



Kinetic catalytic determination of trace levels of iodide based on the oxidation of basic dyes with hydrogen peroxide monitored potentiometrically using simple PVC electrodes

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ABSTRACT

Four sensitive catalytic potentiometric methods have been developed for trace levels determination of iodide based on its catalytic effects on the oxidation of four dyes: viz. variamine blue (VB), rhodamine B (RB), methylene blue (MB) and malachite green (MG), with H₂O₂ in H₃PO₄ medium at 25 ± 0.5 °C. The catalyzed reaction rates were estimated potentiometrically by monitoring the potential of the corresponding dye-PVC ion selective electrodes. To select the optimized reaction conditions offering the highest sensitivity of the method, parallel studies were carried out on each dye catalyzed reaction including: the effect of reactant concentration, reaction medium and temperature. The working calibration curves were linear over the concentration range from 0.32 to 2.54 mg L⁻¹ iodide for VB method and from 3.2 to 12.7 mg L⁻¹ for other ones. The tolerance limits of more than 20 interfering species were listed indicating the high selectivity of the method. Trace iodide in edible salt and pharmaceutical samples was determined without the need for separation or preconcentration procedures.

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1. Introduction

Iodine is an essential part of the thyroid hormones that play an important role in the development of brain function and cell growth. Deficiency of iodine causes serious delay in neurological development, while an excess of iodine can cause goiter and hypothyroidism as well as hyperthyroidism [1,2]. Salt fortification and the use of pharmaceutical preparations containing potassium iodide are highly effective methods used to avoid iodine deficiency disorder (IDD), therefore, it is essential to monitor the concentration of iodine in the diet and pharmaceutical preparations.

Several analytical methods have been applied for iodide determination, including: titrimetry [3], electrochemistry [4,5], chemiluminescence [6], ion [7] and ion-pair reversed-phase [8] high performance liquid chromatography. Neutron activation analysis [9] and inductively coupled plasma-mass spectrometry [10,11] have also been described for the determination of iodide. However, such methods [3–6] lack in sensitivity and selectivity while others [7–11] require expensive instruments and time-consuming for sample preparation.

Kinetic-spectrophotometric methods are attractive alternative ones, as trace determination can be achieved without the use of expensive or special equipment with lower probability to receive interferences [12–15]. Several catalytic procedures for iodide determination were found in the literature which is based on its catalytic affect on the oxidation of different organic and inorganic compounds with various oxidizing agents [16–22]. The catalyzed reaction rates were followed spectrophotometrically by monitoring the absorbance of the colored species. Due to the interferences that may accompany the spectrophotometric measurements and fading of the colored species, potentiometric measurements have also been suggested for following the catalyzed reaction using simple indicator ion selective electrodes [23–28]. In contrast to spectrophotometric techniques, potentiometric measurements have analytical and economic advantages including simple instrumentation, fast response, application to turbid or colored solutions and the ability of construction of portable measuring system for field measurements. Catalytic potentiometric procedures based on the fabrication of methyl violet, crystal violet, MG, or RB electrodes were applied for the catalytic potentiometric determination of nitrite [23,28], manganese [24,25,27] or tungsten [26] and no reported catalytic potentiometric method was suggested for iodide determination.

The present work described catalytic potentiometric methods for the determination of iodide based on its catalytic effect on the

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oxidation of different organic dyes namely; VB, RB, MG and MB with H_2O_2 . The catalyzed reactions were followed potentiometrically using the corresponding dye PVC electrodes where the reaction rates were estimated from the potential–time curves of the dye electrodes.

2. Experimental

2.1. Reagents

All reagents were of the analytical grade and bidistilled water was used throughout the experiments. Iodide stock solution ($10^{-2} \text{ mol L}^{-1}$) was prepared by dissolving potassium iodide (Analar) previously dried at 105°C for 2 h in 100 mL bidistilled water. Working solutions were prepared daily by appropriate dilution with water and standardized by visual titration method [33].

Stock dye solutions were prepared by dissolving the appropriate weight of each dye (VB-HCl, $\text{C}_{13}\text{H}_{14}\text{N}_2\text{O}\cdot\text{HCl}$, BDH; MB: $\text{C}_{16}\text{H}_{12}\text{ClN}_3\text{S}$, Merck; RB, $\text{C}_{28}\text{H}_{31}\text{ClN}_2\text{O}_3$, Merck; and MG, $\text{C}_{23}\text{H}_{25}\text{N}_2\cdot\text{C}_2\text{HO}_4$, BDH) in 100 mL bidistilled water. The exact concentration of each dye solution was determined via potentiometric titration against standardized sodium tetraphenylborate (NaTPB) using the simple PVC-electrode [29–32].

Hydrogen peroxide solution ($10^{-3} \text{ mol L}^{-1}$) was prepared using 30% H_2O_2 (Merck) which was standardized by permanganate titration. Other oxidant solutions were prepared by dissolving the appropriate amounts of potassium bromate (KBrO_3 , BDH), potassium iodate (KIO_3 , BDH), potassium periodate (KIO_4 , Analar) or potassium persulphate ($\text{K}_2\text{S}_2\text{O}_8$, Analar) in bidistilled water. Acid solutions; H_3PO_4 , H_2SO_4 , HCl, HNO_3 or acetic acid were prepared by diluting the analytical grade stock with bidistilled water.

2.2. Samples

2.2.1. Edible salt samples

The edible salt samples, collected from local stores, were oven dried at 120°C overnight and stored in desiccator until constant weight. Sample solutions were prepared by dissolving an accurate weight of salt in water (*note*: filtration may be necessary for some sample solutions that contain particulate matter). However, some salt samples are supplemented with potassium iodate for a longer shelf life; in such a case addition of ascorbic acid into salt solution was required for the reduction of iodate. The samples were analyzed directly using the proposed catalytic method and the visual titration one [33].

2.2.2. Pharmaceutical preparations

Betadine sample (antiseptic solution, povidone–iodine solution (2-pyrrolidinone, -l-ethenyl-homopolymer compound) with iodine, Nile Company for Pharmaceutical and Chemical Industries) was purchased from local drug stores. The iodine content was assayed with the proposed catalytic method and potentiometric titration with silver nitrate [34,35].

Eltroxine tablets ($100 \mu\text{g}$ thyroxine sodium BP, Glaxo Smith Kline GmbH, Egypt) were purchased from local drug stores. Weighed grounded samples were burnt in oxygen atmosphere using a combustion flask by “Schoniger’s method” [36], where the combustion products were absorbed in 10 mL hydrazine sulphate solution. The obtained solution was transferred to a 25 mL measuring flask and filled to the mark with water.

2.3. Apparatus

All potentiometric measurements were recorded using Jenway 3510 pH meter (UK) with PC interface, accompanied with conven-

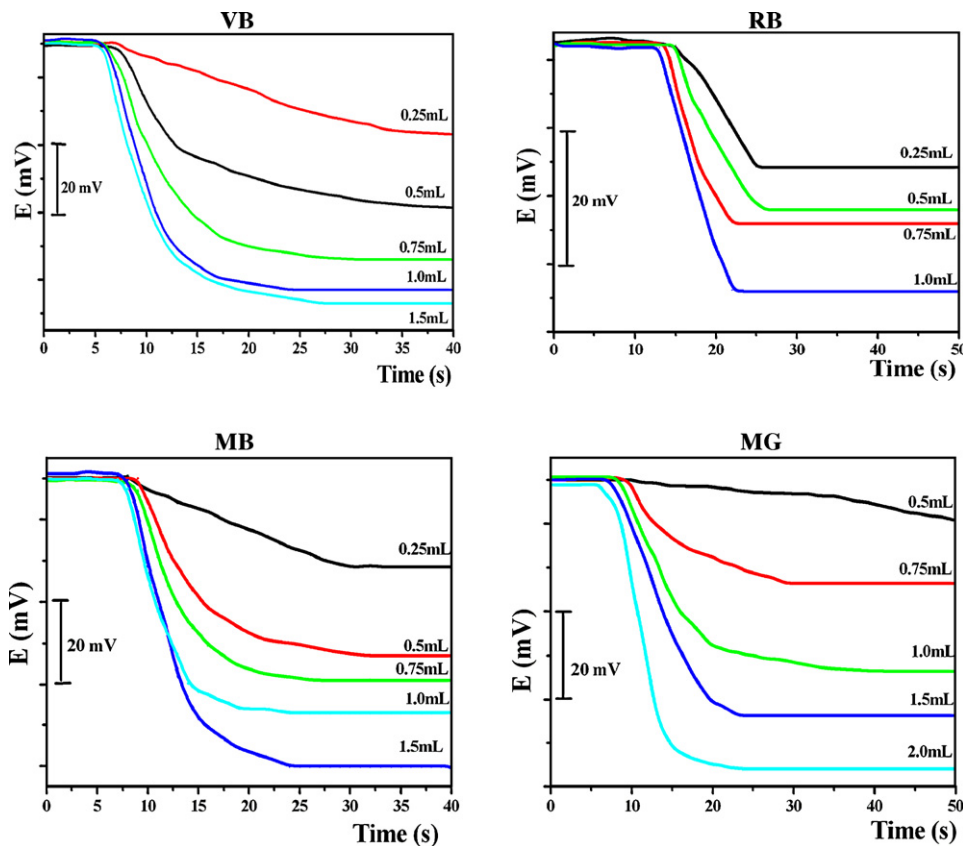


Fig. 1. Influence of dye concentration on the reaction rates. Conditions: 1.27 mg L^{-1} iodide in case of VB, and 12.7 mg L^{-1} iodide in case of other catalyzed reactions, 2 mL of $10^{-3} \text{ mol L}^{-1} \text{ H}_2\text{O}_2$ and $0.05 \text{ mol L}^{-1} \text{ H}_3\text{PO}_4$ at 25°C .

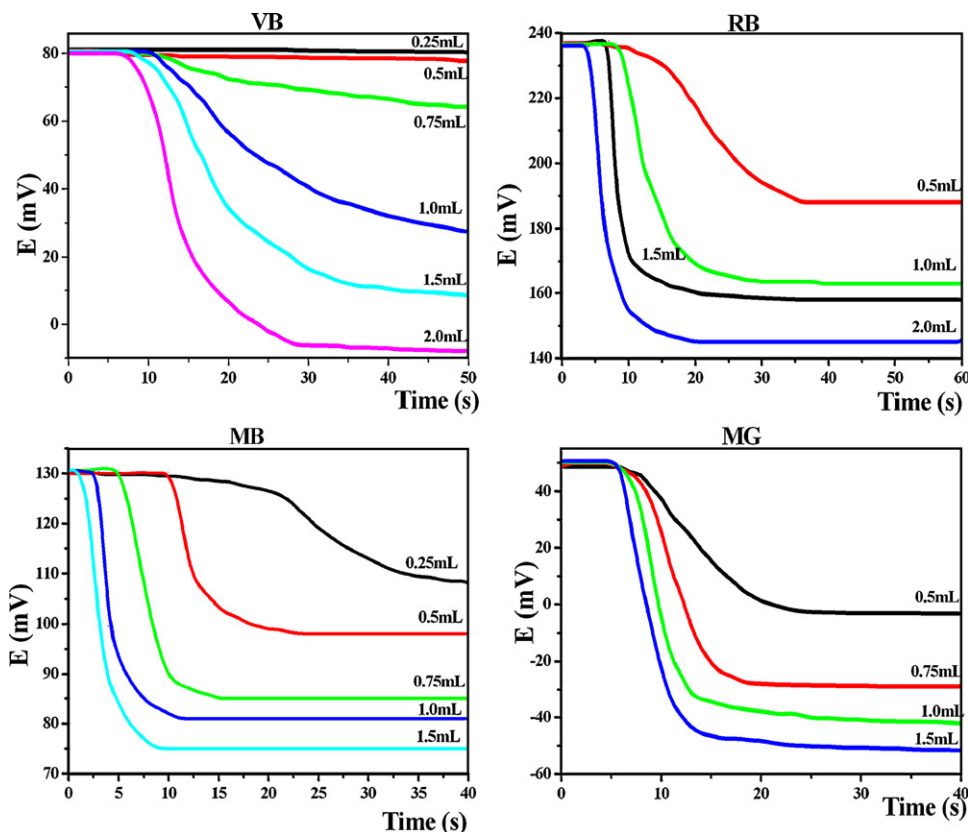


Fig. 2. Influence of H_2O_2 concentration on the reaction rates. Conditions: 1.27 mg L^{-1} iodide in case of VB, and 12.7 mg L^{-1} iodide in case of other catalyzed reactions.

tional macroscopic Ag/AgCl double-junction reference electrode and combined pH glass electrode. Simple PVC-electrodes were fabricated for each tested dye following the procedures described in details elsewhere [29–32]. The dye–TPB ion pairs were incorporated in the PVC electrodes matrix using *o*.nitrophenyloctyl ether as the plasticizer. Potentiometric measurements were carried out in a double-jacket and thermostated glass cell with an HAAK thermostetting circulating water bath with temperature stability of 25 ± 0.1 °C.

2.4. Procedures

Aliquots of iodide solution were transferred to the reaction cell containing the selected volume of the dye solution, 0.5 mL of 1 mol L^{-1} H_3PO_4 and 5 mL water. The corresponding dye-PVC electrodes in conjugation with reference electrode were immersed in the measuring solution with continuous stirring. The reaction was initiated by the addition of appropriate H_2O_2 volume and the reaction mixture was completed to 10 mL with bidistilled water. The catalyzed reactions were monitored potentiometrically by monitoring the potential of the corresponding dye-PVC electrode. The reaction rates were estimated from the potential–time curves of the dye electrodes and calibration curves were obtained by plotting the reaction rate against iodide concentration.

3. Results and discussion

3.1. Electrode behavior

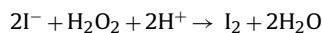
Different dye ion-selective electrodes have been fabricated and optimized for the potentiometric determination of each corresponding dye under direct potentiometry and titration modes [29–32]. The fabricated electrodes showed near-Nernstian

responses over the concentration ranges from 1.0×10^{-6} to 1.0×10^{-3} , 1.0×10^{-6} to 1.0×10^{-2} , 1.0×10^{-6} to 1.0×10^{-3} and 1.0×10^{-7} to $1.0 \times 10^{-3} \text{ mol L}^{-1}$ for MG, VB, RB and MB-PVC electrodes, respectively, with detection limits reaching 3.5×10^{-7} , 4.6×10^{-7} , 3.0×10^{-7} and $7.0 \times 10^{-8} \text{ mol L}^{-1}$ for the aforementioned electrodes in the same order. For analytical applications of novel sensors, the fast electrode response with stable potential measurement is of critical importance, especially when monitoring kinetic reactions or incorporation of the electrode in flow injection systems. The proposed sensors possessed fast response times of 12, 8, 8 and 10 s, respectively, and were suitable for monitoring the catalytic reactions.

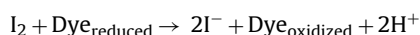
3.2. Catalytic potentiometric determination of iodide

In the present study, the fabricated VB-, RB-, MB- and MG-PVC electrodes were used for monitoring the catalyzed reactions by following the change in the corresponding dye concentration throughout the catalyzed reaction instead of spectrophometric measurements.

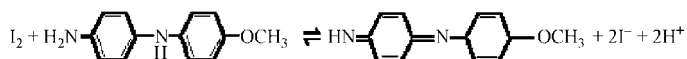
In the proposed catalyzed system, iodide was oxidized in acidic medium into iodine according to the following reaction:



The iodine formed can oxidize the dye present in the reaction medium to its oxidized product and iodide:



Oxidation of VB was reported to take place through the transfer of two electrons to give rise to N-(4-methoxyphenyl)-quinonedimine (VB_{ox}) with deep violet blue color [37], while the oxidation of the other tested dyes resulted in their decolorization:



Using the nominal dye ion-selective electrode, the concentration of such dye can be followed throughout the catalyzed reaction by measuring the potential reading within the reaction time. The reaction rate of these catalyzed reactions can be expressed according to the following equation:

$$v = -\frac{d[\text{dye}]}{dt} = k[I^-][\text{dye}]^m[\text{oxidant}]^n$$

where k is the rate constant.

Because the condition of $[\text{oxidant}] \gg [\text{dye}]$ is fulfilled, $[\text{oxidant}]$ can be considered constant and m was found to be 1. By integrating the above equation and incorporating the simplest potential-concentration dependence,

$$E = k + \frac{RT}{F} \ln[\text{dye}]$$

The final expression can be obtained as [28]:

$$(E_0 - E_t) \frac{F}{RT} = \ln \frac{[\text{dye}]_0}{[\text{dye}]_t} = k \times [I^-] t$$

This relation can be used for rate constant measurement using the corresponding dye ion-selective electrode. From the last equation given above, a linear relationship can be obtained when plotting $\Delta E/\Delta t$ (slope of potential-time curves) against iodide concentration.

3.2.1. Effect of variables on the catalyzed reaction

Parallel studies were carried out on each catalyzed reaction including: the effect of reactant concentration, reaction medium and temperature, to select the best reaction conditions offering the highest sensitivity of the method. It was found that the oxidation of iodide takes place in acidic medium; therefore, the catalyzed reactions were done in different acidic medium (viz. H_3PO_4 , H_2SO_4 , HCl or acetic acid). It is noteworthy to mention that all the fabricated dye electrodes showed stable and fast potential reading in such acidic media and the highest reaction rate was achieved in H_3PO_4 . Furthermore, the effect of the phosphoric acid concentration was studied over the concentration range from 0.02 to 0.08 mol L^{-1} and 0.05 mol L^{-1} was selected.

Different increments of 7.5×10^{-5} , 6.9×10^{-5} , 8.4×10^{-5} or 10^{-4} mol L^{-1} of VB, MB, RB or MG stock solutions were added to the reaction medium and in each case the reaction rate was estimated (Fig. 1). All the tested dye concentration lies in the linear range of the fabricated dye sensors and addition of 1, 1.5 or 2 mL of aforementioned dyes were selected as it gave the highest reaction rate compared with other tested concentrations.

Under the recommended dye concentrations and in the absence of iodide, different oxidizing agents such as persulphate, periodate, bromate, iodate and hydrogen peroxide can oxidize the tested dyes to give a deep violet blue color in case of VB, and cause decolorization of other dyes. Oxidation was instantaneous in the presence of persulphate and periodate, while in the presence of bromate or iodate it is not as fast and application of such oxidizing agents was unsatisfactory for the catalytic determination of iodide. On the other hand, oxidation with hydrogen peroxide undergoes at slow

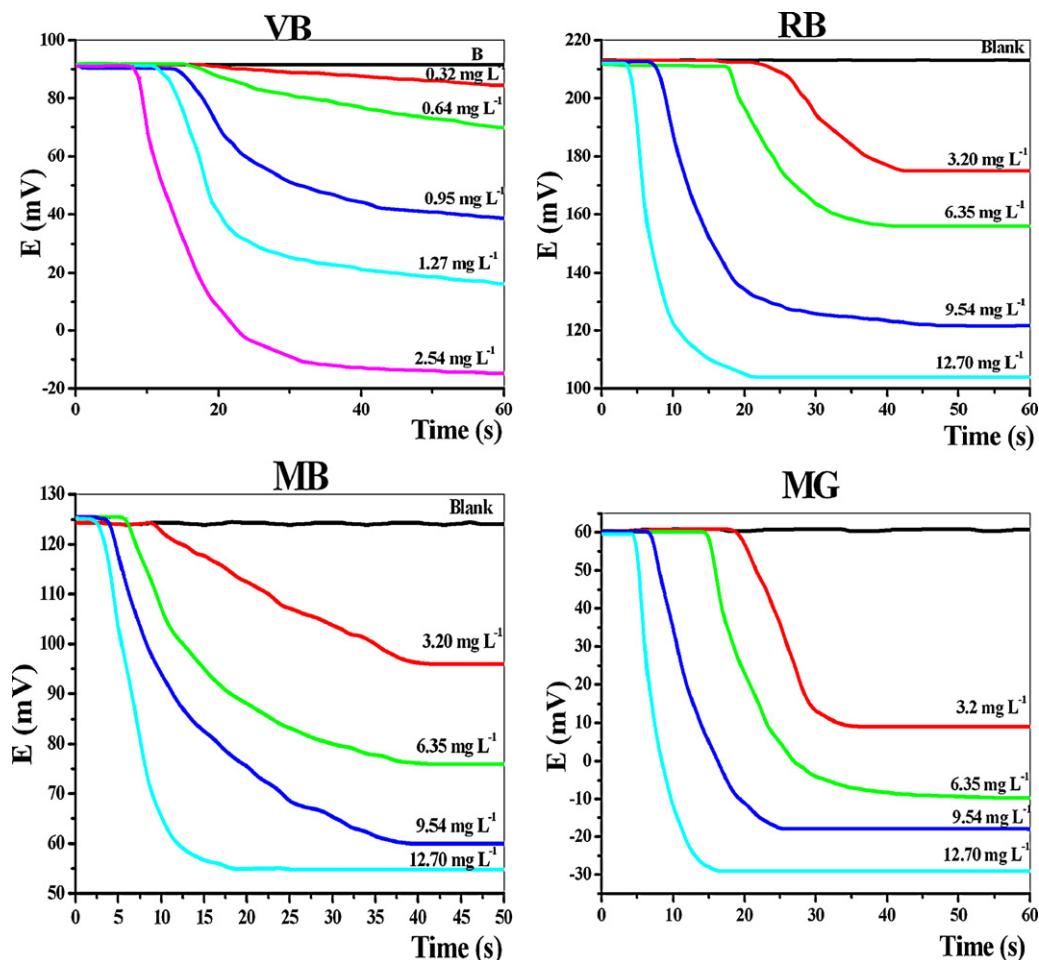


Fig. 3. Catalytic potentiometric determination of iodide based on its catalytic effect on oxidation of different dyes with H_2O_2 using the corresponding dye-PVC electrodes.

Table 1
The analytical characteristics of the four suggested procedures.

Method	VB	RB	MB	MG
Dye concentration (mL)	1.0	1.0	1.5	2.0
H ₂ O ₂ concentration (mL)	2.0	2.0	1.5	1.5
Linear range (mg L ⁻¹)	0.32–2.54	3.20–12.70	3.20–12.70	3.20–12.70
Regression equation ^a				
Slope (b)	-3.043	-1.023	0.742	-0.877
Intercept (a)	0.184	0.090	0.381	0.248
Correlation coefficient	0.9966	0.9998	0.9955	0.9986
LOD (mg L ⁻¹)	0.02	0.05	0.35	0.19

^a $\Delta E/\Delta t = a + bc$, C is the concentration of iodide in mg L⁻¹.

rates, which are accelerated in the presence of trace iodide. The influence of H₂O₂ concentration was studied by the addition of different H₂O₂ (10⁻³ mol L⁻¹) volumes. 2.0 mL of H₂O₂ was selected in case of VB and RB; while 1.5 mL was suitable for MB and MG catalyzed reactions, respectively (Fig. 2).

At the optimum concentration of both the dye and the oxidant, the effect of reaction medium temperature was also studied. It is noteworthy to mention that all the fabricated electrodes have low isothermal coefficient (from 0.505 to 0.70 mV °C⁻¹), and reasonable thermodynamic ionic exchange process at the membrane/dye solution interface can be achieved with good mechanical stability up to 70 °C [29–32]. Rising of the reaction temperature from 25 to 50 °C resulted in a noticeable decrease in the reaction rates, and operating at 25 °C was selected as it showed the highest reaction rate.

3.2.2. Analytical characterization

Under the optimum working conditions reported above for each catalyzed reaction, the potential of the corresponding dye-PVC electrodes decreased via addition of iodide (Fig. 3). Calibration graphs were obtained by plotting the reaction rate (slope of the first linear part of potential–time curve; $\Delta E/\Delta t$) against iodide concentration. The regression equations and detection limit of the four listed catalyzed reactions were shown in Table 1 and Fig. 4. Linear calibration curves were obtained over the range from 0.32 to 2.54 mg L⁻¹ iodide for VB procedure, and from 3.20 to 12.7 mg L⁻¹ iodide for other ones, with limit of detection (three times of standard deviation of the slope) ranged from 0.02 to 0.35 mg L⁻¹ iodide. It could be concluded that the four methods showed high sensitivity and VB method was the best.

3.2.3. Interferences

In order to investigate the analytical applicability of the proposed method, the effect of several interfering ions was examined by operating the catalyzed reaction in the presence of 1.27 mg L⁻¹ iodide and different interfering ions, where the maximum amount of substance causing an error of $\pm 5\%$ was denoted as the tolerance limit (Table 2).

Table 2
Maximum tolerance limits of diverse ions in the determination of 1.27 mg L⁻¹ iodide using VB procedure.

Element	Tolerance limit	Recovery (%)	Element	Tolerance limit	Recovery (%)
Cd ²⁺	500	101	V (V)	50	110
Ag ⁺	30	93	Fe ²⁺	150 ^a	107
Pb ²⁺	1000	103	Fe ³⁺	150 ^a	104
Cu ²⁺	300 ^b	106	NO ₃ ⁻	1000	100
Sn ⁴⁺	100	97	NO ₂ ⁻	1000	100
Hg ²⁺	100	95	F ⁻	1000	98
Cr ³⁺	50	104	Cl ⁻	1000	102
Cr ⁶⁺	15	107	Br ⁻	300	101
Mn ²⁺	1000	101	CN ⁻	100	103
Zr ⁴⁺	100	99	EDTA	1000	99
Au ³⁺	50	97	Ascorbic	1000	98

^a The tolerance limits were in the presence of EDTA.

^b The tolerance limit was in presence of triethylenetetramine.

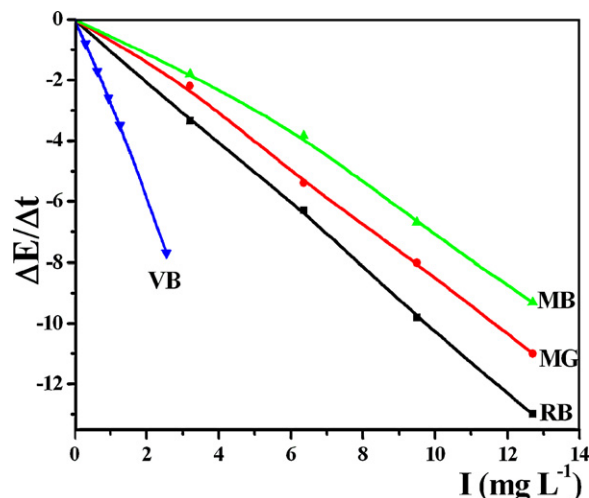


Fig. 4. Linear calibration graphs for the potentiometric determination of iodide based on its catalytic effect on the oxidation of different dyes with H₂O₂ using the corresponding dye-PVC electrodes.

Table 3
Catalytic potentiometric determination of iodide in different samples using VB procedure.

Sample	Taken (mg L ⁻¹)	Recovery (%)	S.D. ^a
Authentic sample	0.64	96.50	3.20
	0.95	98.20	2.10
	1.27	100.5	1.50
	2.54	101.20	1.20
Edible salt 1	0.58	96.20	2.80
Edible salt 2	0.58	97.80	2.10
Povidone–iodine	1.05	99.70	2.30
Eltroxine	2.10	102.50	1.10
	1.31	98.50	2.90

^a Mean recovery and standard deviations for five determinations.

Iron (II, III) caused serious interference by catalyzing the oxidation of VB with H₂O₂ [38], and addition of ethylenediaminetetraacetic acid (EDTA) was required to reduce the interference of iron up to 150 folds without a noticeable effect on the iodide determination. The interference of copper can be suppressed using triethylenetetramine as complexing agents. Sulfamic acid is an effective reagent for nitrite decomposition, and addition of 2 mL of 3% sulfamic acid solution improved the interfering effect of nitrite to 1000-folds.

However, the tolerance limits for these interfering ions are greater than the levels normally present in analyzed samples, and the proposed method can directly be applied for the determination of iodide without the need of separation or pretreatment procedures.

3.3. Analytical applications

To validate the proposed method, it was applied for iodide determination in edible salt and pharmaceutical samples. Results (Table 3) showed non-significant difference between the proposed and the official methods. The recovery was found to be quantitative and the repeatability of the method was satisfactory with short analysis time less than 3 min.

4. Conclusions

The present work demonstrated that catalytic potentiometric methods can be simply applied for trace determination of iodide compared with spectrophotometric ones. The proposed method has many advantages of permitting simple, accurate and precise determination of iodide down to microgram levels using of simple and inexpensive equipments. The sample analysis time was very short when compared with some previously published methods, and carried out at more ambient conditions in one step reaction. The method was successfully applied for iodide determination in different samples with recoveries agreed with that of the standard method. The behavior of a selected system allowed the development of a kinetic method for the determination of trace amounts of iodide without any separation or preconcentration step.

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