

Novel PVC-Based Coated Graphite Electrode for Selective Determination of Quinoline Yellow

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Novel coated graphite electrode (CGE) for the determination of quinoline yellow (QY), an artificial food colorant, was evaluated based on the use of tetraphenylphosponium-QY ion-pair complex as the electroactive substance. The electrode revealed linear emf-pQY response over wide concentration ranges ($1.0 \times 10^{-1} \sim 5.0 \times 10^{-5}$ M) with a slope -30.1 ± 0.2 mV decade⁻¹ and a limit of detection of 4.0×10^{-5} M. The electrode showed good stability, reproducibility and fast response (<5 s). It can be used in wide pH range (4.7-10.7) and was successfully applied to determination of quinoline yellow in artificial mixtures and commercial soft drinks. The results obtained with the electrode were in good agreement with the value obtained by using HPLC measurements, as an official method.

Keywords: Ion-selective electrode, Quinoline yellow, Potentiometer, Food analysis, Synthetic food colorant

INTRODUCTION

The use of synthetic colorants has been extensively increasing in the past two decades in food industries compared to natural dyestuffs, because of their higher brightness, more stability, cheapness and the wider range of shades [1-3]. Colorants are very important ingredients in many convenience products such as gelatin desserts, snacks and beverages, since without these they would be colorless and appear undesirable. FDA certified synthetic colors are widely used in food, pharmaceutical, and chemical industries [3]. The concentration of these additives must be carefully controlled as they may have various harmful effects on human health. Health-related aspects of the use of synthetic colorants have been investigated extensively [4-8]. Research has shown that dyes induce DNA damage in the gastrointestinal organs at a low dose [4], in young children with attention deficit hyperactivity

disorder (ADHD) an elimination diet can lead to a statistically significant decrease in symptoms [5], dyes induced increase in sperm abnormalities [6], consumption of Red No. 3 (erythrosine), which has estrogenlike growth stimulatory properties, could be a significant risk factor in human breast carcinogenesis [7], and reduced mobility of sperm in mice [6], amaranth and tartrazine (Red No. 2 and Yellow No. 5) were found to suppress the immune system.

Quinoline yellow, FD&C No: 10 (E104), is widely used as an additive in soft drinks, lipsticks, hair products, colognes and in a wide range of medications. Numerous children's products have also been reformulated, including dolly mixtures and flying saucers, which contained quinoline yellow. It may cause asthma, rashes and hyperactivity. Aspirin sensitive people must also avoid it [8].

In many countries their uses are strictly limited, and it is important to detect and analyze them in different products. The regulation of colors and the need for quality control relating to their purity and amounts have made the

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development of new analytical methods necessary.

Different analytical methods have been developed for the qualitative and quantitative analysis of food dyes, chromatography, spectrometry and voltammetry, or various combinations of them [9-14]. Chromatographic techniques have the disadvantage of requiring expensive equipment and expert operators. Other methods require long analysis times and are overly complex.

Polymeric membrane-based potentiometric sensors which are selective to a variety of ionic species have attracted increasing interest because of their potential to be used extensively in biological, chemical and pharmaceutical analysis [15-17]. The inherent advantages of ion selective electrodes (ISEs) are simplicity, short time measurement, low cost, adequate precision and accuracy, adequate detection limit, wide analytical range, and particularly the ability to measure the activity of various species selectively, and in most cases, without prior separation of the target molecule from the formulation matrix [18-20]. These make ISE potentiometry very attractive for chemical and pharmaceutical analysis. Several drug selective electrodes were constructed based on ion-pair complexes of ionic drugs with a high molecular weight counter ions [21-24]. Most food colorants contain sulfonate groups that are ionized and carry negative charges at pHs found in most foods. They are very similar to ionic drugs; therefore, it is expected that they form insoluble ion-pair complex with large molecular weight counter ions such as tetrabutylammonium. It is worth mentioning that, to the best of our knowledge, there is no previous literature report on development of selective electrode for artificial food colorants.

In this work, a Quinoline Yellow coated graphite electrode (CGE) and a polymeric membrane electrode (PME) were developed based on the use of ion-pair complex of tetraphenylphosphonium-quinoline yellow (TPP-QY) embedded in a polyvinylchloride matrix as electro-active substance. Coated graphite electrode displayed a low detection limit and high selectivity and sensitivity to quinoline yellow determination in food products. The performance of electrode is described. The electrode was successfully applied to determination of quinoline yellow using direct potentiometric method. The results obtained with the electrode were in good agreement with the value obtained by using the official method (HPLC measurements).

EXPERIMENTAL

Reagents and Chemicals

Reagent-grade dioctyl phthalate (DOP), benzyl acetate (BAC), dibutyl sebacate (DBS), dibutyl phthalate (DBP), 2-nitrophenyl octyl ether (NPOE), tetraphenylphosphonium bromide (TPPB), high relative molecular weight PVC, tetrahydrofuran (THF) and tetrabutylammonium bromide (TBAB) were purchased from Merck chemical company and used as received. Quinoline yellow (E104) FD&C Red No.10 was obtained from Institute of Standard and Industrial Research of Iran. Reagent-grade sodium salts of the anions used (all from Merck) were of the highest purity available and used without any further purification except for vacuum drying over P₂O₅. Triply distilled water was used throughout.

The ion pair complex was prepared by shaking 5.0 cm³ of a 0.01 M QY solution with an equal volume of a 0.02 M of tetraphenylphosphonium bromide. The resulting TPP-QY ion pair precipitates was centrifuged, filtered, thoroughly washed with water and dried under vacuum over P₂O₅ for 72 h.

Electrode Preparation

The general procedure to prepare the PVC membrane was to mix thoroughly 30 mg of powdered PVC, 12 mg of TPP-QY, 54 mg of dioctyl phthalate, 4 mg TBAB and 2 mg TPPB as an additive. Then, the mixture was dissolved in 5 ml of THF. The resulting mixture was transferred into a glass 2-cm-diameter dish. The solvent was evaporated slowly until an oily concentrated mixture was obtained. A pyrex tube (3 mm) was dipped into the mixture for ~10 s so that a nontransparent membrane of ~0.3 mm thickness formed. Next, the tube was pulled out from the mixture and kept at room temperature for ~1 h. Then the tube was filled with internal filling solution (1.0 × 10⁻³ M QY). Finally the electrode was conditioned for 4 h by soaking in a 1.0 × 10⁻³ M solutions of QY. Also a silver/silver chloride electrode was used as an internal reference electrode.

To prepare coated graphite electrodes, spectroscopic-grade graphite rods 10 mm long and 3 mm in diameter were used. A shielded copper wire was glued to one end of the graphite and the electrode was sealed into the end of a PVC tube of about the same diameter with epoxy resin. The working surface of the electrode was polished with fine alumina slurries on a

polishing cloth, sonicated in distilled water and dried in air. The polished graphite electrode was dipped into the membrane solution mentioned above and the solvent was evaporated. A membrane was formed on the graphite surface and the electrode was allowed to stabilize over night. The electrode was finally conditioned by soaking in a 1×10^{-2} M solution of QY for 12 h.

Emf Measurements

All emf measurements were carried out with the following assembly:

Ag-AgCl, KCl (3 M) | internal solution, 1.0×10^{-3} M Na NO₃ | PVC membrane | test solution [Hg-Hg₂Cl₂, KCl (satd.)] (PME)

Graphite surface | PVC membrane | sample solution || Hg-Hg₂Cl₂, KCl (satd.) (CGE)

A 713 Metrohm pH/mV meter was used for potential measurements at 25.0 ± 0.1 °C. The emf observations were made relative to a double-junction saturated calomel electrode (SCE, Metrohm) with the chamber filled with an ammonium nitrate solution. Activities were calculated according to the Debye-Huckel procedure [25].

Food Sample Treatment

The method was applied to determine quinoline yellow in commercial soft drinks (lemon and banana flavored). Fifty milliliters of the sample was transferred to a 100 ml flask, boiled and stirred continuously to remove the carbon dioxide. The pH of these samples was then adjusted to 5 by addition of 20% citric acid.

RESULT AND DISCUSSION

Some important features of PVC membrane, such as the nature and amount of the plasticizer, additives used and the membrane composition are reported which significantly influence the sensitivity and selectivity of ion-selective electrodes [26-28]. Thus, the different aspects of membranes were optimized; the results are summarized in Table 1. It is obvious that a membrane composition of 30% PVC, 12% TPP-QY, 54% dioctylphthalate, 4% TBAB and 2% TPPB, as an additive, resulted in a CGE, showing high sensitivity with the Nernstian slope over a wide dynamic range (Fig. 1).

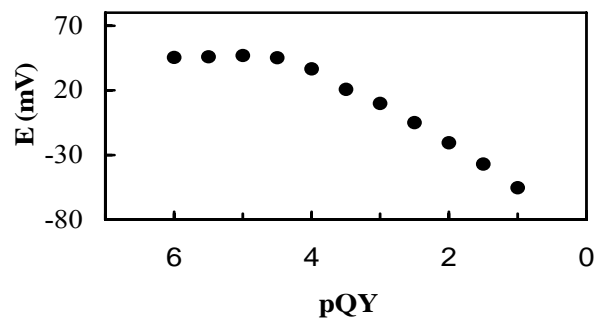


Fig. 1. Calibration graph for the CGE at pH 6.

The critical response characteristics of the proposed electrodes were assessed according to IUPAC recommendations [29]. The slopes and linear ranges of the resulting emf-pQY graph are given in Table 2. The limits of detection, defined as the concentration of QY obtained when the linear ranges of the calibration graphs are extrapolated to the base line potentials, are also included in Table 2. It is obvious that the performance characteristics of the CGE improved compared to those of PME. It is presumably originated from the coated graphite technology, where an internal 1.0×10^{-3} M QY solution, in the case of PME, has been replaced by a graphite of much higher electrical conductivity [30-33].

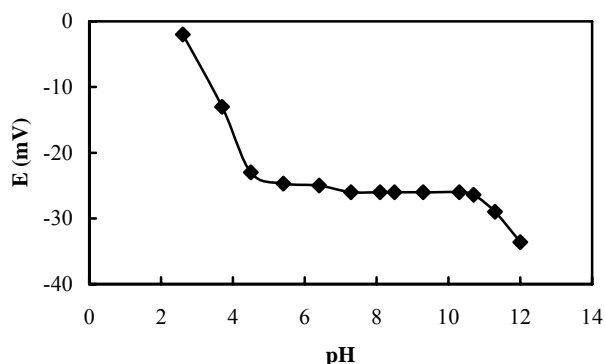
The average time required for the electrodes to reach a potential response within ± 1 mV of the final equilibrium value after successive immersion in a series of QY solutions, each having a 10-fold difference in concentration, was studied. The static response time of the electrodes thus obtained for concentration of $\leq 1.0 \times 10^{-3}$ M is listed in Table 2. The prepared CGEs were kept in air when unused and conditioned in 10^{-3} M QY solution 2hr before experiments. The CGEs can be used frequently for 2 months, without any measurable divergence. The influence of the pH of the test solution on the potential response of the CGE in the presence of 1.0×10^{-4} M QY ion is shown in Fig. 2. As can be seen, the potential remains constant from pH 4.7 to 10.7, beyond which it changes considerably. The observed drift at lower and higher pH values could be due to the protonation of an ionophore in acidic media that decrease its ion exchange properties and for alkali media, it seems that OH⁻ will strongly compete with

Table 1. Optimization of Membrane Ingredients. Variation of Potentiometric Responses were Measured at the Concentration Range of $1.0 \times 10^{-1} \sim 5.0 \times 10^{-4}$ M of Quinoline Yellow Solutions in Phosphate Buffer of pH 7.0 at 25 °C

No.	Composition (%)				Slope (mV decade ⁻¹)	
	PVC	Plasticizer	Additive	TPP-QY	PME	CGE
1	30	DBS,64	TBAB,2	5	-4.0 ± 0.1	-12.1 ± 0.1
2	30	DBP,64	TBAB,2	5	-6.2 ± 0.2	-20.3 ± 0.1
3	30	BAC,64	TBAB,2	5	-7.1 ± 0.3	-8.4 ± 0.3
4	30	NPOE,64	TBAB,2	5	-5.2 ± 0.1	-14.2 ± 0.2
5	30	DOP,64	TBAB,2	5	-11.1 ± 0.2	-22.6 ± 0.2
6	30	DOP,63	TBAB,4	5	-9.0 ± 0.3	-22.2 ± 0.2
7	30	DOP,65	TBAB,0	5	-5.2 ± 0.2	-8.3 ± 0.3
8	30	DOP,65	TBAB,6	5	-8.4 ± 0.5	-14.5 ± 0.3
9	30	DOP,65	TBAB,4 + OAC,8	5	-16.4 ± 0.1	-21.4 ± 0.2
10	30	DOP,61	TBAB,2 + TPPB,2	5	-17.1 ± 0.4	-23.2 ± 0.2
11	30	DOP,58	TBAB,2 + TPPB,2	8	-16.3 ± 0.2	-26.4 ± 0.1
12	30	DOP,56	TBAB,2 + TPPB,2	10	-22.1 ± 0.1	-28.5 ± 0.1
13	30	DOP,54	TBAB,2 + TPPB,2	12	-20.2 ± 0.1	-30.1 ± 0.2
14	30	DOP,56	TBAB,2 + TPPB,2	16	-10.1 ± 0.3	-19.3 ± 0.2
15	30	DBP,54	TBAB,2 + TPPB,2	12	-14.5 ± 0.3	-27.8 ± 0.1

Table 2. Response Characteristics of the QY Ion-Selective Electrodes

Electrode	Slope (mV decade ⁻¹)	Linear range	Limit of detection (M)	Response time (s)	Working pH range	Life time (month)
CGE (NO.13)	-30.1 ± 0.2	5.0×10^{-5} - 1.0×10^{-1}	3.2×10^{-5}	<10	4.7-10.7	2

**Fig. 2.** pH dependence of potential response of the quinoline yellow CGE.

analyte ion for exchange in the membrane.

The repeatability of the potential reading for electrode CGE was examined by subsequent measurements in 1.0×10^{-3} M of QY solution immediately after measuring the first set of solution at 1.0×10^{-2} M of QY solution (Fig. 3). The standard deviation of measuring emf for 5 replicate measurements was 0.20 mV. This means that the repeatability of potential response of the electrode is good.

The influence of interfering ions on the potential response behavior of the ion-selective membrane electrode is usually described in terms of the selectivity coefficients [15]. In this

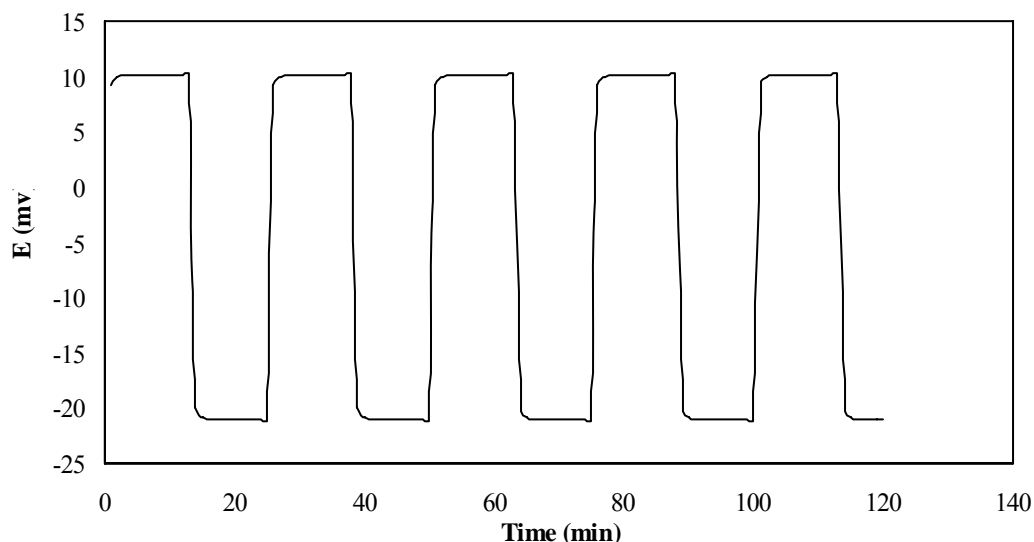


Fig. 3. Dynamic response of quinoline yellow sensor during successive immersion in a 1.0×10^{-2} and 1.0×10^{-3} solution of QY, in phosphate buffers (pH 7.0), 25 °C.

Table 3. Selectivity Coefficients of Various Interfering Ions

Interfering ion	k^{pot}	Interfering ion	k^{pot}
CH_3COO^-	9.6×10^{-3}	Cl^-	1.0×10^{-5}
CO_3^{2-}	1.0×10^{-5}	PO_4^{3-}	8.8×10^{-3}
NO_2^-	8.0×10^{-2}	HPO_4^{2-}	1.4×10^{-2}
NO_3^-	8.6×10^{-2}	H_2PO_4^-	4.3×10^{-2}
Citrate	1.2×10^{-3}	Ascorbate	2.3×10^{-3}
Benzoate	3.4×10^{-3}	Glucose	1.0×10^{-5}

work, the matched potential method (MPM), which is totally independent of the Nicolski-Eiseman equation, was used for determination of selectivity coefficients [34]. According to the MPM, the selectivity coefficients are defined as the activity ratio of the primary ion (A) and the interfering ion (B) that gives the same potential change in a reference solution. Thus, one should measure the change in potential upon changing the primary ion activity. Then the interfering ion would be added to an identical reference solution until the same potential change is obtained. The selectivity coefficient, k^{pot} is determined as:

$$k^{\text{pot}} = \Delta a_A / a_B$$

where $\Delta a_A = \acute{a}_A - a_A$ and \acute{a}_A and a_A are the initial primary ion activity and the primary ion activity in the presence of the interfering ion a_B , respectively. The resulting values are summarized in Table 3. The basic ingredients of soft drinks are always a sweetener, an acid (generally ascorbic acid, citric acid), carbon dioxide, preservative (generally benzoic acid) and color. As is seen, for all diverse ions used, the selectivity coefficients are in the order of 10^{-3} or smaller, indicating that they would not significantly disturb the electrode behavior

Table 4. Recovery of Quinoline Yellow

Added ($\mu\text{g ml}^{-1}$)	Found ($\mu\text{g ml}^{-1}$)	Recovery (%)
5.00	4.8	96 \pm 0.4
8.50	7.9	93 \pm 1.4
12.00	11.4	95 \pm 0.7

except for nitrate and nitrite ions. However, these ions generally are not used in soft drink formulation. Ingredients in soft drinks such as citrate, ascorbate, carbonate and benzoate ions do not influence the QY determination.

The reliability of the proposed QY ion-selective electrode (CGE) for quantification of quinoline yellow was assessed by determining the synthetic samples of quinoline yellow solutions using the direct potential method and the obtained data shown in Table 4. Average of five determinations is found and the mean of recovery and the mean standard deviation were 102.25% and 0.87%, respectively.

The direct potential method was applied to the determination of quinoline yellow in food products (soft drink) and compared with the HPLC method [9]. The mean value and the relative standard deviation obtained using quinoline yellow selective electrode was $5.71 \pm 0.03 \text{ mg Kg}^{-1}$ and 1.4% ($n = 5$) for lemon flavor and $2.52 \pm 0.02 \text{ mg Kg}^{-1}$ and 1.25% ($n = 5$) for banana, respectively. The measure values found to be in satisfactory agreement with the values obtained using HPLC technique (*i.e.*, $5.12 \pm 0.01 \text{ mg Kg}^{-1}$ for lemon and $2.1 \pm 0.01 \text{ mg Kg}^{-1}$ for banana).

CONCLUSIONS

Novel coated graphite electrode (CGE) for the determination of quinoline yellow (QY) was prepared based on tetraphenylphosphonium-QY ion-pair complex as the electroactive substance. The electrode prepared was successfully applied to the determination of quinoline yellow in food products. The proposed method is rapid, simple, inexpensive, and sensitive with a low detection limit of $4.0 \times 10^{-4} \text{ M}$.

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Novel PVC-Based Coated Graphite Electrode

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