

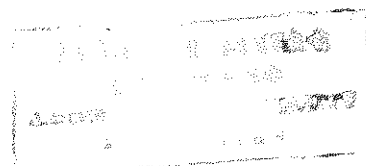
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**HEXAFLUOROTANTALATE(V)-SELECTIVE  
COATED GRAPHITE ELECTRODE  
BASED ON MALACHITE GREEN**

**A Thesis Presented to  
the School of Graduate Studies  
Addis Ababa University**

**In Partial Fulfilment of the  
Requirements for the Degree of Master of Science  
in Chemistry**

by  
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**JUNE 1996**

ADDIS ABABA UNIVERSITY  
SCHOOL OF GRADUATE STUDIES

HEXAFLUOROTANTALATE(V)-SELECTIVE COATED GRAPHITE ELECTRODE  
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## ACKNOWLEDGMENTS

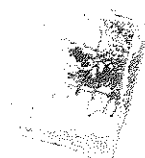
I am very much indebted to my research advisors Dr. B.S. Chandravanshi and Dr. Ghirma Moges for their constant supervision, guidance, constructive comments, and encouragement at all stages of the work.

I would like to express my deep pleasure of gratitude to Dr. Wendimagegn Mammo for his kindly and friendly help in searching CD-ROM for invaluable abstracts for the theoretical aspect of the work.

I wish to gratefully acknowledge Ato Gelebo Sengego (Awasa Water Supply and Sewerage Agency) for his kindness in providing the reference electrode. My heartfelt thanks shall be extended to Negussie Megersa for his concern in the work and relevant suggestion and Ahmed Mustefa whose encouragement and friendly cooperation have contributed a lot to the preparation of the thesis in time. Help from other staff members of the Chemistry Department of Addis Ababa University shall never be overlooked.

I also owe much to my friends and my colleagues who paid due attention to my work and exerted their utmost effort to bring the work to completion.

Finally, the Ministry of Education and the Swedish Agency for Research Cooperation with Developing Countries (SAREC) are highly acknowledged for sponsorship and financial assistance, respectively.



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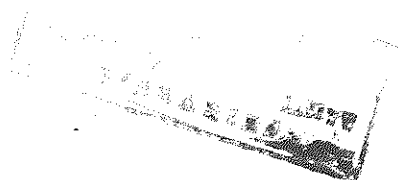
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## HEXAFLUOROTANTALATE(V)-SELECTIVE COATED GRAPHITE ELECTRODE BASED ON MALACHITE GREEN

### ABSTRACT

*An attempt was made to develop hexafluorotantalate(V)-selective coated graphite electrodes based on Malachite Green, Crystal Violet, and Ethyl Violet using 1-chloronaphthalene, tri-n-butyl phosphate, and dimethylphthalate as plasticizers. The electrode prepared by coating Malachite Green-hexafluorotantalate(V) extract in 1-chloronaphthalene with a PVC matrix on a graphite rod was found to give a Nernstian response and hence was studied in detail. Potential measurements with the coated graphite electrode were made against a plastic sleeve HF-resistant Ag/AgCl external reference electrode. Optimum response of the electrode was observed in test solutions made 1 mol/L in both sulphuric and hydrofluoric acids. The response characteristics of the electrode were evaluated. The linear range, slope, and detection limit were found to be  $1.0 \times 10^{-5}$  -  $1.0 \times 10^{-2}$  mol/L tantalum(V),  $58.0 \pm 1.5$  mV/decade, and  $3.98 \times 10^6$  mol/L tantalum(V), respectively. The precision of the method developed with the electrode was estimated to be 2% and the electrode functioned properly for three months. The effects of diverse ions on the electrode response to hexafluorotantalate(V) were studied, and the potentiometric selectivity coefficients were evaluated. The electrode was found to be highly selective to hexafluorotantalate(V). It was found that the response of the electrode to hexafluorotantalate is free from interference of niobium which commonly occurs with tantalum. The analytical application of the electrode to the determination of tantalum in synthetic matrices and real ore samples was also studied. The results obtained using four potentiometric techniques are in good agreement with the actual or certified values.*



the electrode is selective [58].

**2.3.1 The Potentiometric selectivity coefficient.** As it is already pointed out, ideal selectivity is not a feature of real ISEs. Furthermore, the activity range over which an electrode will give a Nernstian response (a response according to Eq.(2.1)) to the primary ion is limited in practice, even in the absence of interfering ions [59].

When the test solution contains ions other than those to which the electrode is essentially reversible, the electrode potential depends upon the selectivity of the membrane. For an electrode responding to an ion  $i$  of activity  $a_i$  and charge  $z_i$  in the presence of an interfering ion  $j$  of activity  $a_j$  and charge  $z_j$  the potential is given by the Nicolsky-Eisenman equation:

$$E = \text{constant} \pm (RT/z_i F) \ln [a_i + k_{ij} a_j^{z_i/z_j}] \quad (2.2)$$

Where  $k_{ij}$  is the potentiometric selectivity coefficient. The selectivity coefficient has also been called the selectivity constant and the selectivity factor. The former term is inappropriate because selectivity coefficients are seldom constant for all experimental conditions and ratios of  $i$  to  $j$  [59]. The latter term, while being as accurate as 'selectivity coefficient', has not received wide acceptance.

The potentiometric selectivity coefficient,  $k_{ij}$ , is a measure of the degree of selectivity of the ISE for the primary ion  $i$  with respect to the interfering ion  $j$ . When the electrode is very selective for  $i$  in comparison with  $j$ ,  $k_{ij}$  will be much less than unity. Conversely, if, as occasionally happens, the electrode responds preferentially to  $j$  rather than  $i$ ,  $k_{ij}$  will be greater than unity [59]. Thus, in analytical applications the selectivity for the primary ion should be as large as possible, so that the electrode potential has a Nernstian dependence on this ion activity over as large a range of activities as possible. This condition is fulfilled when the selectivity coefficient  $k_{ij}$  for the interfering ion is very small; in such a case the relation  $a_i \gg k_{ij} a_j^{z_i/z_j}$  is valid even if the interfering ion is greatly in excess in comparison with the primary ion [58]. Consequently, Eq.(2.2) reduces to Eq.(2.1).

The value of  $k_{ij}$  is never constant for all activities of  $i$  and  $j$ , although it is sometimes constant for a given ratio of the activity of  $i$  to  $j$  [59]. The experimentally determined values of the selectivity coefficient may also be different, depending upon

the method of determination (separate or mixed solution, see Section 2.3.2), the measurement technique (the time elapsed for observing potential, stirring, etc.), chemical conditions (composition, levels of ion concentration), etc. [72]. As a rationalization of this fact the term selectivity coefficient was introduced (and the use of the term selectivity constant almost abandoned). Therefore, for any quoted value of  $k_{ij}$  to be of use and comparable to other values, full details must be available of both the method of determination and the experimental procedure used to derive the data [59].

### 2.3.2 Methods of determination of the selectivity coefficient.

Several methods have been described for the experimental determination of selectivity coefficients. These methods are based on potential measurements either in separate solutions, or in mixed solutions containing the primary and the interfering ion [58,59,73]. Thus the methods fall into two categories: (i) separate solution methods and (ii) mixed solution methods.

**i. Separate solution methods.** In these methods the potential of the electrode under investigation is measured first in solutions containing the interfering ion  $j$  with no  $i$  present. Similarly, the electrode potential is measured in solutions containing the primary ion  $i$  with no  $j$  present. The  $k_{ij}$  is calculated by using any one of the following methods [56,58,73-75].

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

$$E_i = \text{constant} \pm (RT/z_i F) \ln a_i \quad (2.3)$$

If the solution is without  $i$  (i.e.,  $a_i = 0$ ) and containing only ion  $j$ , then Eq.(2.2) becomes

$$E_j = \text{constant} \pm (RT/z_j F) \ln k_{ij} a_j^{z_i/z_j} \quad (2.4)$$

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

$$\pm(E_j - E_i)z_i F/RT = \ln k_{ij} + [(z_i/z_j) - 1] \ln a_i \quad (2.5)$$

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

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

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

These separate solution methods of measuring  $k_{ij}$ , although simple to perform, cannot be recommended, as they do not give reliable results. This is because the conditions for potential measurements are not well defined probably due to electrode surface contamination by solution of  $i$  while making measurements in solution of  $j$  [56]. The methods are unsatisfactory because they do not reflect the real situation of measurements with normal samples which almost contain more than one ion pair [76]. In addition, in a statistical approach to estimation of selectivity parameters of ISEs, it has been proved [77] that parameters which would be obtained from the separate solution methods were meaningless, and no value could be attached to them. In many cases, the response of an electrode in pure solutions of an interfering ion is also very slow, liable to drift and, hence, unsatisfactory.

**ii. Mixed solution methods.** The mixed solution methods entail the measurement of the electrode potential in a range of solutions containing different activities of both  $i$  and  $j$  [58,59]. This can be done by measuring the potential in solutions of fixed  $a_j$  and varied  $a_i$  or fixed  $a_i$  and varied  $a_j$ . IUPAC [66] has recommended the method in which a constant interfering activity and a variable measured ion activity are employed.

Thus, the electrode potential in solutions containing both ions becomes

$$E^* = \text{constant} \pm (RT/z_i F) \ln[a_i + k_{ij}a_j^{z_i/z_j}] \quad (2.7)$$

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

$$E^* - E_i = (RT/z_i F) \ln[(a_i + k_{ij}a_j^{z_i/z_j})/a_i] \quad (2.8)$$

If a range of solutions with constant  $a_j$  and varying  $a_i$  are prepared and the electrode potentials in these solutions measured and then plotted against  $-\log a_i$ , a curve of the type shown in Fig.2 is usually obtained (see Fig.3 for alternative behaviour). In the region PQ the electrode is responding in a Nernstian manner to the primary ion  $i$ . As  $a_i$  decreases, the electrode potential is increasingly affected by the constant activity of  $j$  and in the region QR the electrode shows a mixed response to both  $i$  and  $j$ . From R to S the electrode is responding entirely to the constant  $a_j$  and the effect of the decreasing  $a_i$  is not detectable. Ideally, the line RS will be straight; however, as already described, in pure solutions of  $j$  the potentials may drift and give transitory peaks. In such cases, RS will not be a straight line.

There are several methods (mixed solution methods) for calculating  $k_{ij}$  from the plot of  $E^*$  versus  $-\log a_i$  ( see Fig. 2 and Fig. 3).

**Method 1.** The first method depends on finding graphically the point T at which the electrode is responding equally to both ions, i.e.  $a_i = k_{ij} a_j^{z_i/z_j}$  (from Eq.(2.6)). If the line RS is straight and parallel to the abscissa, then T is the point of intersection of the extrapolations of PQ and SR, as shown in Fig.2. Thus  $k_{ij}$  may be calculated from the activity of  $i$  at point T,  ${}_T a_i$ , and the constant  $a_j$  using the equation

$$k_{ij} = {}_T a_i / a_j^{z_i/z_j} \quad (2.9)$$

This method is suitable if RS is a straight line.

**Method 2.** This more generally applicable method does not depend on the form of RS, but instead relies on PQ and QR. Again, from Eq. (2.6), both ions are contributing equally to the electrode response when

$$a_i = k_{ij} a_j^{z_i/z_j} \quad (2.10)$$

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

$$E = \text{constant} \pm (RT/z_i F) \ln[a_i' + k_{ij} a_j^{z_i/z_j}] \quad (2.11)$$

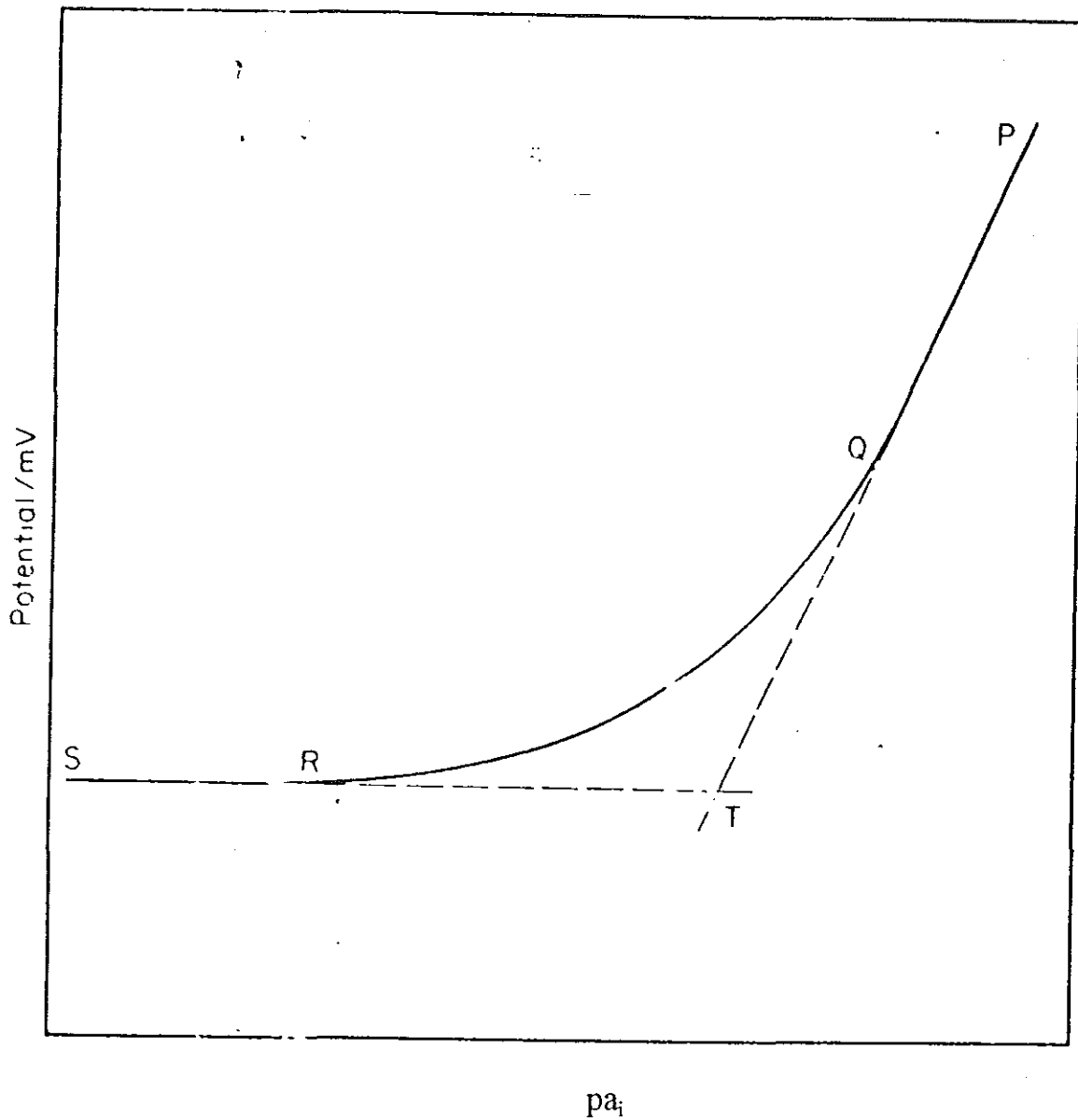


Fig.1. Typical curve for selectivity coefficient calculations by method 1 (mixed solution method)

3144 hsp  
WS 21  
1907 1907  
1907 1907

$$E = \text{constant} \pm (RT/z_i F) \ln[2a_i'] \quad (2.12)$$

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

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

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

$$\Delta E = 18/z_i \text{ mV at } 25^\circ\text{C}$$

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. Then,  $k_{ij}$  is calculated by substituting  $a_i'$  into the equation

$$k_{ij} = a_i'/a_j^{Z_i/Z_j} \quad (2.13)$$

In general mixed solution methods of selectivity coefficient determination are always preferred to the separate solution methods. A new twist on the mixed solution method [78], similarly preferred by Solsky [79], fixes the sum of logarithms of the activities of the interfering ions constant so that a graphical treatment of the data yields the selectivity coefficient.

#### 2.4 Analytical Measurement Techniques

The response behaviour of ISEs in solutions containing ionic species for which the electrodes are selective is described by the Nernst equation ( Eq.(2.1)). Thus, ISEs sense the activity of the ion, which can be related to concentration by taking the activity coefficient of the sample solution into account [54]. Furthermore, if the relationship between the activity and concentration of the ion to be determined can be fixed by adding a constant concentration of an inert electrolyte to all samples to swamp out minor variations in sample composition, then an electrode may be used directly for

concentration measurement [59].

Generally, two variations of measuring methods are distinguished [80]. In one case, the ISE is made to sense either the ion to be determined itself or some other material obtained by chemical transformation from the substance to be determined. These methods are called 'direct methods'. In the second case, the material to be determined is allowed to quantitatively react with another species, and the concentration of the reagent or the substance arising from the reaction is followed by ISE detection. These are called indirect analytical methods. Below are briefly discussed the most widely adopted analytical techniques using ion-selective electrodes.

**2.4.1. Calibration methods.** The most straight forward technique and thus the technique of choice whenever possible, as its name implies, is the direct method [59]. The potential is plotted versus the activity or concentration of the ion of interest in standard solutions and a linear calibration curve is constructed for the standard solutions. The potential of the sample solution is measured and then related to the activity or concentration of the ion of interest from the calibration graph. A single measurement, therefore, gives the activity or concentration of the ion [81].

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 and the range is broad, it is usually sufficient to prepare one standard per decade of activity. 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

$$E_x - E_s = S \log(a_x/a_s) \quad (2.14)$$

which can be rearranged to give

$$a_x = a_s 10^{\Delta E/S} \quad (2.15)$$

where  $S$  is the experimental slope and  $\Delta E$  is the difference in electrode potentials for the sample and for the standard. The value of  $S$  can be determined using two solutions of

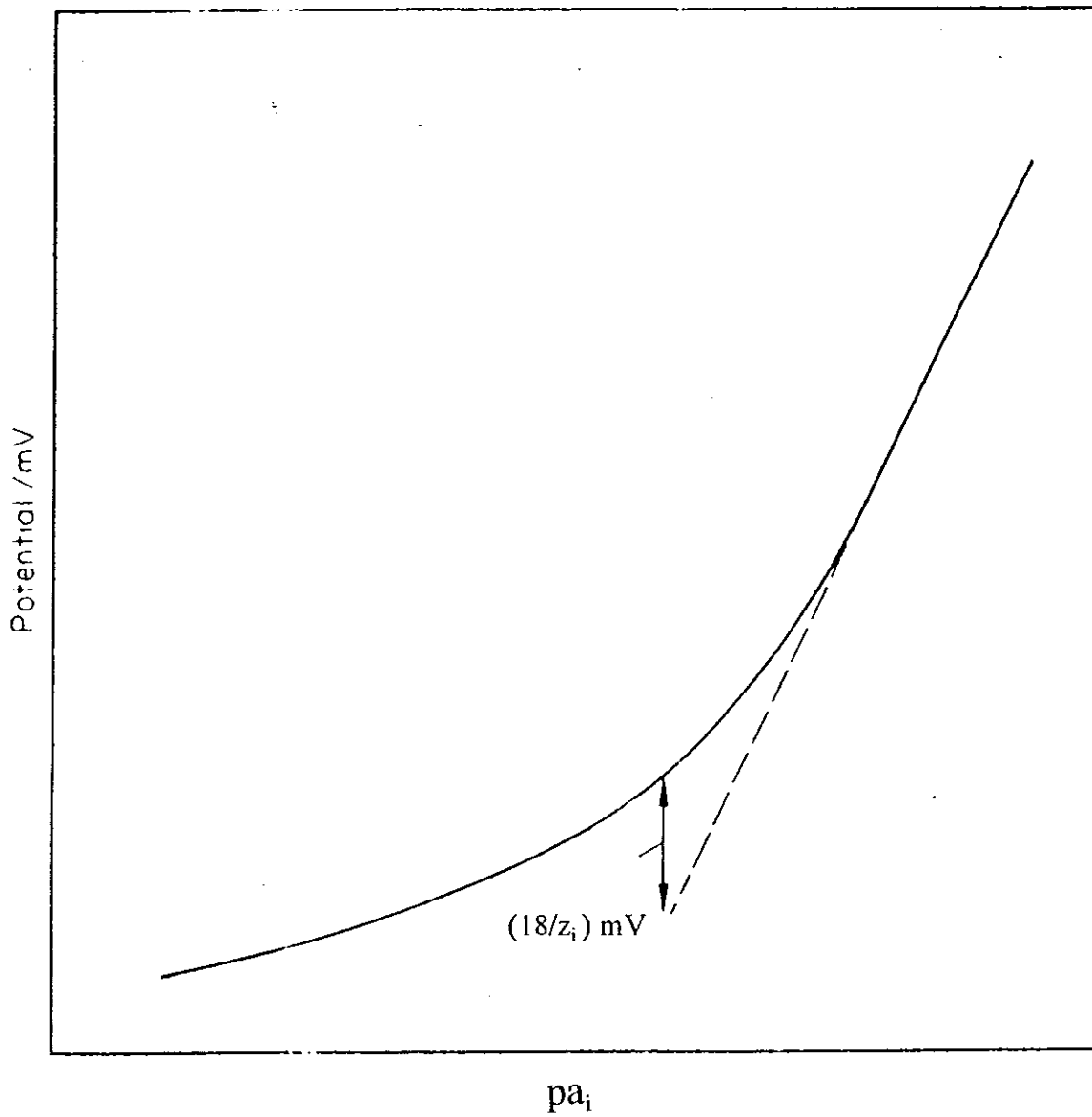


Fig. 2. Calibration graph, illustrating method 2 for selectivity coefficient determination (mixed solution method)

known activities. This approach requires no knowledge of the standard potentials of the electrode pair. The assumption made here is that the slope is constant, and that there is a linear relationship between the potential and logarithm of activity or concentration.

A more complicated version of this method involves the use of two standard solutions in which the analyte activities ( $a_1$  and  $a_2$ ) bracket the unknown activity ( $a_x$ ). Then, applying the Nernst equation,  $a_x$  can be calculated from

$$(E_x - E_1)/(E_1 - E_2) \log(a_1/a_2) = \log(a_x/a_1) \quad (2.16)$$

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

**2.4.2 Known addition methods.** Known addition methods have the advantage of being rapid and easy to perform, and when the electrode is well behaved (selectivity, working range, Nernstian response) the errors are negligible [58].

Two different methods are distinguished. In the first, a known volume of standard solution is added to a known sample volume and the change in the electrode potential is recorded, and in the second, a known volume of the sample is similarly added to a known volume of the standard.

**Standard addition to a sample.** To a known volume ( $V_x$ ) of the sample solution containing an unknown concentration ( $C_x$ ) is added a known volume ( $V_s$ ) of a standard solution of concentration  $C_s$ . Then, the change in the electrode potential is recorded. According to the Nernst equation, the initial potential of the sample solution of unknown concentration  $C_x$  is given by [56]

$$E_1 = E^\circ \pm (RT/z_1F) \ln(C_x \gamma_x) + E_L \quad (2.17)$$

where  $\gamma_x$  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 ( $V_s$  ml of  $C_s$  concentration) to the initial volume  $V_x$ , the new potential is given by

$$E_2 = E^0 \pm (RT/z_1F) \ln\{[C_x V_x + C_s V_s]/(V_x + V_s)\gamma_x'\} + E_L \quad (2.18)$$

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

$$\Delta E = E_2 - E_1 = (RT/z_1F) \ln[(C_x V_x + C_s V_s)/(V_x + V_s)C_x] \quad (2.19)$$

On rearrangement Eq.(2.19) becomes

$$\Delta E/S = \log [(C_x V_x + C_s V_s)/(V_x + V_s)C_x] \quad (2.20)$$

where  $S$  is the slope ( $= 2.303RT/z_1F$ ) experimentally determined by using a series of known standard solutions. Eq.(2.20) may be rearranged to give

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

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

$$C_x = C_s (V_s/V_x) [10^{\Delta E/S} - 1]^{-1} \quad (2.22)$$

Several assumptions are made in the derivation of these equations. It is, therefore, worthwhile listing these and further assumptions which may be made to simplify the procedure or the calculation [59].

- (i) The change in sample volume caused by the addition of the standard is negligible (Eq.(2.22)).
- (ii) The change in the liquid junction potential is negligible.
- (iii) The activity coefficient and the degree of complexation of the determinand remains constant.

(iv) No interferences are present in the sample.

(v) The ISE has a theoretical Nernstian slope.

Advantages of this technique over the other techniques are that electrode calibration is unnecessary, 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, also known as the analate addition technique, is a variation, strictly speaking, the reverse, of the standard addition method. In this case, the potential of a known volume  $V_s$  of the standard solution of known concentration,  $C_s$ , is measured. Then, a known volume  $V_x$  of the sample solution is added, and the new potential is measured. The concentration of the analyte,  $C_x$ , is then calculated by using the equation [55,56,58]

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

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

The prime advantage of this technique is that it may be used for the analysis of volumes of sample so small that they can not be measured by any other method, because there is insufficient to immerse the end of the electrode [59].

**Gran's Plot.** Another variation of the standard addition technique, known as Gran's Plot, involves a graphical procedure. It was devised by Gran [84] as a way of linearizing the data obtained in potentiometric titrations and thus easily and precisely locating the equivalence points of titrations. The plot is also used with ISEs for this original purpose and also for linearizing data from multiple standard addition procedures [59].

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. Thus, Eq.(2.18) can be rearranged to give

$$(V_x + V_s) 10^{E/2.303RT} = 10^{(\text{constant} + EL)/2.303RT} \gamma_x (C_x V_x + C_s V_s) \quad (2.24)$$

A plot of  $(V_x + V_s)10^{E2F/2.303RT}$  versus  $V_s$  gives a straight line which intercepts the abscissa for a value of  $V_s$  called  $V_e$  where  $C_x V_x = -C_s V_e$ . Thus,  $C_x$  can be evaluated since  $V_e$ ,  $V_x$ , and  $C_s$  are known [56].

The concentration of the standard, instead of volume, can alternatively be used in Gran's plot [85]. Initially the potential of  $V_x$  volume of unknown concentration  $C_x$  is measured. Then  $V_s$  ml of the standard solution of  $C_s$  concentration is added, and the new potential is measured. The process may be repeated as many times as desired. The concentration of the determinand after  $n$  additions of the standard solution will be

$$(C_x)_n = (C_x V_x + n C_s V_s) / (V_x + n V_s) \quad (2.25)$$

The measured electrode potential after  $n$  additions is

$$E_n = \text{Constant} \pm S \log(C_x)_n \quad (2.26)$$

Rearranging and taking the antilog,

$$\text{antilog} [\pm(E_n/S)] = \text{constant} \times [(V_x C_x + n C_s V_s) / (V_x + n V_s)] \quad (2.27)$$

A plot of  $\text{antilog} [\pm(E_n/S)]$  versus  $n C_s V_s / (V_x + n V_s)$  is a straight line which on extrapolation intercepts the abscissa at  $-(C_x V_x) / (V_x + n V_s)$ . Thus  $C_x$  can be easily calculated from the x-intercept.

**Standard subtraction method.** The standard or known subtraction method is different from the standard addition one only in that the standard solution added to the sample is not a determinand solution but a solution of a species which reacts quantitatively with the determinand (through precipitation or complexation) [55,59]. Thus, a decrease in determinand concentration is produced with the corresponding change in the 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 equation [59]

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

Further assumption that dilution effect brought about by the addition of the standard solution is negligible reduces Eq.(2.28) to a form given by

$$C_x = C_s V_s / V_x [1 - 10^{-\Delta E/S}]^{-1} \quad (2.29)$$

Eqs.(2.28) and (2.29) hold true, as already pointed out, for a 1:1 stoichiometry of the reaction; the equations become more complex, otherwise.

## 2.5 Response Time

An important factor which commends the use of an ISE for a particular application is the response time of the electrode [58,59]. The response time of an ISE is defined by IUPAC as the time needed for the potential of the electrode to reach a value 1 mV from the final equilibrium potential after a supposedly instantaneous change in determinand activity [59]. A ten-fold increase or decrease of determinand activity (concentration) is specifically used [58] in defining the response time.

Very few people have ever used this particular definition, and each group of workers has defined the response time in their own way. For example, Fleet and co-workers [82] defined the response time as the time interval within which the electrode potential reaches 95 per cent of the steady state value. Thus, values of response time quoted in the literature do not usually permit any more than a rough comparison of different electrodes, since the bases of the calculations are nearly all different, and often insufficient practical information is given on the circumstances of measurement, upon which so much depends [59]. For a quoted value of the response time to be useful, therefore, it is essential to know the experimental conditions on which the response time is experimentally dependent. These include initial and final determinand activities, stirring rate, and the way in which the activity was changed.

## 2.6 Detection Limit

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 [83]. 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 electrodes is defined, as recommended by IUPAC, as the concentration of the determinand,  $i$ , at which the extrapolated, linear portion of the calibration curve at extreme dilution of the determinand intersects the extrapolated, Nernstian part of the curve; this would correspond to the point T in Fig. 1 [59].

### 3. EXPERIMENTAL

#### 3.1 Chemicals and Reagents

Tantalum pentoxide (Riedel-de Haen), potassium nitrate (BDH), potassium carbonate (BDH), sulphuric acid (98%(w/w), BDH), tartaric acid (Hopkin & Williams), ammonium fluoride (Fluka), tetraphenylarsonium chloride (Riedel-de Haen), Malachite Green (Hopkin & Williams), Ethyl Violet (Aldrich), Crystal Violet (Aldrich), hydrofluoric acid (40%(w/w), BDH), sodium sulphate (anhydrous, BDH), Poly(vinyl chloride) (Fluka), 1-chloronaphthalene (Fluka), tri-n-butyl phosphate (BDH), dimethylphthalate (BDH), and tetrahydrofuran (Fluka). All chemicals and reagents were used without further purification. Distilled water was used throughout to prepare aqueous solutions. Plasticwares were used wherever hydrofluoric acid was involved.

#### 3.2 Preparation of Solutions

**3.2.1 Preparation of tantalum(V) stock solution.** A weighed amount (1.0 g) of well-powdered tantalum pentoxide ( $Ta_2O_5$ ) was thoroughly mixed with 2.5 g of potassium carbonate ( $K_2CO_3$ ) and 2.5 g of potassium nitrate ( $KNO_3$ ) (2:5:5 weight ratio) in a 30-mL platinum crucible. The mixture was fused in a muffle furnace at 740-760°C for about 15 min. The melt was cooled to room temperature, and treated with about 25 mL of concentrated sulphuric acid. The extract was quantitatively transferred to a 500-mL Kjeldhal flask, evaporated to dryness, and allowed to cool. The residue was then dissolved in 100 mL of 20%(w/v) tartaric acid by heating and continuous swirling. The clear solution obtained was transferred to a 250-mL volumetric flask and made to the mark with 20%(w/v) tartaric acid solution [35,37].

**3.2.2 Standardization of tantalum(V) solution.** A 9.0 mL of aliquot of tantalum(V) stock solution was transferred into a 500-mL plastic beaker. To this was added 10 mL of concentrated nitric acid, and the solution was diluted to 200 mL with water. About 1 g of ammonium fluoride was added to the solution and the content was gently heated over a steam bath for 15 min. A 5.0 mL aliquot of 2%(w/v) tetraphenylarsonium chloride was added dropwise and the solution was allowed to stand for 30 min to ensure complete precipitation of tantalum(V) as tetraphenylarsonium-hexafluorotantalate(V).

The precipitate was filtered and then heated in a porcelain crucible over a bunsen flame for one hour. It was allowed to cool to room temperature and weighed as  $Ta_2O_5$  [19].

**3.2.3 Preparation of sample solutions and solutions of diverse ions.** A weighed amount (0.5 g) of well-powdered real ore sample (collected from EIGS, Ethiopian Institute of Geological Surveys) was thoroughly mixed with 1.25 g of each of  $KNO_3$  and  $K_2CO_3$  (2:5:5: weight ratio) in a 30-mL 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 quantitatively transferred to a 100-mL volumetric flask and made to the mark with 5 mol/L sulphuric acid [35,37].

Solutions of synthetic matrices of definite composition were prepared by mixing known amounts of solutions of different ions. The final solutions were made 1 mol/L in sulphuric acid (100 mL each).

Solutions of diverse ions were prepared for interference study. Oxides, nitrates, chlorides, or sulphates were used to prepare solutions of cations while solutions of anions were prepared from their sodium, potassium, or ammonium salts. The concentrations of all solutions were  $5.0 \times 10^{-2}$  mol/L with respect to the ion in question except for niobium(V) and EDTA which were  $2.0 \times 10^{-3}$  mol/L and  $2.0 \times 10^{-2}$  mol/L, respectively.

A niobium(V) solution was prepared by fusing 0.1439 g of  $Nb_2O_5$  (Fluka) with 3.6 g of potassium pyrosulphate (Merck-Darmstadt) in a platinum crucible until a clear melt was obtained. The cooled melt was dissolved in 100 mL of 20%(w/v) tartaric acid by heating. The solution was cooled to room temperature, transferred to a 500-mL volumetric flask, and diluted to volume with water [86,87].

A solution of titanium (IV) was prepared by fusing 0.4 g of  $TiO_2$  with 4 g of potassium hydrogensulphate. The cooled melt was leached with 10% (v/v) sulphuric acid and diluted to 100 mL with 10%(v/v) sulphuric acid [87].

Solutions of  $Ag^+$ ,  $Cu^{2+}$ ,  $Ca^{2+}$ ,  $Cd^{2+}$ ,  $Zn^{2+}$ ,  $Pb^{2+}$ ,  $UO_2^{2+}$ ,  $Fe^{3+}$ ,  $Cr^{3+}$ ,  $La^{3+}$ , and  $Y^{3+}$  were prepared by dissolving the corresponding nitrate salts in water.  $Mg^{2+}$ ,  $Ba^{2+}$ ,  $Sr^{2+}$ , and  $Ni^{2+}$  solutions were prepared by dissolving their chloride salts in water.

Solutions of Sn(II), Bi(II), Er(III), and Zr(IV) were prepared by dissolving stannous chloride, bismuth nitrate, erbium oxide, and zirconyl chloride, respectively in 1 mol/L hydrochloric acid. Dissolutions were carried out by heating to obtain clear solutions.

Solutions of Hg(II), Al(III), Ce(IV), and Th(IV) were prepared by dissolving mercuric nitrate, aluminium chloride, ceric sulphate, and thorium nitrate in 0.5 mol/L hot sulphuric acid. Sulphates of Co(II) and Mn(II) were dissolved in water to prepare solutions of the respective ions.

Sodium salts were dissolved in water to prepare solutions of perchlorate, periodate, EDTA, tungstate, antimonate, and arsenate while thiocyanate, molybdate, and metavanadate solutions were prepared by dissolving the corresponding ammonium salts in water. Potassium salts were dissolved in water to prepare solutions of nitrate, chloride, and sulphate.

Boric acid and Oxalic acid solutions were prepared by dissolving the solid compounds in water.

### **3.3 Preparation of Malachite Green-, Ethyl Violet-, and Crystal Violet-Hexafluorotantalate(V)-Coated Graphite Electrodes**

**3.3.1 Preparation of solutions of cationic dyes.**  $1.8 \times 10^{-2}$  mol/L stock solutions of Malachite Green, Ethyl Violet, and Crystal Violet were prepared by dissolving 0.8343 g of oxalate salt of Malachite Green (FW 927.03), 0.8859 g of chloride salt of Ethyl Violet (FW 492.15), and 0.7344 g of chloride salt of Crystal Violet, respectively, in about 50 mL of water in 100-mL beakers by continuous stirring. The solutions were then quantitatively transferred to 100-mL volumetric flasks and diluted to volume by washing the beakers several times with water.

**3.3.2 Preparation of the electroactive materials.** Aliquots of 22 mL of  $1.8 \times 10^{-2}$  mol/L 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  $1.84 \times 10^{-2}$  mol/L Malachite Green solution, and the volume of aqueous phase was adjusted to 50 mL with water. The mixture was vigorously shaken for 2 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 in a 100-mL plastic beaker containing about 1 g of anhydrous sodium sulphate. The extract was transferred into a small plastic bottle.

Similar procedures were followed for the extraction of Ethyl Violet- and Crystal Violet-hexafluorotantalate(V) ion-association complexes in 1-chloronaphthalene, tri-n-butyl phosphate, and dimethylphthalate.

These extracts, i.e., Malachite Green-, Ethyl Violet-, and Crystal Violet-hexafluorotantalate(V) in 1-chloronaphthalene as well as in the other two plasticizers were used as the electroactive materials for the proposed potentiometric sensor.

**3.3.3. Preparation of the coating mixtures.** A Poly(vinyl chloride), PVC, solution in tetrahydrofuran (THF) was prepared by dissolving 0.1 g of the polymer powder in about 3.25 mL of THF. To this was added 0.25 mL of the ion-association extracts in the plasticizers, respectively. These mixtures were used as the membrane matrices for the preparation of the coated graphite electrodes.

**3.3.4. Preparation of the hexafluorotantalate(V)-selective coated graphite electrodes.** One end (about one-third) of a graphite rod (3.6 cm long and 3 mm in diameter, Ringsdorff-Werke, GmbH, RWO) was cleaned with a wet smooth emery paper, washed with water and dried. The other end of the rod was tightly fixed to one end of a glass tube so that a coil of copper wire, housed in the glass tube, is in contact with it.

The cleaned part of the graphite rod was dipped into the coating mixtures several times with an interval of 2 min until the graphite surface was completely covered by a dark-green film. The assembly was then kept in a hood for 6 h to evaporate the THF. The remainder and some of the coated portion of the rod was tightly wrapped with a paraformaldehyde film (American Can Company) to prevent direct contact of the rod with the test solutions. The resulting assemblies, after conditioning by soaking the coated-graphite tip in a  $1.0 \times 10^{-2}$  mol/L tantalum(V) solution made 1 mol/L in both sulphuric and hydrofluoric acids for 30 min, were ready for use as hexafluorotantalate(V)-selective coated graphite electrode. The electrodes were stored between use by suspending the coated end in brown dropper bottles saturated with the corresponding plasticizer to prolong their life time [44]. The electrodes were reconditioned immediately before use by soaking them in the conditioning solution. The



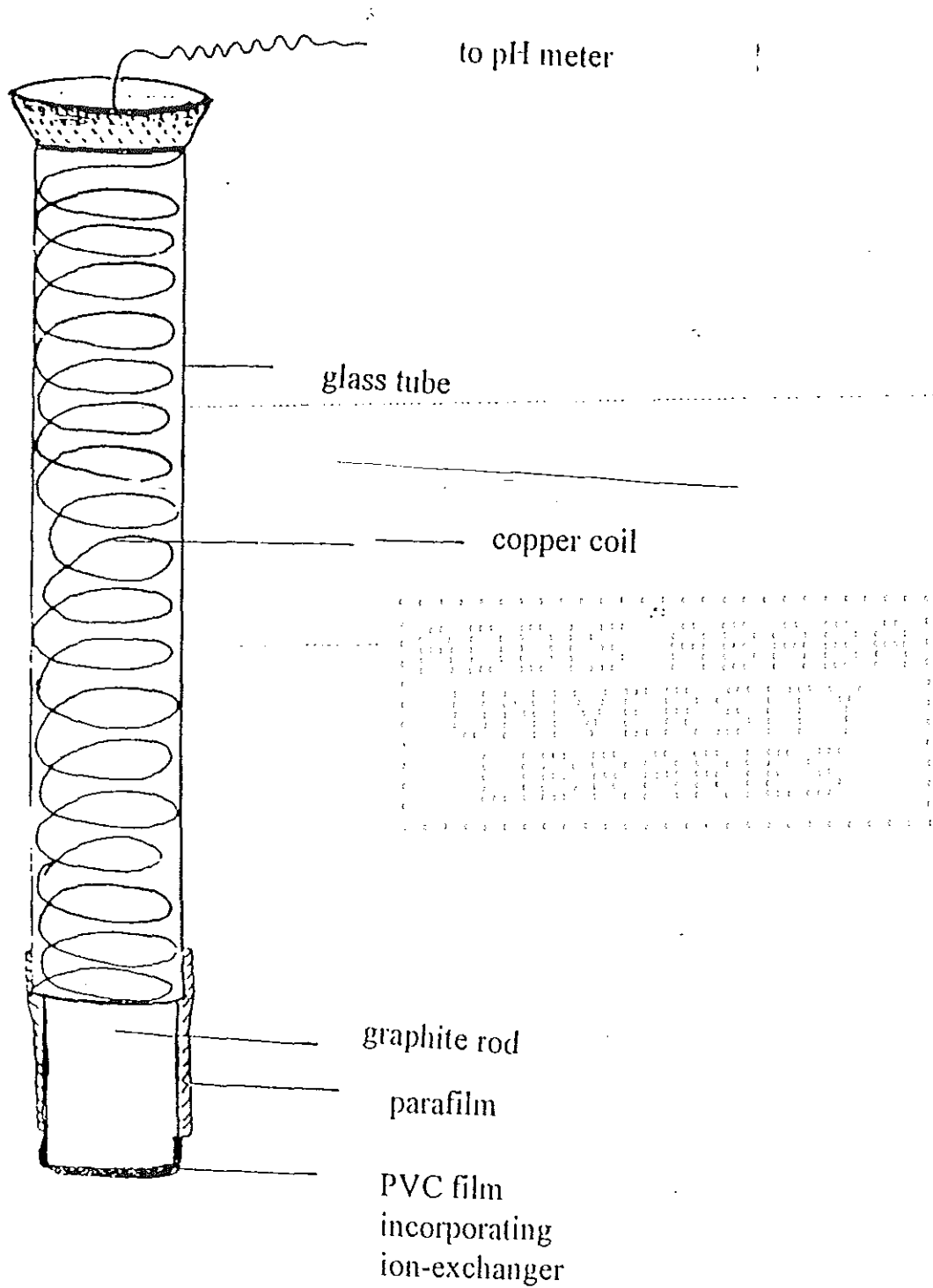


Fig. 3. The hexafluorotantalate(V)-selective coated graphite electrode.

### 3.6 Interference Study

The effect of diverse ions on the response characteristics of the electrode was evaluated and of the potentiometric selectivity coefficients were determined using the mixed solution method as described below.

Aliquots (5.6 mL) of  $1.8 \times 10^{-2}$  mol/L tantalum(V) solution, 1.1 mL of concentrated  $\text{H}_2\text{SO}_4$ , 0.9 mL of 40%(w/w) HF, and 8 mL  $5.0 \times 10^{-2}$  mol/L (with respect to the particular ion) solution of the interfering ion were added to 100-mL plastic beakers. Serial dilution with water and then adjustment of the acidity with  $\text{H}_2\text{SO}_4$  and HF were made to obtain a series of 20 mL solutions,  $5.0 \times 10^{-6}$  -  $5.0 \times 10^{-3}$  mol/L in tantalum(V) and 1 mol/L in both  $\text{H}_2\text{SO}_4$  and HF. The potentials of the resulting solutions were measured and the calibration curves were constructed. The selectivity coefficient were calculated from the detection limits of the curves using Eq.(2.13).

### 3.7 Sample Analysis

**3.7.1 Direct potentiometry.** The potentials of 20 mL of the sample-containing solutions (made 1 mol/L in both sulphuric and hydrofluoric acids) were measured. The concentration of tantalum in the sample solutions was then determined from the calibration curve, E(mV) vs  $-\log [\text{Ta(V)}]$ .

**3.7.2 Standard addition technique** The potential ( $E_1$ ) of 20 mL ( $V_x$ ) of a dilute sample solution (1 mol/L in both sulphuric and hydrofluoric acids) was first measured. This was followed by the addition of 2 mL ( $V_s$ ) of a  $1.0 \times 10^{-3}$  mol/L ( $C_s$ ) standard tantalum(V) solution (also 1 mol/L in both acids) to the stirred sample solution. The new potential ( $E_2$ ) was measured, and the concentration ( $C_x$ ) of tantalum in the sample solution was then calculated using Eq.(2.21).

**3.7.3 Sample addition technique.** The potential ( $E_1$ ) of a 20 mL ( $V_s$ ) of  $2.0 \times 10^{-5}$  mol/L tantalum(V) solution ( $C_s$ ) (1 mol/L in both sulphuric and hydrofluoric acids) was initially measured. Then 2 mL ( $V_x$ ) of a sample of about 100-fold higher concentration ( $C_x$ ) (also 1 mol/L in both acids) was added, and the new potential ( $E_2$ ) was recorded. The concentration of tantalum(V) in the unknown was calculated by making use of

Eq.(2.23).

**3.7.4 Gran's plot.** The potential of 20 mL ( $V_x$ ) of a 100-fold diluted sample solution of unknown concentration  $C_x$  (1 mol/L in both sulphuric and hydrofluoric acids) was initially measured. Then, 2, 4, 6, 8, and 10 mL of a  $1.0 \times 10^{-3}$  mol/L ( $C_s$ ) standard tantalum(V) solution (also 1 mol/L in both acids) were added in 2 mL ( $V_s$ ) portions, and the new potentials ( $E_n$ ) were recorded after each addition. A plot of  $\text{antilog}(-E_n/S)$  vs  $nC_s V_s / (V_x + nV_s)$  gave a straight line which, on extrapolation, intercepts the abscissa at  $-C_x V_x / (V_x + nV_s)$ . Then,  $C_x$  was calculated from the value of the x-intercept (Fig. 5 in Section 4.7).

## 4 RESULTS AND DISCUSSION

### 4.1 Selection of Membrane Plasticizer

The properties of polymeric membrane ISEs strongly depend on the composition of the polymeric membrane (polymer, electroactive material, solvent mediator and / or plasticizer) [79,88]. Plasticizers (solvents) are required in polymeric membrane ISEs in order to increase ionic mobility in the membrane [89].

Selectivity studies of both cation and anion-selective CWEs [90,91] reveal the importance of solvent extraction parameters in quantitatively determining the selectivity of the membranes. From solvent extraction studies and from calculated extraction constants [92], the observed close one-to-one correspondence between extraction constants and selectivity coefficients also shows the advantage of considering the properties of the solvent (plasticizer) for the desired selectivity of the particular membrane to be used.

Thus, the choice of the plasticizer has a drastic effect on the selectivity of the membrane since the latter is governed by the mobility of the ions in the membrane and the equilibria existing at the membrane-solution interface (partition coefficients, ion-exchange equilibrium constants) [56,93].

A plasticizer in PVC matrix membrane ISEs, in addition to its plasticizing function, must be chosen so as to satisfy the following requirements [54,55]: immiscibility with water, low volatility, high viscosity, and the ease with which it allows considerable association of ions in the membrane (relatively of low dielectric constant). Furthermore, it must be a good solvent for the ion-association salt and promote the desired selectivity [80].

Three different plasticizers, namely, 1-chloronaphthalene, tri-n-butyl phosphate, and dimethylphthalate were examined. The Malachite Green-, Ethyl Violet- and Crystal Violet-hexafluorotantalate(V) ion-association salts were found to be poorly extractable into tri-n-butyl phosphate and dimethylphthalate and hence it was not possible to prepare CGEs using these plasticizers while the complexes were found to be easily and quantitatively extractable into 1-chloronaphthalene. Furthermore, 1-chloronaphthalene meets the requirement [94] for a good plasticizer and is also a good solvent for the PVC matrix. It has an additional advantage over most of the conventional plasticizers such as dioctylphthalate in that it does not participate in pH dependent equilibria when the

membrane plasticized with 1-chloronaphthalene is in contact with the test solution [95]. It also helps in prolonging the life time of the membrane electrode when it is used in the coating matrix [42]. Hence, 1-chloronaphthalene was used as the membrane plasticizer for the proposed hexafluorotantalate(V)-selective electrodes.

#### 4.2 Selection of Internal Conductive Substrate

The development of potentiometric sensors must take into account the properties of the substrate material employed in their construction. Thus, in order to achieve the desired quality in terms of sensitivity, response time, and stability, it is essential to choose a suitable solid internal contact.

In a previous study [37] to develop a hexafluorotantalate(V)-selective CWE based on Brilliant Green, an electrode employing silver wire as an internal contact failed to function satisfactorily when used in strongly acidic test solutions, and no attempt was made to prepare an electrode using silver wire as an internal conductive substrate.

In the present investigation, a graphite rod which is relatively inert and has no 'memory' effect [54] was chosen as an internal contact for the proposed electrode and found to function well, and hence no attempt was made to test other internal contacts.

#### 4.3 Selection of Cationic Dye

Three different hexafluorotantalate(V)-selective CGEs based on Malachite Green, Ethyl Violet, and Crystal Violet were prepared and their response behaviour were examined in the range  $1.0 \times 10^{-7}$  -  $1.0 \times 10^{-2}$  mol/L tantalum(V) made 1 mol/L in both sulphuric and hydrofluoric acids. The results are given in Table 1.

It can be seen from Table 1 that among the three dyes examined Malachite Green was found to give nernstian response (slope  $58 \pm 1.5$  mV per decade) in a wider linear response range ( $1.0 \times 10^{-5}$  -  $1.0 \times 10^{-2}$  mol/L Ta(V)). Hence the electrode prepared using Malachite Green-hexafluorotantalate(V) ion-association complex was used for further investigation.

Table 1. Effect of cationic dye on the response behaviour of the hexafluorotantalate(V)-selective CGE

Cationic dye	Linear range Ta(V), mol/L	Average slope* mV per decade
Malachite Green	$1.0 \times 10^{-5} - 1.0 \times 10^{-2}$	$58 \pm 1.5$
Ethyl Violet	$1.0 \times 10^{-4} - 1.0 \times 10^{-2}$	$58 \pm 2.0$
Crystal Violet	$5.0 \times 10^{-4} - 1.0 \times 10^{-2}$	$57 \pm 2.5$

\* Average of triplicate measurements

#### 4.4 Effect of Exchanger Concentration

The effect of the ion-exchanger concentration in the membrane on the electrode response behaviour was studied by varying the Malachite Green to tantalum(V) mole-ratio in the aqueous phase used for the extraction of Malachite Green-hexafluorotantalate(V) in 1-chloronaphthalene (thereby varying the concentration of the Malachite Green-hexafluorotantalate(V) ion-association salt in the membrane). The results are given in Table 2.

The electrode prepared using the extract from a 1:2 Malachite Green to tantalum(V) mole-ratio aqueous phase exhibited a wider range of linear response with a better slope and shorter response time (5-15 s). Thus, this electrode was used for further study.

#### 4.5 Study of Effect of Variables

Tantalum forms fluoro-complexes of various compositions in aqueous hydrofluoric acid [7]. The formation as well as the composition of these complexes is dependent on the pH and fluoride concentration of the solution.

Therefore, the effect of the concentrations of sulphuric and hydrofluoric acids in the test solutions on the response behaviour of the CGE was studied to establish the optimum concentrations which would lead to well behaved electrode response to

hexafluorotantalate(V).

Table 2. Effect of the composition of the aqueous phase used for the extraction of Malachite Green-hexafluorotantalate(V) into 1-chloronaphthalene on the response behaviour of the CGE (the concentration of the stock solutions of both tantalum(V) and Malachite Green used was  $1.8 \times 10^{-2}$  mol/L)

Mole-ratio MG:Ta(V)	Linear range [ Ta(V) ]	Average slope* mV per decade	Response
1:3	$1.0 \times 10^{-4} - 5.0 \times 10^{-3}$	$55.5 \pm 3.5$	unstable
1:2	$1.0 \times 10^{-5} - 1.0 \times 10^{-2}$	$58 \pm 2$	fast
1:1	$1.0 \times 10^{-4} - 1.0 \times 10^{-2}$	$56 \pm 3$	slow
1:05	$5.0 \times 10^{-4} - 1.0 \times 10^{-2}$	$54 \pm 1.5$	slow

\* Average of triplicate measurements.

**4.5.1 Effect of sulphuric acid concentration.** Tantalum(V) is easily hydrolyzed in aqueous solutions. In order to avoid the hydrolysis sulphuric acid was used in the test solutions.

The effect of sulphuric acid was studied by varying its concentration in the range 0.0-2.0 mol/L, keeping the hydrofluoric acid concentration 1.0 mol/L in the test solutions. The results are shown in Table 3.

The slope of the potential response decreased with increasing sulphuric acid concentration (the effect being more pronounced at lower tantalum(V) concentrations) and remained practically constant in the range 0.5 - 1.25 mol/L sulphuric acid with Nernstian response slope  $58 \pm 1.5$  mV per decade. The decrease in slope upon increasing sulphuric acid concentration might be due to the protonation of the electroactive dye and also to the contribution of the graphite rod imparted from the pH change [96].

Although higher response slopes were observed at lower sulphuric acid concentrations ( $< 0.5$  mol/L), the potential readings were not stable, probably due to hydrolysis of tantalum(V) in low acid concentration. It should also be noted that potential

Table 3. Effect of sulphuric acid concentration in test solutions on the response slope of the CGE

( [ HF ] = 1 mol/L in the test solutions, Ta(V) concentration: (a)  $1.0 \times 10^{-3}$  -  $1.0 \times 10^{-2}$ , (b)  $1.0 \times 10^{-4}$  -  $1.0 \times 10^{-3}$ , and (c)  $1.0 \times 10^{-5}$  -  $1.0 \times 10^{-4}$  mol/L )

[ H <sub>2</sub> SO <sub>4</sub> ]	Average slope ( mV per decade )*		
	a	b	c
0.000	62.5	60.5	58.0
0.125	62.0	60.5	57.5
0.250	61.5	60.0	57.0
0.500	61.0	60.0	56.5
0.750	60.5	59.5	56.5
1.000	59.5	59.0	56.5
1.250	59.0	58.5	55.0
1.500	58.0	58.0	54.0
2.000	57.0	57.0	51.

\* Average of triplicate measurements.

measurements at zero concentration of the acid were made immediately to avoid the hydrolysis.

**4.5.2 Effect of hydrofluoric acid concentration.** Since the electrode responds to hexafluorotantalate(V) (and not to tantalum(V)) it was necessary to convert Ta(V) to TaF<sub>6</sub><sup>-</sup>. Hence hydrofluoric acid was used in the test solutions.

The effect of the concentration of hydrofluoric acid in the test solutions on the response slope of the CGE was similarly studied by varying its concentration in the range 0.25 - 2.0 mol/L while keeping the sulphuric acid constant concentration at 1 mol/L. The results are given in Table 4.

The slope was observed to increase up to 0.75 mol/L and then remained practically constant indicating that the complexation of tantalum(V) is practically complete at about 0.75 mol/L hydrofluoric acid. Further increase in the concentration of

hydrofluoric acid does not have an adverse effect on the complexation of tantalum and thus on the response slope of the electrode as well.

It can be seen from Table 4 that the optimum concentration range of hydrofluoric acid for the response of the CGE to hexafluorotantalate(V) is 0.75 - 1.25 mol/L. Particularly at 1 mol/L hydrofluoric acid, the electrode gave the best average slope of  $58 \pm 1.5$  mV per decade in the range  $1.0 \times 10^{-5}$  -  $1.0 \times 10^{-2}$  mol/L tantalum(V).

Table 4. Effect of hydrofluoric acid concentration on the response slope of the CGE ([H<sub>2</sub>SO<sub>4</sub>] = 1.0 mol/L in the test solutions, Ta(V) concentration (a)  $1.0 \times 10^{-3}$  -  $1.0 \times 10^{-2}$ , (b)  $1.0 \times 10^{-4}$  -  $1.0 \times 10^{-3}$ , and (c)  $1.0 \times 10^{-5}$  -  $1.0 \times 10^{-4}$  mol/L)

[ HF ]	Average slope (mV per decade)*		
	a	b	c
0.25	54.0	55.0	53.0
0.50	57.5	56.5	55.0
0.75	59.0	58.0	56.0
1.00	59.5	59.0	56.5
1.25	60.5	60.0	56.5
1.50	61.0	60.5	57.5
2.00	61.5	61.0	57.5

\* Average of triplicate measurements.

#### 4.6 Response Behaviour of the Electrode

The Malachite Green-hexafluorotantalate(V) CGE was found to respond to hexafluorotantalate(V). The response behaviour of the electrode was studied in the concentration range  $1.0 \times 10^{-7}$  -  $1.0 \times 10^{-2}$  mol/L tantalum(V) in test solutions made 1 mol/L in both sulphuric and hydrofluoric acids. The electrode was found to respond linearly in the range  $1.0 \times 10^{-5}$  -  $1.0 \times 10^{-2}$  mol/L tantalum(V) with a Nernstian slope of

58.0  $\pm$  1.5 mV per decade and detection limit of  $3.98 \times 10^{-6}$  mol/L tantalum(V). The response time of the electrode was found to be 5-15 s. The precision of the method was estimated by determining the concentrations of six different samples each containing  $5 \times 10^{-4}$  mol/L tantalum(V), i.e., at the middle of the linear range. The relative standard deviation was found to be 2%.

Table 5. Optimum conditions and response characteristics of the Malachite Green-hexafluorotantalate(V) CGE

Parameter /characteristic	Value
Sulphuric acid concentration in test solutions, mol/L	1
Hydrofluoric acid concentration in test solutions, mol/L	1
Linear range, Ta(V)concentration,mol/L	$1.0 \times 10^{-5}$ - $1.0 \times 10^{-2}$
Slope, mV per decade	$58.0 \pm 1.5$
Detection limit, Ta(V) concentration, mol/L	$3.98 \times 10^{-6}$
Response time, s	5-15
Life time of the electrode, month	3
Precision, R.S.D. at $5 \times 10^{-4}$ mol/L Ta(V) (n = 6)%	2

The electrode was found to respond properly (with constant slope and linear range) with no deterioration in the linear range and detection limits for three months. 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 [93,97]. A potential drift of not more than 2 mV was noted in 24 hours. The drift was evaluated by measuring the potentials of four known concentrations of the analyte ( $1.0 \times 10^{-5}$  -  $1.0 \times 10^{-2}$  mol/L

tantalum(V)) at least three times in 24 hours. 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 rod with the test solutions and no hysteresis of the sensor was observed. The electrode was stored by dipping its coated end in a brown dropper bottle saturated with 1-chloronaphthalene.

The reproducibility and consistency between the electrodes prepared at different times were found to be very good. Six electrodes were prepared and used at the various stages of the work. With each electrode, potentials of series of solutions in the concentration range  $1.0 \times 10^{-7}$  -  $1.0 \times 10^{-2}$  mol/L tantalum(V) were measured. The calibration curves were constructed and the slopes were determined. The calibration curves were found to be reproducible with the linear range of  $1.0 \times 10^{-5}$  -  $1.0 \times 10^{-2}$  mol/L tantalum(V) and an anionic slope of  $58 \pm 1.5$  mV per decade.

The optimum conditions and response characteristics of the Malachite Green-hexafluorotantalate(V) CGE are summarized in Table 5. The calibration curve is shown in Fig. 4.

#### 4.7 Interference Study

The effect of forty-four diverse ions on the response of the Malachite Green-hexafluorotantalate(V)-CGE was studied. The mixed solution method was employed; and the selectivity coefficients were evaluated by using Eq. (2.13) together with the calibration curve. The selectivity coefficients calculated for several anions and for cations (which form fluoro-complexes in the test solutions made 1 M in both sulphuric and hydrofluoric acid) are shown in Table 6.

The anions  $H_2Y^{2-}$  (EDTA),  $C_2O_4^{2-}$ ,  $SO_4^{2-}$ ,  $NO_3^-$ , and  $Cl^-$  did not impart serious interference on the response behaviour of the CGE to hexafluorotantalate(V). No serious interference was also noted from arsenate, molybdate, and metavanadate. However, mild interference was noted from  $SCN^-$ ,  $ClO_4^-$ ,  $Bi^{3+}$ , and  $IO_4^-$ , the relative interference decreasing in that order (Table 6).

Although  $Hg^{2+}$  is suggested to form fluoro-complexes, there is no structural information [98]. Its presence, however, imparted no series interference. There is no any information on the fluoro-complex formation with  $Y^{3+}$  and  $La^{3+}$  [98]. Precipitation in the presence of these ions was noted due to formation of insoluble fluorides. However, these

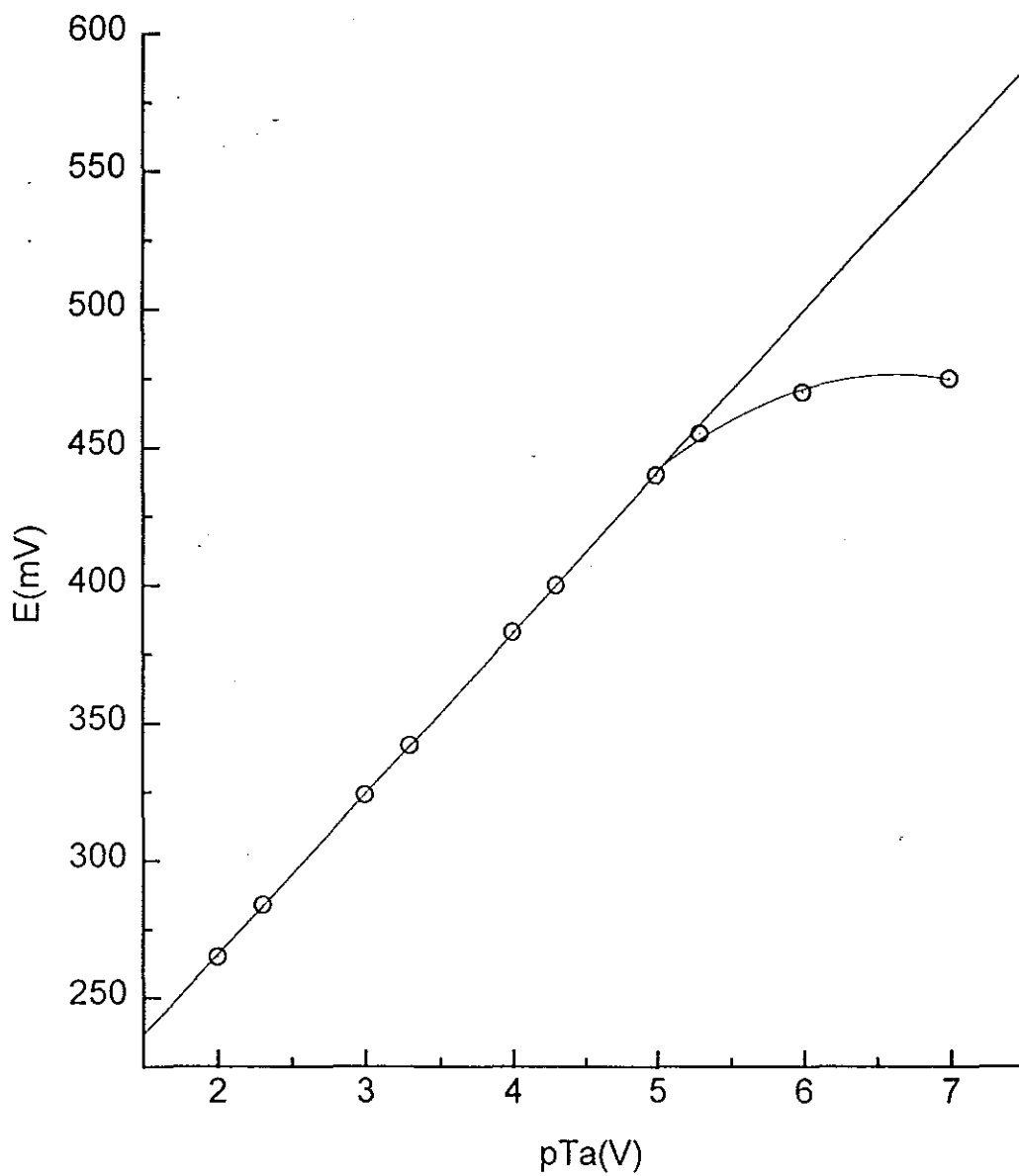


Fig. 4. Calibration curve for hexafluorotantalate(V)- selective coated graphite electrode

Table 6. Selectivity coefficients of the Malachite Green-hexafluorotantalate(V)-coated graphite electrode

Interferent	Most probable fluoro complex in 1 mol/L HF and 1 mol/L H <sub>2</sub> SO <sub>4</sub>	Reference	$k_{ij}$ , $i = \text{TaF}_6^-$
SCN <sup>-</sup>	-	-	$4.68 \times 10^{-3}$
ClO <sub>4</sub> <sup>-</sup>	-	-	$2.63 \times 10^{-3}$
Bi <sup>3+</sup>	BiF <sub>4</sub> <sup>-</sup>	101	$2.45 \times 10^{-3}$
IO <sub>4</sub> <sup>-</sup>	-	-	$1.99 \times 10^{-3}$
Ce <sup>4+</sup>	CeF <sub>6</sub> <sup>2-</sup>	102	$1.51 \times 10^{-3}$
B <sup>3+</sup>	BF <sub>4</sub> <sup>-</sup>	100	$1.29 \times 10^{-3}$
Cu <sup>2+</sup>	CuF <sub>4</sub> <sup>2-</sup>	98	$1.23 \times 10^{-3}$
Cl <sup>-</sup>	-	-	$1.12 \times 10^{-3}$
Ca <sup>2+</sup>	CaF <sub>4</sub> <sup>2-</sup>	100	$1.02 \times 10^{-3}$
Cd <sup>2+</sup>	CdF <sub>4</sub> <sup>2-</sup>	98	$9.12 \times 10^{-4}$
UO <sub>2</sub> <sup>2+</sup>	UO <sub>2</sub> F <sub>4</sub> <sup>2-</sup>	99	$8.31 \times 10^{-4}$
Sn <sup>2+</sup>	SnF <sub>4</sub> <sup>2-</sup>	101	$7.94 \times 10^{-4}$
Ti <sup>4+</sup>	TiF <sub>6</sub> <sup>2-</sup>	98	$7.41 \times 10^{-4}$
NO <sub>3</sub> <sup>-</sup>	-	-	$6.64 \times 10^{-4}$
W <sup>6+</sup>	WF <sub>8</sub> <sup>2-</sup>	98	$6.02 \times 10^{-4}$
Pb <sup>2+</sup>	PbF <sub>4</sub> <sup>2-</sup>	101	$5.62 \times 10^{-4}$
Cr <sup>3+</sup>	CrF <sub>5</sub> (H <sub>2</sub> O) <sup>2-</sup>	99	$4.36 \times 10^{-4}$
Nb <sup>5+</sup>	NbOF <sub>5</sub> <sup>2-</sup>	35, 37	$3.38 \times 10^{-4}$
SO <sub>4</sub> <sup>2-</sup>	-	-	$5.01 \times 10^{-5}$
Ag <sup>-</sup>	AgF <sub>3</sub> <sup>2-</sup>	98	$4.19 \times 10^{-5}$
Al <sup>3+</sup>	AlF <sub>6</sub> <sup>3-</sup>	99	$8.51 \times 10^{-5}$
Fe <sup>3+</sup>	FeF <sub>6</sub> <sup>3-</sup>	99	$6.60 \times 10^{-5}$
Mg <sup>2+</sup>	MgF <sub>4</sub> <sup>2-</sup>	100	$1.51 \times 10^{-3}$
C <sub>2</sub> O <sub>4</sub> <sup>2-</sup>	-	-	$9.12 \times 10^{-4}$
EDTA	-	-	$2.29 \times 10^{-5}$

ions did not interfere seriously.

Although trivalent hexafluoro-complexes of  $\text{Fe}^{3+}$  and  $\text{Al}^{3+}$  are known [99] no serious interference was noted in the presence of these ions. The presence of  $\text{Zr}^{4+}$ ,  $\text{Sb}^{3+}$ ,  $\text{As}^{3+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Co}^{2+}$ , and  $\text{Ni}^{2+}$  did not impart strong interference probably due to greater tendency of these cations to form stable sulphates in sulphuric acid solutions [98,100].

Precipitation was also noted in the presence of  $\text{Pb}^{2+}$ ,  $\text{Th}^{4+}$ ,  $\text{Ce}^{4+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Er}^{3+}$ , and  $\text{Ba}^{2+}$  ions. However, none of these ions was found to interfere seriously. Several cations such as  $\text{Bi}^{3+}$ ,  $\text{Sn}^{2+}$ ,  $\text{UO}_2^{2+}$ ,  $\text{W}^{6+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Ti}^{4+}$ ,  $\text{Ag}^+$ ,  $\text{B}^{3+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{Ca}^{2+}$  form fluoro-complexes of various compositions. However, the calculation of the selectivity coefficients is based on the very frequently occurring fluoro-complexes (Table 6).

The study of niobium is of special concern due to the fact that tantalum is found in nature together with niobium. Niobium forms an oxy-fluorotantalate,  $\text{NbOF}_5^{2-}$ , in 1 mol/L  $\text{H}_2\text{SO}_4$  and 1 mol/L HF [35,37]. No appreciable interference was noted, as can be seen from the small value of the selectivity coefficient (Table 6). Hence the CGE can be used for determining tantalum in natural samples which invariably contain niobium. It can be seen from Table 6 that most of the ions do not interfere on the response of the newly developed CGE to hexafluorotantalate(V). The results indicate that the proposed CGE is highly selective to hexafluorotantalate(V). Hence the proposed method can be applied to the determination of tantalum in diverse samples.

#### **4.8 Application of the Malachite Green-hexafluorotantalate(V)-coated Graphite Electrode**

The proposed CGE was applied to the determination of tantalum in Ethiopian tantalite-columbite ores collected from the Ethiopian Institute of Geological Surveys, EIGS using four different potentiometric techniques, namely, direct potentiometry, standard addition, sample addition, and Gran's plot. The results are given in Table 7. A typical Gran's plot is shown by Fig. 5. The results are in good agreement with the certified values indicating the reliability of the proposed method.

The results obtained by the four potentiometric methods were compared with the certified values to assess the advantages of one method over others. The comparison shows that the percentages of tantalum found in the two ores by the four methods are

in agreement with the certified values within an error of about 1%, although the precision of the direct potentiometry is lower than the three addition methods. Hence any of the four methods may be used for determination of tantalum in samples of complex matrices.

Since the ores analyzed were of high tantalum content, the applicability of the proposed electrode was further tested by determining low level tantalum content in synthetic matrices of different compositions to represent the most important tantalum-bearing ores. The tantalum content of the matrices was determined by the proposed electrode using direct and standard addition potentiometric techniques. The results obtained (Table 8) are in good agreement with the actual amount added, indicating the reliability of the proposed method.

Thus, the effects of diverse ions and the applicability of the proposed method to the determination of tantalum in tantalite-columbite ores and synthetic matrices suggest that the proposed method can be applied to determine tantalum in diverse samples with reasonable precision and accuracy.

Table 7. Determination of tantalum in Ethiopian tantalite-columbite ores

Potentiometric method	EIGS No. 334101 Ta <sub>2</sub> O <sub>5</sub> %(w/w) found*	EIGS No. 334107 Ta <sub>2</sub> O <sub>5</sub> %(w/w) found*
Direct potentiometry	64.70 ± 3.01	48.43 ± 3.15
Standard addition	64.72 ± 1.22	48.60 ± 1.76
Sample addition	64.51 ± 1.38	48.64 ± 1.68
Gran's plot	65.01 ± 0.84	50.27 ± 1.33
<b>Certified value</b>	<b>65.50</b>	<b>49.50</b>

\* Mean ± 95% confidence limit for triplicate measurements.

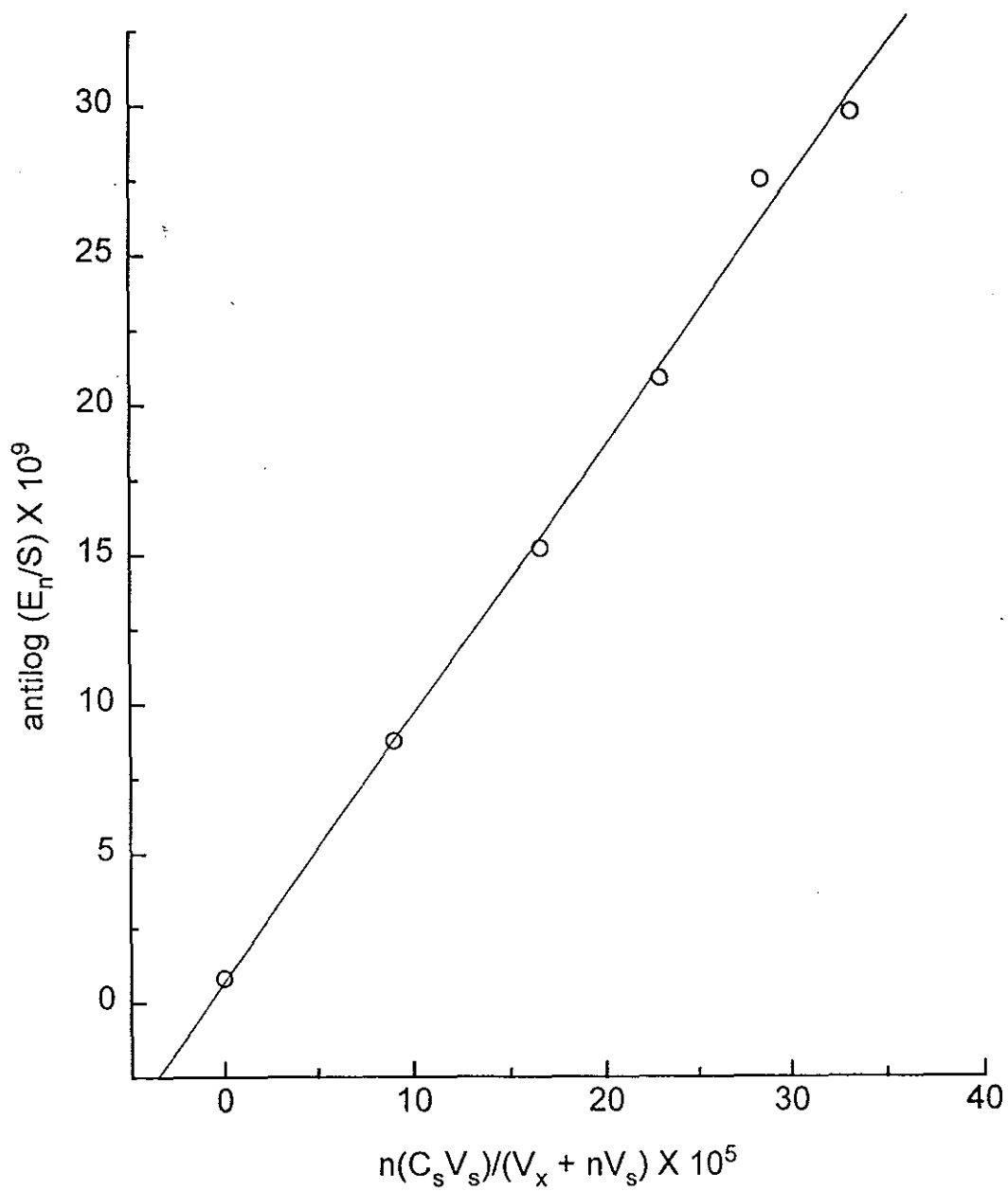


Fig. 5. Gran's plot for the determination of tantalum in Ethiopian tantalite-columbite ore.

Table 8. Determination of tantalum in synthetic matrices

No.	Composition of matrix	Tantalum found* by direct potentiometry, $\mu\text{g}$	Tantalum found* by the standard addition, $\mu\text{g}$
1	10 mg $\text{Nb}^{5+}$ + 12 mg $\text{Mn}^{2+}$ + 12 mg $\text{Cr}^{3+}$ + 4 mg $\text{Pd}^{2+}$ + 40 mg $\text{Fe}^{3+}$ + 200 $\mu\text{g}$ $\text{Ta}^{5+}$	201.57 $\pm$ 8.1	201.6 $\pm$ 4.5
2	6 mg $\text{Nb}^{5+}$ + 48 mg $\text{Fe}^{3+}$ + 8 mg $\text{Ni}^{2+}$ + 8 mg $\text{Ti}^{4+}$ + 4 mg $\text{Al}^{3+}$ + 4 mg $\text{Co}^{2+}$ + 200 $\mu\text{g}$ $\text{Ta}^{5+}$	198.4 $\pm$ 6.6	201.7 $\pm$ 4.2
3	8 mg $\text{Nb}^{5+}$ + 20 mg $\text{Ca}^{2+}$ + 30 mg $\text{Na}^+$ + 200 $\mu\text{g}$ $\text{Ta}^{5+}$	198.5 $\pm$ 7.1	201.6 $\pm$ 3.5
4	10 mg $\text{Nb}^{5+}$ + 20 mg $\text{Y}^{3+}$ + 10 mg $\text{Er}^{3+}$ + 20 mg $\text{Ce}^{4+}$ + 20 mg $\text{La}^{4+}$ + 32 mg $\text{U}^{6+}$ + 200 $\mu\text{g}$ $\text{Ta}^{5+}$	203.5 $\pm$ 6.8	198.6 $\pm$ 3.8
5	8 mg $\text{Nb}^{5+}$ + 20 mg $\text{Y}^{3+}$ + 40 mg $\text{U}^{6+}$ + 60 mg $\text{Fe}^{3+}$ + 40 mg $\text{Th}^{4+}$ + 8 mg $\text{Ti}^{4+}$ + 200 $\mu\text{g}$ $\text{Ta}^{5+}$	201.60 $\pm$ 7.3	202.1 $\pm$ 4.0

\* Mean  $\pm$  95% confidence limit for triplicate measurements.

#### 4.9 Comparison of the proposed Electrode with Other Hexafluorotantalate(V)-Selective Electrodes.

The response characteristics of the proposed electrode has been compared with those of the previously reported hexafluorotantalate(V)-selective electrodes (Table 9). It should be noted, however, that there is no complete set of information to make the comparison on the basis of each electrode characteristic.

Table 9. Comparison of the response characteristics of the proposed hexafluoro-tantalate(V)-selective CGE with other hexafluorotantalate(V)-selective electrodes.

Electroactive material	Membrane solvent or matrix	Slope mV per decade	Linear range, [Ta(V)]	Response time, s	Ref.
Solvent mediator	PVC matrix	*	$1.0 \times 10^{-5}$ - $1.0 \times 10^{-4}$	*	27
Tetraoctylammoniumhydrogen sulphate	Chloroform PVC	-57	$2.0 \times 10^{-6}$ - $1.0 \times 10^{-2}$	*	31
Triheptyldodecylammonium iodide	Liquid ion exchanger	*	$1.0 \times 10^{-6}$ - $1.0 \times 10^{-1}$	*	33
Brilliant Green	Nitrobenzene PVC	-58.5	$2.0 \times 10^{-6}$ - $1.0 \times 10^{-2}$	20 - 120	35
Brilliant Green	1-Chloronaphthalene PVC on graphite	-58	$5.0 \times 10^{-6}$ - $5.0 \times 10^{-3}$	4 - 15	37
Malachite Green	1-Chloronaphthalene PVC on graphite	-58	$1.0 \times 10^{-5}$ - $1.0 \times 10^{-2}$	5 - 15	Proposed

\* Data not available.

One can see from the table that the proposed electrode is well-behaved, showing a Nernstian response slope with very short response time. The response behaviour of the proposed electrode has been extensively studied in the presence of diverse ions, and also reliably applied to the determination of tantalum in a variety of matrices while most of the electrodes reported were not studied in detail with respect to their selectivity and application or their response characteristics suffer from a number of limitations. The proposed electrode is easy to prepare, simple to use and does not require an internal reference system and thus is cheaper than those employing internal reference electrodes. Furthermore, the proposed electrode has a short response time and hence a number samples can be analyzed in a relatively short period of time.

## 5 CONCLUSION

A hexafluorotantalate(V)-selective coated graphite electrode based on Malachite Green has been developed. The newly developed electrode was found to exhibit Nernstian response behaviour to hexafluorotantalate(V). The study on the effect of diverse ions on the response characteristics of the electrode also indicates that the electrode is highly selective to hexafluorotantalate(V).

The analytical application of the electrode to the analysis of tantalum in both synthetic and real ore samples was tested using four potentiometric techniques. The results are in good agreement with the standard and certified values. The electrode can, therefore, be reliably applied to the determination of low levels of tantalum in ores and complex materials.

The electrode is easy to construct, simple to use, sturdy, inexpensive, and does not require an internal reference electrode. The electrode can be made of use in fast assay methods for quantification of tantalum in tantalite-columbite mineral ores with reasonable precision and accuracy.

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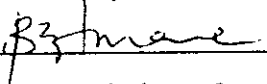
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## DECLARATION

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

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Place and date of submission June 25, 1996

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