New selenite ion-selective electrodes based on 5,10,15,20-tetrakis-(4-methoxyphenyl)-21H,23H-porphyrin-Co(II)

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New polymeric membrane (PME), modified carbon paste (MCPE), and coated wire (CWE) selenite ion-selective electrodes based on 5,10,15,20-tetrakis-(4-methoxyphenyl)-21H,23H-porphyrin-Co(II) (CoTMeOPP) are reported. The best composition was the electrode containing 2% CoTMeOPP as the active material and 49% TCP as plasticizer. The electrodes reveal a Nernstian behavior over a concentration range of 5.5 × 10⁻² to 1.1 × 10⁻² M for PME, 5.2 × 10⁻⁵ to 1.2 × 10⁻² M for MCPE and 1.2 × 10⁻³ to 4.4 × 10⁻³ M for CWE. The potentiometric response is pH dependent, since selenous acid is a diprotic acid. The slope of the selenite PVC electrode was −57.0 mV for the monovalent anion at pH 6.47, and −26.0 mV for the divalent anion at pH 11.00. The detection limits were 3.4 × 10⁻⁵ and 4.7 × 10⁻⁵ M at pH values 6.47 and 11.00, respectively. The electrodes manifest advantages of low resistance, very short response time (15 s), and most importantly good selectivities relative to a wide variety of other anions. In fact, the proposed selenite ion-selective electrodes show a great improvement compared to previously reported electrodes for selenite ion. The electrode was used for the determination of selenite in selenite/selenate mixture, in sodium selenite raw material powder, and in VitaFit Selenium ACE antioxidant tablets with recovery ranges of 90.0–103.3%.

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1. Introduction

In the recent years, there has been increasing interest in the trace determination of selenium. Apart from natural sources (mainly metal–sulfur minerals), selenium compounds are widely spread out from the combustion of fossil fuels, and used in the glass, electronic industries and in agriculture [1]. The toxicity and essential nature of selenium depends on its chemical form. Selenium naturally exists in several oxidation states in inorganic and organic forms. The inorganic species most frequently found in water and soil are selenite (SeO₃²⁻) and selenate (SeO₄²⁻).

The development of reliable techniques to study the speciation of selenium in environmental and biological samples is necessary to understand the biochemical cycle, mobility, and uptake of selenium, as well as its toxicity. Many problems in selenium speciation analysis are associated with the low concentration of each species to be determined. Significant errors may also arise by losses of volatile selenium compounds, instability of its chemical species specially in analytical methods involving many chemical treatments [1].

Selenium occurs naturally in a number of inorganic forms, including selenide, selenite and selenate. Selenium is an essential trace element for plants, animals and humans. The biological functionality of selenium shows dual characteristics, it can cause disease by its deficiency but is toxic at level relatively close to those required for health [2]. Elemental selenium and most metallic selenides have relatively low toxicities because of their low bioavailability. By contrast, selenite and selenate are very toxic and have modes of action similar to that of arsenic. Speciation of selenium in environmental and biological samples is necessary to understand the biochemical cycle, mobility and uptake of selenium, as well as its toxicity.

Hydride generation coupled to atomic absorption spectrometry (AAS), inductively coupled plasma (ICP) or atomic fluorescence spectrometry (AFS) are the techniques that most commonly used for the speciation of inorganic selenium [3–6]. Detection limits were 0.1–0.4 ng/l. Since this reaction is specific for Se(IV), these techniques can be applied for total inorganic selenium (the sum of Se(IV) and Se(VI)) after quantitative reduction of selenate to selenite. The content of selenate is obtained as the difference between that of selenite. Elemental selenium and most metallic selenides have relatively low toxicities because of their low bioavailability. By contrast, selenite and selenate are very toxic and have modes of action similar to that of arsenic. Speciation of selenium in environmental and biological samples is necessary to understand the biochemical cycle, mobility and uptake of selenium, as well as its toxicity.

The use of ion-selective electrodes has gained importance because of their ease of handling and their selectivities on specific ions. There are only a few investigations regarding selenite ion-selective electrodes. Ion-selective electrodes for the determini-
nation of selenite were constructed by compressing either HgSeO₃ or a mixture of HgSeO₃ and Hg₂Cl₂ [7]. Cai et al. [8] had developed selenite ion-selective electrode using 4,6-dibromopiaselenole as active material, PVC as membrane matrix and dibutyl phthalate as plasticizer. Three different selenite-selective electrodes were fabricated, the first was developed using solid salts of Ag₂Se and Cu₂S [9]. Piaselenol (PIS) was used in the form of 1,2-phenylenediamine selen complex as the active material for ion-selective electrode membrane sensitive to selenite ion [10]. Silicon rubber [11] was used as the active membrane matrix for selenite-selective electrode consisted of 4% dialkyldimethylammonium chloride, and QAD 86 PI. A self-made ion-selective electrode was made using Ag₂Se as electroactive material [12], and used for the determination of selenium in biological materials. It can be observed that in all papers reported in the literature, there is no mention about selenious acid species as a function of pH.

It was, therefore, felt worthwhile to develop a better sensor for selenious ions using 5,10,15,20-tetraakis-(4-methoxyphenyl)-21H,23H-porphyrin-Co(II) (CoTMeOPP) (Fig. 1) as an electroactive phase in PVC matrix or carbon paste.

An unusual feature of porphyrin chelate is that the metal ion is bonded to four nitrogen atoms, which are themselves linked together in a conjugated system. This imparts a high degree of mesomerism whereby a substitution anywhere in the porphyrin nucleus can relay its electron donating and attracting tendency to all the four coordinating atoms that makes metalloporphyrins so versatile [13].

PVC membranes, coated wires, and modified carbon paste electrodes based on CoTMeOPP as ionophore for selenite ions were prepared, optimized, and checked at different concentration ranges for selenite. The electrodes were used for the determination of selenite in pure solutions, selenite/selenate mixture, in raw material of sodium selenite, and in VitaFit Selenium ACE antioxidant tablets.

2. Experimental

2.1. Apparatus and reagents

For potential measurements a JENWAY 3010 digital pH/mV meter was used. A SENTEK R1/2MM Ag/AgCl electrode was used as the outer reference electrode. Millipore Elix S (Automatic Sanitation Module, ASM) was used for obtaining the deionized water. CARY 50 Probe UV–Visible spectrophotometer, Varian was used for the spectrophotometric measurements.

Anhydrous sodium selenite (Na₂SeO₃) was purchased from Loba Chemie Pvt LTD., India. 5,10,15,20-tetraakis-(4-methoxyphenyl)-21H,23H-porphyrin-Co(II) [C₄₈H₃₆CoN₄O₄], poly(vinyl chloride) (PVC) of high relative molecular weight, graphite powder, tetrahydrofuran (THF), AgNO₃, tris(hydroxymethyl)-aminomethane and the plasticizers, α-nitrophenol,ctyl ether (α-NPOE), dibutyl phthalate (DBP), diocyl phthalate (DDBP), and tricresyl phosphate (TCP) were purchased from Aldrich chemical company, USA.

2.2. Solutions

Stock solution of 0.1 M sodium selenite was prepared by dissolving 1.73 g Na₂SeO₃ in 100 ml deionized water. The solution was kept in refrigerator.

Acetate buffer solution of pH 5.89 was prepared by mixing 95 ml of 0.1 M sodium acetate solution with 5 ml 0.1 M acetic acid solution. Phosphate buffer solutions of pH values, 5.59, 6.47, and 7.38 were prepared by mixing the appropriate volumes 0.01 M KH₂PO₄ and 0.01 M Na₂HPO₄ solutions [14]. Tris–HCl buffer solution pH 8.5 was prepared by the addition of 0.01 M HCl to 50 ml 0.01 M tris solution [15]. Ammoniacal buffer solution of pH 9.5 was prepared by the addition of the required volume of 0.01 M NH₄OH to 50 ml 0.01 M NH₄Cl solution then completed to 100 ml using deionized water. Sodium chloride–sodium hydroxide solution of pH 10.2 and 11.0 were prepared by the addition of the required volume of 0.01 M NaOH to 50 ml 0.01 M NaCl solution then completed to 100 ml using deionized water.

To investigate the selectivity of the proposed electrodes, 0.5 M sodium salt solution of each of the following ions, Cl⁻, Br⁻, NO₃⁻, SO₄²⁻, and 0.1 M sodium salt solution of each of the following ions, SO₃²⁻, F⁻, SO₄²⁻, PO₄³⁻, and 0.1 M potassium salt solution of SeO₄²⁻, SCN⁻ were prepared in deionized water.

2.3. Preparation of the electrodes

2.3.1. Preparation of PVC-membrane electrodes

Membranes of different compositions and plasticizers were prepared. The membrane was prepared by dissolving the required amount of PVC and plasticizer in 5 ml THF. The calculated amount of ionophore was dissolved in THF and mixed with the PVC/plasticizer solution in Petridish (5.0 cm diameter). The total weight of constituents in each batch is fixed at 0.2 g. The membranes were left to dry in air (not less than 24 h) to obtain homogeneous and uniform thickness. The membranes formed as a film in the bottom are taken out carefully and glued to a homemade electrode bodies with an adhesive of PVC dissolved in THF. The electrodes were filled with 10⁻¹ M NaCl and 10⁻³ M sodium selenite solution and preconditioned by soaking in 10⁻² M selenite solution for 24 h.

2.3.2. Preparation of coated wire electrodes

Pure silver, graphite, glassy carbon and cupper rods of 1 mm diameter and 12 cm in length were insulated leaving 2 cm at one end for coating and 1 cm at the other end for connection. The polished rod surface of each type was coated with active membrane by dipping the exposed end into the coating solution, as previously described in membrane preparation, and allowing the film to dry in air for about 1 min. The process was repeated until a plastic film of approximately 1 mm thickness was formed (about 10 times). The prepared electrodes were preconditioned by soaking for 1 h in 10⁻¹ M selenite solution.
2.3.3. Preparation of carbon paste electrodes

A teflon holder (12 cm length) with a hole at one end (7 mm diameter and 3.5 mm depth) for the carbon paste filling served as the electrode body. Electrical contact is made through a stainless steel rod through the center of the holder. This rod can move up and down by screw movement to press the paste down when renewal of the electrode surface is needed. The modified paste was prepared by mixing the appropriate weight of ionophore and high purity graphite with acetone. The mixture was homogenized, left at room temperature to evaporate acetone, then a weighed amount of plasticizer was added and a very intimate homogenization was then achieved by careful mixing with agate pestle in agate mortar. The paste was then packed into the hole of the electrode body. The carbon paste was smoothed onto a paper until it had a shiny appearance and used directly for potentiometric measurements without preconditioning.

2.4. Selectivity of the sensor

Potentiometric selectivity factor was evaluated using the matched potential method [16]. According to this method, the activity of analyte was increased from \( a_A = 1.0 \times 10^{-5} \) M (reference solution) to \( a'_A = 1.0 \times 10^{-3} \) M, and the change in potential (\( \Delta E \)) corresponding to this increase in activity is measured. Then, 0.1 M solution of an interfering ion is added to a new 1.0 \( \times 10^{-5} \) M analyte reference solution until the same potential change \( (\Delta E) \) is recorded [17], the concentration of the added amount is thus \( a_B \). The selectivity coefficient \( K_{\text{MPM}}^{A,B} \) for each interferent was calculated using the following equation:

\[
K_{\text{MPM}}^{A,B} = \frac{a'_A - a_A}{a_B}
\]

2.5. Potentiometric determination

The standard addition method was applied [18]. In this method, the proposed electrode was immersed into a sample of 25 ml with unknown concentration (\( \sim 10^{-7} \) to \( 10^{-4} \) M) sample solution and the equilibrium potential of \( E_0 \) was recorded, then 0.1 ml of \( 1.0 \times 10^{-3} \) M of standard selenite solution was added into the test solution and the equilibrium potential \( E_s \) was obtained. From the potential change \( \Delta E = (E_0 - E_s) \) one can determine the concentration of the test sample using the equation:

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

where \( C_s \) is the concentration to be determined, \( V_x \) is the volume of the original sample solution, \( V_s \) and \( C_s \) are the volume and concentration of the standard solution added to the sample to be analyzed, respectively, \( \Delta E \) is the change in potential after the addition of certain volume of standard solution, and \( S \) is the slope of the calibration graph.

3. Results and discussion

3.1. PVC-membrane electrodes

3.1.1. Effect of pH on the electrode response

Calibration graphs (electrode potential vs. \( -\log \) [selenite]) were constructed using standard selenite solution adjusted to different pH values in the range of 5.5–11.0 using acetate, phosphate, and tris buffers. The slope of the calibration graphs, Fig. 2, Table 1 was found to be in the range of 50–60 mV/concentration decade for selenite samples buffered at pH 5.59–7.38 indicating that the electrode responds to the monovalent anion at this pH range. Increasing the
pH of selenite samples leads to a decrease in the slope of the calibration graphs until they reach to about 23–30 mV at pH 8.50–11.00 indicating that the electrodes also respond to the divalent anion. This in agreement with the fact that selenine acid is a diprotic acid with pK₁ = 2.62 and pK₂ = 8.32, thus [19]:

\[ \text{H}_2\text{SeO}_3^- = \text{H}^+ + \text{HSeO}_3^- \quad \text{pK}_1 = 2.62 \]

\[ \text{HSeO}_3^- = \text{H}^+ + \text{SeO}_3^{2-} \quad \text{pK}_2 = 8.32 \]

As indicated from the distribution curve of selenine acid species as a function of pH, Fig. 3, it is obvious that the monovalent HSeO₃⁻ ions are the predominating species within the pH range 4.5–6.5 and at pH higher than 10.0, the divalent SeO₃²⁻ ions are the predominating species. Accordingly, the electrode response has to be measured at fixed pH value using an appropriate buffer.

3.1.2. Composition of membrane electrodes

On using an ion-selective electrode in analytical determination, there are many factors that should be taken into consideration as they affect the performance of the electrode towards its respective ion. Some of these factors are: composition of the membranes and the amount of ionophore, plasticizer, the effect of soaking time on life span and the effect of operational conditions such as temperature, response time, presence of interferents and pH, etc. These studies have been performed according to the recommendation of the IUPAC [18].

The composition of the membrane was varied so as to reach the optimum composition exhibiting the best performance characteristics (slope of calibration graph, linear concentration range and reproducibility of the results). In preliminary experiments, membranes with and without ionophore were constructed. The membrane with no ionophore displayed no measurable response towards the studied selenite ion, whereas, in the presence of the proposed ionophore for selenite-selective electrode, the optimized membrane demonstrated Nernstian response and remarkable selectivity for the respective selenite ion over several common inorganic anions. The key ingredient of poly(vinyl chloride) (PVC) membrane electrodes is the incorporated ionophore, which defines the selectivity of the electrode. In plastic membrane electrodes, the amount of this ionophore should be sufficient to obtain reasonable response at the gel layer-test solution interface which is responsible for the membrane potential. Also, the amount of the plasticizer should be to the extent that produces a membrane of good physical properties and at the same time plays efficiently its role as a solvent mediator for the ionophore.

Investigations reveal that, the performance characteristics reported for a given PVC membrane may vary depending on the membrane composition and the nature of solution to which the electrodes are exposed [20–22]. Thus, several membranes of varying nature and ratio of ionophore/PVC/plasticizer were prepared for the systematic investigation of each membrane composition. The amount of ionophore was found to seriously affect the sensitivity of the membrane electrodes, experimental trials proved that certain percentage of ionophore was optimum as indicated by the Nernstian behavior of the electrode. However, further increase of the ionophore over this percentage resulted in a diminished response slope of the electrode, most probably due to some inhomogenities and possible saturation of the membrane [23].

The amount of ionophore should be sufficient to obtain a reasonable ionic exchange at the gel layer-test solution interface, which is responsible for the membrane potential. Also, the amount of the plasticizer should be to the extent that produces a membrane of good physical properties and at the same time plays efficiently its role as a solvent mediator for the ionophore. It is evident that the change of composition affects significantly the response of the electrode (Table 2). The data collected in Table 2, shows that a PVC membrane plasticized with TCP and containing 1.0% CoTMeOPP has a slope of −47.80 mV while the one containing 2.0% CoTMeOPP has a −57.00 mV slope and the 3% CoTMeOPP membrane shows a diminished response of −54.00 mV slope. The detection limit was 4.70 × 10⁻⁵ M for both 1.0% and 3.0% CoTMeOPP membrane composition while it was 3.40 × 10⁻⁵ M for the 2.0% CoTMeOPP composition. The electrode containing 2.0% CoTMeOPP has a linear working range (5.50 × 10⁻⁵ to 1.00 × 10⁻² M) which is wider than the other two compositions (Table 2).

3.1.3. Effect of plasticizer

Besides the critical role of the nature and the amount of ionophore on the characteristics of the sensors, some other important features such as the nature of the solvent mediator, the plasticizer/PVC ratio and the nature of any additives used, are known to significantly influence the sensitivity and selectivity of ion-selective electrodes [24–26].

The nature of the plasticizer influences both dielectric constant of the membrane and the mobility of the ionophore [27]. The solvent mediator has a dual function, it acts as liquefying agent, enabling homogeneous solubilization and modifying the distribution constant of the ionophore used. For plasticizer to be adequate for use in sensors, it should gather certain properties and characteristics, such as having high lipophilicity, high molecular weight, low vapor pressure, and high capacity to dissolve the substrate and other additives present in the matrix [28]. The influence of the plasticizer type and its quantity on the characteristics of the studied sensors was investigated using five plasticizers with different polarities including DBP, DOP, DBBP, TCP and NPOE.

As shown in Fig. 4(a) and (b), the electrode containing TCP generally shows better potentiometric responses, i.e. sensitivity and linearity range of the calibration plots. This is due to its high dielectric constant and relatively high molecular weight. The results given in Table 2 indicate that the sensor composed
Table 2: Composition, slopes, linear ranges, and detection limits of calibration curves for selenite PVC membranes, chemically modified carbon paste and coated wires electrodes.

<table>
<thead>
<tr>
<th>% Conventional composition</th>
<th>Slope, mV/decade pH 6.67</th>
<th>Detection limit, M</th>
<th>Linear range, M</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ionophore</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PVC</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Plasticizer</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbon paste</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ionophore</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Graphite</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Plasticizer</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coated wires (2% ionophore + 49.0% TCP)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Type of bed</td>
<td>Slope, mV</td>
<td>Detection limit, M</td>
<td>Linear range, M</td>
</tr>
<tr>
<td></td>
<td>pH 6.47</td>
<td>pH 11.00</td>
<td>pH 6.47</td>
</tr>
<tr>
<td>Ag</td>
<td>−45.90</td>
<td>−32.20</td>
<td>5.80 × 10⁻⁵</td>
</tr>
<tr>
<td>Ag (1% graphite)</td>
<td>−61.80</td>
<td>−39.00</td>
<td>9.10 × 10⁻⁵</td>
</tr>
<tr>
<td>Graphite</td>
<td>−23.60</td>
<td>−15.70</td>
<td>3.20 × 10⁻⁵</td>
</tr>
<tr>
<td>Copper</td>
<td>−43.00</td>
<td>−19.40</td>
<td>4.70 × 10⁻⁴</td>
</tr>
<tr>
<td>Glassy carbon</td>
<td>−19.60</td>
<td>–</td>
<td>3.20 × 10⁻⁵</td>
</tr>
</tbody>
</table>

* The optimum composition chosen.

Fig. 4. Effect of plasticizer on potential response of PVC membrane containing 2.0% CoTMeOPP at pH 6.47 (a) and pH 11.00 (b).
of 2.0% ionophore, and TCP as plasticizer gives best sensitivity with near Nernstian slope of $-57.00 \text{ mV/decade}$ at pH 6.47 with detection limit of $3.4 \times 10^{-5} \text{ M}$ over a linear range of $5.50 \times 10^{-5}$ to $1.00 \times 10^{-2} \text{ M}$ and $-26.00 \text{ mV/10-fold}$ at pH 11.00 with detection limit of $4.70 \times 10^{-5} \text{ M}$ over a linear range of $6.60 \times 10^{-5}$ to $1.20 \times 10^{-2} \text{ M}$. Therefore, this composition was used to study various operation parameters of the electrode. The same composition and plasticizer was taken as the optimum composition of a coating mixture for the CWE.

### Table 3

<table>
<thead>
<tr>
<th>Soaking time</th>
<th>Slope, mV/decade</th>
<th>Linear range, M</th>
<th>Response time, s</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 h</td>
<td>$-38.80$</td>
<td>$8.30 \times 10^{-3}$ to $2.90 \times 10^{-1}$</td>
<td>$&lt;20$</td>
</tr>
<tr>
<td>1 day</td>
<td>$-57.00$</td>
<td>$8.30 \times 10^{-3}$ to $2.90 \times 10^{-1}$</td>
<td>$&lt;20$</td>
</tr>
<tr>
<td>4 days</td>
<td>$-49.80$</td>
<td>$8.30 \times 10^{-3}$ to $2.90 \times 10^{-1}$</td>
<td>$&lt;20$</td>
</tr>
<tr>
<td>6 days</td>
<td>$-44.00$</td>
<td>$8.30 \times 10^{-3}$ to $2.90 \times 10^{-1}$</td>
<td>$&lt;20$</td>
</tr>
</tbody>
</table>

3.1.4. Effect of soaking on life span of the PVC-membrane electrodes

The performance characteristics of the investigated electrodes were studied as a function of soaking times. For this purpose, the electrode was soaked in $1.00 \times 10^{-3} \text{ M}$ selenite solution for different intervals and then the effect of soaking on the calibration graph slope, usable concentration range and the response time were measured (Table 3). As shown in the table, while the slope of the electrode after 1 h was $-38.80 \text{ mV/decade}$, it changed to $-57.00 \text{ mV/decade}$ after 1 day. The membrane loses its sensitivity after 4 days, as the slope decreased to $-49.80 \text{ mV/decade}$. This negative effect of soaking is attributed to the leaching of the ionophore and plasticizer to the bathing solution which is related to the distribution equilibria and diffusion rates. Another explanation can be related to the penetration of the water molecules from the bathing solution to the membrane and consequently slow solvation of the lipophilic salts in situ, so they are slowly leached out and limit the electrode life [29]. However, it was noted that, the electrode in use if kept dry in refrigerator showed good preservation of its slope value and response extending to 2 months with refreshing the electrode by immersing into soaking solution for 30 min or after a set of measurements.

3.2. Coated wire electrodes (CWEs)

The main advantage of these electrodes towards other types of ion-selective electrodes arises from the fact that, there is no need for an inner electrolyte solution. The electrodes, simply, consist of conductive bed coated with a coating mixture containing an electroactive material. The optimum composition of a coating mixture is that which exhibits a Nernstian slope and a wide dynamic range of concentration when it was used as PVC membrane.

3.2.1. Effect of electrode bed

To investigate the effect of the bed nature on the efficiency of coated wire electrodes, the optimized coating mixture was used in the preparation of electrodes with different conductive beds, namely silver, copper, graphite and glassy carbon. After conditioning, each electrode was examined in the concentration range $1.00 \times 10^{-2}$ to $1.00 \times 10^{-4} \text{ M}$ of selenite solution. The dynamic range of concentration and the limit of detection for the electrodes were evaluated according to the IUPAC recommendations [18]. As can be noticed from Table 2, all wires give unsatisfactory response towards selenite except silver wire. Ag wire coated electrode has a slope $-45.90 \text{ mV}$ at pH 6.47 and a Nernstian behavior with slope $-32.20 \text{ mV}$ at pH 11.00. This is attributed to the lowest resistivity

(1.62 $\mu \Omega \text{ cm}^{-1}$) of silver. A significant improvement of CWE was obtained when transducer layer with electronic conductivity was applied between the substrate and the ion-selective membrane, to yield the so-called “all-solid-state ion-selective electrode” [30]. In this type of electrodes, electrochemically synthesized conducting polymer is electrodeposited directly onto an electric conducting substrate or a conducting polymer is included in the cocktail of ion-selective membrane components and the mixture is casted directly on a solid conducting substrate [31–33]. It was found that very fine pure graphite powder can be used as electrically conducting additive added to the membrane matrix instead of using conducting polymer. This type of potentiometric sensors result in a significant improvement of charge transfer between the substrate and the membrane phase. As a result, stability of the sensor potential and lowering of detection limits were observed [17]. In this work, a small mass percentage (1.0% graphite) was added to the plastic ion-selective membrane phase of selenite and coating the silver wire. The results show good improvement in the electrode characteristics, slope, and response time. Fig. 5 represents the improvement of the slope of the coated silver wire electrode when doped with 1.0% graphite in which the slope has increased from $-45.90$ to $-61.80 \text{ mV}$ for the monovalent selenite ion in acidic medium pH 6.47 over linear range of $1.20 \times 10^{-4}$ to $4.40 \times 10^{-3} \text{ M}$ with detection limit $9.10 \times 10^{-5} \text{ M}$. While, for the divalent selenite ion in basic medium pH 11.00 the slope increased from $-32.20$ to $-39.00 \text{ mV}$ over a linear range of $7.90 \times 10^{-6}$ to $1.30 \times 10^{-3} \text{ M}$ with detection limit $3.90 \times 10^{-6} \text{ M}$ (Table 2).

3.3. Chemically modified carbon paste electrode (CMCPE)

CoTMeOPP as a carrier was found to be highly sensitive to selenite with respect to several other anions. Therefore, we studied in details the performance of the CMCPE containing this ionophore for selenite in aqueous solutions. It is well known that the selectivity, linear dynamic range and sensitivity obtained for a given CMCPE depends significantly on the paste composition [34] and the nature of the solvent mediator [35,36].

The amount of the ionophore in the paste affects the response of the electrode. The results in Table 2 show that the electrode containing 1.0% CoTMeOPP has a slope of $-55.48 \text{ mV}$, while that containing 2.0% CoTMeOPP has a slope of $-65.00 \text{ mV}$, then the slope decreased to $-50.33 \text{ mV}$ when 3.0% of CoTMeOPP was used. The
three electrodes have the same detection limit and almost the same linear range.

3.3.1. Effect of plasticizer on CMCPE

It is noteworthy that the nature of the solvent influences the mobility of ions and provides the appropriate conditions for the incorporation of selenite ion into the paste prior to its exchange with the soft ionophore.

Four plasticizers with different polarities including TCP, DBBP, NPOE, and DOP were studied and the optimum composition for the electrode was given in Table 2. The use of TCP as a solvent mediator, as low polarity compound, in this electrode results in a Nernstian linear plot over a concentration range of $5.20 \times 10^{-5}$ to $1.20 \times 10^{-2}$ M, $8.70 \times 10^{-5}$ to $1.20 \times 10^{-2}$ M with slopes of $-65.00$ and $-29.40$ mV at pH 6.47 and 11.00 respectively. Whereas, in case of other solvent mediators; the potentiometric response is much different from the expected Nernstian value.

3.4. Response time

The response time [18] of the electrode was tested by measuring the time required to achieve a steady state potential (within $\pm 1$ mV) after successive immersion of the electrode in a series of its respective selenite solution, each having a 10-fold increase in concentration from $1.00 \times 10^{-4}$ to $1.00 \times 10^{-1}$ M. The resulting potential–time plots for PVC electrode is shown in Fig. 6. The PVC-membrane electrode yielded steady potentials within 20 s while the CMCPE reaches the steady state potential within 15 s. The CWE shows better response time shorter than both PVC and CMCP electrodes (5 s). The relatively higher response time of the PVC and CMCP electrodes may be attributed to the higher noise originated from the higher resistance of the liquid-contact membranes, which was as a consequence of their large thickness [37]. The potential readings stay constant, to within $\pm 1$ mV, for at least 4 min. This indicates the fast response time of the suggested electrodes and their high stability after attending the steady state value.

3.5. Selectivity of selenite electrode

The selectivity coefficient is the main source of information concerning interferences on the electrode response. In analytical applications, the response for the analyte must be as high as possible, i.e. the response for foreign substances must be very small, so that the electrode exhibits a Nernstian dependence on the pri-
mary ion over a wide concentration range. The selectivity of the ionophore of the electrode sensor depends on the selectivity of the ionophore process at the sensor-test solution interface and the membrane phase. Comparison to other anions tested and the rapid exchange kinetics of the anion between the aqueous and membrane phase.

The selectivity sequence of the studied electrodes for different interferences, as selectivity is concentration dependent. The selectivity sequence significantly differs from the so-called Hofmeister selectivity sequence (i.e. that is to say selectivity based solely on the lipophilicity of anion). Table 7 shows that thiocyanate ions may cause some interference as the slope of its graph is near Nernstian but at low concentration it would not cause any interference, as selectivity is concentration dependent.

Two specialized IUPAC committees were held concerning the determination of potentiometric selectivity coefficients [41]. In the first IUPAC committee, held in 1975 [42], the separate solution method (SSM) was recommended only if the electrode exhibits Nernstian response, but it was considered less desirable compared to the fixed interferences method (FIM), because it does not represent as well the actual conditions under which the electrode is used. In 2002, the second IUPAC committee on methods for representing the selectivity coefficients recommended the matched potential method (MPM) which is independent of Nikolsky–Eisenman equation [16]. The selectivity coefficient values were calculated by applying the matched potential method and collected in Table 4.

### 3.6. Analytical applications

#### 3.6.1. Determination of selenite in pure solution and in sodium selenite raw material powder

The electrode was successfully used for the potentiometric determination of selenite in pure solution by applying standard addition method (Table 5), the recovery percents range from 95.0%

### Table 4

<table>
<thead>
<tr>
<th>Interferent</th>
<th>PVC membrane</th>
<th>CMCPE</th>
<th>CWE</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>pH 6.47</td>
<td>pH 11.00</td>
<td>pH 6.47</td>
</tr>
<tr>
<td>Cl&lt;sup&gt;-&lt;/sup&gt;</td>
<td>3.60</td>
<td>3.10</td>
<td>3.60</td>
</tr>
<tr>
<td>Br&lt;sup&gt;-&lt;/sup&gt;</td>
<td>3.30</td>
<td>3.00</td>
<td>3.50</td>
</tr>
<tr>
<td>SO&lt;sub&gt;4&lt;/sub&gt;²⁻</td>
<td>2.80</td>
<td>2.60</td>
<td>3.70</td>
</tr>
<tr>
<td>SO&lt;sub&gt;3&lt;/sub&gt;²⁻</td>
<td>3.50</td>
<td>2.80</td>
<td>3.60</td>
</tr>
<tr>
<td>S&lt;sup&gt;-&lt;/sup&gt;²⁻</td>
<td>2.30</td>
<td>1.10</td>
<td>2.00</td>
</tr>
<tr>
<td>SeO&lt;sub&gt;4&lt;/sub&gt;²⁻</td>
<td>3.10</td>
<td>2.30</td>
<td>2.00</td>
</tr>
<tr>
<td>F&lt;sup&gt;-&lt;/sup&gt;</td>
<td>3.00</td>
<td>2.70</td>
<td>3.50</td>
</tr>
<tr>
<td>NO&lt;sub&gt;3&lt;/sub&gt;⁻</td>
<td>2.70</td>
<td>3.10</td>
<td>2.50</td>
</tr>
<tr>
<td>SCN&lt;sup&gt;-&lt;/sup&gt;</td>
<td>0.59</td>
<td>0.69</td>
<td>0.20</td>
</tr>
</tbody>
</table>

### Table 5

<table>
<thead>
<tr>
<th>Interferent</th>
<th>Taken, M</th>
<th>Found, M</th>
<th>Found, M by ICP-AES</th>
<th>RSD, %</th>
<th>Recovery, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure selenite solutions</td>
<td>1.00 × 10⁻³</td>
<td>9.50 × 10⁻⁶</td>
<td>9.90 × 10⁻⁶</td>
<td>0.32</td>
<td>95.00</td>
</tr>
<tr>
<td>Selenite/Selenate mixture</td>
<td>1.00 × 10⁻³</td>
<td>9.70 × 10⁻⁵</td>
<td>9.99 × 10⁻⁵</td>
<td>0.21</td>
<td>97.00</td>
</tr>
<tr>
<td>Sodium selenite raw material powder</td>
<td>1.00 × 10⁻³</td>
<td>9.60 × 10⁻⁶</td>
<td>9.89 × 10⁻⁶</td>
<td>0.52</td>
<td>96.00</td>
</tr>
<tr>
<td>Antioxidant Vitafit Selenium tablets</td>
<td>1.00 × 10⁻³</td>
<td>9.70 × 10⁻⁵</td>
<td>1.00 × 10⁻⁵</td>
<td>0.56</td>
<td>97.00</td>
</tr>
</tbody>
</table>

For Carbon paste electrode, HSeO<sub>3</sub><sup>-</sup> > SCN<sup>-</sup> > SO<sub>4</sub>²⁻ > S²⁻ > NO<sub>3</sub>⁻ > SO<sub>3</sub>²⁻ > SeO<sub>4</sub>²⁻ > Br⁻ > Cl⁻ > SO<sub>4</sub>²⁻ > Br⁻ > Cl⁻ > SO<sub>4</sub>²⁻ > SeO<sub>4</sub>²⁻ > S²⁻ at pH 6.47, and SeO<sub>2</sub>²⁻ > SCN<sup>-</sup> > NO<sub>3</sub>⁻ > SeO<sub>4</sub>²⁻ > Br⁻ > Cl⁻ > SO<sub>4</sub>²⁻ > S²⁻ at pH 11.00.
to 103.0%. The electrode was also used for the determination of selenite in raw material powder Na₂SeO₃ with recovery percents (95.0–98.9%).

3.6.2. Determination of selenite in selenite/selenate mixture

It is known that selenite and selenate are the most mobile and biogeochemically important forms of selenium. A solution was prepared by mixing definite amounts of selenite and selenate solutions, and the pH was adjusted with buffer of pH 6.47. The electrode under investigation (Table 2), composed of 2.0% CoTMeOPP and TCP as plasticizer, is successfully able to determine the concentration of selenite in the presence of selenate with a percentage of recovery ranging from 96.0% to 101.0% (Table 5).

3.6.3. Determination of selenite in VitaFit Selenium antioxidant tablets

The tablet weighing 1.3348 g was ground well then dissolved in deionized water and transferred to a 250-ml volumetric measuring flask. The potential of this solution is measured by the new selenite-selective electrode, then standard additions are made and the potential changes are recorded. From these potential values the quantity of selenite is calculated. The results are in a good agreement with those obtained by inductive coupled plasma (ICP-AES) measurements (Table 5).

3.6.4. Potentiometric titrations

Selenite was previously determined argentometrically by Masson [43]. The lower solubility of silver selenite salt (−log \( K_{sp} \) = 14.74–15.58) is sufficient to produce analytically useful titration curves [44–46]. Thus, the newly developed sensor was successfully used as indicator electrode for the titration of selenite with silver nitrate at pH 6.47. For this, 1, 3, 5, and 8 ml of 0.01 M selenite solution were transferred into the titration cell and completed to 25 ml with buffer of pH 6.47 and titrated against 0.01 M silver nitrate solution.

3.6.5. Statistical treatment of the results

The calculated \( F \) values were less than the tabulated \( F \) value (6.39) where \( v_1 = 4 \) and \( v_2 = 4 \) at 95% confidence level. \( t \)-Test [47] was also done at 99.9% confidence level (tabulated \( t \) = 8.61) and

---

**Table 6**

<table>
<thead>
<tr>
<th>Type of electrode</th>
<th>F-test</th>
<th>t-Test</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVC vs. CMCP</td>
<td>3.67</td>
<td>5.01</td>
</tr>
<tr>
<td>PVC vs. CW</td>
<td>4.23</td>
<td>5.46</td>
</tr>
<tr>
<td>CMCP vs. CW</td>
<td>2.24</td>
<td>4.03</td>
</tr>
</tbody>
</table>

Tabulated \( F \) value = 6.39. 
Tabulated \( t \) = 8.61.

---

**Table 7**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Recovery, %</th>
<th>F-test</th>
<th>t-Test</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure solution</td>
<td>97.6</td>
<td>1.133</td>
<td>4.98</td>
</tr>
<tr>
<td>Selenite raw material powder</td>
<td>99.0</td>
<td>1.012</td>
<td>1.56</td>
</tr>
<tr>
<td>Selenite/selenate mixture</td>
<td>100.5</td>
<td>0.909</td>
<td>5.28</td>
</tr>
<tr>
<td>VitaFit antioxidant tablet</td>
<td>99.5</td>
<td>1.023</td>
<td>2.57</td>
</tr>
</tbody>
</table>

---

**Table 8**

<table>
<thead>
<tr>
<th>Ion recognition</th>
<th>Slope, mV</th>
<th>Detection limit, M</th>
<th>Linear range, M</th>
<th>Response time, s</th>
<th>Interfering ions</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>4,6-dibromo-piaseleone</td>
<td>−23.6</td>
<td>1.00 × 10⁻⁶</td>
<td>1.00 × 10⁻⁶ to 1.00 × 10⁻¹</td>
<td>–</td>
<td>–</td>
<td>[8]</td>
</tr>
<tr>
<td>HgSeO₃ or a mixture of HgSeO₃ and HgCl₂</td>
<td>−29.5</td>
<td>6.00 × 10⁻⁵</td>
<td>6.00 × 10⁻⁵ to 1.00 × 10⁻¹</td>
<td>–</td>
<td>–</td>
<td>[7]</td>
</tr>
<tr>
<td>1,2-phenylene-diamine selen complex PIS</td>
<td>−21.0</td>
<td>1.00 × 10⁻⁵</td>
<td>1.00 × 10⁻⁵ to 1.00 × 10⁻¹</td>
<td>180</td>
<td>Cl⁻ , Br⁻</td>
<td>[10]</td>
</tr>
<tr>
<td>Ag₂Se and Cu₂S</td>
<td>−28.0</td>
<td>1.00 × 10⁻⁶</td>
<td>1.00 × 10⁻⁶ to 1.00 × 10⁻¹</td>
<td>60–120</td>
<td>S²⁻ , Ag⁺ , Cu²⁺</td>
<td>[9]</td>
</tr>
<tr>
<td>Diallyl(dimethyl) ammonium chloride</td>
<td>−19.0</td>
<td>1.00 × 10⁻⁶</td>
<td>1.00 × 10⁻⁶ to 1.00 × 10⁻¹</td>
<td>240–300</td>
<td>–</td>
<td>[11]</td>
</tr>
<tr>
<td>Ag₂Se</td>
<td>−28.0</td>
<td>4.50 × 10⁻⁷</td>
<td>6.00 × 10⁻⁷ to 1.00 × 10⁻⁴</td>
<td>&lt;90</td>
<td>SO₄²⁻ , Ni²⁺</td>
<td>[12]</td>
</tr>
<tr>
<td>CoTMeOPP</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PVC membrane (pH 6.47)</td>
<td>−57.0</td>
<td>3.40 × 10⁻⁵</td>
<td>5.50 × 10⁻⁵ to 1.00 × 10⁻²</td>
<td>15</td>
<td>SCN⁻</td>
<td>This work</td>
</tr>
<tr>
<td>PVC membrane (pH 11.00)</td>
<td>−26.0</td>
<td>4.70 × 10⁻⁵</td>
<td>6.60 × 10⁻⁵ to 1.20 × 10⁻²</td>
<td>15</td>
<td>SCN⁻</td>
<td>This work</td>
</tr>
<tr>
<td>Carbon paste (pH 6.47)</td>
<td>−65.0</td>
<td>3.50 × 10⁻⁵</td>
<td>5.20 × 10⁻⁵ to 1.20 × 10⁻²</td>
<td>15</td>
<td>SCN⁻</td>
<td>This work</td>
</tr>
<tr>
<td>Carbon paste (pH 11.00)</td>
<td>−29.4</td>
<td>7.70 × 10⁻⁵</td>
<td>8.70 × 10⁻⁵ to 1.20 × 10⁻²</td>
<td>15</td>
<td>SCN⁻</td>
<td>This work</td>
</tr>
<tr>
<td>Coated Ag wire (pH 6.47)</td>
<td>−61.8</td>
<td>9.10 × 10⁻⁵</td>
<td>1.20 × 10⁻⁵ to 4.40 × 10⁻⁵</td>
<td>10</td>
<td>SCN⁻</td>
<td>This work</td>
</tr>
<tr>
<td>Coated Ag wire (pH 11.00)</td>
<td>−39.0</td>
<td>3.90 × 10⁻⁶</td>
<td>7.90 × 10⁻⁶ to 1.30 × 10⁻³</td>
<td>10</td>
<td>SCN⁻</td>
<td>This work</td>
</tr>
</tbody>
</table>
the results are shown in Tables 6 and 7. The method applied with the use of conductive electrode does not exhibit significant differences in comparison to with the official method which reflects the accuracy and precision of this method.

4. Conclusion

New selenite-selective electrodes that are highly selective and sensitive to selenite have been developed using CoTMeOPP as electroactive material. Experiments show that the PVC based electrode containing 2.0% CoTMeOPP, and TCP as plasticizer exhibits linear response for the monovalent selenite ion HSeO₃⁻ with slope −57.00 mV at pH 6.47 and linear response for the divalent selenite SeO₃²⁻ with slope −26.00 mV at pH 11.00. The detection limit is 3.40 × 10⁻⁵ and 4.70 × 10⁻⁵ M at pH values 6.47, and 11.00 respectively and the response time is within 5–15 s. The carbon paste electrode exhibits linear response for monovalent selenite of slope −65.00 mV with detection limit 3.50 × 10⁻⁵ M at pH 6.47 and linear response for divalent selenite of slope −29.40 mV with detection limit 7.70 × 10⁻⁵ M at pH 11.00. Table 8 compares the slope, response time, detection limit, and major interfering ions of the proposed selenite electrodes with those of selenite-selective electrode, Pure Appl. Chem. 74 (2002) 923–954.


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