92	84
	90	86
	94	83
	Mean: 92.25% S.D. 1.71	Mean: 84.5% S.D. 1.3

Conclusion

The developed SW-AdSV method for the determination of Eosin-Y was found to be simple, sensitive (DL ≈ $8.73x10^{-10}$ mol L^{-1}) and rapid. It also offered several advantages in terms of low cost, good precision (0.64 RSD%) and adequate accuracy (Recovery 107%±1.6). The stripping voltammetric response was evaluated with respect to various experimental parameters and the optimal values estimated at acetate buffer pH5, 30 s accumulation time, 0.0 V accumulation potential, 400 mVs^{-1} scan rate, 80 mV pulse amplitude and 60 Hz SW frequency. The analytical application of voltammetric method was studied by determination of Eosin Y in Varnish and sea water.

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