HEXAFLUOROTANTALATE(V)-SELECTIVE COATED GRAPHITE ELECTRODE BASED ON BRILLIANT GREEN

BY

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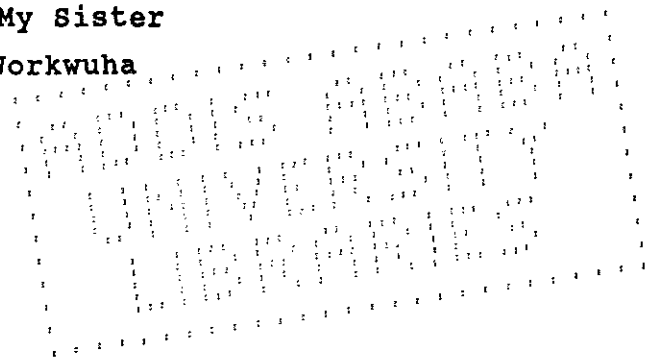
To My Sister

Workwuha



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ABSTRACT

HEXAFLUOROTANTALATE(V) - SELECTIVE COATED-GRAPHITE ELECTRODE

BEREKET TEWOLDE

The Hexafluorotantalate(V)-selective coated-graphite electrode was prepared by using a Brilliant Green-hexafluorotantalate(V) extract in 1-chloronaphthalene with a PVC matrix. The electrode body was prepared by fixing a graphite rod to one end of a glass tube housing a copper coil, so that the electrode is in contact with it. The potential measurement with the coated-graphite electrode was made against a sintered ground glass diaphragm (Ag/AgCl) external reference electrode. The concentrations of sulphuric and hydrofluoric acids, for optimum response of the electrode to hexafluorotantalate(V) were found to be 1 M in the test solutions. The response characteristics of the electrode have been evaluated, and the electrode was found to respond to hexafluorotantalate(V) in the concentration range of 5.0×10^{-6} - 5.0×10^{-3} M tantalum(V) with a Nernstian slope (58±1 mV per decade) and the detection limit of 8.0×10^{-7} M.

The effects of forty diverse ions on the electrode response to the hexafluorotantalate(V) have been studied to evaluate the selectivity of the electrode, and the electrode was found to be highly selective to hexafluorotantalate(V). The newly developed coated-graphite electrode has been applied to the determination of tantalum in tantalite-columbite ores and several artificial matrices by direct, standard addition, sample addition and Gran's plot potentiometric techniques. The experimental results are found to be in good agreement with the actual or certified values.

1. INTRODUCTION

Tantalum (Ta) is a chemical element of atomic number 73 and atomic weight 180.95. It is a member of the fifth group of the periodic table, and is in the 5d transition series. It's valence electronic configuration is $5d^3 6s^2$, which accounts for its max
imum oxidation state of +5[1-3].

1.1. Occurrence and Uses of Tantalum

The metal does not occur naturally in the free state. It is found in a number of oxide minerals, which almost invariably contain niobium also. In terms of abundance, tantalum does not appear on the list of the first 65 elements that are found in sea water. It does not also appear on the list of the first 36 elements that occur in the earth's crust, and hence is relatively scarce. The element occurs in the earth's crust to the extent of 2.1×10^{-4}%[1-4].

Tantalum is always found in nature in the Ta(V) oxidation state. The most important tantalum-bearing minerals are tantalite and columbite which are variations of the same natural compound $(Fe,Mn)(Ta,Nb)_2O_6$. Tantalite-columbite occurs in some pegmatites in quantities which seldom exceed a few pounds per ton and in alluvium derived from such pegmatites. Other tantalum minerals except microlite, $(Na,Ca)_2Ta_2O_6(O,OH,F)$, have little significance as a source of tantalum. These are manganotantalite, $Mn(Ta,Nb)_2O_6$, tapiolite, $Fe(Ta,Nb)_2O_6$,

Skogbolite, $FeTa_2O_6$, simpsonite or calogerasite, $Al_2Ta_2O_8$ with CaO as an impurity, thoreaulite, $SnTa_2O_7$ with CaO and Nb_2O_5 as impurities,

stibiotantalite, $(Sb,Bi)(Ta,Nb)O_4$, Yttrotantalite, $(Fe,Ca)_2(Y,Er,Ce,U)_2(Ta,Nb)_4O_{15}+4H_2O$, and euxonite, $(Y,Er,Ce,U)(Ta,Nb)(Ti)O_6$ [1,3-6].

Tantalum is best known as a refractory metal with a combination of unique properties making it useful in a great variety of commercial applications, though its applications are inhibited somewhat by its relatively high cost. It is used widely, although in small quantities, in the manufacture of capacitors for electronic equipment including band radios, heart pacemakers, emitters, getters, and automobiles[2]. The extreme corrosion-resistance of tantalum at normal temperatures (due to the presence of an exceptionally tenacious film of oxide) leads to its application in the construction of chemical plants, especially where it can be used as a liner inside cheaper metals. The corrosion resistance of tantalum has been compared with that of glass. Additionally, the metal has a high heat transfer coefficient, and is easy to fabricate. Consequently, it finds use in equipment that must resist strong corrosive attack, as in the manufacture of HCl, hydrogen peroxide, in chromium plating baths, in bromine heaters and stills, and in the preparation of corrosive fine chemicals. The metal has also been used in resistance heaters in very high temperature furnaces and for some nuclear reactor parts[7-9].

Moreover, tantalum has got several important surgical and

dental applications because of the inertness of the metal to body fluids and the tolerance of the body for the metal. It may be placed in the skull, or other body parts without rejection. Strips and screws made of tantalum are used for holding broken pieces of bone, and the wire mesh is used for surgical staples, braid for sutures, and reinforcements[2,3,6].

Tantalum is also added to nickel and nickel-cobalt super-alloys for gas-turbine and jet engine parts. Tantalum-base alloys are used for aerospace structures and space power systems, principally because of the high temperature stability and strength of these alloys[6].

A tantalum-tungsten alloy is used for fabricating spring for high temperature, high vacuum applications. The tensile strength of ternary alloys of tantalum (tantalum with 30% niobium and 5% zirconium or vanadium) at room temperature is about three times that of tantalum alone, and the alloy finds several uses in industry and aerospace structures. Other metals such as hafnium, molybdenum and rhenium are also added to tantalum, though in small amount, to give significant tensile strength. The ferrotantalum, which is added to austentitic steels to reduce the intergranular corrosion, has also many uses in several related areas[1-4].

In the last few years exploration and exploitation of tantalum-bearing minerals (tantalite-columbite) has been one of the major mining projects going on in this country with particular attention to the site at Shakiso (Legedenbi area in Sidamo). One of the major assessment problems of this project

tantalum and niobium, are of relatively minor importance. Thus, apart from the halide chemistry, the vast majority of characterized compounds of the metals are pentavalent, although compounds with formal oxidation states of +4, +3, +2, +1,0 and -1 have been reported, these oxidation states, in particular the first three, are less well characterized.

In contrast to vanadium, for which the species VO^{+} and, particularly VO^{+}_{2} play important roles, tantalum and niobium have virtually no cation chemistry. Their oxides, Ta_2O_5 and Nb_2O_5, are appreciably basic, while that of vanadium, V_2O_5, is amphoteric. There is also considerable similarity in the chemistry of lower halides, of tantalum and niobium, where metal-metal bonding is important, and in their numerous integral valence stable cluster compounds.

Differences are also observed, though not profound ones, between the chemistries of tantalum and niobium[4]. For example, it is well established that tantalum(V) is less readily reduced than niobium(V), and is more readily hydrolysed in aqueous hydrochloric acid solutions. Moreover, there are differences in the structural chemistry of the respective peroxides, in the stability of the pentavalent oxyhalides, and the nature of oxysulphates obtained from aqueous solutions.

The pentoxide, Ta_2O_5, can be obtained by heating the metal in oxygen or by dehydration of the hydrated oxide. The pentoxide is a white, air stable, and water insoluble solid which is an important starting material for tantalum production. The pentoxide is hardly attacked by mineral acids

with the exception of hydrofluoric acid. It can be melted by fusion with alkali metal pyrophosphates, potassium hydroxide or carbonate, and a mixture of potassium carbonate and potassium nitrate. The resulting melt may be dissolved in acidic solution or, depending on its composition, in water[4].

Several lower oxides of tantalum, of compositions TaO_x ($2<x<2.5$) have also been reported, though no discrete TaO and TaO_2 compounds are known[12]. They are formed by active metal reduction. TaO_2 forms, with alkali metals, the metatantalates, $MTaO_3$, the orthotantalate, M_3TaO_4, and pyrotantalates, $M_4Ta_2O_7$, as well as the polytantalates of composition $M_8Ta_6O_{19}$ which require fusion with alkali hydroxides[6].

Tantalates are obtained by fusing the pentoxide with alkali hydroxides or carbonates, which hydrolyse to oxide upon washing with water. The melt can be extracted into aqueous potassium hydroxide, and upon treating the extract with ethanol, a product of composition $K_8Ta_6O_{19}.16H_2O$ precipitates. The anion, $Ta_6O^{8-}_{19}$, also exists in aqueous solution in the pH range of 10-13, without being subjected to further polymerization, depolymerization or protonation. Upon acidification the hydrous oxide precipitates. Although it is called tantalic acid, it is insoluble in aqueous bases, but soluble in acidic solutions, and salts of compositions $KTaF_6$, K_2TaF_7 and K_3TaF_8 can be crystallized from aqueous solutions of different fluoride concentrations[1-3].

In aqueous fluoride media there exists a distribution of a series of fluorotantalate complexes of composition $Ta^{V}F_n^{5-n}$

(n<8)[4]. The formation of various complexes depends on many factors: viz, the concentration of tantalum, and the acidity of the medium. Predominant species in specific solutions, as deduced from Raman and n.m.r. spectra, are $[TaF_6]^-$ in 24 M HF, (no $[TaF_7]^{2-}$), $[TaF_7]^{2-}$) in 5.2 M NH_4F, (no $[TaF_6]^-$), and a mixture of $[TaF_6]^-$ and $[TaF_7]^{2-}$ in 3.1-11.0 M HF, with the formation constants of 4.6×10^3, 1.26×10^3 and 4.5 for $[TaF_6]^-$, $[TaF_7]^{2-}$ and $[TaF_8]^{3-}$, respectively[4]. The $[TaF_8]^{3-}$ anion has not been detected by the Raman technique in hydrofluoric acid solutions upto 24 M. There is conflicting evidence for the existence of $[TaF_9]^{4-}$ in aqueous fluoride media and no solid complexes containing this anion have yet been prepared. The preparation of the fully halogenated, Cl, Br and I, (i.e. non-oxygenated) compounds require the use of non-aqueous solvents[4].

1.3. Methods of Determination of Tantalum

A large number of instrumental as well as chemical methods have been reported in the literature for the determination of tantalum in ores and various natural samples. Only few of the most commonly used ones are described below.

Tantalum is determined most frequently by spectrophotometric methods using a variety of reagents. Pyrogallol is, perhaps, one of the most important of such reagents[13]. It reacts with tantalum(V) in a medium of 4 N HCl and 0.0175 M $H_2C_2O_4$ to form a soluble complex compound. The molar extinction

coefficient of the complex solution is 4.8 x 10^3 M^{-1} cm^{-1} at 325 nm. Beer's law holds for tantalum concentration up to 40 ug/ml. Mo(VI), W(VI), U(VI), and Sn(IV) interfere with the determination. The effect of Nb(V), Ti(IV), Cr(III), V(V), Bi and Cu is insignificant and can be compensated for by adding these ions into the blank solution. Platinum and fluoride ions interfere with the determination of tantalum. Thus, platinum crucible should not be used to fuse the sample if the metal is to be determined by pyrogallol.

Gravimetric methods of analysis generally involve precipitation of the metal ion with suitable reagents followed by ignition of the precipitate to the pentoxide. Benzohydroxamic acid derivatives[14-15] quantitatively precipitate tantalum from aqueous solution at pH 0.5 - 1.8. These reagents are also employed for the separation of tantalum from niobium by selecting the appropriate pH range (3.5-6.5 for Nb(V), and 0.5-1.8 for Ta(V)). The interference of Ti(IV) and Zr(IV) can be eliminated by masking with fluoride and EDTA, respectively. However, Mo(VI) and W(VI) interfere seriously. The method is fairly selective, but tedious, less sensitive and not effective for the determination of small quantities of the element.

Titrimetric methods have not been widely applied to the determination of tantalum because the +5 oxidation state of the metal is the only stable state. However, indirect titrimetric methods have been reported[16,17]. These methods involve the titrimetric application of outer-sphere complex formation of

the anionic fluoro-complex of tantalum(V) in aqueous dimethyl sulphoxide. Heptafluorotantalate(V) forms a soluble outer sphere complex with potassium ion in a medium of aqueous 90% (v/v) dimethyl sulphoxide. Such complex formation can be used for spectrophotometric titration of microgram amount of tantalum with 1 to 100 mM KCl at 626 nm using nitrosulphonazo(III)[16], and nitchroazo[17] as indicators. In practical analysis, the method is not very common since compounds of tantalum(V) are not reduced in aqueous solution[13].

The Atomic-absorption Spectroscopic method for the determination of tantalum(V), in industrial raw materials[18] and intermediates such as niobates and tantalates[19], has been used into a nitrogen-separated nitrous oxide-acetylene flame. However, the method suffers from strong interferences and has a poor limit of detection.

The determination of tantalum by the potentiometric titration technique has been achieved in non-aqueous media. Tantalum(V) reacts with 3-aminopyrazinoic acid to form a 1:1 complex[20]. The metal, in dimethyl formamide, was determined by direct and reverse potentiometric titration with 0.01 M of the reagent in the solvent. However, interference from some ions such as niobium(V), titanium(IV), iron(III), and tungsten(VI) was noted, and the method is not favourable for the determination of small quantities of tantalum. Potentiometric titration of tantalum(V) with bis(quinolin-8-ol) has also been reported[21].

Ion-selective electrodes for the determination of tantalum have been developed recently based on cetylpyridinium chloride-hexafluorotantalate(V)[22], which was applied to potentiometric titrations[23], and tetraoctylammonium -hexafluorotantalate(V) liquid membranes responding to hexafluorotantalate(V)[24]. The application of the former electrode has been extended to the determination of tantalum in niobium[25], and in steel samples[26]. However, this electrode suffers from interferences of several ions such as Nb(V), Ni(II), Fe(III), Al(III),and Ti(IV). Moreover, the electrode response was a linear function of hexafluorotantalate(V) in the concentration range of only 10^{-5} - 10^{-4} M. The latter electrode, i.e. the electrode with tetraoctylammonium active material, had a better range of response (2.0×10^{-6} - 1.0×10^{-2} M) but applications of this electrode was not mentioned in the report. In addition, the selectivity study was performed only for a few ions such as Cl^-, NO_3^-, HSO_4^-, $NbOF_5^{2-}$, and ClO_4^-.

A general anion-selective PVC membrane electrode based on tetradodecylammonium iodide[27] was prepared and it was observed to respond to twenty anions, one of which is hexafluoro- tantalate(V). The authors concluded that the study of this general anion-selective electrode further confirmed that the mechanism of ion-association type ion-selective electrodes is a nonspecific ion-selective electrode.

Triheptyldodecylammonium iodide was found to be useful as the active material for ion-selective electrodes[28]. This active material was used for tetrafluoroborate(III), picrate,

and hexafluorotantalate(V) anion-selective membrane electrodes. The linear detection ranges and detection limits, were 10^{-6}-10^{-1} M and 8.0 x 10^{-7} M for tetrafluoroborate(III), 10^{-6} - 10^{-2} M and 5.0 x 10^{-7} M for picrate, and 10^{-6} - 10^{-1} M and no data for the detection limit of hexafluorotantalate(V). Furthermore, there is no report of a selectivity study nor any application of the electrode given.

A radiotracer study with ^{182}Ta showed that PVC matrix membranes containing a liquid ion-exchanger based on triheptyldodecylammonium-hexafluorotantalate(V) sensor plus bis(ethylhexyl)phthalate mediator are permselective to hexafluorotantalate(V)[29]. The information available for selectivity is only for ClO^-_4, NO^-_2, Br^-, and Cl^- ions. Moreover, the characteristics of the electrode were not tested with either real or artificial samples.

Very recently Brilliant Green-hexafluorotantalate(V) extract in nitrobenzene was used to prepare a hexafluorotantalate(V) - liquid membrane electrode with PVC support[30]. The electrode body was made from concentric polypropylene tubes joined with a cork. The cell with the liquid membrane electrode consisted of a fluoride- selective electrode as internal reference and sintered glass diaphragm (Ag/AgCl) electrode as the external reference electrode. The concentration of both sulphuric and hydrofluoric acids, for optimum response of the electrode to hexafluoro - tantalate(V) were found to be 1.0 M in the test solutions. The response characteristics of the electrode was evaluated, and the linear

response to hexafluorotantalate(V) was linear on the concentration range 2.0 x 10^{-6} - 1.0 x 10^{-2} M tantalum(V) with slope and detection limit of -58.5 mV/decade and 3.69 x 10^{-7} M tantalum(V), respectively. The effects of forty diverse ions on the electrode response to the hexafluorontantalate(V) were reported and the electrode was found to be highly selective to the hexafluorotantalate(V). The electrode was applied to the determination of tantalum in tantalite-columbite ores by different potentiometric techniques. However, this electrode, i.e., the Brilliant Green-hexafluorotantalate(V) liquid membrane electrode had the traditional 'barrel-type' configuration and required an internal reference electrode system. In general, the large size of this type of ISE along with the requirement that it be used in a nearly upright position renders it somewhat cumbersome to use and unnecessarily expensive[31].

Thus the foregoing discussion clearly reveals that few ISEs have been developed for hexafluorotantalate(V) during the last decade, and the studies of the behaviour of these electrodes and/or their construction modes were insufficiently well. Some of the inherent problems associated with liquid membrane electrodes could be overcome by coating the sensing element on wire electrodes such as silver, platinum and graphite. Such electrodes are known as coated wire electrodes, CWEs[31,32]. CWEs are easy to prepare and their preparation has led to miniaturization of ISEs. The simplicity of the CWE lies in the fact that the same conductor after cleaning can be repeatedly

used for coating when the electrode deteriorates in its response. Thus it is worthwhile to develop a coated conductor electrode. For reasons explained in the Results and Discussion section the successful candidate was the CGE. This electrode, like the CWEs, is easy to use, inexpensive, compact and sturdy and eliminates the use of an internal reference electrode for the quantitative determination of tantalum in diverse samples.

1.4. Aim and Scope of the Present Investigation

The triphenylmethane dyes, such as Brilliant Green, crystal violet, etc., are monovalent cationic species forming ion-pairs with anions, having a number of desirable properties e.g., they can be extracted into water immiscible solvents. These cationic dyes have been used as ion-exchangers in electrodes selective to different organic and inorganic anions including tetrathio - cyanatozincate(II)[32], perchlorate[33,34], tetrafluoro - borate[35], salicylate[36], phthalate[37], detergent anions[38],tetrachloroferrate(III)[39], and saccharin[40].

The Brilliant Green-hexafluorotantalate(V) ion-association complex has been employed for the extraction-spectrophotometric deter- mination of tantalum[41]. As indicated earlier, it has also been used as a potentiometric sensing element in the preparation of a liquid membrane electrode for the determination of tantalum [30].

It is, therefore, worthwhile to undertake the development

of a coated conductor electrode for the determination of tantalum based on the Brilliant Green-hexafluorotantalate(V) ion association complex. Thus the objectives of the present research project were:

1. to prepare a tantalum solution by fusing Ta_2O_5 .
2. to standardize the tantalum solution,
3. to prepare a coated conductor electrode (e.g. graphite rod, silver wire) sensitive to hexafluorotantalate(V) based on Brilliant Green-hexafluorotantalate(V),
   - 3.1. electrode body preparation
   - 3.2. extraction of electroactive material.
4. to study the basic electroanalytical parameters of the electrode; such as dynamic (linear) range, slope, the effect of sulphuric and hydrofluoric acid concentrations, and the effect of other ions (selectivity coefficient determinations), to establish the optimal conditions, and
5. to study the analytical applications of the newly made electrode for the determination of tantalum in artificial and real (Ethiopian columbite-tantalite ores) samples by potentiometric measurement techniques.

2. THEORETICAL CONSIDERATIONS

2.1. Membrane Electrodes[42,43]

The term 'ion-selective electrodes' is applied to a range of membrane electrodes which respond selectively towards one (or several) ionic species in the presence of others[43]. They are, in practice, based on electrochemical membranes, i.e., on phases consisting of solid or liquid electrolytes, perfectly separating two electrolyte solutions[44].

The word 'membrane' is used here, in its broadest sense, to denote a thin section of electrically conducting material that regulates the movement of charged species across it, thereby creating conditions for the generation of an electric potential[42]. It is used, in a phenomenological sense, to indicate all types of electrodes that act reversibly as a membrane electrode, irrespective of the mechanism involved.

The Electrical potential arising across the membrane when they separate two electrolyte solutions is called the membrane potential. The membrane potential may arise as a diffusion potential across the membrane due to differences in the mobilities of the ions. There are also other ways in which a potential might arise across the membrane. The simplest way is to have it arise as an ohmic potential drop by passing electric current from an external source of emf through the system. Another way would be to have it arise as a static potential by

adding to one of the compartments some charged species that cannot pass through the membrane[42].

Ion-selective electrodes (ISE) are used for the determination of the membrane potential which is dependent on the concentration (more accurately the activity) of a particular ion in solution which develops across the electrode/electrolyte interface[45].

The membrane potentials cannot be determined directly, but can easily be derived from the emf values for the complete electrochemical cell using the Nernst equation[46]. These cells comprise the membrane which is in contact, on one side with a solution containing the ion of interest (test solution) in which the external reference is immersed and, on the other side, either with a solid conductor or a solution containing the ion of interest at a constant concentration, (internal solution). A schematic representation of such cell assembly is shown in cell I:

Test solution / membrane/ solid conductor

or Cell I

internal solution

The conventional ISE utilizes an internal solution of constant composition in contact with the membrane and an internal reference electrode. When the ISE is placed in a sample solution containing the particular ion to which the electrode is reversible, it passes from the solution of higher

concentration through the membrane to that of lower concentration thus producing an electric potential difference known as the diffusion potential. Consequently the transmembrane difference of electrode potential (Donnan potential) is generated which eventually stops further diffusion of the particular ionic species[47].

The emf of this electrochemical cell is related to the ion activities in the sample solution[48] by the extended Nikolsky equation.

$$E = E^{o} + (RT/z_iF)\ln[a_i + k_{ij}^{pot}(a_j)^{z/z}] \qquad (2.1)$$

E: cell potential (emf)

E^{o}: constant reference potential

a_i: activity of a primary ion I^{zi} in the sample solution

a_j: activity of an interfering ion J^{zj} in the sample solution

k_{ij}^{pot}: potentiometric selectivity coefficient, characteristic of a given membrane.

where: (+) is for a cation and (-) for anion.

Electrodes with solid internal contacts[49,50], which do not require the conventional internal reference system, have been developed. The membranes are generally prepared by incorporating the ion-exchanger components (sensor plus mediator/plasticizer) in an inert matrix, e.g. PVC with a plasticizer and the aid of a solvent such as tetrahydrofuran or cyclohexanone : the solvent is allowed to evaporate, leaving a tough, flexible membrane with the ion-exchanger components

trapped in the inert matrix[43].

The solid internal contacts (substrates) can be divided into two broad classes, carbon or graphite on the one hand, and metals such as platinum, silver or copper on the other.In many cases, the selectivities of the coated-substrate ISEs were significantly better than the conventional, 'barrel-type' counterparts[51]. This along with absence of the traditional internal reference electrode, raised fundamental questions about the charge conduction mechanism occurring in the membrane and at the polymer-substrate interface. Calculation of activation energies from the temperature dependence of conduction suggested that an electronic mechanism was operative, such as that observed in organic semiconductors[52]. However, later studies of the pressure dependence of conduction gave strong evidence for ionic conduction, because much larger activation volumes than could be expected from an electronic mechanism were obtained[53,54]. As such the existence of a redox couple at the polymer-substrate interface probably functions[55] as an 'internal reference'. This hypothesis is further reinforced when one considers that conditional standard potentials shift by significant and reproducible amounts from one type of substrate to another.

Electrodes based on organic ion exchangers

A liquid ion exchange membrane is usually formed by dissolving a liquid ion exchanger in a water- immiscible solvent. The ionogenic groups (sites) of liquid ion exchangers are mobile. Depending on the solvent used to form the ion-

exchange membrane, the sites would be completely dissociated (dielectric constant of the solvent is high) or highly associated (dielectric constant of the solvent is low) into ion pairs[42].

The conditions existing in these ion-exchange membrane system are shown in Fig.1.

The species A^+ and X^- are in chemical equilibrium with the species AX in the membrane. Thus

$$\overline{A}^+ + \overline{X}^- \rightleftharpoons \overline{AX}$$

The chemical potential of the species everywhere in the membrane are related as

$$\mu_{AX} = \mu_A + \mu_X$$

Assuming $\tau_i = 1$, applying the law of mass action gives

$$K_{AX} = \frac{\overline{C}_{AX}}{\overline{C}_A \overline{C}_X}$$

At the boundaries, the electrochemical potential of i are equal. So

$$\mu_i^o + RT\ln a_i' + Z_i F E' = \overline{\mu}_i^o + RT\ln\overline{C}_i' + Z_i F \overline{E}'$$

The selectivity coefficient[90] can be calculated using

$$k_{ij}^{pot} = \exp\left(\frac{-VF}{RT}\right)$$

Where V is the membrane potential.

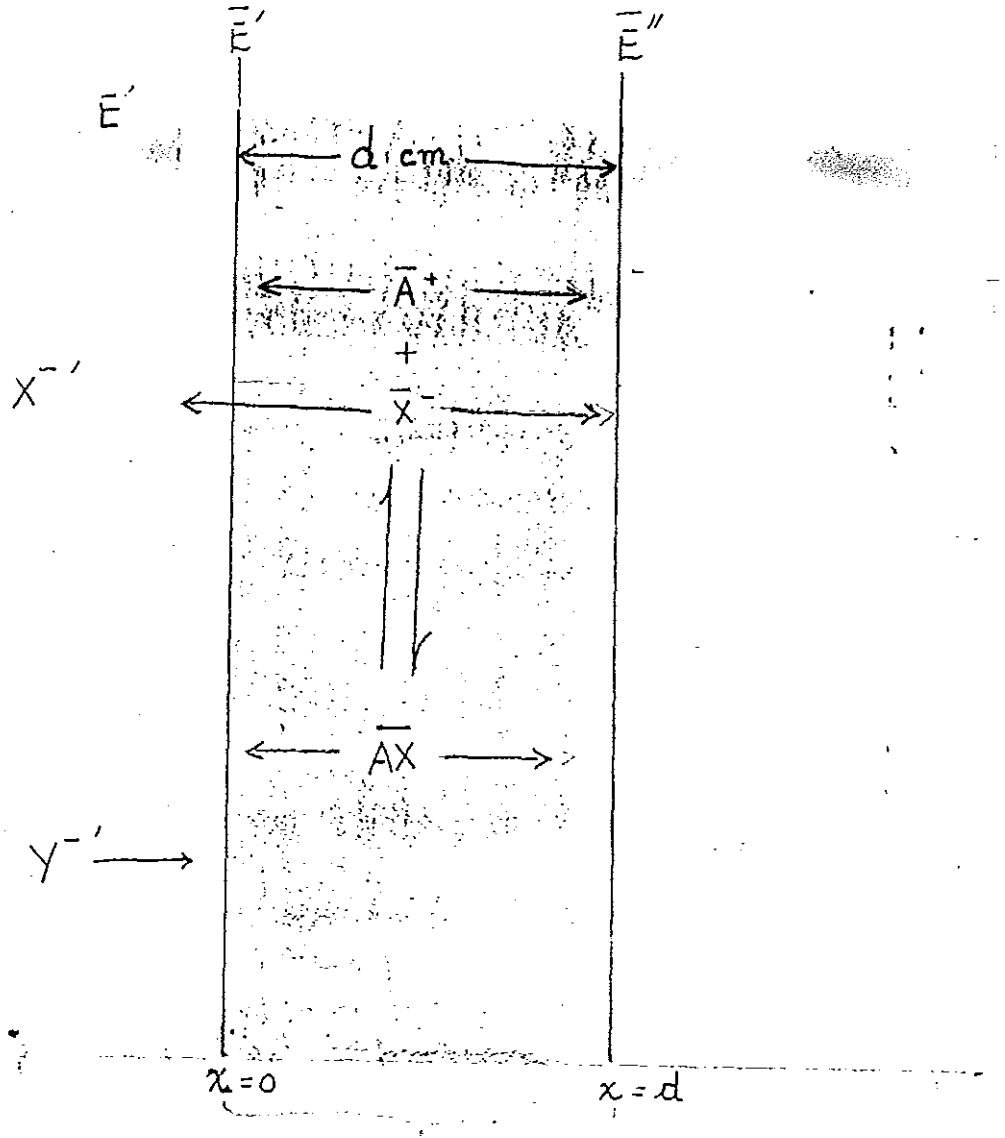

Fig 1 Schematic diagram of ion exchange membrane system containing the ion-exchanger A^+ to the determind X^- in the presence of interfering ions, Y^-. $\bar{AX}$ is the mobile ion pair. X^- freely permeates the membrane - solution interface, whereas A^+ is confined to the membrane phase. The E's are the electrical potentials and overbars refer to the membrane phase. (') regers to the solution phase.

2.2. Selectivity of Membranes[47]

ISEs have the advantage that they can in principle be produced for any ionic species, but the difficulty of distinguishing between different ions (particularly those of the same sign), is an important limitation of the method. The selectivity of an electrode is represented by its ability to distinguish between different ionic species present in the test solution.

The factors responsible for the selectivity of the membrane include difference in the mobilities of the ions in the membrane, strengths of association between the ions in the solution and in the membrane, the ionic strengths and the ion concentration ratios[42].

2.2.1. The potentiometric selectivity coefficients[45]. The potentiometric selectivity coefficients of an ISE (k_{ij}^{pot}) is a measure of the degree of selectivity of an electrode for the primary ion i of charge z_i relative to the interfering ion j of charge z_j. It is defined by the Nikolsky equation[42],i.e.,it is given by rearrangement of Eq.(2.1)

$$k_{ij}^{pot} = \{ \exp [(z_iF/RT)(E - E^\circ)] - a_i \} / (a_j)^{z/z} \qquad (2.2)$$

The potentiometric selectivity coefficient, k_{ij}^{pot}, represents the sensitivity (or selectivity) ratio : interfering ion/measured

ion. Thus, if $k_{ij}^{pot} > 1$, the selectivity of the electrode to the interfering ion,j, is more than to that of the primary ion, i. On the other hand, if $k_{ij}^{pot} < 1$, the electrode is more selective to the primary ion,i, than the interfering ion,j.

2.2.2. Determination of selectivity coefficient. Selectivity coefficients give basic information on the role played by various interfering ions on the performance of a given ISE. The majority of the methods for determining selectivity coefficients are based on the following assumptions[56].

(i) sufficiently rapid establishment of ion-exchange equilibrium, the rate of which may depend on the concentration of both the primary and interfering ions;

(ii) maintenance of the same conditions in the solution at the membrane surface as those in the bulk of the solution,i.e., here the disturbance of concentration conditions due to the exchange reaction and the transport rate, leading to compensation of the concentration changes, plays a role;

(iii) operation of a simple membrane mechanism.

Methods of experimental determination of the selectivity coefficients are based on potential measurements either in separate, or in mixed solutions containing the primary ion i (for which the electrode is designed) and the interfering ion j[57,58]. Thus, two types of method are employed for determining the selectivity coefficient: (A) the separate

Thus, the selectivity coefficients can be calculated by using either Eq.(2.5) or Eq.(2.6).

The separate solution method is only successful if the electrode shows a true mixed response, that is, it functions reversibly in the presence of the interferent[43].

B. Mixed solution method. In this method, potential selectivity coefficient values are obtained by measuring the emf in solutions containing both ions. Thus, the ISE potential becomes

$$E = E^{o} + (RT/z_iF)\ln[a_i + k_{ij}^{pot}(a_j)^{z/z}] \qquad (2.7)$$

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

$$E - E_i = (RT/z_iF)\ln\{[a_i + k_{ij}^{pot}(a_j)^{z/z}]/a_i\} \qquad (2.8)$$

which on rearrangement becomes

$$k_{ij}^{pot} = a_i/(a_j)^{z/z}\{[\exp(z_iF/RT)(E - E_i)] - 1\} \qquad (2.9)$$

This is done by adding increasing quantities of either the interferent to the primary ion or the primary ion to the interferent ion solution. The IUPAC has recommended a method in which a constant interfering ion activity and variable primary ion activities are employed. The potential E is measured for different solutions containing variable primary ion activities but constant interfering ion activities. Thus E^{*} according to

Eq. (2.1) can be written as

$$E^{*} = E^{o} + (RT/z_iF)\ln[a_i + k_{ij}^{pot}(a_j)^{z/z}] \qquad (2.10)$$

Combining Eqs. (2.3) and (2.10) gives

$$k_{ij}^{pot} = a_i/(a_j)^{z/z}\{[\exp(z_iF/RT)(E^{*} - E_i)] - 1\} \qquad (2.11)$$

There are several methods for calculating k^{pot}_{ij} from the plot of E^{*} versus pa_i.

Method 1. The first method depends on finding graphically the point T at the which the electrode is responding equally to both ions, i.e., $a_i = k_{ij}^{pot}\, a_j^{z/z}$ (from Eq. 2.6). If the line RS (see Fig.2) is straight and parallel to the abscissa, then T is the point of intersection of the extrapolation of PQ and SR as shown in Fig. 2. k_{ij}^{pot} may then be calculated from the activity of i at point T, ${}_Ta_i$, and the constant a_j by means of the equation [56,68]

$$k_{ij}^{pot} = {}_Ta_i^z / a_j^z \qquad (2.12)$$

The method is only suitable if RS is a straight line.

Method 2. The more generally applicable method is one that

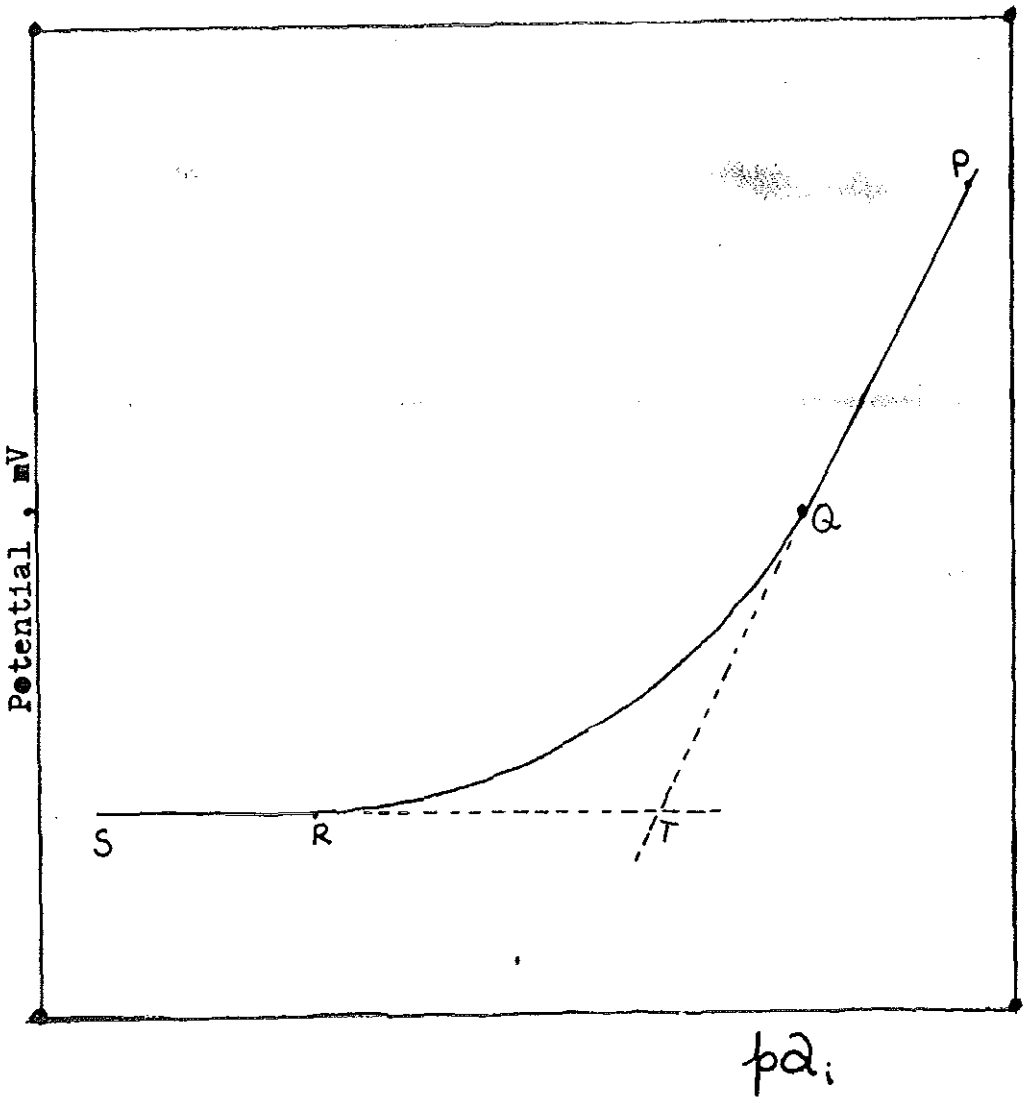

Fig. 2 Typical curve for the calculation of k_{ij}^{pot} using mixed solution method (method 1)

does not depend on the form of RS, but instead relies on PQ and QR (Fig. 2). From Eq. (2.1) both ions are contributing equally to the electrode response when [56]

$$a_i = k_{ij}^{pot}\, a_j^{z/z} \qquad (2.13)$$

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

$$E = E^{\circ} + (RT / z_i F) \ln(2a_i) \qquad (2.14)$$

The response of the electrode in the absence of j is given by the extrapolation of PQ 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 [56]:

$$\Delta E = (RT / z_i F) \{\ln 2a_i' - \ln a_i'\}$$

$$\Delta E = (RT / z_i F) \ln 2$$

$$= 18 / z_i \ \text{mV} \qquad \text{at } 25\,^{\circ}\text{C}$$

Thus by finding on the graph the activity of i at which the experimental line QR differs from the extrapolation of PQ by $18/z_i$ mV (as in Fig. 3), the activity a_i' is determined. k_{ij}^{pot} is then calculated by substitution into the equation

$$k_{ij}^{pot} = a_i'^{z}i / a'^{z}_{j}j \qquad (2.15)$$

In addition to the procedures described above other workers have used different methods for the determination of the selectivity coefficient [56].

The value of the selectivity coefficient is never constant for all activities of i and j, although it is sometimes constant for a given ratio of i to j [71].

It must be emphasized that for any quoted value of k_{ij}^{pot} to be of use and comparable to other values, full details must be available of both the method of calculation and the experimental procedure used to derive the data [56].

2.3. Analytical Measurement Techniques

The unique and reproducible correlation between the membrane potential and the concentration or activity of the chemical species for which the electrode is selective, is the fundamental characteristic of any ion-selective membrane electrode and is the basis for quantitative determinations by ISE potentiometry. Actually, the ISEs sense the activity, rather than the concentration, of ions in solution. The

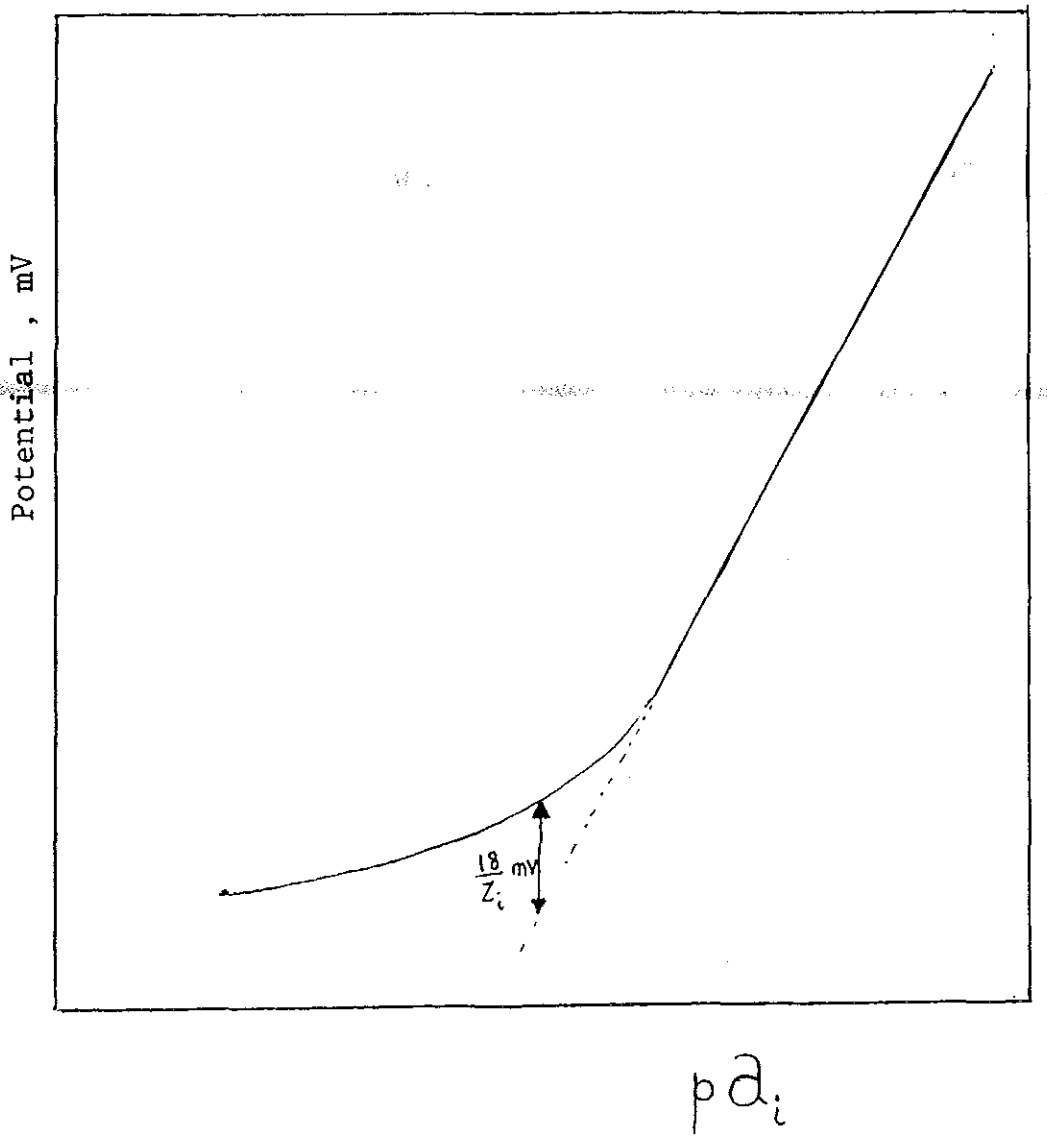

Fig . 3 . Typical Curve for the Calculation of k_{ij}^{pot} using mixed solution method (method 2)

relation between activity (a) and concentration(c) is given by

$$a = fc \qquad (2.16)$$

Where f is the activity coefficient. But if the relationship between the activity and concentration of the analyte can be fixed by adding a constant concentration of an inert electrolyte (i.e. not sensed by the ISE) to all samples to swamp out minor variations in sample composition measurements[56] then the difference between a and c ceases to be a problem.

The measurement techniques used to obtain reproducible and meaningful results and the conversion into analytical results are briefly discussed below.

2.3.1. Calibration Methods. An empirical calibration curve, whereby the electrode potential is related to the logarithm of activity or concentration of the ion of interest, is the most straight forward method and the technique of choice whenever possible.The sample to be analyzed is pretreated as required and the electrodes are immersed in it. The equilibrium potential is then measured and related to the determinand activity or concentration by means of the calibration curve[56].

A series of solutions can also be prepared spanning the anticipated range of activity or concentration of the determinand in the sample. If the calibration curve is expected

to be linear with theoretical Nernstian slope and the range is broad, it is usually sufficient to prepare one standard per decade of activity. The determination of the sample activity or concentration can then be made by single point calibration. It follows from the Nernst equation that:

$$E_{sample} - E_{standard} = S \log(a_{sample}/a_{standard}) \qquad (2.17)$$

which can be rearranged to give

$$a_{sample} = a_{standard}\ 10^{\Delta E/S} \qquad (2.18)$$

Where S is the experimental slope whose value can be determined using two standard solutions of known different concentrations. This approach requires no knowledge of the standard potential of the electrode pair. The assumption here is that the value of the slope is constant and that there is a linear relationship between the potential and log. activity or concentration.

A more complicated version of this method involves the use of two standard solutions in which the analyte activities are a_1 and a_2, which bracket the unknown activity a_x (for concentration the activities (a's) are changed to concentrations (C's)). Then applying the Nernst equation to all these three solutions, a_x can be calculated from

$$[(E_x-E_1)/(E_1-E_2)]\log(a_1/a_2) = \log(a_x/a_1) \qquad (2.19)$$

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

2.3.2. Standard (or known) addition method. Known addition methods offer the advantage that they are rapid, easy to perform and also diagnostic as they provide information about the buffer capacity of the ion to be determined. These methods, however, make some assumptions[56],

(i) the change in sample volume caused by to addition of the aliquot is negligible;

(ii) the change in liquid junction potential, El, is negligible;

(iii) the activity coefficient and the degree of complexation of the ion to be determined remains constant;

(iv) interference is negligible;

(v) the ISE has a theoretical Nernstian response slope.

Two different methods are distinguished here.

Standard addition to a sample. A known volume, V_s ml, of the standard solution of concentration C_s is added to the sample solution, V_x ml, containing the unknown concentration C_x, and the potential change of the electrode is recorded[42].The observed initial potential of the sample solution of unknown concentration, C_x, is given by the Nernst equation. Thus,

$$E_1 = E^\circ + (RT/z_iF)\ln[C_x\gamma_x] + E_l \qquad (2.20)$$

E_l being the liquid junction potential.

On additon of a known amount of test ion, (V_s ml of known concentration, C_s, to the initial volume, V_x ml), the new potential measured is given by:

$$E_2 = E^\circ + (RT/z_iF)\ln\{[(C_xV_x + C_sV_s)/(V_x + V_s)]\gamma_x'\} + E_l \qquad (2.21)$$

Assuming the constancy of E_l and $\gamma_x = \gamma_x'$, subtracting Eq. (2.20) from Eq. (2.21) gives

$$\Delta E = E_2 - E_1 = (RT/z_iF)\ln\{[(C_xV_x + C_sV_s)/(V_x + V_s)C_x]\} \qquad (2.22)$$

On rearrangement Eq. (2.22) gives

$$\Delta E/S = \log\{[(C_xV_x + C_sV_s)/(V_x + V_s)C_x]\} \qquad (2.23)$$

where S is the Nernst slope (= 2.303 RT/z_iF) experimentally determined by using a series of known standard solutions. Equation (2.23) may be rearranged to give

$$C_x = [C_s\ V_s/(V_x + V_s)]\{10^{\Delta E/S} - [V_x/(V_x+V_s)]\}^{-1} \qquad (2.24)$$

Thus C_x can be evaluated. If there is no change in volume V_x of sample, upon addition of the standard Vs is negligible (i.e. V_x >> Vs), then Eq. (2.24) becomes

$$C_x = [C_s\ V_s/V_x]\ \{10^{\Delta E/S} - 1\}^{-1} \qquad (2.25)$$

Or

$$\Delta E = S \log [\ 1 + (C_sV_s/C_xV_x)\ ] \qquad (2.26)$$

Or

$$10^{\Delta E/S} - 1 = C_s\ V_s/C_xV_x \qquad (2.27)$$

Equation (2.27) indicates that C_x may be calculated from the single addition method or preferably determined from the slope of a plot of $10^{\Delta E/S} - 1$ vs V_s, where several addition of standards are made.

Advantages of this techique over other techniques are that electrode calibration is uneecessary, only one standard solution is required and calibration drift is unimportant; however, two potential measurements per sample are necessary.

Sample addition to a standard. This method is the reverse of the foregoing one, and called the 'analate addition' technique. First the potential of a known volume, V_s, of the standard solution of a known concentration, C_s, is measured. Then, a known volume, V_x, of the solution to be analysed is added, and the new potential measured. The concentration of the unknown sample solution, C_x, can then be calculated from the equation[42,44,46],

$$C_x = C_s \left[(V_s + V_x/V_s)(10^{E/S}) - (V_s/V_x) \right] \qquad (2.28)$$

This rearranged equation is derived by replacing C_s in place of C_x in Eq. (2.21) and subtracting from Eq. (2.22).

Gran's plot method[45]. Gran[61] proposed a procedure for determining the equivalence point of potentiometrically indicated titrations by means of extrapolating a linearized titration curve[62,63].

Gran's method is based on the idea that a linear titration curve is obtained if the concentration of the indicated ion is plotted rather than the corresponding cell potential. Eq.(2.21) can be rearranged to give

$$(V_x+V_s)\ 10^{E\,F/2.3RT} = 10^{(E+E)F/2.3RT}\ \gamma_x'\,(C_xV_x+C_sV_s) \qquad (2.29)$$

A plot of $(V_x + V_s)\ 10^{E\,F/2.3RT}$ vs. V_s gives a straight line which intercepts the abscissa for a value of V_s called V_c where $C_x\ V_x = -\ C_s\ V_c$. Thus C_x can be evaluated since V_c, V_x, and C_s are known[42].

Standard subtraction method. The standard or known subtraction method is different only in that the standard solution added to the sample is not the analyte solution but a solution of a species which reacts quantitatively with the determinand. Thus, a decrease in the analyte concentration is produced with a corresponding change in cell potential; this potential change

may be used to calculate the intitial analyte concentration in the sample by means of the following equation.

$$C_x = C_s V_s / [V_x - (V_s + V_x) 10^{\Delta E/S}] \qquad (2.30)$$

The assumption here is that, a 1:1 stoichiometry of the reaction between the analyte and the added species is considered. The equation becomes complex if there is a different stoichiometry[56,64].

2.4. Response Time

The response time of an electrode pair is the time required for the potential to come within a specified range of the final steady value[43], a potential 95 percent[44] of the steady-state value or differing [65] by 1 mV from the steady-state value.

2.5. Detection Limit[66]

The detection limit of an analytical procedure is regarded as being the lowest concentration of the analyte that can be distinguished with reasonable confidence from a field blank, here defined as a hypothetical sample containing zero concentration of analyte.

Detection limit is estimated in the response (or signal) domain, but is usually reported in terms of concentration or

amount (mass). The relationship between the respone and concentration domain is the calibration function.

The IUPAC has recommended[66] 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 certainity in a given analytical procedure.

The detection limit with ion-sensitive detection techniques is defined by IUPAC 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 (i.e., at 25°c, $59.1/z_i \times \log 2 = 18/z_i$) [45].

3. EXPERIMENTAL

3.1. Materials and Reagents

Tantalum pentoxide (BDH, 99.9%), Potassium nitrate (BDH, analar), Potassium carbonate (Riedel-de Haen), Poly(vinyl chloride) (Fluka), sulphuric acid (BDH, 40% (w/w)), ammonium fluoride (Fluka), tetraphenylarsonium chloride (Merck), Brilliant Green (Fluka), anhydrous sodium sulphate (BDH), 1-chloronaphthalene (Fluka) were used as received without further purification.

3.2. Preparation of Solutions

3.2.1. Preparation of tantalum solutions [68,69]. 1.0 g of well-powdered Ta_2O_5 was thoroughly mixed with 2.5 g of K_2CO_3 and 2.5 g of KNO_3 (2:5:5 weight ratio) in a platinum crucible. The mixture was fused in a muffle furnace at 740-760°C for about 15 min. The fused melt was cooled to room temperature and treated with about 25 ml of concentrated sulphuric acid. The extract was quantitatively transferred to a 300-ml Kjeldhal flask, evaporated to dryness, and cooled. The residue was then dissolved in 100 ml of 20% (w/v) tartaric acid by heating and continuous stirring. A clear solution was obtained, and it was quantitatively transferred to a 250-ml Volumetric flask and made up to the mark with 20% (w/v) tartaric acid solution.

3.2.3. Preparation of sample solutions[30]. 0.5 g of a well-powdered Ethiopian tantalite - columbite ore sample was thoroughly mixed with 1.25 g each of KNO_3 and K_2CO_3 (2:5:5 weight ratio) in a platinum crucible. The mixture was fused in a muffle furnace at 740 - 760°C for about 15 min. The fused melt was cooled to room temperature and treated with about 15 ml of concentrated sulphuric acid. The extract was quantitatively transferred to a 300-ml Kjeldhal flask, evaporated to dryness, and cooled. The residue was dissolved in 80 ml of 25% (w/V) tartaric acid by heating and continuous swirling. The solution obtained was then quantitatively transferred to a 100-ml volumetric flask and made up to volume with approximately 20 ml of 5 M sulphuric acid.

Other artificial samples (matrices) of definite composition were prepared by mixing known quantities of the solutions of different ions. The solutions were acidified with 1 M sulphuric acid to known volumes (100 ml each).

3.2.4. Solutions of diverse ions. Solutions of cations were prepared from their oxides, nitrates or sulphates, while solutions of anions were prepared from their sodium, potassium or ammonium salts. The concentrations of all the solutions prepared were 5.0×10^{-2} M with respect to the ion in question except for niobium(V) which was 1.0×10^{-3} M.

A niobium solution was prepared by fusing 0.1439 g of Nb_2O_5 (Johnson and Mathey, 99%) with 3.6 g of potassium pyrosulphate

(Riedel - de Haen) in a Silica crucible. The cooled melt was dissolved in 100 ml of 20% (w/v) tartaric acid (BDH, Analar) solution by heating over a sand bath. The solution was cooled to room temperature, transferred to a 1-litre volumetric flask, and diluted to volume with distilled water[71,72].

A solution of titanium(IV) was prepared by fusing 0.4 g of TiO_2 (BDH) with 4 g potassium hydrogen sulphate (BDH). The cooled melt was leached with 10% (v/v) sulphuric acid and diluted to 100 ml with 10% sulphuric acid[72].

Solutions of Sn (II), Er(III), Zr(IV) and Bi(III) were prepared by dissolving stannous chloride, erbium oxide, zirconium chloride and bismuth nitrate (BDH), respectively, in 1.0 M hydrochloric acid solution. Dissolutions were carried out by heating to obtain clear solutions.

Solutions of Al(III), Hg(II) and Ce(IV) were prepared by dissolving the respective sulphate salts (BDH or Riedel-de Haen) in 0.5 M hot sulphuric acid solutions. Sulphates of Co(II) and Mn(II) in distilled water were also used to study the effect of these cations.

Solutions of Fe(III), Zn(II), Cu(II), Ni(II), Ca(II), Cd(II) La(III), Cr(III), UO_2(II), Pb(II), Y(III) and Ag(I) nitrates were prepared by dissolving each salt (BDH or Riedel-de Haen) in distilled water.

Potassium salts were used to prepare aqueous solutions of nitrate, chloride and sulphate; perchlorate, periodate, EDTA, tungstate, antimonate and arsenate solutions were made from their sodium salts; and for thiocyanate, molybdate and

metavanadate the ammonium salts (BDH, or Riedel-de haen) were used in distilled water.

Oxalic acid (Riedel-de haen) and boric acid (May & Baker) solutions were prepared by dissolving the solid compound, in distilled water.

3.3. Preparation of the Coated- Graphite electrode

3.3.1. Preparation of Brilliant Green solution. A 2.0×10^{-2} M stock solution of Brilliant Green was prepared by dissolving 0.9653 g of the salt in about 50 ml of distilled water by continuous stirring for 2 min, to ensure complete dissolution. The solution was then quantitatively transferred to a 100-ml volumetric flask and diluted to volume by washing the beaker several times.

3.3.2. Preparation of electroactive material. Aliquots of 22 ml of 1.8×10^{-2} M of the tantalum(V) stock solution, 2.7 ml of concentrated sulphuric acid and 2.3 ml of 40% (w/w) hydrofluoric acid were transferred into a 250-ml polypropylene separatory funnel. To this was added 11 ml of 2.0×10^{-2} M Brilliant Green solution and the volume of the aqueous phase was adjusted to 50 ml with distilled water. The mixture was vigorously shaken for 3 min with 10 ml of 1-chloronaphthalene (2 x 5 ml) and the two phases were allowed to separate for 30 min during each extraction. The organic phase was collected into a 100-ml plastic beaker containing 1 g of anhydrous sodium

sulphate. The dried extract was transferred into a 25-ml volumetric flask. This solution, i.e., the solution of Brilliant Green-hexafluoro- tantalate(V) ion association complex in 1-chloronaphthalene, was used as the electroactive material for the potentiometric sensor.

3.3.3. Preparation of the coating mixture. A poly(Vinyl chloride), PVC, solution was prepared by dissolving 100 mg of the polymer in about 3.25 ml of tetrahydrofuran (THF). To this was added 0.25 ml of the Brilliant Green-hexafluorotantalate(V) extract in 1- chloronaphthalene.

3.3.4. Preparation of Brilliant Green-hexafluorotantalate(V) Coated graphite electrode. About two-third of a 12-mm graphite rod (Ringsdorff-Werke, GmbH, RWO, diameter 3.1 mm) was cleaned with a wet smooth emery paper, washed with distilled water and dried for 1 h at 105°C. The other end of the rod was tightly fixed to one end of a glass tube (internal diameter 3 mm) so that a coil of conducting copper, housed in the glass tube, was in contact with it.

The cleaned part of the graphite rod was dipped into the coating mixture six to eight times with an interval of two min to partially evaporate the THF. This allowed the graphite surface to be completely covered by a dark-green film. The electrode was then kept in a hood for 6 h to completely evaporate the THF. the uncoated and some of the coated portion of the rod was tightly wrapped with paraformaldehyde film

(Parafilm, American Can Company) to prevent direct contact of the graphite rod with the test solutions. The resulting coated-graphite tip (about 3 mm) was then conditioned for 30 min in a 5.0×10^{-3} M tantalum(V) solution made 1 M in both sulphuric and hydrofluoric acids. The electrode was then ready for use. When not in use, it was stored by suspending the electrode in a brown dropper bottle, saturated with 1-chloronaphthalene to prolong its life-time [32]. The design of the electrode is shown in Fig.4.

3.4. Instrumentation

Potentiometric measurements were made at room temperature (20 ± 2°C) using a Philips 9409 digital pH/mV meter with the coated-graphite electrode (CGE) against a sintered glass diaphragm Ag/AgCl external reference electrode (Orion). Equilibrium potentials of the test solutions were recorded after continuous stirring with a Teflon-coated magnetic stirring bar for 4-20 seconds to obtain a constant potential reading. The complete electrochemical cell is represented as follows:

CGE / test solution / external reference electrode

3.5. General Procedures

3.5.1. Study of the electrode behaviour. Potential measurements were made by dipping the CGE and external reference electrode into 20 ml aliquots of 1.0×10^{-7} - 1.0×10^{-2} M tantalum (V) in 1.0 M sulphuric acid and 1.0 M hydrofluoric acid in 100-ml polypropylene beakers. A constant potential was recorded within 4-20 seconds at room temperature (20 ± 2 °C).

3.5.2. Study of experimental parameters. The effect of the organic ion exchanger in the PVC membrane as well as sulphuric and hydrofluoric acid concentrations in the test solution was studied by recording the potential of the system according to the general procedure, keeping all other experimental parameters constant except the one under study.

3.6. Procedure for Selectivity Coefficient Determination

3.6.1. Separate solution method[59]. The potential (E_i) of 5.0×10^{-5} M (C_i) tantalum(V) solution in sulphuric and hydrofluoric acids, both 1.0 M, was initially measured, followed by potential measurements (E_j) of 5.0×10^{-6} - 5.0×10^{-2} M of the interfering ion, which were again 1.0 M in both sulphuric and hydrofluoric acids. The selectivity coefficients were then determined by using Eq.(2.5).

3.6.2. Mixed solution method[56,73]. Aliquots (8 ml each) of

5.0 x 10^{-2} M solutions of the interferring ion in 1.0 M sulphuric acid and 1.0 M hydrofluoric acid were added to 5.0 x 10^{-6} - 5.0 x 10^{-3} M tantalum(V) solution, which was also in 1.0 M sulphuric and 1.0 M hydrofluric acids. The potentials of the resulting solutions were measured and the selectivity coefficients were evaluated from the detection limits of the calibration curves using Eq. (2.10).

3.7. Procedures for sample analysis

3.7.1. Direct potentiometry[56]. The potentials of aliquots (20 ml each) of the sample solutions, 1.0 M in both sulphuric and hydrofluric acids, were measured following the general procedure described for the electrode behaviour. The tantalum concentration in the sample solution were determined from the calibration curve (E (mV) vs -log [Ta(V)]). Alternatively, the tantalum concentration in the sample solution could reliably be calculated based on a single point calibration [64] using Eq. (2.17) or by use of two standard solutions from Eq.(2.19).

3.7.2. Standard addition technique[56]. The potential (E_x) of 20 ml (V_x) of a dilute sample solution, 1.0 M in both sulphuric and hydrofluric acids, was first measured. This was followed by additions of 1 or 2 ml of 1.0 x 10^{-3} M (C_s) standard tantalum(V) solution, 1.0 M in both sulphuric and hydrofluoric acids, to the stirred sample solution and the new potential (E_s) was recorded. the concentration (C_x) of tantalum in the sample

solution was then calculated using Eq.(2.31).

3.7.3. Sample addition technique[74,75]. The potential (E_s) of 20 ml (V_s) of 2.0 x 10^{-5} M tantalum solution (C_s) in 1.0 M sulphuric acid and 1.0 M hydrofluoric acid was initially measured. Addition of 1 or 2 ml (V_x) of solution containing x-fold higher sample concentration (in the same acidity medium) was followed and then the new potential (E_t) recorded. The concentration (C_x) of tantalum in the sample was calculated based on Eq.(2.28).

3.7.4. Gran's plot[62,76]. The potential (E_x) of 20 ml dilute sample solution (about 1.0 x 10^{-5} M Ta(V)), in 1.0 M sulphuric acid and 1.0 M hydrofluric acid was initially measured. 2, 4, 6, 8 and 10 ml (V_s) of 1.0 x 10^{-3} M standard tantalum(V) solution, (C_s), (again in 1.0 M sulphuric acid and 1.0 M hydrofluoric acid) was added in 2 ml portions and the new potentials (E_2) were recorded after each addition. The quantity of $(V_x + V_s)\ 10^{E/S}$ was plotted versus V_s(equation 2.29) which gave a straight line intercepting the abscissa at a value of V_s called V_e ; where $C_xV_x = -C_sV_e$. The concentration of the sample solution (C_x) was calculated from the values of V_e , V_x and C_s.

4. RESULTS AND DISCUSSION

4.1. Selection of internal conductive substrate

There have been a large number of attempts to prepare ISEs with suitable solid state internal contacts, thus eliminating the internal reference system and achieve considerable technical advantages[43]. Metal wires, carbon rods, metal disc electrodes, etc., have all been utilized as internal conductive substrates onto which either inorganic precipitates or ion-exchange resins have been coated. Alternatively, the precipitates or solid exchangers have been incorporated into membrane form[77].

In order to achieve the desired electrode quality in terms of sensitivity, response time and stability, it is essential to choose a suitable solid internal contact.

In this study graphite rod and silver wire have been tried as the internal conductive substrates onto the surface of which the Brilliant Green-hexafluorotantalate(V), incorporated in PVC matrix,was coated.

These solid substrates were examined with a PVC coating mixture incorporating Brilliant Green-hexafluorotantalate(V) extracts in 1-chloronaphthalene. The coated conductor electrodes with a sintered glass diaphragm Ag/AgCl external reference electrode, were tested to measure the potentials of

$1.0x10^{-7}$ - $1.0x10^{-2}$ M tantalum(V) solutions. The cell used in the study is schematically represented below.

Ag/AgCl	/ test solution	/ Coated solid
(F-resistant,plastic body)	Ta(V)in 1M HF,	conductor
	1M H_2SO_4	electrode

The electrode with silver wire as internal conductive substrate was not found to function satisfactorily when used in the strongly acidic test solutions (pH < 1).This is because the dark-green coating film on the surface of the wire slowly turned white and the wire surface turned dark brown indicating the formation of an oxide film in acidic media, resulting in high specific resistance [78].This might have changed the composition of the dye rendering the electrode practically non functional.

Silver(I) oxide is known to catalyze the reduction of nitrogen-containing organic compounds such as hydrazines [78]. It is not known, however, if silver oxide catalyses decomposition of Brilliant green. No further investigation was made on this observation.

It should be noted, however, that previously Brilliant Green-tetrathiocyanatozincate(II) in PVC matrix coated on silver wire was applied satisfactorily for the potentiometric determination of zinc in mildly acidic solutions(pH 4.7 -5.8) [32]. The electrode prepared by coating the surface of the comparatively inert graphite rod was found to function well as will be discussed in later section with more detail.

Further studies were thus made using the graphite rod as a solid internal contact.

4.2. Selection of Membrane Solvent

A solvent (plasticizer) is required in a polymer membrane ion-selective electrode in order to increase ionic mobility in the polymeric membrane[79]. The choice of the plasticizer has,then, a drastic effect on the selectivity of the membrane since the selectivity of the membrane is governed by both the mobility of the ions in the membrane and the equilibria existing at the membrane solution interface[80].

A plasticizer in PVC matrix membrane ISEs, in addition to its plasticizing function, must be immiscible with water, relatively nonvolatile, and be a good solvent for the ion-association salt. Furthermore, it must promote the desired ionic selectivity and possess sufficiently high viscosity[43].

1-Chloronaphthalene having low miscibility with water, higher viscosity, nonvolatility and high dielectric constant, is a good plasticizer for the PVC matrix.It has an additional advantage over other plasticizers such as dioctylphthalate, in that it does not participate in pH or acidity dependent equilibria when the PVC membrane electrode with 1-Chloro - naphthalene as plasticizer is subjected to the test solution [81]. It also helps in prolonging the life time of the electrode when it is used in the coating matrix[32]. A summary of the physical properties of 1 - Chloronaphthalene is given in

Table 2.

Table 2. Some physical properties of 1-Chloronaphthalene.

Property	1-Chloronaphthalene
M.W.,g/mole	162.61
b.p., °C	263
m.p., °C	-20
n_D^{20}	1.6332
D_4^{20}	1.1938

Further it was found that the Brilliant Green-hexafluorotantalate(V) ion-association complex is easily and quantitatively extracted into 1-chloronaphthalene.

Thus 1-Chloronaphthalene, which fulfils most of the requirements of the membrane solvent, was used to extract the Brilliant Green-hexafluorotantalate(V) salt and this extract was used for the preparation of the coated graphite electrode in the present investigation. Hence, other PVC plasticizing solvents were not tried.

4.3. Influence of Exchanger Concentration

The effects of the composition of the aqueous phase, (i.e., the ratio of the concentration of tantalum(V) to that of Brilliant Green in the aqueous phase used for the extraction of Brilliant Green-hexafluorotantalate(V) in 1-chloronaphthalene) and consequently the concentration of the Brilliant Green-

hexafluorotantalate(V) in the extractant on the response behaviour of the coated graphite electrode has been studied. The results are given in Table 3.

Table 3. Effects of the composition of the aqueous phase used for extraction of $BG^+TaF_6^-$ ion-pair into 1-chloronaphthalene and the concentration of BG^+TaF_6 in the extract on the CGE (the concentrations of the stock solutions used were [Ta(V)] = 1.8 x 10^{-2} M; [BG^+] = 2.0 x 10^{-2} M).

Vol. ratio BG:Ta	Mole ratios BG:Ta	Linear range Ta(V), M*	average slope mV/decade*	remark
1:4.80	1:4.32	$1.0x10^{-5}$-$1.0x10^{-3}$	55.5+1	Slow response
1:2.00	1:1.80	$5.0x10^{-6}$-$5.0x10^{-3}$	58.0+1	Fast response
1:1.00	1:0.90	$5.0x10^{-5}$-$1.0x10^{-3}$	54.0+2	Slow response
1:0.50	1:0.45	-------	---	Unstable
1:0.21	1:0.19	-------	---	Erratic

* Average of duplicate measurements.

In each case the extraction was carried out with 10 ml (2x5 ml) of 1-chloronaphthalene from 50 ml of aqueous phase.

The electrode prepared from 2.20 x 10^{-2} M BG^+TaF_6 (which was extracted from the aqueous phase having the composition 22 ml of tantalum ($1.8x10^{-2}$ M) and 11ml Brilliant Green ($2.0x10^{-2}$ M)

stock solutions) gave relatively wide linear response range with a better slope and shorter response time. Thus this prepared electrode was used for further study.

At least 30 minutes of conditioning time was found to be necessary in order to obtain a constant potential readings with the CGE.

4.4. Study of the Effect of Variables

Tantalum forms fluoro-complexes of various compositions in aqueous hydrofluoric acid [4]. The formation and composition of fluoro-complexes of Ta(V) is dependent on pH and fluoride concentration.

Study of the extraction of the fluoro-complexes of tantalum with Brilliant Green in organic solvents suggested that singly charged anions are extracted with substantially larger distribution coefficient than others. Thus, in the process of extraction, the TaF_6^- complex is transferred to the organic phase predominantly. To facilitate this by preventing the hydrolysis of tantalum(V), sulphuric acid was used in the aqueous phase[24,27]. Therefore, the effects of sulphuric and hydrofluoric acid concentrations were studied to establish the optimum conditions for the potentiometric determination of tantalum in various matrices and real samples by the proposed CGE.

4.4.1. The effect of Sulphuric acid concentration.

The effect of sulphuric acid was studied by varying its concentration from 0.0 to 2.0 M keeping the concentration of hydrofluoric acid constant at 1.0 M. This study was done in two different modes. In the first mode of study a series of tantalum solutions were prepared in which the concentration of tantalum was kept constant and the sulphuric acid concentration was varied. This was to find out the effect of sulphuric acid concentration on the potential values of the system. In the second mode several series of tantalum solutions were prepared in which sulphuric acid was kept constant from series to series while varying tantalum in each series. This was to find out the optimum linear range.

The potential was found to increase with increasing concentration of sulphuric acid. The increase in potential may be due to the increasing extent of complexation. However, at higher concentrations of the acid (> 1.6 M) the slope decreased, and the effect was more pronounced at lower tantalum concentration(Table 4).

A decreasing trend in the slope of the potential response of the CGE with increasing concentration of sulphuric acid has been noticed, however, the slope remained practically constant and Nernstian in the range 0.5-1.2 M of sulphuric acid (i.e., 58.5 ± 1 mV per decade).

Table 4. Effect of the concentration of sulphuric acid on the slope of $BG^{+}TaF_{6}^{-}$ coated graphite electrode. [HF]=1.0

decreased and the effect was more pronounced at lower tantalum concentrations (Table 4) which might be associated with pH response of the graphite rod[82]. A 1.0 M sulphuric acid concentration was, therefore, chosen for further study, at which the linear response range and slope were 5.0×10^{-6}-5.0×10^{-3} M tantalum(V) 58 ± 1 mV/decade, respectively.

4.4.2 The effect of hydrofluoric acid concentration.

The concentration of sulphuric acid was kept constant at 1.0 M, to study the effect of hydrofluoric acid, varying the latter between 0.1 and 2 M. This study was done in two different modes. In the first mode of study a series of tantalum solutions were prepared in which the concentration of tantalum was kept constant and the hydrofluoric acid concentration was varied. This was to find out the effect of hydrofluoric acid concentration on the potential values of the system. In the second mode several series of tantalum solutions were prepared in which hydrofluoric acid was kept constant from series to series while varying tantalum in each series. This was to find out the optimum linear range.

The potential was observed to increase up to 0.5 M and then remained practically constant. This may be due to the decrease in the degree of dissociation of hydrofluoric acid (a weak acid) at higher concentrations in 1.0 M sulphuric acid.

The electrode responded with a Nernstian slope up to about 5.0×10^{-6} M tantalum(V) from 0.8 to 1.6 M hydrofluoric acid in

the concentration of ions in solution according to the Nernst equation

$$E = \text{constant} + S \log a_i$$

where S is the experimental slope and a_i is the activity of the ion,i. The constant is the emf of the electrochemical cell with a solution in which $\log a_i = 0$, i.e., $a_i = 1$.

The relationship between the activity and concentration of an ion can be expressed by the equation

$$a_i = f_i c_i$$

where f is the activity coefficient and c the concentration of the ion i.

The relationship between the activity and concentration can be fixed by adding a constant higher concentration of an 'inert' electrolyte, hence

$$E = \text{constant}^* + S \log C_i$$

where C_i is the concentration of the analyte ion, and constant* is a new constant incorporating the activity coefficient, and depends, among other things, on the type of reference electrode employed.

The $BG^+TaF_6^-$ coated graphite electrode was found to respond to TaF_6^- ions. The response behaviour of the electrode was

studied in the concentration range of $1.0x10^{-7}$ - $1.0x10^{-2}$ M tantalum(V) in solution that were 1 M in both sulphuric and hydrofluoric acid. However, the electrode responded linearly in the concentration range of $5.0x10^{-6}$ - $5.0x10^{-3}$ M tantalum(V) with a Nernstian slope of 58 ± 1 mV per decade. A typical calibration curve is shown in Fig. 5.

The detection limit as defined by the IUPAC was found to be

$8.0x10^{-7}$ M tantalum(V). The response time was found to be 4-15 seconds in the linear range.

The electrode was found to give a constant slope during the analysis of 300 samples with no deterioration in the linear range and detection limit. Then the slope from the lower part of the calibration curve gradually decreased resulting in higher detection limits. The reason might be due to the leaching of the plasticizer and/or the electroactive material into the test solutions[83]. Whenever the electrode was not in use it should be stored by tightly suspending the coated end in a brown dropper-bottle saturated with 1-chloronaphthalene.

A potential drift of 1-2 mV was noted during 24 hours. The drift was evaluated by measuring the potentials of four known concentrations of the analyte at least three times in 24 hours.

The response curve was obtained by plotting the measured potential E (mV) vs. - log C_i (Fig. 5).

The optimum conditions and response characteristics of the Brilliant Green-hexafluorotantalate(V) CGE are summarized in Table 6.

Table 6. Optimum conditions and response characteristics of the $BG^{+}TaF_{6}^{-}$-coated graphite electrode.

	Parameter/characteristics	Values
1	conditioning time, min	30
2	H_2SO_4 concentration in the test solutions,M	1
3	HF Concentration in the test solutions,M	1
4	Linear range,Ta(V) concentration, M	$5.0x10^{-6}$- $5.0x10^{-3}$
5	Detection limit,Ta(V)concentration,M	$8.0x10^{-7}$
6	Slope, mV/decade	58+1
7	Response time, sec	4-15
8	Precision, R.S.D(n=6),%	1.99
9	Number of samples analyzed during life time of an electrode	300

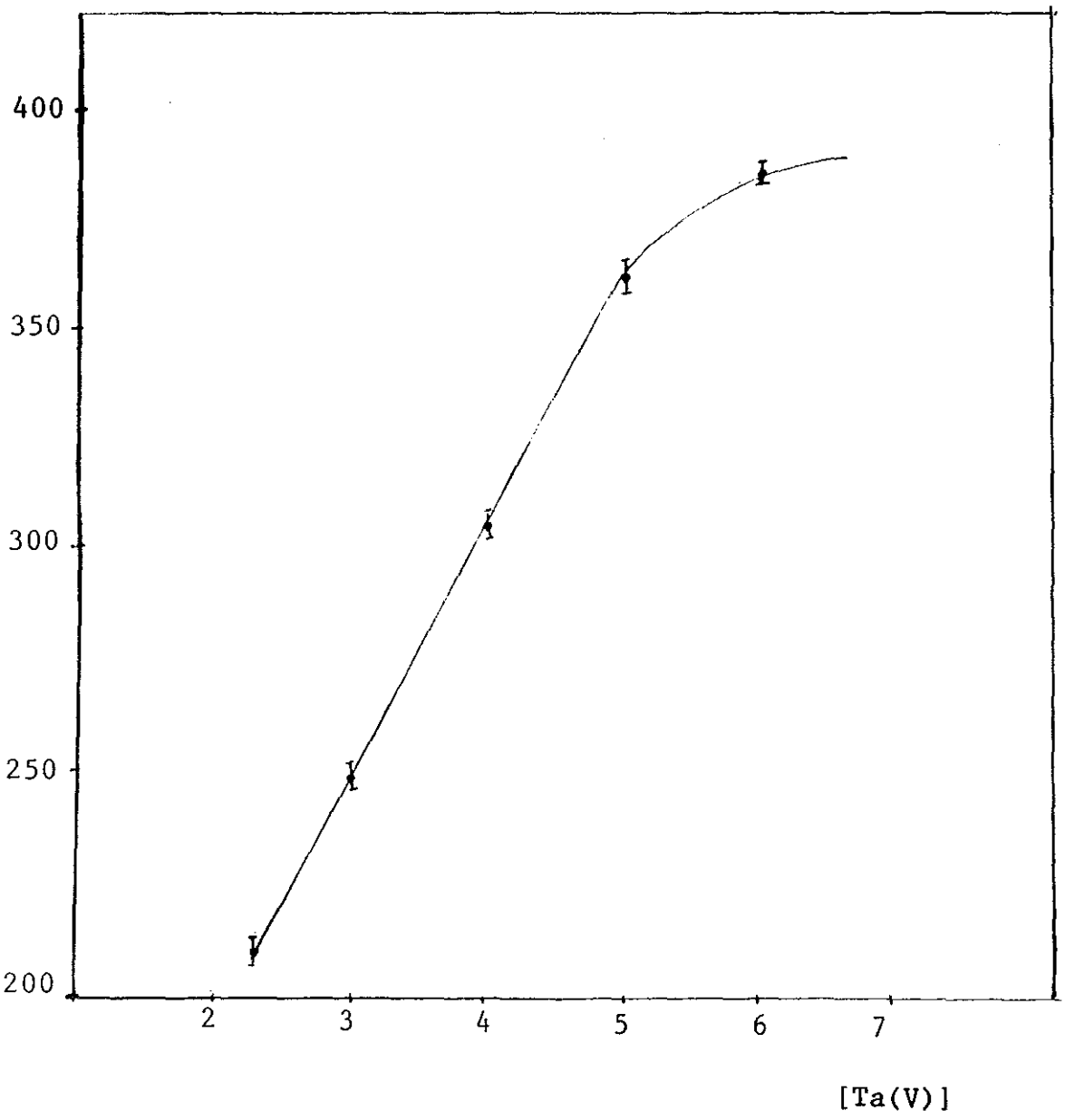

Fig.5. Calibration curve for the determination of tantalum (V)

Table 7. Selectivity coefficients of Brilliant Green-hexafluorotantalate(V) coated graphite electrode.

Interfering ion	most probable fluoro-complex in 1 M HF and 1 M H_2SO_4	Reference	$logk^{Pot}_{ij}$* separate solution method	$logk^{Pot}_{ij}$* mixed solution method
B	BF^-_4	88	2.16	3.07
Bi	BiF^-_4	89	1.83	2.40
Cl^-	_	-	2.17	3.33
ClO^-_4	_	-	2.01	2.41
IO^-_4	_	-	1.97	2.49
NO^-_3	_	-	2.21	3.46
SCN^-	_	-	2.12	3.74
Ag	AgF^{2-}_3	86	3.04	3.92
Ca	CaF^{2-}_4	88	2.39	3.41
Cd	CdF^{2-}_4	86	2.36	3.33
Ce	CeF^{2-}_6	-	2.36	2.52
Cr	$CrF_5H_2O^{2-}$	87	3.03	3.23
Cu	CuF^{2-}_4	84	2.40	3.08
Nb	$NbOF^{2-}_5$	24	3.09	3.54
Pb	PbF^{2-}_4	89	2.38	2.77
Sn	SnF^{2-}_4	89	2.94	
SO^{-2}_4	_	-	2.30	2.82
Ti	TiF^{2-}_6	86	2.49	3.09
UO^{2+}_2	$UO_2F^{2-}_4$	87	2.41	3.23
W	WF^{2-}_8	-	2.97	2.92
Al	AlF^{3-}_6	87	4.43	4.31
Fe	FeF^{3-}_6	87	3.13	4.30

* Average of triplicate measurements

The preference of the prepared electrode was 1000 times more to

tantalum relative to niobium.

Fe^{3+} and Al^{3+} ions tend to form hexafluoro-complexes[87], but the interference of these tervalent complexes with the CGE was very small.The presence of Zr^{4+}, Sb^{3+} and As^{3+} did not interfere seriously.These cations mainly have a strong affinity to form compounds with sulphate[86,88].There was also no serious interference due to Mn^{2+}, Zn^{2+}, Co^{2+} and Ni^{2+}. This might be due to the greater tendency of these cations to form the sulphates in sulphuric acid solutions[86]. The sulphates of these cations are more stable than their fluorides and fluoro-complexes.

There is no information on fluoro-complex formation with Y^{3+} and La^{3+} ions[86]. The presence of these ions in the solution showed no significant interference. Though the formation of fluoro-complex was reported for Hg^{2+}, there is no structural information[86]. However,the presence of Hg^{2+} showed some interference.

In both the separate and mixed solution methods Er^{3+} and Ce^{4+} ions form precipitates upon addition of hydrofluoric and sulphuric acids. However, the formation of these precipitates did not affect the stability of the potential readings and their presence did not interfere on the response of the electrode to hexafluorotantalate(V) anion. Several cations such as Bi^{3+},Pb^{2+}, Sn^{2+},UO^{2+}_2,W^{6+},Cr^{3+},Ti^{4+},Ag^{+},B^{3+},Cu^{2+},Cd^{2+} and Ca^{2+} form fluoro-complexes of various compositions. However, the calculation of the selectivity coefficients is based on the very frequently occurring fluoro-complexes(Table 5). The results indicate that these ions do not cause strong interference on the response of the Brilliant Green-hexafluorotantalate(V) CGE to TaF_6^-.

4.7. Application of the Brilliant Green-hexafluorotantalate(V) Coated Graphite Electrode.

The developed Brilliant Green-hexafluorotantalate(V) coated graphite electrode was applied to standard and real samples in

order to evaluate the reliability of the potentiometric technique for the quantification of tantalum.

The reliability of the proposed CGE was assessed by determining the content of tantalum in five different matrices prepared in such away as to represent the most important tantalum-bearing ores. The matrices were prepared by mixing the required quantities of the salt solutions(section 3.2). The tantalum content of the matrices were determined by the proposed electrodes using direct and standard addition potentiometric techniques. The results obtained(Table 8) are in good agreement with the actual value.

Table 8. Analysis of five matrices

No.	Composition of matrix	Amount μg, of Tantalum	Tantalum found direct potentiom	Using the CGE, μg* standard addition
1	5mg Nb^{5+}+3mg Mn^{2+} +3mg Cr^{3+} +50μg Ta^{5+} +1mg Pd+10mg Fe^{3+}	50	52±0.14	52.08±0.44
2	3mg Nb^{5+}+12 mg Fe^{3+}+ 2mg Ni^{2+}+2mg Ti+ 1mg Al^{3+}+1mg Co^{2+}+50μg Ta^{5+}	50	50.95±0.17	51.7±0.35
3	4mg Nb^{5+}+ 5mg Ca^{2+} + 7.5mg Na^{+} +50μg Ta^{5+}	50	48.97±0.11	50.74±0.39
4	5mg Nb^{5+}+5mg Y^{3+}+ 2.5mg Er^{3+}+5mg Ce^{4+} + 5mg La^{4+} +8mg U^{6+} + 50μg Ta^{5+}	50	53.00±0.24	53.23±0.48
5	4mg Nb^{5+}+5mg Y^{3+} + 10mg U^{6+} +15mg Fe^{3+} + 10mg Th^{4+} + 2mg Ti^{4+} + 50μg Ta^{5+},	50	47.19±0.20	46.72±0.26

*Mean±95% confidence limits for triplicate measurements

To further test the reliability of the proposed CGE , it was applied for determination of the tantalum content of two Ethiopian tantalite-columbite ore samples (which were collected from Ethiopian Institute of Geological Surveys, EIGS) using four different potentiometric techniques; viz., direct potentiometry, standard addition , sample addition and Gran's plot. The results are summarized in Tables 7 and 8 .

Table 9. Analysis of Ethiopian tantaliat-columbite ore sample EIGS sample No. 334101 (Ta_2O_5 certified by EIGS was 65.5%)

Method	Ta_2O_5 found percent*	Eq. No. used for calculation
Direct potentiometry	66.81±3.3%	2.19
Standard addition	63.15±1.3%	2.25
Sample addition	63.00±1.2	2.29
Gran's plot	66.3±1.5	2.29

* Mean±95 % confidence limit for triplicate measurements

Table 10. Analysis of Ethiopian tantalite-columbite ore EIGS sample No. 334107 (Ta_2O_5 certified by EIGS was 49.5%)

Method	Ta_2O_5 found percent*	Eq. No. used for calculation
Direct potentiometry	48.61±2.01	2.19
Standard addition	51.21±1.05	2.25
Sample addition	48.52±0.80	2.28
Gran's plot	49.04±1.20	2.29

* Mean±95% confidence limit for triplicate measurements

4.8. Comparison with Other Hexafluorotantalate(V)-Selective Electrodes

The performance characteristics of the TaF_6^--selective CGE were compared side by side with those of the previously proposed TaF_6^--selective electrodes. The reported data are summarized in Table 11.

Table 11. Comparison of the response characteristics of the TaF_6^--selective CGE with other TaF_6^--selective electrodes.

Electroactive material	membrane solvent or matrix	Slope mV per decade	Linear range, Ta(V),M	Response time,s	Reference
Solvent mediator	PVC matrix	*	1.0x10-1.0x10	*	22
Tetraoctyl ammonium hydrogen sulphate	chloro-form PVC	-57	2.0x10-1.0x10	*	24
Triheptyldodecyl ammonium iodide	solid	*	1.0x10-1.0x10	*	28
Brilliant Green	nitroben zene PVC	-58.5	2.0x10-1.0x10	20-120	30
Brilliant Green	1-chloro naphthal ene PVC on graphite rod	-58	5.0x10-5.0x10	4-15	propo sed

* Data not given

5. CONCLUSION

A coated graphite electrode sensitive to hexafluoro - tantalate(V) anion based on ion-pair formation between Brilliant Green and hexafluorotantalate(V) in a plasticized PVC membrane was developed .

The electrode showed linear responses with Nernstian slope over a wide range of concentrations and with a short response time. It might be suitable for use in flow-injection systems because of its fast response and mechanical strength.

Investigation of various potentiometric techniques, with the electrode, showed the method developed to be highly selective and analytically reliable. Furthermore, the electrode was applied to different tantalite-columbite ore samples. Thus, it can used to determine tantalum in diverse samples reliably.

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