ADDIS ABABA UNIVERSITY

SCHOOL OF GRADUATE STUDIES

DEVELOPMENT OF PERCHLORATE SELECTIVE COATED GRAPHITE ELECTRODE BASED ON CRYSTAL VIOLET AND ITS APPLICTION TO THE DETERMINATION OF ETHYLENE GLYCOL, GLYCEROL, GLUCOSE AND MANNITOL VIA PERIODATE OXIDATION

A Project Presented to the School of Graduate Studies Addis Ababa University

In partial Fulfillment of the Requirement for the Degree of Master of Science In Chemistry

Advisors:

Dr. Ghirma Moges

Dr. Negussie Megersa

By

Atnafu Guadie

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DEDICATION

To my mother Banchiayehu Ayele who always inspire me to make progress in life.

DECLARATION

I, the undersigned, declare that this project paper is my original work and has not been presented for a degree in any other university. All sources of materials used for the project work have been duely acknowledged.

Name Atnafu Guadie

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This project has been submitted for examination with my approval as university advisor

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Place and date of submission _____

Department of Chemistry

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DEVELOPMENT OF PERCHLORATE-SELECTIVE COATED GRAPHITE ELECTRODE BASED ON CRYSTAL VIOLET AND ITS APPLICTION TO THE DETERMINATION OF ETHYLENE GLYCOL, GLYCEROL, GLUCOSE AND MANNITOL VIA PERIODATE OXIDATION

ABSTRACT

An attempt was made to develop perchlorate-selective coated graphite electrode based on crystal violet using 1-chloronaphthalene as plasticizer. The electrode prepared by coating crystal violet-perchlorate ion association in 1-chloronaphthalene both as the plasticizer and the solvent with a PVC matrix on a graphite rod was found to give a Nernstian response to perchlorate in a wide concentration range. Proper response of the electrode was observed in test solutions made in 0.1 moleL^{-1} potassium nitrate solution. The linear range, slope, and detection limit from the plot of E vs log [ClO_4^-] were found to be 1.0 x 10^{-5}-1.0 x 10^{-1} mol L^{-1}, 58±1.5 mV/decade and 3.16 x 10^{-6} mole L^{-1} perchlorate respectively. The electrode was also used to detect periodate with linear range, slope and detection limit of 1.0 x 10^{-4}-1.0 x 10^{-2} mol L^{-1}, 57±1.5 mV/decade and 5.7 x 10^{-5} mole L^{-1} periodate respectively. The response time of the electrode was found to be < 20 s for concentrations higher than 1.0 x 10^{-4} M and the electrode functioned properly for four weeks. The effect of the amount of the electroactive ion pair was also studied and it was found that electrode prepared from 20-30 mg of the crystal violet perchlorate was chosen with the best response. The effects of diverse ions on the electrode response to perchlorate were studied and the potentiometric selectivity coefficients were evaluated. The electrode was found to be highly selective to perchlorate and periodate. The analytical application of the electrode was extended to the direct determination of perchlorate and periodate and to the indirect determination of ethylene glycol, glycerol, glucose and mannitol via periodate oxidation.

KEY WORDS: Ion selective electrode (ISE), coated graphite electrode (CGE), ethylene glycol, glycerol, glucose and mannitol.

1. INTRODUCTION

1.1. Some Common Properties of Perchlorate and Method of Determination

Many chemists tried to investigate the different techniques and methods for the determination of perchlorate ion and the need to study it rapidly increases. Among the several reasons that arose the interest are perchlorate salts, especially ammonium perchlorate, are used in missile, rocket and space shuttle propulsion systems. The other reason is that perchlorate salts, usually $KClO_4$, have been used pharmaceutically. Perchlorate and similar oxyanions with similar nature are notified in residues from explosions. There is a need to qualitatively and quantitatively analyze soil and dust for these analytes. The most prominent reason related to our study is that electrochemical sensors are often evaluated in terms of Hofmeister behavior, for which perchlorate represents an extreme case. Thus, there is a need for analysis to ensure quality control in the production of perchlorate [1].

From the stand point of chemotherapeutic use or drinking water contamination, there is a need to determine trace concentrations. The interest in analyzing surface, ground and drinking water for perchlorate related to possible health effects increases rapidly [1, 2]. As a result recent developments for perchlorate determination are a direct consequence of concerns over potable water. Thus, techniques and methods developed for analysis of aqueous solutions may be applied to a variety of sample matrices containing perchlorates.

1.2. Methods of Determination of Perchlorate

A large number of instrumental as well as chemical methods have been reported in the literature for the determination of perchlorate. The different analytical techniques available in the literature for the quantitative determination of perchlorate include spectrophotometry, gravimetric, capillary electrophoresis, ion chromatography, mass spectrometry, flow injection analysis [1-4]. However, these analytical methods up to this point suffered from a wide variety of interferences, limitations in sensitivity as well as complicated methods and need sophisticated instruments.

The lower limits of detection were generally inadequate. Gravimetric determination based on nitron, which is still in use today, suffers from a variety of interferences as nitron precipitates many large anions, including perchlorate, iodide, nitrate (aqueous solution as a solvent), tungstate, bromide and perrhenate [1]. The first indirect atomic absorption method based on perchlorate cuprous complex with reasonable selectivity in the presence of common ions for the determination of perchlorate has been reported [5]. It is also reported in the literature that interference and dye impurities would appear to pose high barriers to spectrophotometric and colorimetric methods at low (ppb) concentrations [6]. The last few years methods based on extraction of ion-pair with protriptylinium cation including spectrophotometric methods have been developed [4, 7]. However the methods suffer from strong interferences of permanganate, bromide, molybdate, thiocyanate, chlorate and poor limit of detection. The absorption maximum was dye dependent and causes a change in absorption maximum due to the disruption of chemoreceptor-dye interactions for the spectrophotometric methods [8]. Flow injection analysis method with automated extraction was another method tried for the determination of perchlorate [9]. However, the method suffers from lack of selectivity in the presence of chlorate, iodide or nitrate aqueous solution as a solvent.

Further more multi-information dyes have not been applied to real matrices yet. Besides molecular design and ease of construction appeared to be the key areas of research to achieve selectivity for the direct determination of perchlorate without prior separation in the presence of common anions at high concentration [3, 8].

Recently anion–selective liquid membrane electrodes based on ion association salts have been reported. Basic dyes such as crystal violet and brilliant green commonly found in analytical laboratories were used as extractants and spectrophotometric reagents for anion and cationic metal complex determinations, as well as acid-base indicators [10]. Besides liquid membrane electrodes selective to ClO_4^-, SCN^-, BF_4^-, NO_3^-, Cl^-, and Br^- based on triphenyl dyes: Malachite green, Fuchsine, Crystal violet, Methyl violet, Gentian violet and Alkali blue have been used as electroactive materials in nitrobenzene [11]. The availability of these dyes has widened their applicability to polymer supported anion-selective

electrodes. Recently these dyes have been used for the preparation of tetrathiocyanatozincate (II) [12], saccharin [13], tetrachloroferrate (III) [14] and hexafluorotantalate (V) [15].

Very recently crystal violet and brilliant green-perchlorate extract in nitrobenzene was used to prepare perchlorate–selective liquid membrane electrode with a PVC support [11]. The response characteristics of the electrode were evaluated and the linear range of response to perchlorate and periodate were 10^{-6}-10^{-1} M, 10^{-6}-10^{-2} M with Nernstian and sub-Nernstian slopes respectively. The effect of diverse ion on the electrode response to perchlorate was studied and the electrode was found to be highly selective to anions in the order: MnO^-_4, $ClO^-_4 \approx IO^-_4$, SCN^-, I^-, $Sacc^-$, Hp^-,ClO^-_3, NO^-_3, Br^-, $BrO^-_3 \approx Cl^-$, and F^-. The application of crystal violet-perchlorate liquid membrane electrode has also been successful for the direct determination of low concentration of perchlorate and periodates and for the indirect determination of glucose, manitol and some amino acids, via periodates oxidation. A structural formal for the chloride salt of crystal violet dye is shown below in Figure 1.

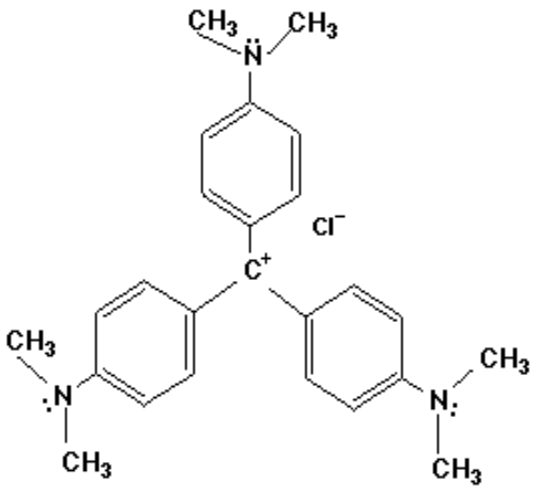


Figure 1. A structural formal for the chloride salt of crystal violet dye

1.3. Scopes and Needs of the Present Investigation

The forgoing discussion reveals that ion selective electrodes (ISEs) have been developed for perchlorate during the last few years and the study of the behavior of the electrode such as selectivity, stability and ranges of practicability were insufficient. Although many applications have been done, there are still many more to be explored. The crystal violet-perchlorate liquid membrane electrode has been used successfully for the direct determination of low concentration of perchlorate and periodate and for the indirect determination of glucose, manitol, ephedrine and two amino acids (serine and threonine) via periodate oxidation. However these electrodes were a bit cumbersome to use as it requires to be in a nearly upright position and expensive since it requires an internal reference system [16]. Thus, the development of new type of ion selective electrode from cheap materials which is simple, sensitive and economical is intended to the indirect determination of some of the anions such as mannitol, glucose, ethylene glycol and glycerol that are not sensed by the electrode via oxidation by the anion, periodate, to which the electrode is selective, in addition to the direct determination of the anions that are detected by the electrode such as periodate and perchlorate. The low cost, simplicity, ease of use and maintenance of brilliant green and malachite green hexafluorotantalate CGE [16, 17] and the applicability of liquid membrane electrode for the direct determination of analytes by dry sample addition methods [13] have stimulated the interest of constructing perchlorate selective coated graphite electrode (CGE) for the determination of anions that are not detected by the electrode. Further more there have been no previous reports about the newly developed CGE selective to perchlorate. The previously reported membrane ISE mentioned in the literature survey also states that the electrode body of ISE responsive to perchlorate needs internal reference electrode and internal filling solution [10, 13-15]. The newly developed method automatically eliminates the need for using these materials. Secondly no attempt has been made for the indirect determination of mannitol and glucose via oxidation by dry sample addition method. The objective of the present project work is, therefore,

1. to develop crystal violet based perchlorate selective coated graphite electrode.
   1.1. to prepare crystal violet-perchlorate ion pair salt.
   1.2. to prepare crystal violet-perchlorate coated graphite electrode.

2. to study the electroanalytical parameters of the electrode (linear range, slope, detection limit, response time etc).
3. to study the analytical application of crystal violet-perchlorate coated graphite electrode for the determination of perchlorate, periodate, ethylene glycol, glycerol, glucose and mannitol.

2. THEORY

2.1. Membrane Electrode Potentials

Potentiometry went through a silent revolution during the past decades [18]. Recently ISE technology has become the subject of rapidly increasing from time to time. The rapid development and ever-increasing range of applications is a measure of the extent to which these devices meet the need for accurate, cheap, reliable analytical information and low cost analysis [11, 16]. In spite of this increasing interest there are still unexplored potential applications being a mastery of laboratories. Broadly speaking these ion selective electrodes (ISEs) consists of electrochemical membrane of solid or a liquid phase perfectly separating two electrolyte solutions which are permeable to only one ion species [19, 20]. In an electrochemical cell, this phase that separates two electrolyte solutions to prevent mass movement between them but allows passage with various degrees of restriction of one or several species constitutes a membrane electrode [21, 22].

The composition and the speeds at which the components of the phase are permeable to the membrane determine the behavior of the membrane electrode [19-23]. These components of the membrane electrode are the electroactive solids or liquids materials containing ionizable groups which have the ability to bind certain ions selectively at the appropriate sites. When the ISEs are placed in solutions containing the particular ion (to which the electrode is reversible), a small number of ions (to which the electrode is selective) pass from the solution of higher concentration to the solution of lower concentration, electrical potential difference known as diffusion potential will be produced [19, 24]. Further diffusion of particular ion species will eventually ceased by transmembrane difference of the electrode potential (Donnan potential) generated. The diffusion potential results from mobility

difference and concentration gradient of ions in the electrolyte but Donnan potential results from complete hindrance of ions across the interface between the electrolytes. The fixed charges within the membrane distinguish among ions according to their charges [20, 23].

The membrane potential cannot be determined directly, but can easily be derived from the e.m.f values for complete electrochemical cell [25]. The cell comprises three components: the reference electrode assembly, the sample (test solution) and the membrane electrode [26]. The electrochemical cell thus, formed may be represented by

Ref. 1/ membrane / Ref. 2 cell (I)

where Ref. 2 are the reference electrode. Ref. 2 may be a conventional reference electrode, where as Ref. 1 may consist of an internal solution with a conventional reference electrode or it may be a conductor in the case of a coated wire electrode. Reference electrode is one of the important elements in the electrochemical measurement by the indicator electrodes. Thus, the sensing (membrane) electrode will dominate the overall response of the potentiometric circuit to external variations of the ion to which it is responsive. Ion selective electrodes (ISEs) have unique characteristics to sense and respond to changes in ionic activities [27] and provide means to easily determine activity coefficients [28]. Further more ISEs usually respond according to Nernst equation to ions to which it is selective. For an ion, i, the Nernstian equation for the response of a cell such as that represented by cell may be written as

$$E = E^{O} \pm \left(\frac{RT}{Z_i F}\right) \ln a_i \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad 2.1$$

where E^0 is the standard potential of the cell, a_i, the activity of i and Z_i is the number of charge on i. The sign in the equation is positive when i, is a cation and negative when it is an anion. Eq. (2.1) describes the pure response of the electrode and thus, assumes that ideal selectivity is not a feature of real electrodes [26].

2.2. Coated-wire Electrodes

Coated-wire electrodes (CWEs) are ISEs whose electroactive mixture are coated over solid internal contacts and thus, do not require the conventional reference system [16]. The solid substances on which the sensing element is directly cast can be carbon (graphite) or metals such as platinum silver or copper [29-31]. The small size of the coated tip (sensing part) of the electrode makes it possible measurements to be performed in a relatively small solution volume [16]. The literature survey also states that the CGE has significantly better sensitivities. The redox couples or ion association at the substrate solution interface probably performs the function of internal reference [16]. For the CGE, however, it was suggested that there might be a different mechanism that keeps interfacial potential difference constant.

2.3. Ion Selectivity of Membranes

The selectivity of polymer membrane based ISEs may be understood from empirical or mechanistic perspectives. Selectivity is, therefore, defined as the thermodynamic ion exchange selectivity of the membrane. Practically, no ISE responds exclusively to the ion for which it is intended to measure, although it is often far more responsive to the primary ion than to any others [18, 26, 29]. Thus, the performance of the membrane can be impaired by the interfering ions [28]. The Selectivity of ISE is, therefore; represented by its ability to distinguish between different ionic species present in the test solution and selectively respond to a particular ion. An electrode is ideally selective, i.e., when its potential is not affected by any ionic species present in the sample solution other than the ion for which the electrode is selective [25, 32].

2.3.1. Potentiometric selectivity coefficient

The potentiometric selectivity coefficient, K_{ij}^{pot}, of an electrode is a measure of its ability to distinguish between different ion species in the sample solution in contact. An electrode is ideally selective, i.e., specific, when its potential is not affected by ionic species present in the sample solution other than the ion for which the electrode is selective. If an interfering ion is present at a concentration which is larger with respect to the primary ion, the electrode

response will have contribution from both the primary and the interfering ions. The thermodynamic ion exchange selectivity of the membrane is described by potentiometric selectivity coefficient, K_{ij}^{pot} where i and j refers to the primary (analyte) ions and interfering ion respectively. The smaller value of the selectivity coefficient, K_{ij}^{pot} signifies better selectivity to the primary ion i. When the electrode is very selective for i in comparison with j, K_{ij}^{pot} will be much less than unity. Conversely, if, as occasionally happens, the electrode responds preferentially to j rather than to i, K_{ij}^{pot} will be greater than unity [26]. For an electrode responding to an ion i of activity a_i and charge Z_i in the presence of an interfering ion j of activity a_j and charge Z_j the potential is given by [19].

$$E = E^{o} \pm \left(\frac{RT}{Z_i F}\right) \ln\left(a_i + K_{ij}^{pot} a_j^{Z_i/Z_j}\right) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad 2.2$$

where K_{ij}^{pot} is the potentiometric selectivity coefficient. The selectivity coefficient has also been called the selectivity constant and the selectivity factor. The former term is inappropriate because selectivity coefficients are seldom constant for all experimental conditions and ratios of i to j [26]. The latter term, while being as accurate as 'selectivity coefficient', has not received wide acceptance [33].

2.3.2. Determination of the selectivity coefficient

Several methods have been described for the experimental determination of the selectivity coefficients. These methods are based on potential measurements either in separate solutions or in mixed solutions containing the primary and the interfering ion [25, 26, 34]. Thus, the methods fall in to two categories: (i) separate solution methods and (ii) mixed solution methods.

(i) Separate solution methods: In this method the potential of the electrode under investigation is measured first in solution containing the interfering ion j with no i present. Similarly, the electrode potential is measured in solution containing the ion of interest i with no j present. The K_{ij}^{pot} is calculated by using any one of the following methods [25, 34-36].

Method 1. For the primary ion i only in solution (i.e., $a_j = 0$), Eq. (2.2) becomes

$$E = E^0 \pm \left(\frac{RT}{Z_i F}\right) \ln a_i \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad 2.3$$

If the solution is without i (i.e., $a_i = 0$) and containing only ion j, then, Eq. (2.3) becomes

$$E = E^0 \pm \left(\frac{RT}{Z_i F}\right) \ln K_{ij}^{pot} a_j^{z_i/z_j} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad 2.4$$

For the condition $a_i = a_j$, Eq. (2.3) and Eq. (2.4) give the relation

$$\pm (E_j - E_i) \frac{Z_i F}{RT} = \ln K_{ij}^{pot} + \left[\left(\frac{z_i}{Z_j}\right) - 1\right] \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad 2.5$$

Method 2. If the concentration of the solution of the ion i and the solution of ion j are so chosen that $E_i = E_j$, then, Eq. (2.3) and Eq. (2.4) give

$$K_{ij} = a_i / (a_j)^{z_i/z_j} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad 2.6$$

Thus, the selectivity coefficient can be calculated by using Eq. (2.5) or Eq. (2.6), accordingly. These separate solution methods of measuring K_{ij}^{pot}, although simple to perform, cannot be recommended, as they do not give reliable results. This is because the conditions for potential measurements are not well defined probably due to electrode surface contamination by solution of i while making measurements in solution j [21]. The methods are unsatisfactory because they do not reflect the real situation of measurements with normal samples which almost contain more than one ion pair [37]. In addition, in a statically

approach to the estimation of selectivity parameters of ISEs, it has been proved [38] that parameters which would be obtained from the separate solution methods were meaningless and no value could be attached to them. In many cases, the response of an electrode in pure solutions of an interfering ion is also very slow, liable to drift and hence, unsatisfactory.

(ii) Mixed solution methods**:** The mixed solution method entail the measurement of the electrode potential in a range of solutions containing different activities of both i and j [25, 26]. This can be done by measuring the potential in solutions of fixed a_i and varied a_j or fixed a_j and varied a_i. IUPAC has recommended the method in which a constant interfering activity and a variable measured ion activity are employed [31].
Thus, the electrode potential in solutions containing both ions becomes

$$E = E^{o} \pm \frac{RT}{Z_i F} \ln(a_i + K_{ij}^{pot} a_j^{Z_i/Z_j}) \quad \text{2.7}$$

Eq. (2.7) can be combined with. (2.3) to give

$$E^{*} \quad E_i = \left(\frac{RT}{Z_i F}\right) \ln(a_i + K_{ij}^{pot} a_j^{Z_i/Z_j}) \quad \text{2.8}$$

If a range of solution with constant a_j and varying a_i are prepared, the measured potential of the electrode shows that the electrode responds to the ion i in Nernst manner at higher concentration of the ion of interest i . As solution becomes more and more diluted, the electrode gives mixed response to both i and j since the potential of the electrode is increasingly affected by the constant concentration of the interfering ion and at a very low concentration of the ion of interest i the electrode responds only to the interfering ion. The potentiometric concentration can then be evaluated by the different mixed solution methods. There are several mixed solution methods for calculating K_{ij}^{pot} from the plot of E^{*} versus – $\log a_i$.

Method 1. The first method depends on finding graphically the point T at which the electrode is responding equally to both ions by extrapolations. Thus, K_{ij}^{pot} may be calculated from the activity of i at point T, ${}_{T}a_i$ and the constant a_j using the equation

$$K_{ij}^{pot} = T\, a_i / (a_j)^{z_i/z_j} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad 2.9$$

Method 2. This is more generally applicable method. Again, from Eq. (2.6), both ions are contributing equally to the electrode response when

$$a_i = K_{ij}^{pot} a_j^{z_i/z_j} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad 2.10$$

If the activity of i at which this equality occurs is a_i and the activity of j is a_j, then, the electrode potential, E, is given by

$$E = E^{O} \pm \frac{RT}{Z_i F} \ln(a_i + K_{ij}^{pot}\, a_j^{Z_i/Z_j}) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad 2.11$$

$$E = E^{O} \pm \frac{RT}{Z_i F} \ln 2a_i' \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad 2.12$$

The response of the electrode in the absence of j is given by the extrapolation of the two linear lines as far as the limit of Nernstian response. The difference between the electrode potentials in solutions of i with activity a_i' with and without j at activity a_j is, therefore, given by

$$\Delta E = \pm \frac{RT}{Z_i F} [\ln 2a_i' - \ln a_i']$$

$$\Delta E = \pm \frac{RT}{Z_i F} \ln 2$$

$$\Delta E = \frac{18}{Z_i} \text{ mV at 25oC}$$

Thus, by finding the graph the activity of i at which the experimental line differs from the extrapolation of the two linear lines by $18/Z_i$ mV, the activity a_i is determined. Then, K_{ij}^{pot} is calculated by substituting a_i' in to the equation

$$K_{ij}^{pot} = a_i / (a_j)^{z_i/z_j} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad 2.13$$

In general mixed solution methods of selectivity coefficient determination are always preferred to the separate solution methods. A new twist on the mixed solution method [39], similarly preferred by Solsky [40], fixes the sum of logarithm of activities of the interfering ions constant so that a graphical treatment yields the selectivity coefficient.

2.4. Analytical Measurement Techniques

Ion-selective electrodes respond to ionic species in solution for which the electrodes are selective and their response characteristics is described by the Nernstian equation (Eq. (2.1)). Thus, ISEs senses the activity of the ions, which can be related to concentration by taking the activity coefficient of the sample solution in to account [19]. The other option is to fix the relation ship between the activity and concentration of the ions to be determined by adding a constant concentration of an electrolyte to all samples to swamp out minor variations in sample composition, then, an electrode can be used directly for concentration measurement [26].

Two measuring methods are generally, distinguished [41]. Direct method: In this method, the ISE is made to sense either the ion to be determined itself or some other material obtained by chemical transformations from substance to be determined. Indirect analytical methods: In this second method, the material to be determined is allowed to quantitatively react with another species and the concentration of the reagent or the substance arising from the reaction is followed by ISE detection. The most adopted analytical techniques using ion selective electrodes are briefly discussed as follow.

2.4.1. Calibration methods

This method involves measurement of potential of the sample solution which can be related to the activity or concentration of the ion of interest from constructed calibration curve of measured potential versus the activity or the concentration of the ion of interest in standard solutions [26]. A single measurement, therefore, gives the activity or the concentration of the ion [42].

The activity or concentration of the sample can then be determined by single point calibration. If a_x and a_s represent the activities of the sample and the standard and E_x and E_s, the corresponding electrode potential, then, it follows from the Nernst equation that

$$E_x - E_s = S \log\left(a_x / a_s\right) \quad \text{..... 2.14}$$

which can be rearranged to give

$$a_i = a_s 10^{-\Delta E / S} \quad \text{..... 2.15}$$

where S is the experimental slope and ΔE is the difference in electrode potentials for the sample and the standard. The value of S can be determined using two solutions of known activities. This approach requires no knowledge of the standard potentials of the electrode

pair. The assumption made here is that the slope is constant and that there is a linear relation between the potential and logarithm of activity or concentration.

The uses of two standard solutions with analyte activities a_1 and a_2 involving unknown activity, a_x , is a complicated version of this calibrated method. Then, applying the Nernst equation, a_x can be calculated from

$$\left(\frac{E_x - E_1}{E_1 - E_2}\right)\log\left(\frac{a_1}{a_2}\right) = \log\left(\frac{a_x}{a_1}\right) \quad \text{..... 2.16}$$

This method does not require any knowledge of standard potential or slope. Moreover, the method concentrates for slow drift in both parameters and a linear response over the range of interest can be assumed.

2.4.2. Standard and Sample addition methods

These methods are also called the known addition methods. The known addition methods are rapid and easy to perform and the errors are negligible when the electrode is well behaved to selectivity, working range and Nernestian response [25].

There are two different known addition methods described here. In the first the known solution of standard is added to a known sample volume and the change in the electrode potential is recorded and in the second one, a known volume of the sample is similarly added to a known volume of the standard.

Standard addition to a sample: This method involves measurement of the potential of the electrode system in a relatively large and accurately measured volume (V_x) of unknown concentration (C_x) of the sample solution which is added to a known small volume (V_s) of a relatively concentrated (C_s) solution of the sought for ion and the change in electrode potential is recorded. The initial potential of the sample solution of unknown concentration (C_x) is given by the Nernst equation as follow [21].

$$E_1 = E^O \pm \frac{RT}{Z_i F} \ln(C_x \gamma_x) + E_L \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad 2.17$$

where γ_X and E_L refer to the activity coefficient of the sample solution and the liquid junction potential respectively. On addition of a known amount of the standard (V mL of C concentration) to the initial volume (V), the new potential is given by

$$E_2 = E^O \pm \frac{RT}{Z_i F} \ln\left\{\left[\frac{(C_x V_x + C_s V_s)}{(V_x + V_s)}\right]\right\} + E_L \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad 2.18$$

Assuming the constancy of E_L and $\gamma_X = \gamma'_X$, subtraction of Eq. (2.17) from Eq. (2.18) gives

$$\Delta E = E_2 - E_1 = \pm \frac{RT}{Z_i F} \ln\left[\frac{(C_x V_x + C_s V_s)}{(V_x + V_s)}\right] \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad 2.19$$

On rearrangement Eq. (2.19) becomes

$$\frac{\Delta E}{S} = \log\left[\frac{(C_x V_x + C_s V_s)}{(V_x + V_s) C_x}\right] \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad 2.20$$

where S is the slope (= 2.303RT/Z_iF) experimentally determined by using a series of known standard solutions. Eq. (2.20) may be rearranged to give

$$C_x = \left[\frac{C_s V_s}{(V_x + V_s)}\right]\left[10^{\Delta E/S} - \frac{V_x}{(V_x + V_s)}\right]^{-1} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad 2.21$$

Thus, C_x can be evaluated. If, as is sometimes the case, the dilution caused by the addition of the standard solution is sufficiently small to be negligible, i.e., $V_x >> V_s$, then, Eq. (2.21) becomes

$$C_x = C_s \left(\frac{V_s}{V_x}\right)\left(10^{\Delta E/S} - 1\right)^{-1} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 2.22$$

In standard addition technique only one standard solution is required and neither calibration drift nor electrode calibration is required. The only thing, two potentials must be recorded per sample.

Sample addition to the standard: This method is the inverse of the standard addition method. The potential of the known volume (V_s) of the standard solution of known concentration (C_s) is first recorded followed by measurement of potential of the solution after the addition of volume (V_x) of the analyte solution and the concentration C_x is determined concomitantly using equation (2.23) [20, 21, 25].

$$C_x = C_s \left\{\left[\frac{(V_x + V_s)}{V_x}\right]10^{\Delta E/S} - \left(\frac{V_s}{V_x}\right)\right\} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 2.23$$

Eq. (2.23) can be divided by using C_s in place of C_x in Eq. (2.17) and subtracting it from Eq. (2.18).

This technique is very important for the analysis of very small volume which is insufficient to soak the electrode tip if it were alone. This is the advantage over the other techniques [26].

Standard subtraction method: In this method the standard solution containing species that reacts quantitatively with the determinand (through precipitation or complexation) is added

to a sample [20, 26]. Thus, a decrease in determinand concentration is produced with the corresponding change in potential. If a 1:1 stoichiometry of the reaction between the determinand and the added species is assumed, the initial concentration of the determinand in the sample is calculated by using the Eq. (2.24) [26].

$$C_x = \frac{C_s V_s}{\left[V_x - (V_x + V_s)10^{-\Delta E/S}\right]} \quad \text{..... 2.24}$$

Assumptions were made that dilution effect brought about by the addition of the standard solution is negligible and Eq. (2.24) reduces to a form given by Eq. (2.25)

$$C_x = \frac{C_s V_s}{\left[V_x(1-10^{-\Delta E/S})\right]} - 1 \quad \text{..... 2.25}$$

Equations (2.24) and (2.25) hold true, as already pointed out, for a 1:1 stoichiometry of the reaction; the equation become more complex, otherwise.

2.5. Response Time

Response time is one of the crucial factors which commend the uses of ISEs in routine analysis [25, 26]. According to IUPAC definition, it is the time needed for the potential of an electrode to reach a value 1 mV from the final equilibrium potential following a supposedly instantaneous change in determinand activity [26]. Fleet and co-workers defined the response time as the time interval with in which the electrode potential reaches 95% of the steady state value [43]. Accordingly, the particular values of the response time differ from author to author and are for rough comparison of the different Nernst response of electrode. The deviation from Nernst equation of the electrode response may arise from time dependent variations between the measured activity, a_i' and the intrinsic sample activity, a_i. Such activity gradients are related to diffusion process within the boundary layers of the sample solution (unstirred layer) which are produced as well by the equilibration between the bulk of the sample and interface in the adjoining boundary of the membrane. For a quoted value of the response time to be implemented, the experimental conditions on which

the response time depends experimentally should, therefore, be known. These conditions include initial and final determinand activities, stirring rate and the way in which the activities were changed.

2.6. Detection Limit

The detection limit of analytical procedure is the lowest concentrations of the analyte that can be distinguished with reasonable confidence with the field blank, here defined as a hypothetical sample containing zero concentration of the analyte [44]. Detection limit is estimated in the response (or signal) domain, but is usually reported in terms of concentration or amount (mass). The response domain is related to concentration by making use of the calibration function. The IUPAC has recommended that the limit of detection, defined in terms of either concentration or amount be related to the smallest measure of response that can be detected with reasonable certainty in a given analytical procedure.

The detection limit with ion-selective detection techniques is analogously defined as the measured ion concentration at which the measured signal is exactly twice as large as the background noise. This is the case, when the deviation from the Nernst equation is $18/Z_i$ mV (at 25^oC, $(59.1/Z_i)x \log 2 = 18/Z_i$) [28]. Ideally, the lower detection limit of an ISE results from interfering ion; hence its values are determined by the concentration of the other ion in the sample and corresponding selectivity coefficients K_{ij}^{pot} of the membrane. For a primary ion i with charge Z_i and dominant interfering ion j with charge Z_j, the lower detection limit is defined by Eq. (2.26) [18].

$$(DL) = K_{ij}^{pot} a_j^{Z_i/Z_j} \quad \text{..} \quad 2.26$$

3. EXPERIMENTAL PROCEDURES

3.1. Chemicals and Reagents

Chemicals and reagents used in the analysis processes were high molecular weight Polyvinyl chloride powder (PVC) (Fluka), 1-chloronaphtalene (Fluka) as plasticizers, Tetrahydrofuran (THF) (Fluka), Sodium salt of perchlorate (BDH), potassium iodide (BDH), potassium periodate (Riedel-Haen), sodium chloride, potassium nitrate aqueous solution as a solvent, potassium salts of anions for interference studies, glycerol anhydrous, D(+) mannitol (Hopkins and Williams), & ethylene glycol. Crystal violet (Hopkins and Williams) for ion association salt preparation. Solvents were used as received, with out further purification.

3.2. Preparation of Stock Solutions

Stock solutions of sodium perchlorate monohydrate, Chloride salt of crystal violet, potassium periodate and other anions under study were prepared by dissolving known amount of the salts in aqueous solution containing 0.1 M potassium nitrate aqueous solution as a solvent to adjust the ionic strength of the solutions and then, serial dilutions (10-fold) were prepared by transferring 10 mL of the consecutive solution in to 100-mL volumetric flask and diluted by 0.1 M potassium nitrate aqueous solution as a solvent to the mark [6, 7, 11].

3.3. Preparation of Crystal violet-perchlorate Coated Graphite Electrode

3.3.1. Preparation of crystal violet solution

A 1.0 X 10^{-2} M stock solution of crystal violet was prepared by dissolving known amount of its Chloride salt in about 50 mL of distilled water in a beaker by continuous stirring. The solution is then, quantitatively transferred to a 100-mL volumetric flask and diluted to volume by washing the beakers several times with distilled water until the filling was up to the mark [7, 11].

3.3.2. Preparation of the electroactive species

Crystal violet- perchlorate salt was prepared by gradual mixing of 100 mL of 1.0 x 10^{-3} M solution of crystal violet with an excess (20 mL) of 1.0 x 10^{-2} M perchlorate solution and shaked for 8-10 minutes. The mixture was saturated with sodium chloride as salting out agent and allowed to stand over night. A highly viscous, sticky product was formed after standing overnight and isolated from the aqueous phase by centrifugation, washed 3-4 times with distilled water and dried at 50-60^{o} for 6-6:30 hours. The resulting precipitate was collected in to a small glass bottle. This ion pair, i.e., crystal violet-perchlorate ion pair was used as the electroactive material for the proposed potentiometric sensor with out characterization.

3.3.3. Preparation of coating mixture

A Poly (vinyl chloride), PVC, solution in a mixture of Tetrahydrofuran (THF) and 1-chloronaphtalene, was prepared by dissolving 100 mg of the polymer powder in about 3 mL of THF and 0.5 mL of 1-chloronaphtalene. To this were added 15, 20, 25, 30, 35 or 40 mg of crystal violet-perchlorate precipitate. This mixture was used as the membrane matrix for the coated graphite electrode.

3.3.4. Preparation of perchlorate selective coated graphite electrode

One end (about one-third) of a graphite rod (3.6 cm long and 3 mm in diameter, Ringsdorff-Werke, GmbH, RWO) was mechanically cleaned with glass paper and immersed in a mixture of HCl & HNO_3, washed with distilled water and dried. The other end of the rod was tightly fixed to one end of the plastic tube so that a coil of copper wire, housed in the glass tube, is in contact with it either by mercury or directly [16, 17].

The clean part of the graphite rod was dipped in to the coating mixture several times with an interval of 2 minute to partially evaporate the THF and was rolled using our hands to make the coating uniform until the graphite surface is completely covered by a dark-violet film. The assembly was kept in the stove adjusted at 40^{o}c for not more than 5 minute or in a Hood

for 6 h to evaporate THF. The remainder and some of the coated portion of the rod were tightly wrapped with Parafomaldehyde film (American Can Company) to prevent direct contact of the rod with the test solutions. The resulting assembly, after conditioning by soaking the coated graphite tip in a 1.0 x 10^{-2} M aqueous solution of perchlorate for 1-2 hours, was ready for use as perchlorate selective coated graphite electrode. The electrode was stored between uses by suspending the coated end in a brown dropper bottle saturated with 1-chloronaphtalene to prolong its life time [16]. It was reconditioned immediately before use by soaking it in the conditioning solution. The design of the electrode is shown in Figure 2.

3.4. Instrumentation

Potential measurements of the solution were made with coated graphite electrode against a saturated calomel electrode (SCE) as external reference electrode (Orion model 90-01-00) at room temperature (25^{o}c) using Philips 9409 digital PH/mV/ ion meter. Stable potentials were recorded within < 1 minute. The test solutions were continuously stirred using a Teflon-coated magnetic stirrer bar during measurement. A schematic representation of the complete electrochemical cell is shown by the following scheme:

Coated graphite electrode/ Test solution / External reference electrode

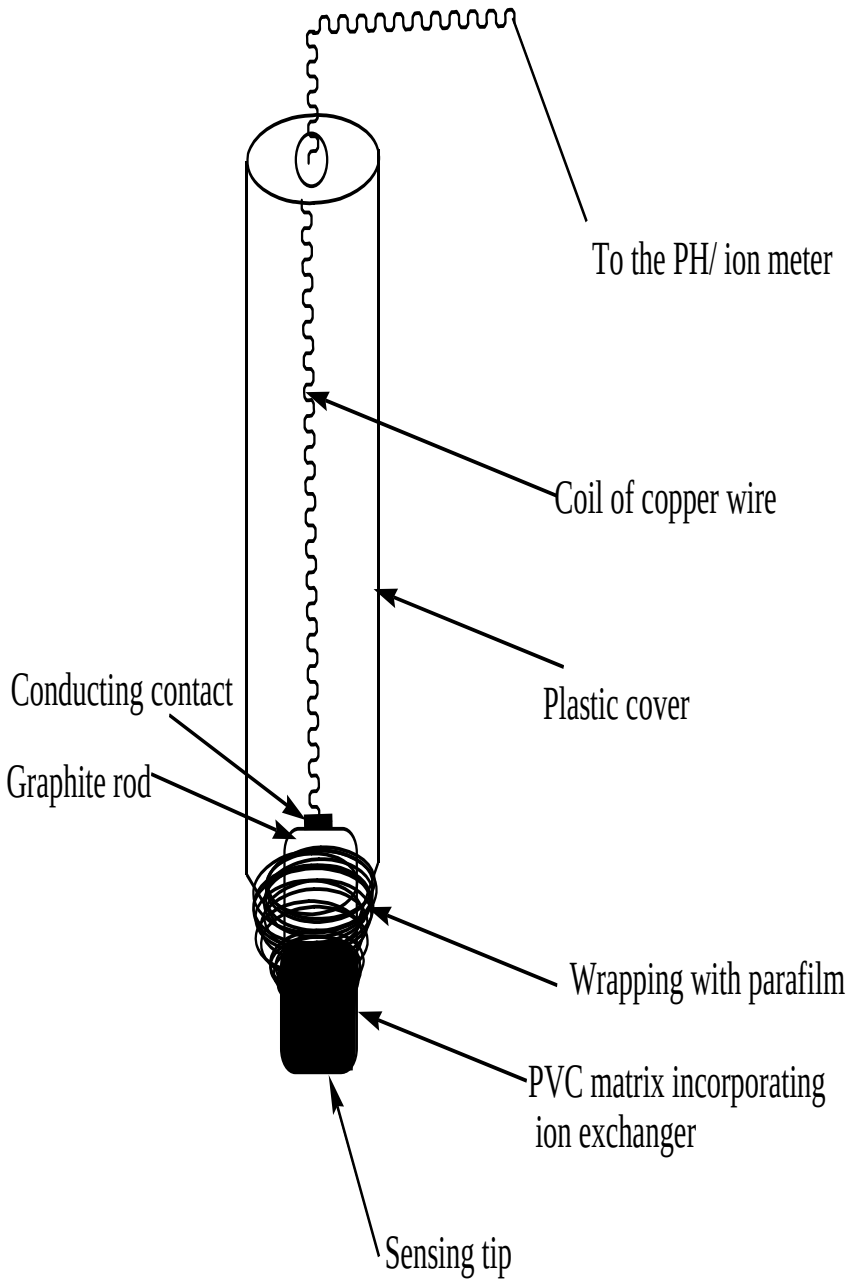


Figure 2. The crystal violet-perchlorate coated graphite electrode

3.5. General Procedures

3.5.1. Electrode calibration

Calibration of electrode responses to the anions was made with the standard solutions of the anions under study. Aliquot (25 mL) of 1.0 x 10^{-6} -1.0 x 10^{-1} M solutions of the anions (ClO_4^-, IO_4^-) were transferred to a 100-mL plastic beaker. The coated graphite electrode in conjunction with the reference electrode was immersed in to the solution and potential (within ±1 mV) was recorded after it becomes stable (within 1 minute). The response characteristics of the CGE were studied by measuring the electrode potentials of 25 mL of these test solutions.

3.5.2. Interference effects and determination of selectivity coefficient (K_{ij}^{pot})

The methods applied to study interference effects of diverse ions were of two kinds; the separate solution method and mixed solution method.

Separate solution method: The potential of aliquot (25 mL) of 1.0 x 10^{-3} M perchlorate solution was first measured. Then, the potential of equimolar amount of the interfering ions j, were measured independently after calibrating the electrode in perchlorate solution concomitantly potentiometric selectivity coefficients, K_{ij}^{pot}, of some selected anions (ClO_4^-, MnO_4^-, IO_4^-, IO_3^- & I^-) were evaluated using Eq. (2.5) [16, 11].

Mixed solution method: The potentials of 1 x 10^{-6} – 1 x 10^{-1} M solutions of i (ClO_4^-) containing a constant concentration of (10 mL), 1.0 x 10^{-3} M solution of the interfering ion j, were measured and selectivity coefficients were evaluated when $E_i = E_j$ using Eq. (2.6).

3.6. Analysis of Sample

3.6.1. The indirect determination of samples potentiometrically

After calibrating the electrode with standard aliquots (25 mL) of 1.0 x 10-6 -1.0 x 10-1 M periodate solutions, a 25 mL aliquot of 1.0 x 10-2 M periodate solution was transferred in to a 100-mL beaker and the coated graphite electrode in conjunction with the reference

electrode was immersed in to the solution and potential (within ±1 mV) was initially recorded within 1 minute. Then, two methods were used to analyse the samples: the dry sample addition method and the sample solution addition method. In the former 1.5-6 mg mannitol and 1.5-6 mg of glucose were directly added to the periodate solution. The potentials were measured after complete oxidation of the compounds (about 5 minute for mannitol and 15 minute for glucose). The amount obtained from mannitol and glucose for the dry sample addition method was evaluated on the basis of single point calibration method. In the later case, 1-5 mL of the sample solution of ethylene glycol and glycerol (containing 5-10 mg of each) were added to the periodate solution. The potentials were again measured after complete oxidation of the compounds (about 6 minute for ethylene glycol and 5 minute for glycerol). 1 mol ethylene glycol ≡ 1 mol IO4- and 1 mol glycerol ≡ 2 mol IO4-. Percent recoveries were calculated from the ratio of the amount obtained by subtracting the blank from the amount calculated to the amount added. Thus, the concentration of these compounds were again calculated from the moles of periodate consumed in the reaction by the sample subtraction method [11, 13], using

$$C_x = \frac{C_s\left[V_s - V_T \times 10^{\Delta E/S}\right]}{V_x \times n} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad 2.26$$

where C_x and C_s are the concentrations of the sample and standard solution respectively, V_x and V_s are the volume of the sample and standard solution respectively. V_T is the total volume of the solution, S is the slope and n is the numbers of moles of periodate consumed by one moles of the compound in the reaction [45, 46].

The electrode was also tried for the determination of ascorbic acid. 25 mg of the tablet was directly added as for mannitol and glucose. The more detail is discussed in the result and discussion part.

3.6.2. Standard addition technique

The potential (E_1) of 25 mL of a dilute sample solution of unknown concentration (in 0.1 M potassium nitrate aqueous solution as a solvent) was first measured. This was followed by the addition of four successive standard perchlorate solution (in 0.1 M potassium nitrate aqueous solution as a solvent) to the stirred sample solution. The new steady potentials (E_n) were recorded and the concentrations (C_x) of perchlorate in the sample solution were then, calculated using Eq. (2.21).

3.6.3. Sample addition technique

The potential (E_1) of 25 mL (V_s) of 1.0 x 10^{-4} M perchlorate solution (C_s) (in 0.1 M potassium nitrate aqueous solution as a solvent) was initially measured. Then, 2, 4, 6, 8 mL (V_x) of a sample of about 100-fold higher concentrations (C_x) (also 1 M in potassium nitrate aqueous solution as a solvent) was added and the new potentials (E_n) were recorded. The concentrations of perchlorate in the unknown were calculated by making use of Eq. (2.23).

4. RESULT AND DISSCUSSION

4.1. Study of Important Factors Affecting the Response Behaviour of the Electrode

The most important properties of polymeric membrane ISEs that determine the response behaviour of the electrode are the selection of the membrane substrate, solvent mediator or plasticizer and the composition of the polymeric membrane (polymer, electroactive material). In this particular work, internal substrate, membrane solvents (plasticizers) and electroactive material are among the properties being studied in detail [16, 47].

4.1.1. Internal conductive substrate

The properties of the substrate material employed for the development of potentiometric sensors in the construction of ISEs plays an important role. The choice of a suitable solid internal contact is, therefore, the decisive factor to be list out in order to get good quality of electrochemical parameters such as sensitivity, response time and stability.

In a previous study [16, 37] some authors have practiced to develop ion-selective CWE based on brilliant green and crystal violet an electrode employing silver wire as an internal contact. But it failed to function satisfactorily when used in strongly acidic test solution and since then, no attempt was made to prepare an electrode using silver wire as an internal conductive substrate.

In this study, no attempt was made to test materials for the internal contacts of the electrode as already pointed out by the previous author. Thus, the present investigation involves a graphite rod as an internal contact for the proposed electrode due to relatively inertness and of no ‘memory’ effect [19]

4.1.2. Membrane plasticizers

The selectivity parameters of the ion selective electrodes are dependent on the natures of the solvents (plasticizers) to promote the ion association of the electroactive materials.

Plasticizers (solvents) are required in polymeric membrane ISEs in order to increase ion mobility in the membrane [45]. The study of the selectivity of ion-selective CWEs [46] notifies solvent extraction parameters that determine the selectivity of the membranes. The advantages of considering the properties of the solvent (plasticizer) for the desired selectivity of the particular membrane to be used has been displayed in solvent extraction studies and from calculation of extraction constants, [47] from which the correlation between extraction constants and selectivity coefficients can be shown.

Selectivity which is the most important electrochemical property of the ISEs strongly depends on the mobility of the ions in the membrane and the reversibility on the membrane-solution interface which are in turn affected by the membrane plasticizer [21, 48]. Thus, a good membrane solvent (plasticizer) includes properties such as immiscibility with water, low volatility, high viscosity and low dielectric constant in order to promote the desired selectivity of ISEs [19, 20, 41].

In this regard, 1-chloronaphtalene both as membrane solvent and plasticizer for the PVC matrix meets most of these requirements. Further more 1-chloronaphtalene doesn't participate in pH dependent equilibrium when the membrane plasticized with 1-chloronaphtalene is in contact with the test solution [49]. It also has the ability for prolonging the life time of the membrane electrode when it is used in coating matrix [16]. Hence, 1-chloronaphthalene was used as membrane plasticizer for the proposed perchlorate selective electrode with out testing it again and no attempt has been made to other plasticizers.

4.1.3. The Effect of the Amount of Electroactive Material on the Response of the Electrode

The effect of the electroactive material in the response behaviour of coated graphite electrode was studied by varying the amount of crystal violet-perchlorate ion association in the coating mixture used to coat the graphite rod in the preparation of the electrode in 1-chloronaphtalene as plasticizer. Various amounts of the crystal violet-perchlorate ion association salts were tried as ion-exchangers. The electrode prepared using 15, 20 & 30 mg

of crystal violet-perchlorate salt exhibited a wider range of linear response with a better slope and shorter response time (< 20 s for 20 & 30 mg and < 90 s for 15 mg electrodes). Thus, these electrodes were used for further study. Particularly the 20 mg and the 30 mg electrodes have given a very stable response within < 20 s for concentration higher than 1.0 x 10^{-4} M. Electrodes prepared from crystal violet-perchlorate salt with > 30 mg give unstable potential responses probably due to the high viscosity of the coating mixture which results difference in diffusion rates (Figure 3. and Table 1).

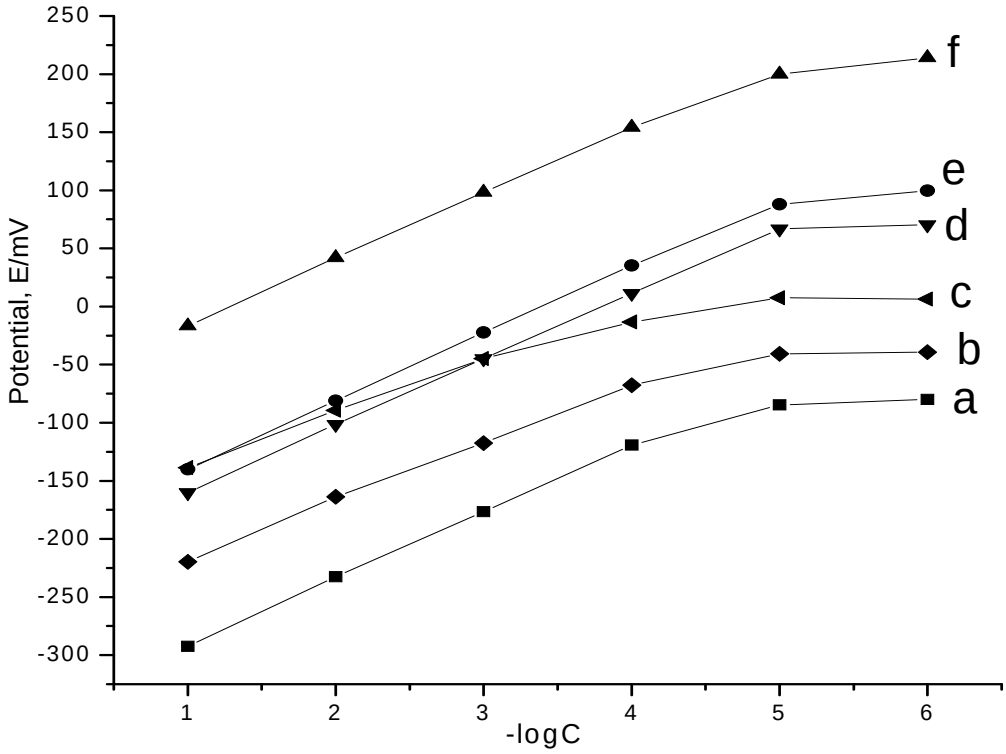


Figure 3. Response characteristics of perchlorate selective coated graphite electrode towards perchlorate with different amount of the crystal violet-perchlorate salt

a) $E_{15\ mg}$ b) $E_{35\ mg}$ c) $E_{40\ mg}$ d) $E_{30\ mg}$ e) $E_{20\ mg}$ f) $E_{25\ mg}$

*E stands for electrode prepared from the given amount of ion pair.

Table 1. Effect of amount of the crystal violet-perchlorate ion association salt in the composition of coating mixture used to coat the graphite rod in 1-chloronaphthalene as plasticizer on the response behavior of the CGE.

Amount of $CVClO_4$	Linear range	Average slope	Response
15 mg	$1 \times 10^{-4} - 1 \times 10^{-1}$	56.5±3.5	Slow, < 90 s
20 mg	$1 \times 10^{-5} - 1 \times 10^{-1}$	58±2	Fast, < 20 s
25 mg	$1 \times 10^{-5} - 1 \times 10^{-1}$	57±3	slow, < 90 s
30 mg	$1 \times 10^{-5} - 1 \times 10^{-1}$	58±1.5	very fast, < 20 s
35 mg	$1 \times 10^{-3} - 1 \times 10^{-1}$	54±3	Unstable
40 mg	$1 \times 10^{-3} - 1 \times 10^{-1}$	53±2.5	Unstable

4.2. Response Characteristics of the Electrode

One of the potential use of ISEs, which have only modest selectivities and respond to a number of ions, is the electrochemical detection of mixture of ions after chromatographic separation. The crystal violet perchlorate CGE was found to respond to perchlorate, periodates permanganates and iodides Figure 4. The electrode response behavior was studied in the concentration range $1 \times 10^{-6} - 1 \times 10^{-1}$ M perchlorate and $1 \times 10^{-6} - 1 \times 10^{-2}$ M periodate and found to respond linearly in the range $5 \times 10^{-5} - 1 \times 10^{-1}$ M for perchlorate with a Nernstian slope of 58±1.5 mV per decade and detection limit of 3.16×10^{-6} M perchlorate and $1 \times 10^{-4} - 1 \times 10^{-2}$ M periodate with Near-Nernstian slope of 56±1.5 mV per decade and detection limit of 5.7×10^{-5} M. This slope is typical of monovalent anions. The response of the newly developed perchlorate selective CGE based on crystal violet has no significant difference in its slope which is Nernstian for higher concentrations and near Nernstian for lower ones, linear response ranges and stable responses within less than a minute. The response time of the electrode was found to be < 20 s for ions of concentration higher than 10^{-4} M and up to 30-70 s for lower ones. The precision of the method was estimated by determining the concentrations of three different samples each containing 5×10^{-3} M perchlorate and 2×10^{-3} M periodate i.e., at the middle of the linear range. This multi-anion selective electrode can be potentially useful for the electrochemical detection of these anions.

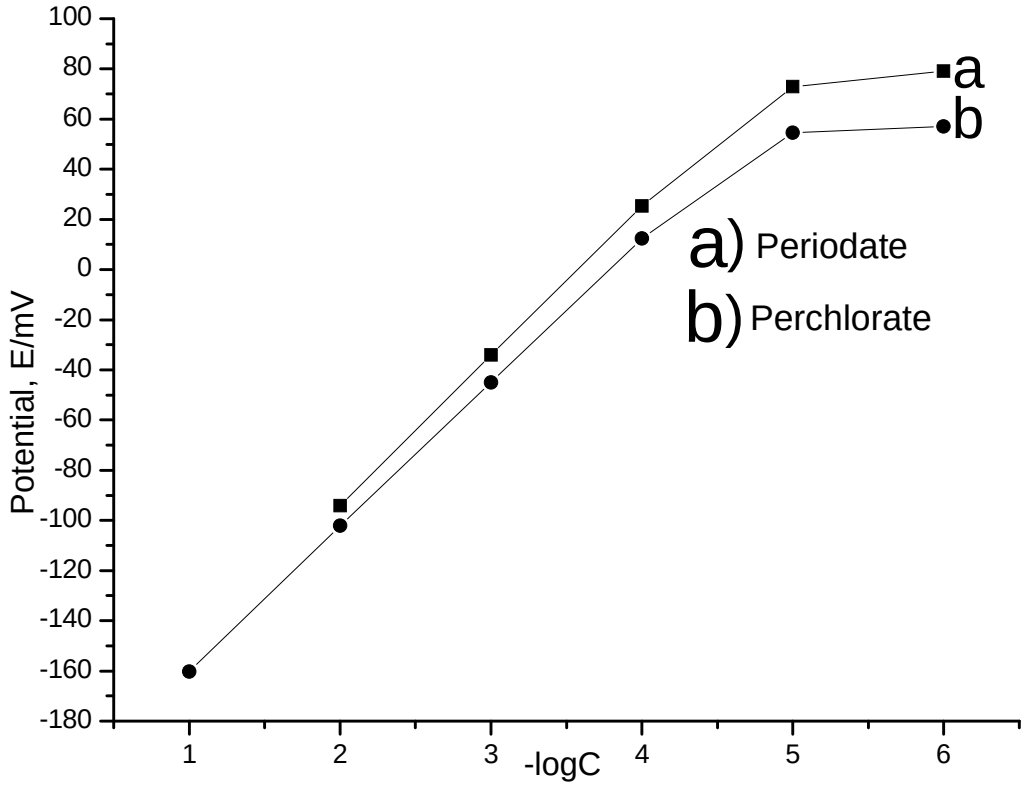


Figure 4. The response curve of the crystal violet-perchlorate CGE periodate and perchlorate

There was an improvement in the slope, linear range and response time after the electrode has been stored between uses by suspending the coated end in a brown dropper bottle saturated with 1-chloronaphtalene to prolong its life time [16]. This was due to inherent renewability of the electrode surface with the solvent [14]. The electrode was found to respond properly with no significant change in slopes, linear range and detection limit with an average life time of 4 weeks. The drift in potential measurement using CGE was evaluated by measuring the potential of three known and constant concentration of perchlorate in 24 hours and it was found to be ±5 to ±10 mV for perchlorate, however the slope obtained was essentially the same. Wrapping of the uncoated and part of the coated portion of the graphite rod with parafilm was found to be highly effective in preventing the direct contact of the solution with the test solutions.

4.3. Interference Study

The response characteristic of the crystal violet-perchlorate selective coated graphite electrode to the ions under study is influenced by other anions present. Investigations were conducted both by Separate and mixed solution methods for some of the selected anions (MnO_4^-, ClO_4^-, IO_4^-, I^- and IO_3^-). These methods are based on potential measurements in separate solutions or in mixed solutions containing the primary and the interfering ions [25, 26, 34]. The results in Table 2 show that the values of the selectivity coefficient are comparable in the two methods. The study was conducted for the selected anions that are expected to pose high interference [11].

Table 2. Selectivity coefficient of crystal violet-perchlorate CGE towards interfering ion j with respect to the ion of interest, i (ClO_4^-).

Interfering ions	Concentration (M)	Selectivity coefficient	
		Separate solution method	Mixed solution method
MnO_4^-	1×10^{-3}	7.92	6.95
ClO_4^-	1×10^{-3}	1.00	1.00
IO_4^-	1×10^{-3}	0.86	0.98
I^-	1×10^{-3}	3.88×10^{-2}	3.54×10^{-2}
IO_3^-	1×10^{-3}	2.66×10^{-4}	9.76×10^{-4}

As can be seen from the table permanganate poses the highest interfering influence since the value of its selectivity coefficient is greater than unity. The interference from periodate is the next highest value. No significant interference is noticed for these ions except

permanganate. The calculated values are in similar order of selectivity for these anions with perchlorate selective liquid membrane electrode and thus, no such study was made for the other anions expecting similar trends [11]. The multi-selective behavior of the electrode is governed by partition coefficient and stability of the solute in the two phases [11, 16, 21]. Multi-component analysis with the same transducer, such as reported electrodes could be made in flow injection analysis and liquid chromatography (LC). The detection of phthalate and nitrate ions was made in LC using membrane electrode [11]. As shown in Figure 4 the electrode also responds to periodate with more selectivity. Hence the electrode can be potentially useful to measure these ions in aqueous solution.

4.4. Application of Crystal Violet-perchlorate Coated Graphite Electrode

4.4.1. Determination of perchlorate

The newly developed perchlorate selective CGE was applied to determination of perchlorate in aqueous sample solutions using direct and standard addition potentiometric techniques displayed in the experimental sections. Three replicate measurements were made on solution containing 2.5 - 50 mg of perchlorate by each method. The results showed a recovery ranging from 96.4 - 102% and a standard deviation ranging from 0.5 – 1.9% (Table 3).

4.4.2. Determination Of periodate

The perchlorate electrode based on crystal violet dye also responds to periodate ion giving sub-Nernstian slope. It can also be applied to the determination of periodate in aqueous solution by direct potentiometric and standard addition methods. Four replicate measurements were made on solution containing 1.5 - 50 mg of Periodate by each method. The results showed a recovery ranging from 97.8 - 101% and a standard deviation ranging from 0.4 - 2.0% (Table 4). Thus, the newly developed electrode can be used reliably to determine perchlorate and periodate in aqueous samples with reasonable precision and accuracy.

Table 3. Determination of perchlorate ion using crystal violet-perchlorate CGE.

Methods	Perchlorate concentration		Recoveries (%)	Standard deviation (%)
	Amount added, mg	Amount obtained, mg		
Direct potentiometry	2.5	2.41	96.4	0.7
	12.5	12.6	100.8	1.3
	25	25.01	100.04	1.7
	50	49.94	99.88	1.8
Standard addition	2.5	2.55	102	0.5
	12.5	12.48	99.8	1
	25	24.9	99.6	1.2
	50	49.73	99.4	1.9

- Average of three determinations

Table 4. Determination of periodate ion using crystal violet-perchlorate CGE.

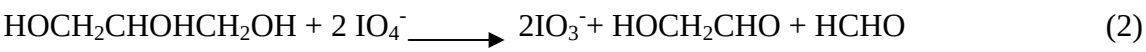
Methods	Periodate concentration		Recoveries (%)	Standard deviation (%)
	Amount added, mg	Amount obtained, mg		
Direct potentiometry	1.5	1.503	100.2	0.4
	12.5	12.43	99.4	1.5
	25	24.55	98.2	1.4
	50	49.9	99.8	2.0
Standard addition	2.5	2.53	101.2	0.5
	12.5	12.4	99.2	1.1
	25	24.47	97.88	1.9
	50	49.12	98.24	1.6

- Average of three determinations

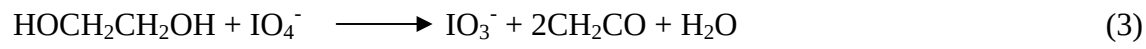
4.5.3. Determination of glucose, mannitol, ethylene glycol and glycerol

The crystal violet-perchlorate CGE has been used successfully for the indirect determination of these reducing substances via periodate oxidation. For one thing periodate ion is a strong oxidizing agent. On the other hand, the electrode doesn't respond to iodate which is the reduced form of periodate during the oxidation of these substances. Alcohols are known to react selectively and stoichiometrically with periodate at room temperature (Malaprade reaction) [50]. The reaction of mannitol, ethylene glycol, glycerol and glucose are given below

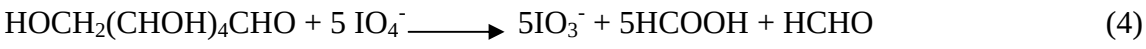
$$HOCH_2(CHOH)_4CH_2OH + 5IO_4^- \longrightarrow 5IO_3^- + 4HCOOH + 2HCHO + H_2O \quad (1)$$



$$HOCH_2CHOHCH_2OH + 2\ IO_4^- \longrightarrow 2IO_3^- + HOCH_2CHO + HCHO \quad (2)$$



$$HOCH_2CH_2OH + IO_4^- \longrightarrow IO_3^- + 2CH_2CO + H_2O \quad (3)$$



$$HOCH_2(CHOH)_4CHO + 5\ IO_4^- \longrightarrow 5IO_3^- + 5HCOOH + HCHO \quad (4)$$

Thus, these reduced substances can be determined indirectly from the amount of periodate consumed in the course of the reaction by the standard subtraction method for ethylene glycol and glycerol and by dry sample addition method for glucose and mannitol. The consumption of periodate brings a change in potential of the electrode by the addition of known amount of the substances to be reduced. The electrode reaches at a potential of its steady state when the reaction is completed at ambient temperature. The time required for the reaction to bring to completion is 4, 5, 6, & 15 minutes for mannitol, glycerol, ethylene glycol and glucose respectively. For the three replicate measurements made for the given amount, the results showed an average recoveries and standard deviations of 98.6, 98.7, 100, 98.5 and 0.8, 1.2, 1.1, 0.7 for mannitol, glycerol, ethylene glycol and glucose respectively.

Table 5. Determination of ethylene glycol and glycerol via oxidation with periodate using crystal violet-perchlorate based CGE by standard subtraction method.

Compound	Amount added, mg/mL	Amount obtained mg/mL	Recoveries (%)	Standard deviation (%)
Ethylene glycol	0.417	0.398	95.4	1.34
	0.140	0.137	98.3	1.05
	0.088	0.09	102.3	0.80
Glycerol	0.257	0.255	99.22	1.20
	0.111	0.11	99.10	1.50
	0.079	0.0782	99.03	1.04

- Average of three determinations

As can be seen from the table 5 above the electrode can be used for the determination of alcohols by oxidation. The results obtained for the determination of 0.088-0.417 mg/mL of ethylene glycol and 0.079-0.257 mg/mL glycerol showed ranges of recoveries and standard deviation of 95.40-102% and 0.80-1.50 for ethylene glycol and 99.03-99.22% and 1.04-1.50 for glycerol respectively.

Table 6. Determination of glucose & mannitol via oxidation with periodate using crystal violet-perchlorate CGE by dry sample addition method.

Compound	Dry Sample added (mg)	Amount obtained (mg)	Recoveries (%)	Standard deviation (%)
Glucose	1.5	1.5	100	0.60
	3	2.98	99.33	0.71
	4.5	4.43	98.44	0.81
	6	5.77	96.20	0.67
Mannitol	1.5	1.48	98.70	1.10
	3	2.88	96.00	0.81
	4.5	4.46	99.11	0.57
	6	6.01	100.6	0.37

- Average of three determinations

The electrode was successfully applied to determine these compounds by dry sample addition method through oxidation by periodate. The results in table 6 above showed lower standard deviation for the dry sample addition because the error that could arise as a result

of measurement process (due to preparation of the solution of different amounts) can be minimized and thus better precision and accuracy of the results are recorded.

4.6. Comparison of the Proposed Electrode with Other Perchlorate selective Electrodes

Attempt has been made to compare the proposed electrode with other perchlorate selective electrodes in terms of its slope, linear range, response time and solvent used (in response to perchlorate ion) as shown in Table 7.

Table 7. Comparison of the response characteristics of the designed electrode with other perchlorate selective electrodes.

Electroactive material	Membrane solvent/matrix	Slope mV/decade	Linear range, M	Response time in second, S	Ref.
Brilliant green perchlorate	Chlorobenzene	57-57.5	10^{-3}- 10^{-1}	____	[51]
Brilliant green perchlorate	Nitrobenzene	56.4	3.8×10^{-6}- 10^{-1}	____	[51]
Crystal violet-perchlorate	Nitrobenzene	59.0	3.5×10^{-6}- 10^{-1}	15-20	[51]
Crystal violet-perchlorate	1-chloronaphthalene PVC on graphite	56.5-59.5	3.16×10^{-5}- 10^{-1}	< 20	This paper

The proposed electrode responds properly giving fairly good Nernstian response in short time compared to most perchlorate selective electrodes (Table 7). As per the membrane solvent is concerned, most of the previously reported perchlorate selective electrodes use nitrobenzene which is carcinogenic while the crystal violet based coated graphite electrode responsive to perchlorate uses 1-chloronaphthalene both as a solvent for the coating mixture and as plasticizer. This is very important from the health effect and economical point of view of the solvent used. The CGE developed doesn't require an internal system (internal filling solution and internal reference electrode) which are the requirements for the membrane electrode. Further more the electrode is easy to prepare, maintain, use and simple to handle. Thus, it is cost effective. The speed of assay procedure and short response time made it possible to analyze a number of samples in a relatively short period of time. The reliable analytical information it has, is another advantage of the electrode to provide accurate, precise and reliable results of measurements.

The electrode was also tried for the determination of ascorbic acid. 25 mg of the tablet was directly added to periodate solution as for mannitol and glucose. There was an immediate rapid response with a very larger change in potential from -229 mV to +350 mV yet the tablet continued to dissolve, but we stopped at 350 mV. The colour of the solution was also change to brown. The tablet continued to dissolve slowly. The color could be due to the dissolving of the dye in the electroactive coating of the electrode. Comparison of this reaction with a test tube reaction has been done side by side. There was no change in colour for the later one. A dark coloured precipitate was also observed in the cell. This was confirmed further by the standard of the ascorbic acid. Similar observation has been taking place. Yet the reaction was not fast as for the tablet. This may probably be due to the presence of additives in the tablet.

5. CONCLUSION

Perchlorate selective coated graphite electrode based on crystal violet-perchlorate ion pair has been developed. This crystal violet dye based CGE can be prepared from commonly available materials in analytical laboratories. 15 mg, 20 mg, 25 mg, 30 mg, 35 mg and 40 mg amounts of the crystal violet-perchlorate ion association salt as electroactive material were tested to ensure the effect on the response characteristics of the electrode. It was found that the electrode prepared from 20-30 mg was very effective giving good electrochemical parameters (linear range, slope, detection limit etc) of the electrode and was chosen for further study. The newly developed electrode was found to exhibit Nernstian and near Nernstian response behavior to perchlorate and periodate respectively. The analytical application of the electrode to the analysis of anions in aqueous samples was tested. The results are reasonably in good precision and accuracy. The electrode can, therefore, be used to detect a number of anions in aqueous system after chromatographic separations of these multianions and enables to quantitatively determine the concentration of ions sensed by the electrode directly and the concentration of reagents or substance (glucose, mannitol, ethylene glycol and glycerol via oxidation by periodate) arising from chemical reaction indirectly. The comparison between the present work and those of the previously done by other methods has been made. The comparison shows that the presently designed method is highly selective with fast response, in a fairly good detection range of concentration and direct application to dry sample determination with out prior pretreatment (no preparation of solution) so that possible errors during preparation of solution can be eliminate or minimized.

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