

Development of perchlorate-selective coated graphite electrode based on crystal violet and its application to the determination of ethylene glycol, glycerol, glucose and mannitol via periodate oxidation

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ABSTRACT

The developed perchlorate-selective coated graphite electrode based on crystal violet (crystalviolet-perchlorate ion association in 1-chloronaphthalene both as the plasticizer and solvent with a PVC matrix on a graphite rod) gave 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 with linear range, slope, and detection limit of 1.0 x 10⁻⁵- 1.0 x 10⁻¹ mol/L perchlorate, 58±1 mV/decade, and 3.16 x 10⁻⁶ moleL⁻¹ 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.

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KEYWORDS

Ion selective electrode (ISE);
Coated graphite electrode
(CGE);
Ethylene glycol; Glycerol;
Glucose and mannitol.

INTRODUCTION

Studies have been tried to investigate the different techniques and methods for the determination of perchlorate ion and many chemists were in keen interest to study it. Ion selective electrodes for the determination

of perchlorate ion have been developed recently. So far few ion selective electrodes have been proposed for the potentiometric determination of perchlorate ion^[1, 2]. The Literature survey reveals that the response behaviour of ion selective electrodes such as its selectivity, reliability, precision, life time and response time

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have not been yet studied in detail and the applications are limited. Thus the need for constructing the sensitive, precise and selective newly developed electrode for the determination of various ions like perchlorate, periodate, and other carbohydrates and proteins was reasonably required^[1-11].

Crystal violet-perchlorate ion association complex has been employed for the potentiometric determination of perchlorate ion. However there was no report in the literature on the possible application of Crystal violet-perchlorate ion association complex as coated graphite in an ion selective electrode to the determination of perchlorate ion potentiometrically. Hence Crystal violet-perchlorate ion association complex in PVC was used as coating matrix to develop a new perchlorate selective coated graphite electrode for the determination of perchlorate ion potentiometrically.

The forgoing discussion reveals that ion selective electrodes (ISEs) have been developed to determine 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 electrode and internal filling solution^[10-17]. 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. Furthermore there have been no previous reports about the newly developed CGE selective to perchlorate ion. Thus, the development of new type of coated graphite ion selective electrode from cheap materials which is simple, sensitive and economical is intended to the direct determination of perchlorate and the indirect determination of some

of the anions such as mannitol, glucose, ethylene glycol and glycerol.

The present investigation deals with the development of a new coated graphite perchlorate ion selective electrode based on crystal violet-perchlorate ion association complex and its application for the direct determination of perchlorate, periodate and for the indirect determination of ethylene glycol, glycerol, glucose and mannitol via periodate oxidation potentiometrically.

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^[18-26]. A single measurement, therefore, gives the activity or the concentration of the ion^[19].

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

$$E_x - E_s = S \log(a_x/a_s) \quad (1)$$

which can be rearranged to give

$$a_i = a_s 10^{\Delta E/S} \quad (2)$$

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 there is a linear relation between the potential and logarithm of activity or concentration^[27-30].

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

$$\left(\frac{E_x - E_1}{E_1 - E_2}\right) \log\left(\frac{a_1}{a_2}\right) = \log\left(\frac{a_x}{a_1}\right) \quad (3)$$

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.

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 Nernstian response^[21].

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 follows^[22].

$$E_1 = E^0 \pm \frac{RT}{Z_i F} \ln(C_x \gamma_x) + E_L \quad (4)$$

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

$$E_2 = E^0 \pm \frac{RT}{Z_i F} \ln \left\{ \left[\frac{(C_x V_x + C_s V_s)}{(V_x + V_s)} \right] \right\} + E_L \quad (5)$$

Assuming the constancy of E_L and $\gamma_x = \gamma'_x$, subtraction of Eq. (4) from Eq. (5) gives

$$\Delta E = E_2 - E_1 = \pm \frac{RT}{Z_i F} \ln \left[\frac{(C_x V_x + C_s V_s)}{(V_x + V_s)} \right] \quad (6)$$

On rearrangement Eq. (6) becomes

$$\frac{\Delta E}{S} = \log \left[\frac{(C_x V_x + C_s V_s)}{(V_x + V_s) C_x} \right] \quad (7)$$

where S is the slope ($= 2.303RT/Z_i F$) experimentally determined by using a series of known standard solutions. Eq. (7) may be rearranged to give

$$C_x = \left[\frac{C_s V_s}{(V_x + V_s)} \right] \left[10^{\Delta E/S} - \frac{V_x}{(V_x + V_s)} \right]^{-1} \quad (8)$$

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., $V_x \gg V_s$, then, Eq. (8) becomes

$$C_x = C_s \left(\frac{V_s}{V_x} \right) \left(10^{\Delta E/S} - 1 \right)^{-1} \quad (8)$$

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: In this 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 using equation (10)^[21, 22, 25].

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

Eq. (10) can be divided by using C_s in place of C_x in Eq. (4) and subtracting it from Eq. (5).

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^[18].

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^[18, 21]. 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. (11)^[18].

$$C_x = \frac{C_s V_s}{\left[V_x - (V_x + V_s) 10^{-\Delta E/S} \right]} \quad (11)$$

Further assumption that dilution effect brought about by the addition of the standard solution is negligible reduces Eq. (11) to a form given by

$$C_x = \frac{C_s V_s}{\left[V_x (1 - 10^{-\Delta E/S}) \right]} - 1 \quad (12)$$

Equations (11) and (12) hold true, as already pointed out, for a 1:1 stoichiometry of the reaction; the equa-

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tion become more complex, otherwise.

RESPONSE TIME

Response time is one of the crucial factors which commend the uses of ISEs in routine analysis^[18-20]. 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^[22-23]. Fleet and co-workers defined the response time as the time interval within which the electrode potential reaches 95% of the steady state value^[32]. 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.

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^[33]. 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 tech-

niques 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°C, $(59.1/Z_i) \times \log 2 = 18/Z_i$)^[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. (13)^[18].

$$(DL) = K_{ij}^{pot} a_j^{Z_i/Z_j} \quad (13)$$

EXPERIMENTAL PROCEDURES

Reagents and solution

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 using 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 into 100-mL volumetric flask and diluted by 0.1 M potassium nitrate aqueous solution as a solvent to the mark^[6,7,11].

Preparation of crystal violet-perchlorate coated graphite electrode

Preparation of crystal violet solution

A 1.0×10^{-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 up to the mark^[7,11].

Preparation of the electroactive species

Crystal violet-perchlorate salt was prepared by gradual mixing of 100 mL of 1.0×10^{-3} M solution of crystal violet with an excess (20 mL) of 1.0×10^{-2} M perchlorate solution and shaken for 8-10 minutes. The

mixture was saturated with sodium chloride as salting out agent and allowed to stand overnight. 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° for 6-6:30 hours. The resulting precipitate was collected in to a small glass bottle. This crystal violet-perchlorate ion pair was used as the electroactive material for the proposed potentiometric sensor without characterization.

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.

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 polished with glass paper, immersed in a mixture of HCl & HNO₃ for a few minutes, washed with distilled water and dried. The other end of the rod was tightly fixed to one end of the rubber tube so that a coil of copper wire, housed in the rubber 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 round 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°C for not more than 5 minutes 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 re-conditioned immediately before use by soaking it in the conditioning solution. The design of the electrode is shown in Figure 1.

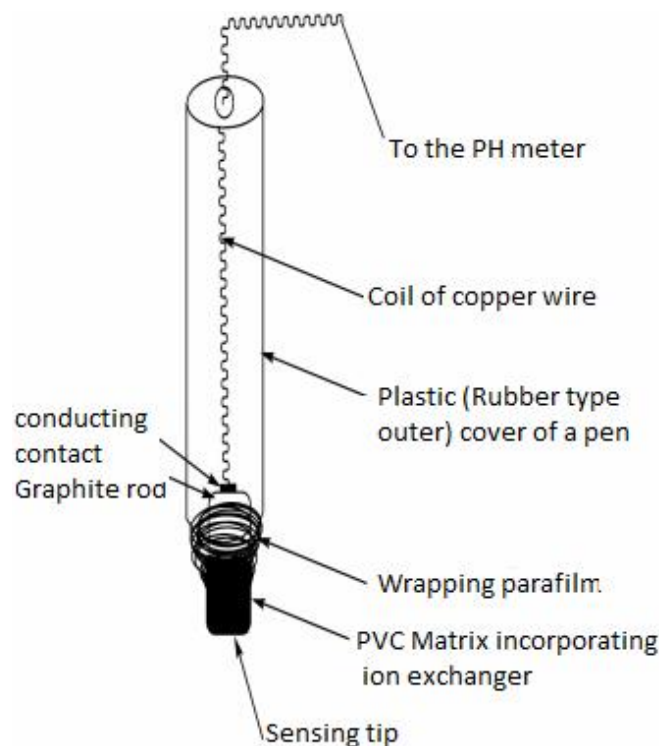


Figure 1 : Coated graphite electrode/ Test solution / External reference electrode

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°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:

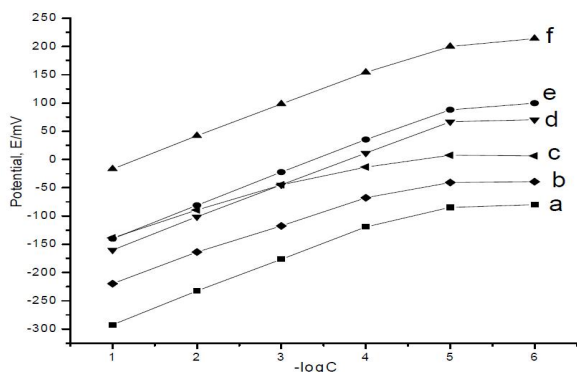
RESULTS AND DISCUSSION

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

The effect of the electroactive material in the re-

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response behaviour of coated graphite electrode was studied by varying the amount of crystal violet-perchlorate ion association, tried as ion-exchangers in 1-chloronaphthalene as plasticizer. 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, the 20 mg and the 30 mg electrodes have given a very stable response in less than 20 s for concentration higher than 1.0×10^{-4} M. Electrodes prepared from greater than 30 mg crystal violet-perchlorate ion association give unstable potential responses (Figure 2. and TABLE 1).



a) E_{15} mg b) E_{20} mg c) E_{25} mg d) E_{30} mg e) E_{35} mg f) E_{40} mg; *E stands for electrode prepared from the given amount of ion pair.

Figure 2 : Response characteristics of perchlorate selective coated graphite electrode towards perchlorate with different amount of the crystal violet-perchlorate salt

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 for perchlorate ion.

Amount of CVCIO_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

Response characteristics of the electrode

One of the potential use of ISEs is the electrochemical detection of mixture of ions. The crystal violet perchlorate CGE was found to respond to perchlorate and periodate ions. Figure 3. The electrode response 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 less than 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.

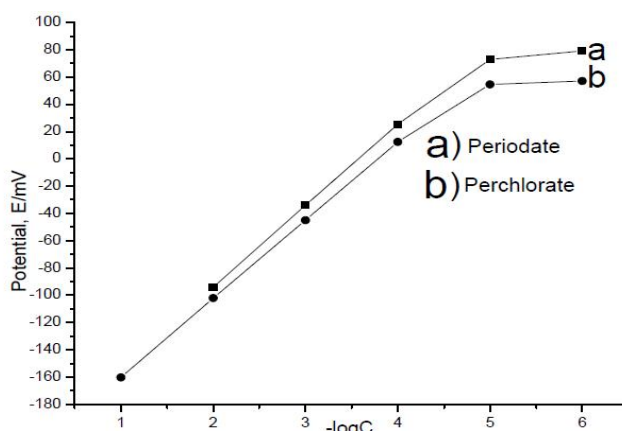


Figure 3 : The response curve of the crystal violet-perchlorate CGE periodate and perchlorate

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 after the electrode has been stored between uses by suspending the coated end in a brown dropper bottle saturated

with 1-chloronaphthalene to prolong its life time due to inherent renewability^[14, 16]. 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.

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

These methods are based on potential measurements in separate solutions or in mixed solutions containing the primary and the interfering ions^[18, 20, 29]. 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 ion poses the highest interfering influence. 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 gov-

erned by partition coefficient and stability of the solute in the two phases^[11, 16, 21]. As shown in Figure 3 the electrode also responds to periodate with more selectivity. Hence the electrode can be potentially useful to measure these ions in aqueous solution.

Application of crystal violet-perchlorate coated graphite electrode

Determination of perchlorate

The newly developed perchlorate selective CGE was applied to the 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).

Determination of periodate

The perchlorate electrode based on crystal violet dye 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
Standard addition	50	49.94	99.88	1.8
	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

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

Methods	Perchlorate 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
Standard addition	50	49.9	99.8	2.0
	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

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)^[34].

The reaction of mannitol, ethylene glycol, glycerol and glucose are given below



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 aver-

age 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	Recoveries mg/mL	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 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 Amount	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	100.60	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.

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.

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

TABLE 7:

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}	—	[12]
Brilliant green perchlorate	Nitrobenzene	56.4	3.8×10^{-6} - 10^{-1}	—	[12]
Crystal violetperchlorate	violetperchlorate	Nitrobenzene	59.0 - 3.5×10^{-6} - 10^{-1}	15-20	[16]
Crystal violetperchlorate	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 other membrane electrode. Furthermore 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.

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