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Ion-Selective Electrodes for the Determination of Periodate IO_4^- Using Periodate - Tetrazolium Chloride (TTC) as an Ion-Pair and its Applications

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الملخص

تم تحضير، وفحص غشاء بولي (كلوريد الفينيل) (PVC) المكون من 2، 3، 5 – تراي فينيل تيترازوليوم كلوريد KIO_4 - (TTC) مع رباعي فينيل بورات الصوديوم (NaTPB) كمستبعد أنيون، وثنائي أوكتيل فثالات (DOP) وثنائي أوكتيل سبيكات (DOS) كمادة ملدنة، ويعمل كقطب انتقائي ل KIO4، ولوحظ أفضل أداء للغشاء الذي يحتوي على مادة الترابط تركيبة من (KIO4 - PVC-TTC) (5mg)، وملدن (DOP) (200mg) و PVC: 100mg وNaTPB رباعي فنيل بورات الصوديوم :5mg، والتي عملت بشكل جيد على مدى تركيز واسع (1.5×10^{-6}–1.0×10^{-1} M) من (50 - 55.0) مللي فولت لكل عقد تركيزات من النشاط بين الرقم الهيدروجيني (3- 10) pH أظهرت هذه الأقطاب الكهربائية وقت استجابة سريعًا من 5 إلى 15 ثانية، وتم استخدامها على مدى 90 صبغة مع قابلية استنساخ جيدة، ومعامل الانتقائية لـ الأنيونات أحادية التكافؤ وثنائية التكافؤ تشير إلى انتقائية ممتازة لـ IO_4^- أيونات على عدد كبير من الأنيونات، تم استخدام المستشعر لتحديد IO_4^- أيونات في آبار المياه في منطقتي أوجلى، وجالو بمنطقة الواحات / ليبيا وكذلك في مياه الصرف.

الكلمات المفتاحية: الأقطاب الكهربائية الانتقائية الأيونية، البيرأيودات، كلوريد تترازوليوم، مياه الصرف.

Abstract

Poly (vinyl chloride) (PVC) membrane-based of 2, 3, 5 –Triphenyltetrazolium Chloride (TTC)- KIO_4 with sodium tetraphenylborate (NaTPB) as an anion excluder and dioctylphthalate (DOP) and dioctylsebacate (DOS) as plasticizer were prepared and studied as a KIO_4^- selective electrode. The best performance was observed with the membrane having the ligand (TTC KIO4 – PVC – plasticizer (DOP) – NaTPB (sodium tetraphenylborate) composition 5: 100: 200: 5mg, respectively, which worked well over a wide concentration range (1.5×10^{-6} M – 1.0×10^{-1}M) with a Nernstian slope of 50–55.0 mV per decade of activity between pH 3 and 10.0. These electrodes showed a fast response time of 5 – 15 s and were used over a period of 90 dyes with good reproducibility. The selectivity coefficient for monovalent and divalent anions indicated excellent selectivity for IO_4^- ions over a large number of anions. The sensor has been used to determine IO_4^- ions from Ojela and Jalu /Libyan water wells and wastewater.

Keywords: Ion-selective electrodes, Periodate, Tetrazolium chloride, Wastewater.

1. INTRODUCTION

Triphenyltetrazolium chloride was used for determining iodate and periodate [1]. Iodonitrotetrazolium chloride and tetrazolium violet were used for determining chromium spectrophotometrically [2], [3]. Triphenyltetrazolium chloride was used for determined mercury in soils spectrophotometrically [4]. 2, 3, 5-Triphenyl-2H-tetrazolium chloride was used as a reagent for sugar determination [5]. Neotetrazolium chloride formed the ion-pair of tetrathiocyanatocobaltate (II) to determine cobalt (II) spectrophotometrically [6]. Tetranitro-blue tetrazolium was used for determined selenium spectrophotometrically [7]. An electrochemical sensor for determined iodate and periodate [8]. Methylene blue was used for determining periodate and iodate spectrophotometrically [9], periodate and iodate were determined spectrophotometrically by calculating the rates of reactions in acidic media with iodide [10].

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IrO_2 nanoparticles are grown on a glassy carbon electrode by electrodepositing method, Iodate and periodate are reduced and the electrochemical properties and electrocatalytic activity of the modified electrode are investigated [11]. Dopamine was determined in pharmaceutical preparations based on its oxidation with (IO_4^-) using a new IO_4^--selective electrode [12], and (IO_4^-) oxidation constrict to the development of selective devices methods of micro-analysis in several fields like electrochemistry, spectrophotometry, chromatography, luminometry, are successful manufacturing of sensors or labeling techniques [13]. The ion-associate of (IO_4^-) extraction balance with HCl was studied spectrophotometrically [14]. Liquid-membrane for determining (IO_4^-) by the ion-selective electrode and its implementation to the potentiometric titration of α-diols and α-amino-alcohols occurred [15], (IO_4^-) -selective electrode was utilized for determining tartaric acid [16], and (IO_4^-) -sensitive ClO_4^- by the ion-selective electrode in the kinetic ultra-micro-determination of manganese (II) was used [17]. Fluorometric analysis of (IO_4^-) based on the oxidation of 2-acetylnaphthol phenyl selenoether and application to the assay were regenerated of (IO_4^-) [18]. The ion-selective membranes were made of PVC with ionophore porphyrin-based sensing systems and cation lipophilic as additive materials was used to

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calculate (IO_4^-) concentration [19]. A method for the determination of reducing sugars in serum was studied; the sample reacted with an excess of (IO_4^-) in a flow system and the decrease in (IO_4^-) [20], and the tubular (IO_4^-) electrode for flow-injection determination of glycerol was devolved [21]. Sucrose $C_{12}H_{22}O_{11}$ was determined in milk products and soft drinks by the acid hydrolysis of sucrose and lactose with the rate of the reaction of (IO_4^-) with quenched aliquots of the solution in which hydrolysis takes place [22], and used nickel (II) Schiff bases, as a neutral carrier to made ion-selective membrane electrodes for the determination of (IO_4^-) [23]. Riboflavin immobilized multi-walled carbon nanotubes amendment electrode GCE/MWCNT-RB was prepared and proved as an electrochemical selective sensor for (IO_3^-) detection [24], and oxalate was determined by the kinetic spectrophotometric method and based on it improved the effect on the oxidation of Mn (II) to MnO_4^-; by KIO_4[25]. IO_4^- consumption by use of an iodide-selective electrode was calculated [26]. An excited state intramolecular proton transfer (ESIPT) fluorescent probe for highly selective and ratio-metric was used for the detection of IO_4^- [27]. Iodate and IO_4^- at the microgram level were determined by a kinetic method [28].

This study used 2, 3, 5-Triphenyl-2H-tetrazolium chloride with periodate as an ion-pair sensor electrode for determining periodate by the ion selective electrode method and applied this method for determining the periodate in wells water, juices, and wastewater.

2. EXPERIMENTAL

2.1. Reagents and Materials

All chemicals were of analytical reagent grade unless otherwise stated and doubly distilled water was used throughout. Periodate KIO_4 (M. wt. = 230) was obtained from Aldrich Chem. Co., polyvinyl chloride PVC powder of Mwt~10000 (THF) tetrahydrofuran solvent 99%, inhibited by 0.025% butylate di-hydroxy toluene, dioctylsebacate DOS, sodium tetraphenylborate (NaTPB) as an anion excluder, and dioctylphthalate DOP as a plasticizer with a purity of ~99%. 10^{-1} M solution of KIO_4 was prepared by dissolving 2.3 g of KIO_4 in 100 ml of (0.05 M) PO_4^{3-} buffer solution pH 7. IO_4^- ion (10^{-1} M – 10^{-6} M) solution was prepared then, dilution of the IO_4^- ion solution by 0.05 M PO_4^{3-}, buffer solution of pH 7, and 2, 3, 5 Triphenyltetrazolium chloride TTC or simply Triphenyltetrazolium chloride as a redox indicator commonly used in biochemical experiments specially to indicate cellular respiration. It is a white crystalline powder, soluble in water, ethanol and acetone but insoluble in ether.

2.2 Apparatus

All Potentiometric Apparatus at 25 ± 1 °C with an Orion pH / mV meter. A double junction Ag / AgCl reference electrode was used, and an electrode (Model 90 – 02) filled with 10% (w/v) KCl was used in the outer closet. A glass electrode (Orion 81– 02) was used for pH measurements.

2.3. Synthesis of (TTC- KIO4) ion pair

1g of TTC was dissolved in 100 ml distilled water + 1g KIO_4 in 100 ml distilled water; white precipitate was formed.

2.4. Preparation of Membrane

Homogeneous membranes of TTC – KIO_4 ion pair were prepared by using PVC as a binder, DOP and DOS as a plasticizer and NaTPB (sodium tetraphenylborate) (anion excluder) were mixed and dissolved the membrane components in diluent THF. Then it was stirred vigorously until the result was a homogeneous syrup. After all the air bubbles were removed, it was poured into glass casting rings resting on a smooth glass plate. The solvent was evaporated at room temperature. After waiting for about 48h, a transparent membrane of about 0.5 mm thickness was obtained from which about 5 mm in diameter was cut away from the inner edge of the cyclic ring and stuck to one end of the polyethylene tube with the membrane by THF.

2.5. Potential Measurement

The membranes were equilibrated with 10^{-2} M KIO_4 solutions for two days and the potential across the membranes was measured with potential membrane used in the outer of reference electrodes in a tube; (10^{-2} M KIO_4 solution + 10^{-2} M KCl) as an internal solution. All the measurements were made at a constant temperature of 25 ± 0.1◦C. Response time was determined after the potential of one solution of 10^{-6} M KIO_4 solution became constant and similar measurements were carried out in another solution of 10–fold higher concentrations. The response time is measured as the time taken to reach an mV of 90% of the potential difference in the two following measurements. Reproducibility can be known as the deviation from the average potential value in the same four dips measurements data.

3. RESULTS AND DISCUSSION

TTC is a redox indicator commonly used in biochemical experiments specially to indicate cellular respiration. The crystalline powder (white) was soluble in water, ethanol and acetone but insoluble in ether [29].

The reaction involves (TTC) with KIO_4; the white precipitate was formed from the TTC-KIO_4 complex used as an ion pair in an ion-selective membrane with (NaTPB) as an anion excluder and (DOP) as a plasticizer. PVC and THF were prepared and studied as a KIO_4–selective electrode for the calculation of the concentration of KIO_4 in water or wastewater or other samples using a calibration curve, and the time of response recorded quadrate the IUPAC recommendation [30].

An electrode membrane contains a solvent mediator (DOP) and DOS; the electrodes achieved an equilibrium response within 15 – 20 s over a whole concentration range of 1.41×10^{-6} M – 1.0×10^{-1} M. The potentials obtained must be still constant for more than 5 min, after a slow variation of data is observed. All potentials were measured periodically and the standard deviation of about 50 mV corresponding measurements was ± 0.4 mV. The lifetime of electrodes based on ion pairs in solvent polymeric membranes depends on the distribution coefficient of the ion pairs and plasticizer between the aqueous and membrane phases. Hence, the lifetime of electrodes must depend on the compositions of the solution and the measured compounds with electrodes. The results experimentally explain that the lifetime of the present electrode was about 15 weeks, the detection limit was stable, and the slope of the electrode was observed to be constant, and remained constant, during this time. The

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electrochemical demeanor of the electrodes gradually degenerates after 15 weeks, which can be due to the senility of the (PVC), DOP plasticizer and ion pair (TTC) (IO_4^-) [31].

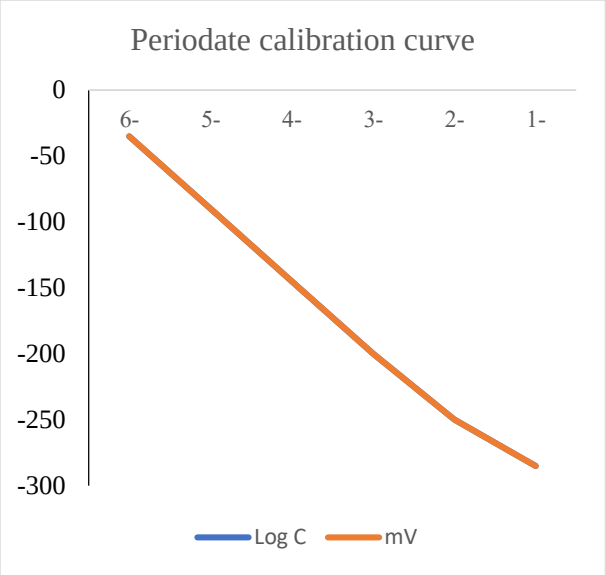


Fig. 1. The relationship between log C in the X- axis and mV in the Y- axis for IO_4^-

KIO_4 -TTC membrane contains the DOP as a plasticizer and shows linearity at the concentration range between 1.0×10^{-5} M, and 1.0×10^{-1} M a slope of about 55 mV ± 0.4 mV per (10) decade. Hence, the membrane electrode was investigated as a KIO_4 selective electrode and all further were studied with this membrane electrode. The salts which incorporated, and which consisted of a hydrophobic cation and a lipophilic anion, e.g., (NaTPB), based on TTC-IO_4 have proved to be beneficial in several respects [32].

Sodium tetraphenylborate (NaTPB) reduces interference by lipophilic anions in the sample by bringing about significant changes in selectivity and boosting the anion selectivity in the case of carriers with poor extraction capability and decreasing the electrical membrane resistance considerably [33,34]. When preparing the electrode without NaTPB, the sensitivity of the electrode and selectivity for KIO_4 was decreased, due to the high resistance of anions in the solution. NaTPB acts as an ion exchanger [35]; hence NaTPB was used, leading to drastic changes in the shape of the slope, and in more response, the membrane electrode becomes more selective.

The electrode potential was investigated over the pH range 2.0 – 12.0 for 1.0×10^{-3} M and 1.0×10^{-4} M of KIO_4. The pH changed with HNO_3 acid or ammonia hydroxide solution. The potential is still stable between pH 3.0 – 9.0 **(Fig. 2)** and the same can act in this working range of pH of the electrode perfectly.

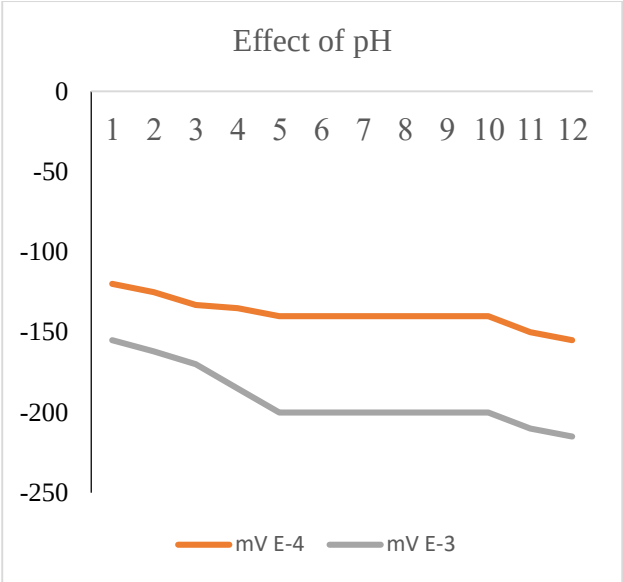


Fig.2. Effect of pH in X- axis and – mV in Y- axis at concentrations 10^{-3} M and 10^{-4} M of IO_4^-

This paper used the Matched Potential Method (MPM) to calculate the selectivity coefficients K^{Pot} IO_4^- [36] at a 1.0×10^{-2} M concentration of some interfering ions. By studying interfering ions and periodate, the electrode was selective to determine KIO_4 concentration (**Table 1**); the reversibility of the membrane electrode which can be calculated in a similar step in the opposite direction was done. The data was placed in the sequence from high values to – low values, i.e., from 1.0×10^{-2} to 1.0×10^{-3} M concentrations of samples, and the results explained that the potentiometric response of the membrane electrodes was reciprocal; although the equilibrium values were reached at the time about (50 s) which is a longer time than that of low to – high concentrations of samples. The lifetime of a membrane or membrane electrode is nearly 2 months [37,38,39,40,41], and the reproducibility of the electrode was studied by using six similarly constructed TTC – KIO_4 electrodes under several conditions. The results explained a good Nernstian slope of about 50 mV (± 0.4 mV) for the membrane electrode.

Table1. Selectivity coefficient data (K^{Pot} IO_4^-) for IO_4^- selective membrane electrode contain TTC- IO_4^- ion-pair.

Interfere	K^{Pot} IO_4^-	Interferes	K^{Pot} IO_4^-
KIO_4	2.3×10^{-5}	K_2CO_3	1.3×10^{-4}
KIO_3	2.2×10^{-5}	$KHCO_3$	1.4×10^{-5}
$KClO_4$	2.1×10^{-4}	$KMnO_4$	1.1×10^{-4}
$KClO_3$	1.2×10^{-4}	K_2CrO_4	2.3×10^{-4}
K_2SO_4	1.3×10^{-4}	$K_2Cr_2O_7$	1.2×10^{-4}
K_2SO_3	1.2×10^{-5}	KH_2PO_4	1.3×10^{-5}
$KHSO_4$	1.4×10^{-5}	K_3PO_4	1.4×10^{-5}
KNO_3	1.1×10^{-4}	CH_3COOK	1.1×10^{-4}
KNO_2	1.2×10^{-4}	$(OH)_2(CH)_2(COOK)_2.5H_2O$	1.3×10^{-4}

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3.1. Application of IO4- Sensor Electrodes

Table 2*:* Determination of IO_4^- in the well water from Ojela and Jalu wells, juices, and wastewater.

Sample	Concentration (ppm)
(Water well 1)	230
(Water well 2)	23
(Water well 3)	12
Orange juice	4
Beetroot	12
Carrot juice	8

4. CONCLUSION

The TTC-IO_4^- membrane electrode incorporating an ion-pair can be seen in the expansion of the IO_4^- ion–selective electrode. The data shows that the (DOP) plasticizer electrode proved to be a good solvent mediator for electrode construction. The suggestion electrode showed high selectivity and sensitivity to IO_4^- ions, and a fast time response with a Nernstian slope of about 55.0 mV/decade to IO_4^- for a large scale of the concentration range of 1.5×10^{-6} M –1.0×10^{-1} M. The proposed electrode revealed excellent selectivity towards IO_4^- and was used to determine IO_4^- in water, wastewater, and different juice samples which may contain IO_4^-.

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