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Determination and Speciation of Tellurium Hazardous Species in Real and Environmental Samples

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Although tellurium is relatively rare in the environment, it is required in a number of important industrial applications such as semiconductor manufacturing, rubber industry, and solar panels. However, it has several environmental hazards and can be accumulated in the body and induce several health issues. It was reported that the toxicity of tellurium depends on its oxidation state with tellurite being the most toxic form. Determination and speciation of tellurite in real and environmental samples have been considered of primary analytical interest. Here, we have developed a simple technique for the analysis of tellurite in different chemical environments without the need for special pre-separation that is currently utilized in the standard quantitative techniques. This method depends on a carbon paste electrode modified with iron(II) phenanthrolin diclofenac ($FephenD_2$) and iron (II) bipyridyl diclofenac ($FebipyD_2$) as electroactive phases in carbon paste. The sensors have the following features: low detection limit (1.42×10^{-5} mol/L), long life time of more than 2 months, high selectivity to tellurite in the presence of a wide range of inorganic and organic ions, high thermal stability (22-56 ºC) and short response time of only 10-20 seconds. The sensors were successfully applied in the determination of tellurite in environmental and biological samples such as waste water, human serum, tellurite culture media, synthetic tellurite-cefotaxime and tellurite/tellurate mixtures. The results show high recovery rates, selective and highly reproducible response, indicating the suitability of the proposed sensors for practical applications.

Keywords: Tellurium, Carbon paste electrode, Environmental samples, Speciation analysis.

1. INTRODUCTION

Tellurium is considered relatively rare in the environment but is known to be extremely toxic. It demonstrates properties similar to those of heavy elements known to be toxic to humans [1]. Tellurium naturally exists in several oxidation states both in organic and inorganic forms. It belongs to the same family as sulfur and selenium and shares some common chemical properties. Specifically, tellurium analogues of organosulfur functional groups are commonly used in the synthesis of

metalorganic vapor phase epitaxy. It also exists in several inorganic species including telluride (Te II), tellurite (Te IV) and tellurate (Te VI). Although tellurium is not widely used in industry, it is required in a number of important industrial applications such as semiconductor manufacturing, glass fiber, rubber industry, optical devices, thermoelectric devices, metallurgy, ceramic colors and solar panels that increases its level in the environment [2]. In microbiology, tellurite-resistant bacteria are obtained by the addition of sodium tellurite to the growth medium [3]. Tellurium compounds need to be handled with care as clinical manifestations of tellurium toxicity are observed at very low concentrations [4]. Furthermore, emission of inorganic tellurium compounds in the environment may induce serious problems due to both acute and chronic toxicity of that element [5].

Tellurium can be accumulated in kidney, spleen, heart and liver and its threshold should not exceed 2.25-2.5 mg/kg. If its concentration exceeds 2.5 mg/kg, it could induce the degeneracy of liver and kidney [6]. Therefore, the Ocupational Safety and Health Administration (OSHA) has set the permissible limit for the exposure of workers to tellurium compounds in the workplace as 0.1 mg/m^3 over an 8-hour workday. Furthermore, the toxicity of tellurium, bioavailability and environmental transport mechanism highly depend on its chemical form and oxidation state. For example, tellurite (IV) is 10-fold more toxic than tellurate (VI) [7]. Tellurite is toxic to more micro-organisms, especially gram negative bacteria. However, it is well-known that tellurite-resistant bacteria can be found in nature having the ability to reduce tellurite to its less toxic elemental form Te^0 [8,9]. The reduced tellurite is deposited as black particles within the cell. The presence of a high concentration of tellurite results in the growth of black colonies of the resistant cells which can be used for the isolation of pathogens including *Corynebacterium diphtheriae*, *Staphylococcus aureus*, *Vibrio cholerae* and *Shigella* spp [10,11].

Tellurium concentration in geological, environmental and biological samples is generally at trace level [12]. Therefore, determination of tellurium is difficult and almost any environmental sample needs a pre-concentration step prior to instrumental measurements. For these reasons, analytical chemists have made great efforts to develop a method for tellurium speciation analysis. Only few analytical techniques have been applied for the speciation and determination of tellurium in environmental and biological samples such as volumetric [13,14], spectral [15-20], chromatographic [21-28] and electrometric [29-33] methods. Most of these methods involve several time-consuming extraction steps, derivatization reactions that are liable to various interferences. A new-generation of potentiometric sensors that are currently used for the determination of several analytical species has been developed using chemically modified carbon paste electrodes (CMCPEs) [34-37]. Unlike other ion selective electrodes (ISEs), these sensors are simple to prepare, can be regenerated easily and do not suffer from the need to internal solution. They also give stable response with a very low ohmic resistance [38,39], corresponding to the formation of a very thin film of a pasting liquid coated onto small particles of graphite powder [40].

There is an increasing need for the development of rapid and sensitive tellurite ion selective electrodes. However, to the best of our knowledge only one study exists under this category [41]. This tellurite ion selective electrode was constructed by comprising a mixture of $HgTeO_3/Hg_2Cl_2$ (1:1) with an internal contact of Hg metal in which a Pt wire was immersed [41]. However, this sensor can only detect tellurite at a concentration of 1.0×10^{-5} mol/L which is higher than tellurite concentration in real

samples. Besides, tellurite was determined in pure solution which is very different from environmental samples that has many sources for interference. In addition, the chemistry of tellurite highly depends on the pH of the solution, which again was not studied in this work. It was therefore felt worthwhile to develop a more accurate sensor for tellurite ions using iron (II) phenanthrolin diclofenac ($FephenD_2$) (Figure 1) and iron bipyridyl diclofenac ($FebipyD_2$) as an electroactive phases in carbon paste.

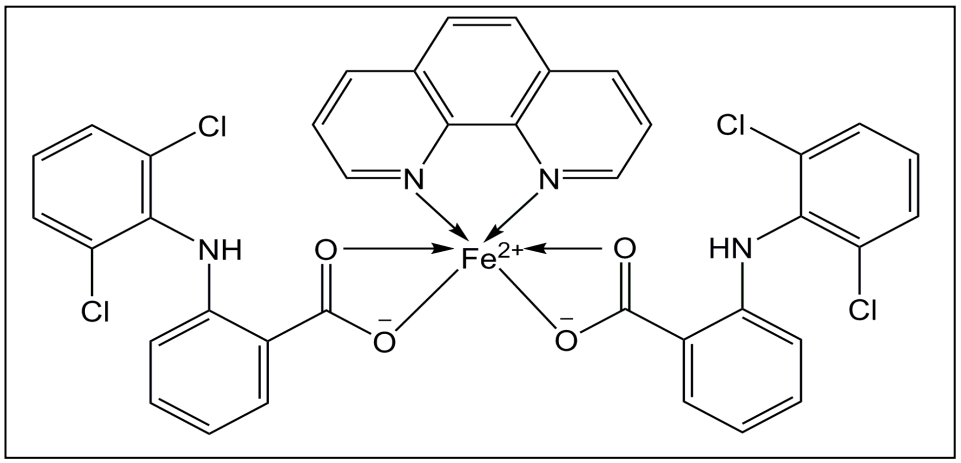

Figure 1. Chemical structure of $FephenD_2$

Macrocycles are widely used in ISEs and are carefully selected based on a few criteria. First, they should provide high complexation or extraction selectivity for a particular anion and enough conformational flexibility for fast ion exchange. In addition, they must have high lipophilic properties in order to prevent its leaching from the paste. Moderate to high molecular weight is also required to allow high mobility. The selected macrocyclic ionophores in this study ($FephenD_2$ and $FebipyD_2$) have attracted interest in the field of construction and design of new sensors capable of detecting definite anions of compatible dimensions in their electron rich heart cavity [42,43]. In addition, these macrocyclic ionophores have several other features such as high stability and selectivity of its metal ion complex, its solubility and high ability to extract tellurite ion into the paste phase. Therefore, $FephenD_2$ and $FebipyD_2$ were explored as active materials in the fabrication of carbon paste sensors for the determination of tellurite.

In the current work, novel and sensitive sensors for tellurite ions as a function of pH were developed. The fabricated sensors were characterized at different concentration range of tellurite, response time and selectivity. The proposed sensors were used in determination of tellurite in pure solutions, waste water, human serum, tellurite culture media, synthetic tellurite/cefotaxim samples and tellurite/tellurate mixtures. In addition, the method can be used for the indirect determination of tellurate by chemical reduction of tellurate to tellurite that determined by proposed sensors.

2. EXPERIMENTAL

2.1. Apparatus and reagents

Potential measurements were carried out using a Jenway 3010 (England) digital pH/mV meter. A WTW packed saturated calomel electrode (SCE) was used as the outer reference electrode. The pH

of the buffer solutions was monitored with a Jenway pH glass electrode. The temperature of the test solution was controlled by a techne circulator thermostat Model C-100 (Cambridge-England) while spectrophotometric measurements were carried out on a CARY 50 probe UV-Visible spectrophotometer (Varian).

Anhydrous sodium tellurite Na_2TeO_3 and 2,2´-bipyridyl were purchased from BDH chemicals Ltd., (England). 1,10-phenanthrolin was obtained from Riedel-de Haën (Germany). Diclofenac sodium was provided by Delta Pharma (Egypt). Tryptone was obtained from Oxford Laboratory Reagents (India), cefotaxime sodium was purchased from Pfizer Company for Pharmaceutical Industries (Egypt). Graphite powder, yeast extract, cetyltrimethylammonium bromide (CTAB), sodium tetraphenylborate (NaTPB) and the plasticizers, dibutyl phthalate (DBP), dioctyl phthalate (DOP), tricresyl phosphate (TCP), bis(2-ethylhexyl) adipate (EHA), 2-Nitrophenyl octyl ether (NPOE) and 2-ethylhexyl salicylate (EHS) were purchased from Sigma-Aldrich chemical company (USA). Potassium tetraphenylborate (KTPB) used in this study was prepared by addition of 100 mL 10^{-2} mol/L KCl to 100 mL 10^{-2} mol/L NaTPB. All experiments were carried out using double distilled water.

2.2. Solutions

Stock solution of 0.01 mol/L of sodium tellurite was prepared by dissolving 0.5539 g Na_2TeO_3 in hot double distilled water and then completed to 250 mL. The solution was kept in glass bottles at room temperature. Working solutions of low concentrations were prepared daily by appropriate dilution.

Acetate buffer solutions of pH 3.42, 3.72, 4.27, 4.63, 4.80, 4.99 and 5.23 were prepared by mixing 95, 90, 70, 50, 40, 30 and 20 mL of 0.1 mol/L of acetic acid with 5, 10, 30, 50, 60, 70 and 80 mL of 0.1 mol/L sodium acetate, respectively [44]. A buffer solutions consisting of sodium chloride and sodium hydroxide of different pH values (8.6, 8.75, 9.1, 9.25 and 10.2) were prepared by adding the required volume of 0.1 mol/L NaOH to 50 mL of 0.1 mol/L NaCl then completed to 100 mL using double distilled water.

To investigate the selectivity of the proposed sensors towards inorganic and organic anions, that usually co-exist in real samples of tellurite, 0.1 mol/L of sodium or potassium salt of each of the following anions was prepared: F^-, Cl^-, Br^-, I^-, NO_2^-, NO_3^-, SO_4^{2-}, SeO_4^{2-}, TeO_4^{2-}, $S_2O_3^{2-}$, $S_2O_8^{2-}$, CH_3COO^-, $C_2O_4^{2-}$ and cefotaxime.

2.3. Preparation of ionophores

The preparation of ionophores, iron (II) phenanthrolin diclophenac ($FephenD_2$) and iron (II) bipyridyl diclophenac ($FebipyD_2$) was achieved in two steps, firstly formation of soluble red complexes of $[Fe(phen)_3]^{2+}$ and $[Fe(bipy)_3]^{2+}$ by addition of 100 mL of 0.01 mol/L $(NH_4)_2Fe(SO_4)_2$ to 100 mL of 0.03 mol/L of 1,10-phenanthrolin or 0.03 mol/L of 2,2´-bipyridyl. After that, the cationic complexes were coupled with 100 mL of 0.02 mol/L of diclophenac anion to form highly insoluble ionophores.

The resulting precipitates were left in contact with their mother liquor overnight to assure complete coagulation. The precipitates were then filtered and washed thoroughly with distilled water and petroleum ether then dried at room temperature and ground to fine powder.

2.3. Sensors Preparation

The sensors were prepared as described elsewhere [45]. Briefly, the modified paste was made by mixing the active ingredients thoroughly in a mortar with pestle. This includes mixing a certain amount of the ionophore with the graphite powder followed by the addition of the sought plasticizer till the slurry becomes homogeneous. The prepared paste was then packed into the hole of the electrode body. The carbon paste was smoothed by rubbing the electrode against a sheet of paper until it had a shiny appearance and used directly for potentiometric measurements after one day of preparation. A fresh surface was obtained by gently pushing the stainless steel screw forward and polishing the new carbon paste surface with paper to obtain a shiny new surface.

2.4. Calibration of the sensors

For construction of the calibration graph, the sensor and reference electrode were immersed in 50 mL the corresponding buffer solution and suitable increments of standard tellurite solution were added. The emf values were recorded at 25±1 ºC then plotted versus the negative logarithm of the tellurite concentration ($pTeO_3^{2-}$).

2.5. Selectivity

Potentiometric selectivity coefficients were evaluated by the matched potential method [46,47]. In this method, selectivity coefficient $K^{MPM}_{tellurite,J}$, is given by the following equation:

$$K^{MPM}_{tellurite,J} = \frac{\Delta a_{tellurite}}{a_B} = \frac{a'_{tellurite} - a_{tellurite}}{a_B}$$

Where $\Delta a_{tellurite}$ is determined by measuring the change in potential upon increasing the concentration by a definite amount of the primary ion activity from an initial value of $a_{tellurite}$ to $a'_{tellurite}$ and a_B represents the activity of the interfering ion added to the same reference solution of activity $a_{tellurite}$ which brings about the same change in potential. The activity of tellurite as the reference solution was taken as 1.0×10^{-4} mol/L in this study.

2.6. Potentiometric determination

Potentiometric determination of tellurite ions was carried out using the standard addition method [48]. In this method, the proposed sensor is submerged into 50 mL of the sample solution

containing an unknown concentration (typically in the range of 10^{-7} –5×10^{-4} mol/L) of tellurite and the equilibrium potential was recorded. This is followed by the addition of small increments of 1.0×10^{-3} mol/L of standard tellurite solution into the test solution and the corresponding equilibrium potential (E_s) was obtained with each addition. From the potential change $\Delta E = (E_u - E_s)$ one can determine the concentration of the test sample using the equation:

$$C_X = C_S\left(\frac{V_S}{V_X + V_S}\right)\left(10^{\,n(\Delta E/S)} - \frac{V_S}{V_X + V_S}\right)^{-1}$$

Where C_x and V_x are the concentration and volume of unknown, respectively, C_s and V_s are the concentration and volume of standard, respectively, S is the slope of the calibration graph and ΔE is the change in millivolt due to the addition of standard.

2.7. Sample analysis

Spiked waste water samples: The analysis of tellurite in an industrial waste water was carried out by spiking waste water by known concentration of tellurite. The samples were analyzed using tellurite sensors and the results were compared to the reference method.

Spiked human serum samples: For the analysis of tellurite in spiked human serum samples, 10^{-3} mol/L of tellurite solution was spiked by introducing 1 mL of serum in 50 mL volumetric flask, then the samples were diluted and potentiometrically analyzed using tellurite sensors.

Tellurite culture media: The determination of tellurite in tellurite culture media is performed by preparation of tellurite agar (Hoyle) [49] by dissolving 1.0 g of yeast extract, 0.5 g NaCl, 1.0 g tryptone and 0.35 g of sodium tellurite in 100 mL volumetric flask. The content of tellurite in this culture medium was determined by standard addition method using the present electrodes.

Synthetic tellurite/cefotaxime samples: Recently, tellurite was used to enhance the antibacterial effect of some antibiotics, where tellurite and cefotaxime act synergistically against *E. coli* [50]. For this reason, the samples containing tellurite and cefotaxime were subjected to potentiometric determination of tellurite by using the proposed sensors.

Tellurate samples: tellurate can be reduced to tellurite by heating with conc. HCl [14] and total amount of tellurite determined using proposed sensor.

3. RESULTS AND DISCUSSION

3.1. Structural characterization of the ionophores.

The chemical compositions of the ionophores were confirmed by C, H, and N elemental analysis using automatic CHN analyzer (Vario El Ementar, Germany) in National Research Center, Dokki, Giza. The C, H, and N percentages are 56.48, 1.97, 7.14 and the corresponding calculated ones are 56.87, 3.55, 6.63, respectively, in case of $FephenD_2$, whereas in case of $FebipyD_2$ the percentage

values found are 55.29, 1.93, and 7.09 and the calculated values are 55.60, 3.65, and 6.82 for C, H, and N, respectively.

In order to clarify the bonding modes of diclofenac (D), and 1,10-phenanthroline (Phen) in the studied ionophore [FephenD$_2$], its spectrum was compared with those of the free ligands and their complexes, FeD$_2$(OH$_2$)$_2$ and [Fe(Phen)$_3$]$^{2+}$ as well as more closely related complex, [NiphenD$_2$] [51]. The shift of the ν(C=N)$_{phen}$ mode (1642 cm^{-1}) of phen to lower wave numbers, 1627 [Fe(Phen)$_3$]$^{2+}$ and 1630 cm^{-1} [FePhenD$_2$] was taken as an evidence for the participation of Phen in the coordination spheres of the metal ion. Comparison between [FePhenD$_2$] and [Fe(Phen)$_3$]$^{2+}$ complexes reveals the presence of two additional bands corresponding to the asymmetric and symmetric stretching mode of COO group at 1579 and 1426 cm^{-1} that are close to the analog nickel complex. In addition, the Δ (= ν(C=O)$_{asym}$-ν(C=O)$_{sym}$) value of 153 cm^{-1} is an indicative for the bi-dentate nature of the carboxylate group, Figure 2. Another important result came from conductance measurements where low molar conductance values were collected for the ionophores under study compared with the previously reported values, indicating their non-electrolytic nature.

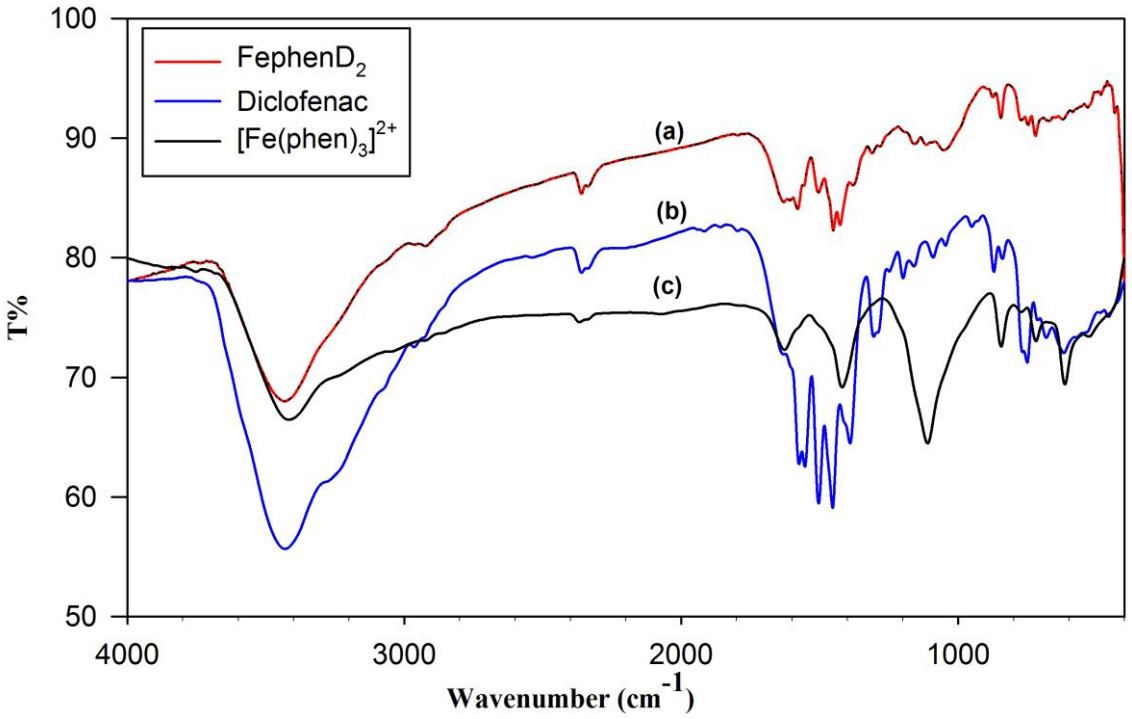

Figure 2. FT-IR absorption spectra of FephenD$_2$ (a), diclofenac (b), and [Fe(phen)$_3$]$^{2+}$ (c).

3.2. Factors affecting the performance of tellurite sensors

3.2.1. Effect of pH on the electrodes response

Calibration graphs (electrode potential vs. −log [Tellurite]) were constructed using standard tellurite solution adjusted to different pH values in the range of 3.42 to 10.2 using acetate and NaOH/NaCl buffers. These data were collected using paste electrodes comprising FePhenD$_2$ and FebipyD$_2$ as ionophores. The calibration graphs shown in Figure 3 and summarized in Table 1 exhibit

slopes in range of -84 to -50 mV/concentration decade for tellurite samples buffered at pH 3.42-5.23. This means that the electrode is detecting the monovalent anion at this pH range. The systematic increase of the pH of tellurite samples leads to a gradual decrease in the slope of the calibration graphs reaching -31 to -45 mV at pH 8.6-10.23, indicating that the electrode is responding to a divalent anion. This is consistent with the nature of tellurous acid being a diprotic acid with pK_1=2.56 and pK_2=7.74 [52], thus:

$$H_2TeO_3 \rightleftharpoons H^+ + HTeO_3^- \qquad pK_1 = 2.56$$

$$HTeO_3^- \rightleftharpoons H^+ + TeO_3^{2-} \qquad pK_2 = 7.74$$

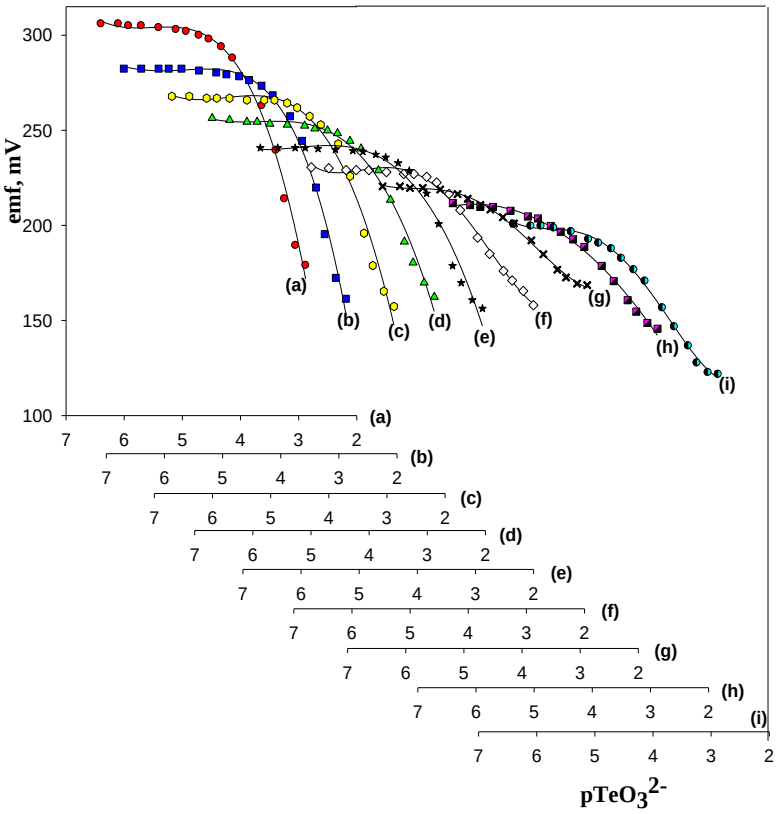

Figure 3. Calibration graphs of FephenD$_2$ CMCPE at different pH values (a) 3.42, (b) 3.72, (c) 4.72, (d) 4.63, (e) 4.80, (f) 5.23, (g) 8.6, (h) 9.1 and (i) 10.2.

Table 1. Slope, linear range, detection limits of FephenD$_2$ and FebipyD$_2$ CMCPEs electrode containing 3% ionophore and 48.5% DBP at different pH values.

pH	Slope (mV/decade)	Linear range (mol/L)	LOD (mol/L)	RSD**	r^2
		FephenD$_2$ CMCPE			
3.42	-84.38±0.45	4.68×10^{-5} –1.32×10^{-3}	4.21×10^{-5}	0.94	0.945
3.72	-82.63±0.98	4.68×10^{-5} -1.32×10^{-3}	4.53×10^{-5}	2.07	0.943
4.27	-76.27±0.52	4.68×10^{-5} –1.32×10^{-3}	4.21×10^{-5}	1.18	0.960
4.63*	-62.32±1.04	4.68×10^{-5} –1.32×10^{-3}	4.21×10^{-5}	3.35*	0.977
4.80	-57.95±1.11	4.68×10^{-5} –1.32×10^{-3}	4.21×10^{-5}	3.34	0.976
5.23	-39.10±0.71	2.86×10^{-5}–1.32×10^{-3}	2.05×10^{-5}	3.14	0.995
8.60	-31.14±0.33	1.17×10^{-5}–5.71×10^{-4}	8.65×10^{-6}	1.84	0.982

9.10*	-31.37±0.84	1.92×10^{-5}–1.32×10^{-3}	1.33×10^{-5}	4.63	0.986
10.20	-37.76±0.72	1.17×10^{-5}–1.32×10^{-3}	1.00×10^{-5}	3.31	0.985
		FebipyD$_2$ CMCPE			
4.63	-73.69±0.21	7.28×10^{-5} –1.34×10^{-3}	6.29×10^{-5}	0.49	0.976
4.80	-70.34±0.51	7.28×10^{-5} –1.34×10^{-3}	5.59×10^{-5}	1.26	0.981
*4.99	-59.73±0.92	4.68×10^{-5} –1.34×10^{-3}	4.46×10^{-5}	2.68	0.983
5.23	-50.13±0.10	2.86×10^{-5} –1.34×10^{-3}	2.32×10^{-5}	0.33	0.985
8.75	-37.13±0.76	1.92×10^{-5} –1.34×10^{-3}	1.59×10^{-5}	3.52	0.992
*9.25	-34.66±0.64	1.92×10^{-5} –1.34×10^{-3}	1.54×10^{-5}	3.17	0.991
10.23	-45.28±0.96	1.92×10^{-5} –1.34×10^{-3}	1.47×10^{-5}	3.67	0.988

*The selected pH of the tellurite solutions.

**Relative standard deviation (three determinations).

pH adjusted using 10^{-3} mol/L acetate and NaOH/NaCl buffers

The distribution curve of tellurous acid species as a function of pH, Figure 4, indicates that the monovalent $HTeO_3^-$ ions are the predominant species within the pH range 4.0 to 5.5, whereas the divalent TeO_3^{2-} anions are the predominate species at pH values higher than 8.0. It is, thus, important to measure the electrode response at fixed pH values using a suitable buffer.

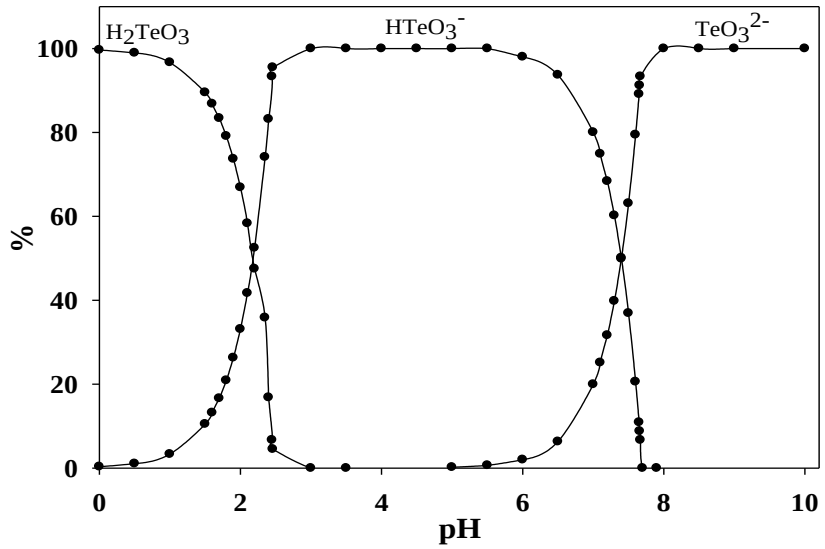

Figure 4. Distribution curves of tellurous acid species as a function of pH.

3.2.2. Potentiometric behavior of tellurite sensors

When using ion selective electrodes in analytical determination, there are several parameters that should be considered as they may have a significant impact on the electrode response towards the analyte under investigation. To name a few, the composition of the carbon paste, the amount of ionophore and type of the plasticizer can have a major effect on the response of the electrode. In addition, electrodes additives may be used to improve the electrochemical performance of the

electrode. Life span is recognized as one of the most important factors that determines the suitability of new sensors in real applications. It is also known that the operation conditions may have a significant effect on the sensor response. This includes temperature, response time, presence of interferents, etc. All of these parameters were studied according to the recommendations suggested by IUPAC [53].

FephenD_2 and FebipyD_2 as ionophores were found to have high sensitivity towards tellurite over several other anions. These complexes are insoluble in many organic solvents, particularly tetrahydrofuran. Therefore, it will be very difficult to prepare polymeric membrane electrode because of the lack of an appropriate solvent. Carbon paste, on the other hand, is a great medium for the dispersion of these ionophores. This work presents a strategy for thoroughly investigating the performances of carbon pastes containing these ionophores as modifiers for the determination of tellurite in aqueous solutions. It is widely accepted that the selectivity, linear range and sensitivity of CPE depend significantly on the paste composition [54], and nature of solvent mediator [55,56].

In preliminary experiments, carbon paste electrodes with and without ionophores were prepared and tested. It was found that the paste with no ionophore displayed no measurable response towards tellurite anion. The addition of the proposed ionophores of FephenD_2 and FebipyD_2 as electroactive modifiers results in Nernstian response towards tellurite ions even in the presence of a wide range of other anionic species.

In order to identify the optimum composition of the electrode, different amounts of FephenD_2 and FebipyD_2 ionohpores were used in different pastes. The potential response of the sensors was tested over a wide concentration range, 4.0×10^{-7}-1.0×10^{-2} mol/L, of tellurite solution and the results are shown in Table 2. Experimental trials showed that optimum response is obtained by increasing the amount of ionophore up to certain percentages, as indicated by the Nernstian behavior of the electrode. However, further increase of the ionophores over this percentage shifts the electrode from Nernstian behavior and reduced slope is obtained. This is likely due to some inhomogenities and possible saturation of the electrode because of the high concentration of the ionophore [57]. As can be seen from data in Table 2 and calibration graphs depicted in Figure 5, at pH 4.63, carbon paste sensor plasticized with DBP and containing 1.0% FephenD_2 has a slope of -75.3 mV and the paste containing 2.0% has a slope of -55.2 mV while 3.0% has -58.3 mV which is near to exact Nernstian value and the 5% FephenD_2 paste has diminished response of -39.7 mV slope. However, at pH 9.10, the increase in the amount of the ionophore improves the sensitivity of the electrode towards tellurite ions and the slope decreased from -65.0 mV for 1% ionophore to -31.3 mV for 3.0 % ionophore to become near to Nernstian value but with lack of reproducibility. Increasing the amount of ionophore (paste containing 5.0%) leads to Nernstain slope with high detection limit. The linear range, detection limit and reproducibility were improved by trying different solvent mediators.

Just like FephenD_2, the amount of FebipyD_2 in the paste at pH 4.99 have a strong effect on the response of the electrode. DBP plasticized paste containing 1.0% FebipyD_2 has a slope of -66.4 mV with a wide linear dynamic range and low detection limit. Increasing the amount of FebipyD_2 ionophore to 3.0 % results in near-Nernstian slope of -58.7 mV but with narrow linear range. Further increase of the ionophore to 5.0% of FebipyD_2 leads to a lower response of -50.4 mV slope. The response of FebipyD_2 modified carbon paste electrodes was also studied at a higher pH of 9.25. Different amounts of the ionophore were incorporated in graphite/DBP matrix and the potential

response of the electrodes was measured. The data depicted in Table 2 indicate that the slope of calibration curves increases by increasing the percentage of ionophore until 2.0% is reached. However, only at a concentration of 3.0% FebipyD$_2$ the electrode shows Nernstian slope of -34.1 mV with a linear range of 1.92×10^{-5}-1.00×10^{-2} mol/L. Further addition of ionophore (5.0%) results in a diminished response and reduced the linear dynamic range.

It is important to point out that the nature of the solvent (plasticizer) has a direct influence on the mobility of ions and provides the appropriate conditions for the incorporation of tellurite ion into the paste prior to its exchange with the soft ionophore. Therefore, the selection of the plasticizer is an important decision for the fabrication of the carbon paste electrode. The plasticizer has to meet several requirements, such as high lipophilicity, high molecular weight and high chemical stability. In addition, the plasticizer should have In addition, the plasticizer should have high capacity to dissolve the substrate and other additives present in the paste. Since the nature of the plasticizer influences the electrical properties of the paste and the mobility of the ionophore molecules, it is expected to play an important role in defining the characteristics of the electrode. It improves the rheology of the electrode and provides liquid channels within the paste which enhances the diffusion of the analyte species and eventually lead to fast response time. Therefore, six different plasticizers namely, DBP, DOP, EHA, TCP, EHS and NPOE were tested with the hope that they can enhance the electrochemical response of the electrode. The results are presented in Table 2.

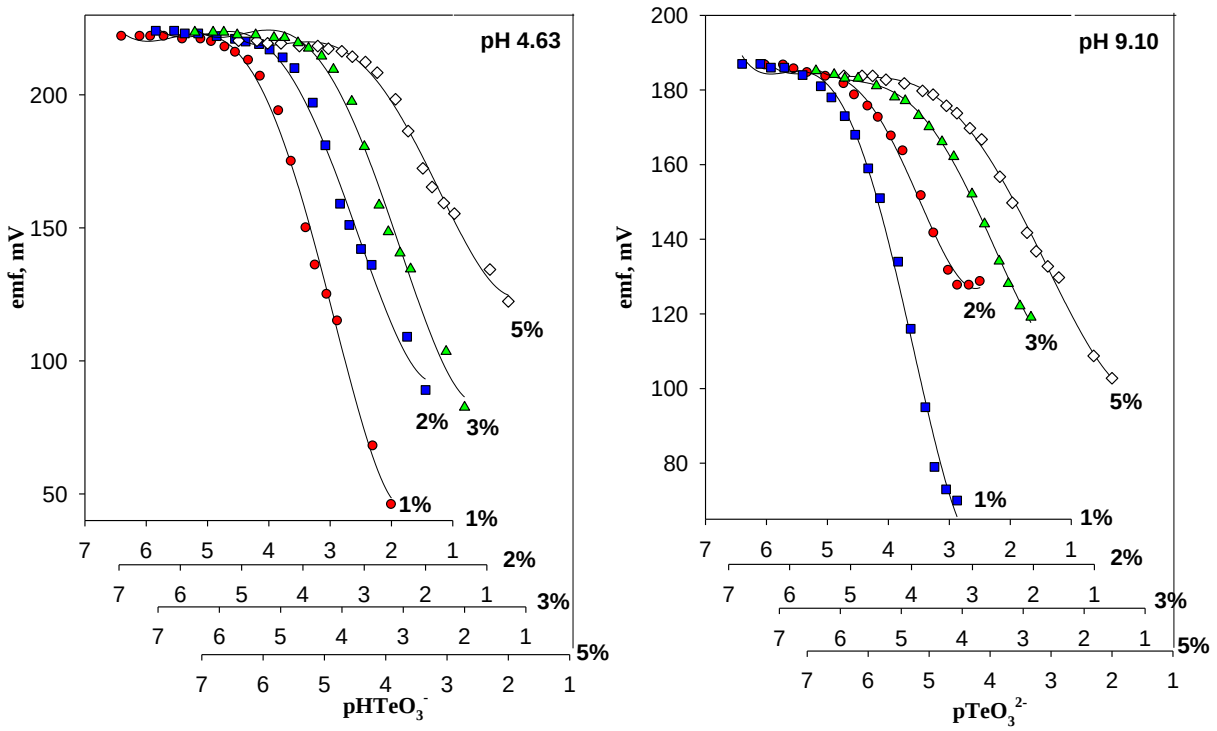

Figure 5. Calibration graphs of FephenD$_2$ CMCPEs using different percentages of ionophore at pH 4.63 and pH 9.10.

For the FephenD$_2$ sensors at pH 4.63, it is observed that DOP, EHA, EHS and NPOE imparted low potentiometric response with slope values -69.5, -76.8, -36.7 and -38.6 mV/decade respectively which is deviated from Nernstian value, while TCP results in improved performance with a near Nernstian slope of -56.7 mV and narrow linear range. Only when using DBP as a plasticizer, the electrode showed Nernstian slope -58.3 mV with a wide linear range 4.68×10^{-5}-1.0×10^{-2} mol/L, and low detection limit 3.99×10^{-5} mol/L, so DBP was selected as a solvent mediator for further studies. Apparently, the electrochemical response is also a function of the pH of the solution. As shown in Figure 6, at pH 9.10, the use of TCP as a plasticizer results in Nernstian slope over a wide concentration range 1.926×10^{-5} to 5.0×10^{-3} mol/L and detection limit 1.42×10^{-5} mol/L with low reproducibility, whereas, other solvent mediators often result in poor potentiometric response with slopes that are highly deviated from the Nernstian value.

Table 2. Composition, slopes, linear ranges and detection limits of calibration curves for tellurite CMCPEs at 25.0±0.1 ºC.

No.	Composition % w/w			Slope±SE (mV/decade)	Linear range (mol/L)	LOD (mol/L)	RSD	r^2
	ionophore	Graphite	plasticizer					
FephenD$_2$ CMCPE				pH 4.63				
1	1.0	49.5	49.5(DBP)	-75.30±0.21	4.68×10^{-5}-1.0×10^{-2}	4.17×10^{-5}	0.48	0.986
2	2.0	49.0	49.0(DBP)	-55.21±0.73	4.68×10^{-5}-1.0×10^{-2}	3.19×10^{-5}	2.27	0.987
3	3.0*	48.5	48.5(DBP)	-58.38±0.45	4.68×10^{-5}-1.0×10^{-2}	3.99×10^{-5}	1.33	0.989
4	5.0	47.5	47.5(DBP)	-39.71±0.51	4.68×10^{-5}-1.0×10^{-2}	2.90×10^{-5}	2.23	0.990
5	3.0	48.5	48.5(DOP)	-69.56±0.87	7.28×10^{-5}-5.0×10^{-3}	5.87×10^{-5}	2.16	0.988
6	3.0	48.5	48.5(EHA)	-76.82±1.19	4.68×10^{-5}-5.0×10^{-3}	2.03×10^{-5}	2.67	0.982
7	3.0	48.5	48.5(TCP)	-56.71±1.05	4.68×10^{-5}-5.0×10^{-3}	4.17×10^{-5}	3.20	0.984
8	3.0	48.5	48.5(EHS)	-36.78±0.33	4.68×10^{-5}-1.32×10^{-3}	2.89×10^{-5}	1.55	0.983
9	3.0	48.5	48.5(NPOE)	-38.61±0.28	4.68×10^{-5}-4.04×10^{-4}	3.54×10^{-5}	1.24	0.981
				pH 9.10				
10	1.0	49.5	49.5(DBP)	-64.05±0.43	1.92×10^{-5}-8.86×10^{-4}	1.54×10^{-5}	1.15	0.975
11	2.0	49.0	49.0(DBP)	-34.01±0.49	1.92×10^{-5}-5.70×10^{-4}	1.54×10^{-5}	2.47	0.981
12	3.0	48.5	48.5(DBP)	-31.37±0.84	1.92×10^{-5}-1.32×10^{-3}	1.33×10^{-5}	4.63	0.986
13	5.0	47.5	47.5(DBP)	-30.22±0.48	7.28×10^{-5}-1.00×10^{-2}	2.37×10^{-5}	2.72	0.995
14	3.0	48.5	48.5(DOP)	-69.04±0.82	2.86×10^{-5}-4.00×10^{-4}	1.19×10^{-5}	2.05	0.978
15	1.0	49.5	49.5(DOP)	-62.68±1.46	1.92×10^{-5}-8.86×10^{-4}	1.53×10^{-5}	3.29	0.982
16	3.0	48.5	48.5(EHA)	-62.50±0.83	2.86×10^{-5}-5.70×10^{-4}	1.42×10^{-5}	2.31	0.979
17	3.0*	48.5	48.5(TCP)	-30.08±0.49	1.92×10^{-5}-5.00×10^{-3}	1.42×10^{-5}	2.80	0.993
18	5.0	47.5	47.5(TCP)	-20.82±0.29	4.68×10^{-5}-1.32×10^{-3}	1.76×10^{-5}	2.38	0.995
19	10.0	40.0	40.0(TCP)	-17.72±0.28	1.92×10^{-5}-1.32×10^{-3}	1.65×10^{-5}	14.62	0.992
20	3.0	48.5	48.5(EHS)	-35.63±0.73	4.68×10^{-5}-1.32×10^{-3}	1.70×10^{-5}	3.64	0.984
21	3.0	48.5	48.5(NPOE)	-42.89±1.19	7.28×10^{-5}-8.86×10^{-4}	2.52×10^{-5}	4.82	0.973
FebipyD$_2$ CMCPE				pH 4.99				
22	1.0*	49.5	49.5(DBP)	-66.44± 0.18	4.68×10^{-5}-1.00×10^{-2}	3.82×10^{-5}	0.46	0.994
23	2.0	49.0	49.0(DBP)	-54.43±0.80	4.68×10^{-5}-1.00×10^{-2}	3.34×10^{-5}	2.54	0.988
24	3.0	48.5	48.5(DBP)	-58.71±0.34	4.68×10^{-5}-5.00×10^{-3}	3.98×10^{-5}	1.00	0.992
25	5.0	47.5	47.5(DBP)	-50.47±0.83	4.68×10^{-5}-1.34×10^{-3}	3.66×10^{-5}	2.83	0.984
26	1.0	49.5	49.5(DOP)	-34.48±0.71	7.28×10^{-5}-1.00×10^{-2}	6.92×10^{-5}	2.89	0.990
27	1.0	49.5	49.5(EHA)	-25.55±0.13	7.28×10^{-5}-1.00×10^{-2}	6.62×10^{-5}	0.85	0.995
28	1.0	49.5	49.5(TCP)	-70.58±0.52	4.68×10^{-5}-1.00×10^{-2}	4.03×10^{-5}	1.28	0.994
29	3.0	48.5	48.5(TCP)	-53.30±1.67	4.68×10^{-5}-5.00×10^{-3}	4.21×10^{-5}	5.42	0.994
30	1.0	49.5	49.5(NPOE)	-45.61±1.57	4.68×10^{-5}-4.05×10^{-4}	4.23×10^{-5}	5.97	0.989
				pH 9.25				
31	1.0	49.5	49.5(DBP)	-39.49±0.70	1.92×10^{-5}-1.00×10^{-2}	1.16×10^{-5}	3.05	0.991
32	2.0	49.0	49.0(DBP)	-43.95±0.82	1.92×10^{-5}-1.00×10^{-2}	1.48×10^{-5}	3.21	0.986
33	3.0*	48.5	48.5(DBP)	-34.17±0.40	1.92×10^{-5}-1.00×10^{-2}	1.53×10^{-5}	2.03	0.991
34	5.0	47.5	47.5(DBP)	-36.20±0.24	1.92×10^{-5}-1.34×10^{-3}	1.69×10^{-5}	1.14	0.980
35	3.0	48.5	48.5(DOP)	-8.56±0.32	2.86×10^{-5}-5.00×10^{-3}	1.94×10^{-5}	6.54	0.984
36	3.0	48.5	48.5(EHA)	-11.42±0.54	7.28×10^{-5}-1.00×10^{-2}	6.33×10^{-5}	8.13	0.981
37	3.0	48.5	48.5(TCP)	-37.41±0.68	1.17×10^{-5}-1.00×10^{-2}	9.28×10^{-6}	3.14	0.992
38	5.0	47.5	47.5(TCP)	-40.10+0.27	2.86×10^{-5}-5.00×10^{-3}	1.54×10^{-5}	1.17	0.991
39	3.0	48.5	48.5(NPOE)	-20.27±0.79	1.16×10^{-5}-1.34×10^{-3}	8.54×10^{-6}	6.73	0.988

*The selected composition of the paste, SE: standard error, r^2: correlation coefficient

Relative standard deviation (three determinations)

In order to understand the behavior of the electrode under these experimental conditions, it is important to discuss a few points. It is widely accepted that the polarity is one of the major parameters that controls the performance of the plasticizer. This is often measured by the value of the dielectric constant of the plasticizer. The dielectric constant of the plasticizers used in this study increase in the following order EHS (3.9) < EHA (5.0) < DOP (5.1) < DBP (6.4) < TCP (6.9) < NPOE (24). Obviously, electrodes using plasticizers with intermediate polarity give more reproducible results with good potentiometric response. Another parameter that is often not discussed in the literature is the possibility of physical bonding between the plasticizer and the ionophore (e.g. hydrogen bonding, van der Walls interactions, etc.). Such interaction can be beneficial to the electrode response, for example by improving the solvation of the ionophore, which allows for higher amounts of the ionophore to be loaded into the electrode. It can also be detrimental to the ion recognition, for example by blocking the complexation site in the ionophore. In case of using DBP as the plasticizer, there is a possible hydrogen bonding between the secondary amine protons in the two diclofenac ligands that are part of the ionophore structure and phthalate functional groups in the DBP molecules. Similar interactions may occur between TCP and the ionophores ($FephenD_2$ and $FebipyD_2$), π-π stacking between the aromatic groups in the ionophores and both DBP and TCP molecules. These interactions explain the excellent electrochemical performance of DBP and TCP electrodes.

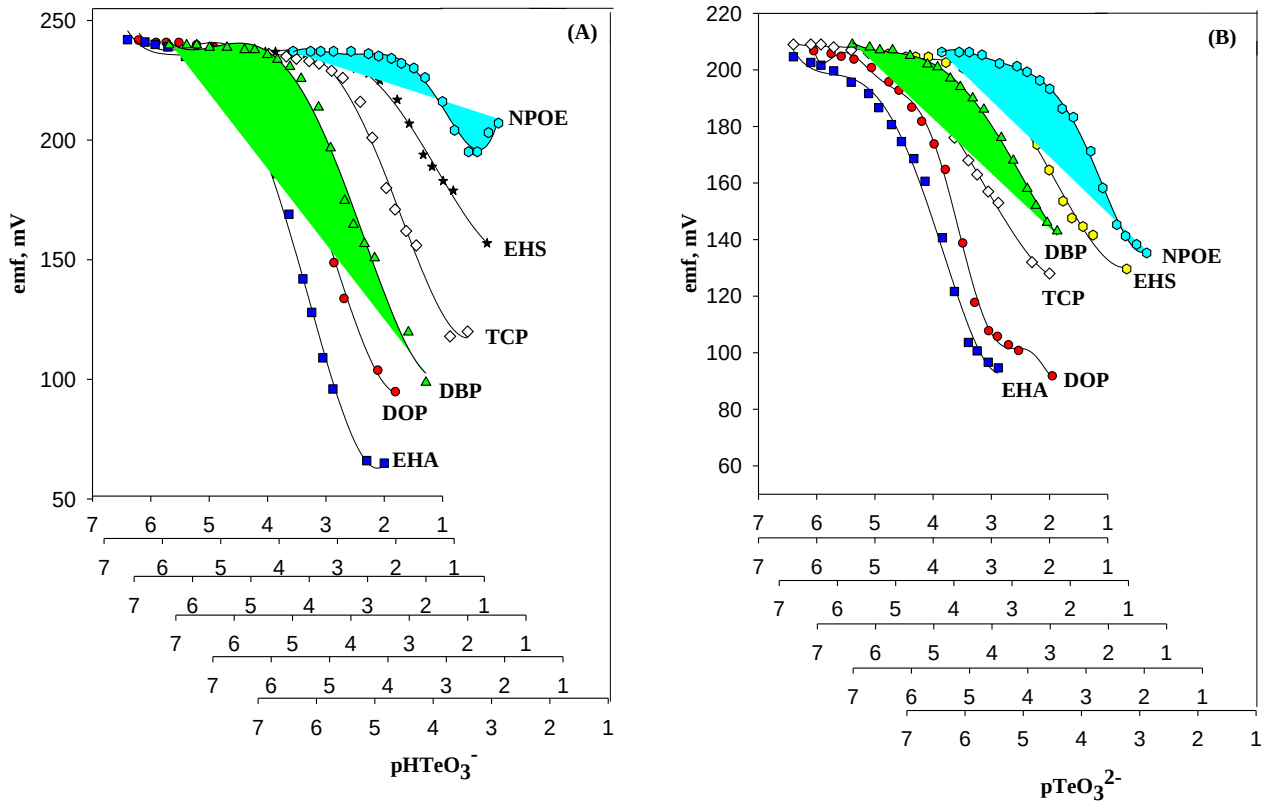

Figure 6. Effect of different plasticizers on the response of $FephenD_2$ CMCPEs at pH 4.63 (A) and pH 9.10 (B).

The effect of plasticizer on the response of the electrode was also studied for $FebipyD_2$ ionohpore. For example, in case of using DBP as a plasticizer for $FebipyD_2$ electrodes at pH 4.99, the sensor showed better potentiometric response compared to other plasticizers, i.e. sensitivity and linear range of the calibration plots, whereas, in the case of other solvent mediators, the slope of the calibration graphs are much different from the expected Nernstian value of -59.5 mV/decade. Similar results were obtained at a higher pH 9.25. Again, the excellent response of the DBP-based electrode originates from its large lipophilicity which improves the solvation and dissolution of the $FephenD_2$ and $FebipyD_2$ ionophores. This in turn enhances the ion recognition capacity of the electrode.

It is widely accepted that lipophilic charged additives have the ability to enhance the potentiometric response of some anion selective electrodes. They do so by reducing the ohmic resistance and improving the response behavior and selectivity of the electrode [54,58]. Thus, the effect of some additives like KTPB as anionic additive and CTAB as cationic additive was studied. Unlike previous results, experiments indicate that these additives had no effect on the electrochemical response of the electrode. That is to say that the slope, linear range and detection limit of the electrode did not change before and after the addition of reagent additives. This is likely due to the weak interaction between the surfactant and tellurite ions. It is also possible that the addition of the surfactants is detrimental to the ion recognition properties of the ionophore. It is, therefore, not recommended to use surfactant additives in the sensors developed in this work.

3.2.3. Life time and regeneration of the electrodes

The constructed electrodes have life times that have been determined by testing the electrode response over a long period of time till the electrodes lost their Nernstian response. The point at which the electrode loses its Nernstian response marks the lifetime of the electrode. The gradual degradation of the electrode response beyond this point can be attributed to the dissolution of the active ingredients (including the ionophore and plasticizer) into the bathing solution. Response of the electrodes including the slope, detection limit and the linear range have been measured by recording the calibration graph at 25 ºC for different time intervals. Life times of the electrodes were found to be 23, 68 days for $FephenD_2$ electrodes at pH 4.63 and 9.10 respectively and 50, 14 days for $FebipyD_2$ electrodes at 4.99 and 9.10, respectively. During these periods, the electrodes showed a slight gradual change in Nernstian slope and lowering of the linear range was also observed. These carbon paste electrodes are stable in some cases for more than 2 months, is relatively longer than the polymeric membrane electrodes. This can be attributed to the diminishing of the ionophore by leaching from the electrode matrix; due to the absence of internal filling solution. The long-term stability is another advantage for the carbon paste electrode potentiometric sensors.

Even after 2 months, the electrode response was regenerated by squeezing the top layer of the exhausted electrode out of the tube and the fresh surface is smoothed by gently rubbing the electrode against a piece of paper [59]. The exhausted $FephenD_2$ electrode has calibration graph of slope -48.09 mV and after regeneration the slope changed to -58.45 mV close to the expected Nernstian value. This

indicates that the electrode response is completely reversible and reproducible. It is also a promising feature that may reduce the price of the CMCPE tellurite sensors developed in this work.

3.2.4. Dynamic response time and repeatability of the electrodes

The dynamic response time is a very important parameter in the characterization of carbon paste electrodes [60]. It is defined as the time passing between the point at which the cell electrodes are brought in close proximity with a test solution and until a stead state potential is reached. The dynamic response time of each electrode was determined by measuring the time required to attain a steady-state potential (within ±1 mV). This if often obtained by immersing the electrode in a series of tellurite solutions, each with 5 fold increase in concentration from 1.0×10^{-4} to 1.0×10^{-2} mol/L. The electrodes yielded steady potentials within 10-20 s as shown in Figure 7. This indicates a rapid diffusion of tellurite ions in the carbon paste electrode, which speeds up the equilibrium between the aqueous layer and the carbon paste phase.

Repeatability of the potential readings for each electrode was examined by subsequent measurement in a low concentration of tellurite solution after measuring in a higher one. The potentiometric response of the sensors showed minimum memory effect, which again reflects the suitability of the current electrodes for real applications.

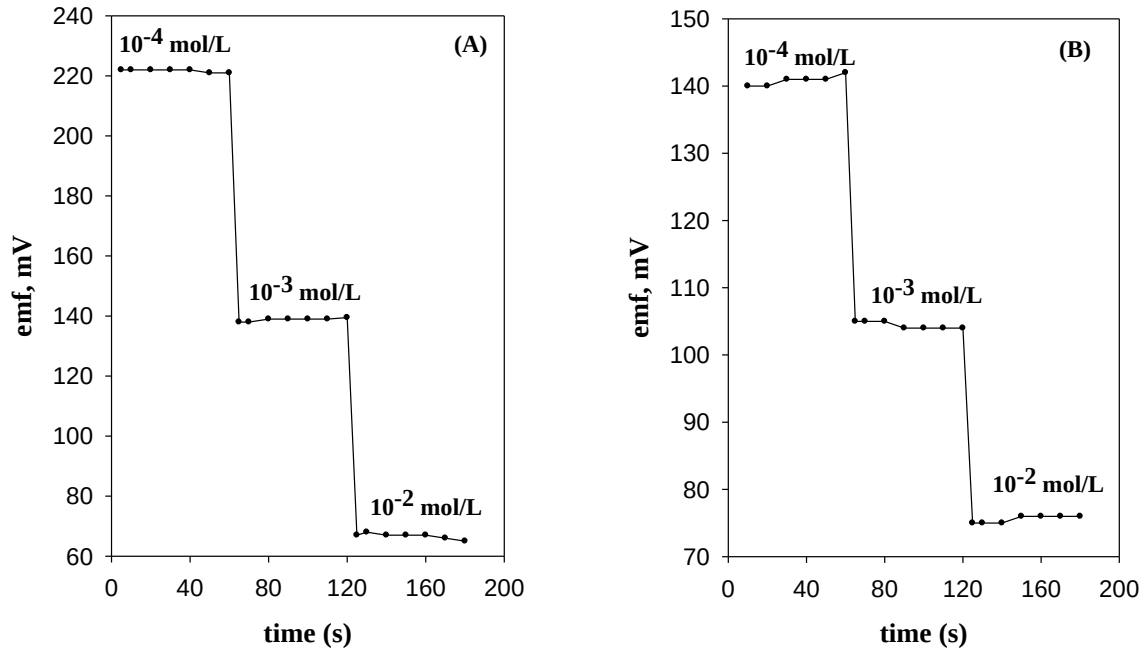

Figure 7. Dynamic response time of FebipyD$_2$ electrodes for step change in tellurite concentration from low to high at pH 4.99 (A) and pH 9.25 (B)

3.2.5. Effect of temperature

When new electrode sensors are developed, it is important to test the performance of the sensor at different temperatures. By knowing the temperature effect on the sensor we can determine the

temperature range required for the safe operation of the sensor. This was accomplished by measuring the calibration graphs (electrode potential vs. p-tellurite) over a wide temperature range from 22 to 52 °C. Here, the study focused on measuring the slope and linear range of the sensor at different test solution temperatures. Figure 9 shows an example of this study for CMCPE using $FebipyD_2$ ionophore. The thermal stability of the electrode was studied by measuring the thermal coefficient (dE_{cell}/dt) which can be obtained directly from the slope of the linear relation between E^o_{cell} and temperature (t-25). In this case, the values of the standard cell potential E^o_{cell} were calculated from the intercept of the calibration plot at p-tellurite = 0. This was used for the calculation of the standard electrode potentials (E^o_{elec}) by adding E^o_{cell} to the standard electrode potential of the calomel reference electrode at different temperatures.

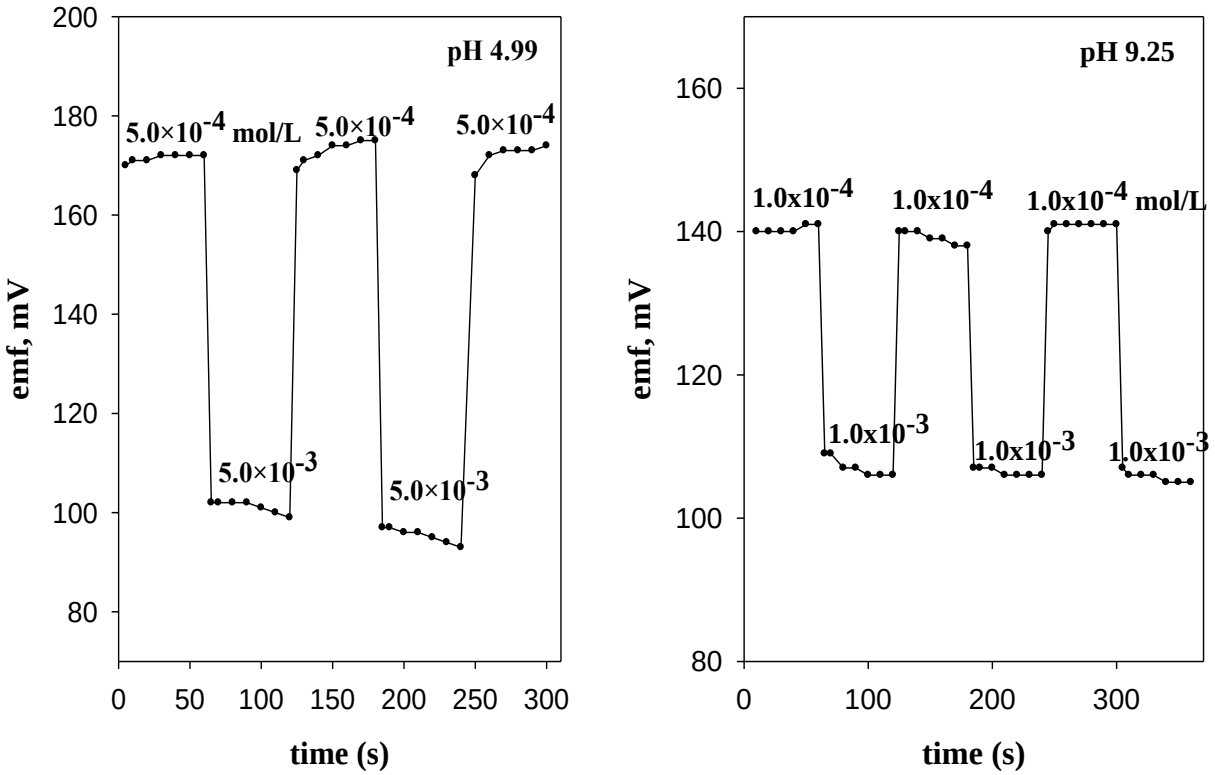

Figure 8. Dynamic response time of $FebipyD_2$ electrodes for several high to low cycles.

The values of dE_{cell}/dt were found to be -0.65, -3.33, -0.198 and -3.09 mV/°C, while the values of dE_{elec}/dt were $-0.61\times10^{-2,}$ -2.67, 0.46 and -3.09 mV/°C for the $FephenD_2$ and $FebipyD_2$ sensors at alkaline and acidic medium, respectively. The results show that the slope of the calibration graphs increased slightly with temperature but is still in the Nernstian range. This reflects the high thermal stability of the sensors developed in this work and confirms their suitability for use in cold and warm environments. This fulfills one of the most pressing needs for the next-generation ion-selective electrodes: high thermal stability over a wide temperature range.

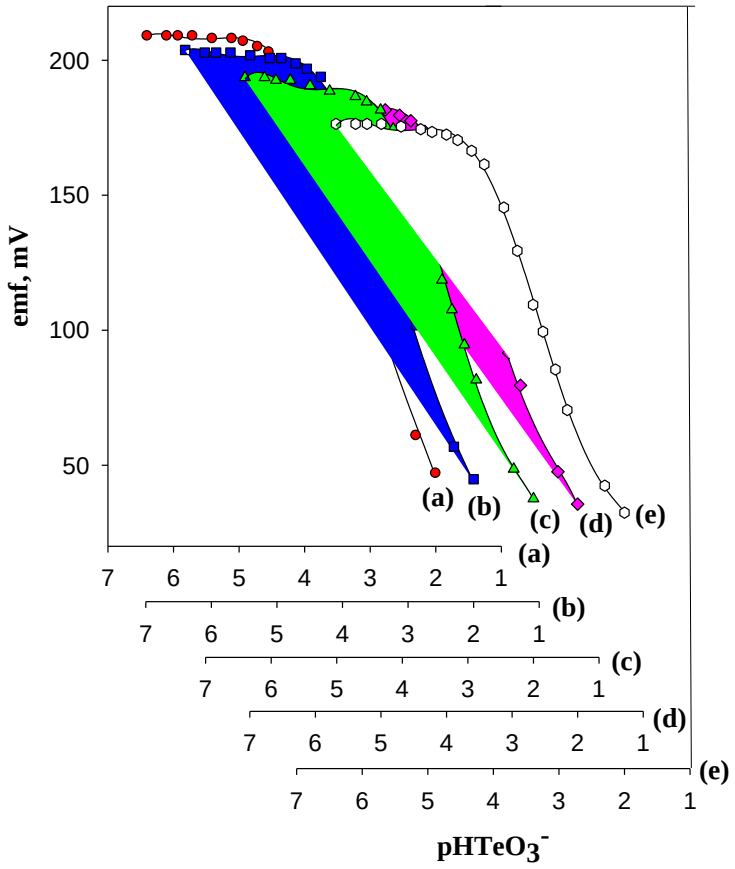

Figure 9. Calibration graphs using $FebipyD_2$ CMCPE at test solution temperatures 22 (a), 32 (b), 36 (c), 42 (d) and 52 °C (e) at pH 4.99.

3.2.6. Selectivity of tellurite sensors

One of the main characteristics of a good sensor is its ability for the selective detection of the analyte species with minimum interference. This is often determined by measuring the potentiometric selectivity coefficient of an electrode towards the ion of interest compared to the other ions that coexist in solution [57]. For electrodes that are known to exhibit non-Hofmeister selectivity, it depends on the selective interaction between the primary ion and the lipophilic ionophore incorporated as well as the mobilities of the respective ions in the matrix of the sensor [61,62]. Here, the response of the sensors toward different anions which may be present in the real samples was tested. In the present study, matched potential method (MPM) was applied and selectivity coefficient values were calculated and presented in Table 3.

The selectivity sequence of the studied sensors for different anions obeys the following order:

For $FephenD_2$ sensors

$HTeO_3^-$> CH_3COO^-> I^-> $C_2O_4^{2-}$> NO_2^-> NO_3^-> F^-> Cl^- ~$S_2O_3^{2-}$ ~SO_4^{2-}> $S_2O_8^{2-}$> Br^-> SeO_4^{2-}> TeO_4^{2-} at pH 4.63, and

TeO_3^{2-}> I^-~ $S_2O_8^{2-}$> CH_3COO^-> NO_2^-> NO_3^-> $S_2O_3^{2-}$> $C_2O_4^{2-}$~ SO_4^{2-}> TeO_4^{2-}> F^-> Br^-> Cl^-> SeO_4^{2-} at pH 9.10.

For $FebipyD_2$ sensors

$HTeO_3^-$> CH_3COO^-> $S_2O_8^{2-}$> I^-> $C_2O_4^{2-}$> TeO_4^{2-}> NO_2^-~ F^-> NO_3^-> SO_4^{2-}> $S_2O_3^{2-}$> Cl^-> SeO_4^{2-} > Br^- at pH 4.99 and

TeO_3^{2-}> $S_2O_8^{2-}$> TeO_4^{2-}> $C_2O_4^{2-}$> I^-> CH_3COO^-> Br^-> F^-> NO_2^-> SeO_4^{2-}> NO_3^-> Cl^-> SO_4^{2-}> $S_2O_8^{2-}$ at pH 9.25.

Table 3. Selectivity coefficient values $-\log K^{MPM}_{Tellurite,J}$ for tellurite sensors.

interferent	$-\log K^{MPM}_{Tellurite,J}$			
	$FephenD_2$		$FebipyD_2$	
	pH 4.63	pH 9.10	pH 4.99	pH 9.25
Cl^-	2.00	2.40	3.33	3.23
Br^-	2.23	1.97	3.74	2.17
F^-	1.95	1.83	2.37	2.30
I^-	1.10	1.23	1.58	1.50
SO_4^{2-}	2.00	1.76	3.30	3.31
$S_2O_3^{2-}$	2.00	1.64	3.32	3.90
$S_2O_8^{2-}$	2.06	1.23	1.22	0.54
SeO_4^{2-}	2.83	2.60	3.51	2.97
TeO_4^{2-}	2.98	1.82	2.35	1.26
NO_2^-	1.77	1.46	2.37	2.79
NO_3^-	1.92	1.54	2.54	3.15
CH_3COO^-	0.6	1.41	1.07	2.01
$C_2O_4^{2-}$	1.17	1.76	1.60	1.28
Cefotaxime	1.87	---	2.28	1.18

The results show that the selectivity of the proposed sensors differs from the so-called Hofmeister selectivity pattern [63]. In other words, the selectivity relies solely on the lipophilicity of anion. In addition, the obtained results show that the selectivity coefficient values are less than one, comparing with the previously reported electrodes, indicating that these anions have negligible effect on the functioning of the tellurite selective electrode.

The potential response of sensors at varying concentrations of interfering anions is shown in Figure 10. Obviously, the calibration graphs of all anions tested show extremely small slopes that are almost insignificant. This indicates that the proposed sensors have high selectivity towards tellurite over all other anions tested.

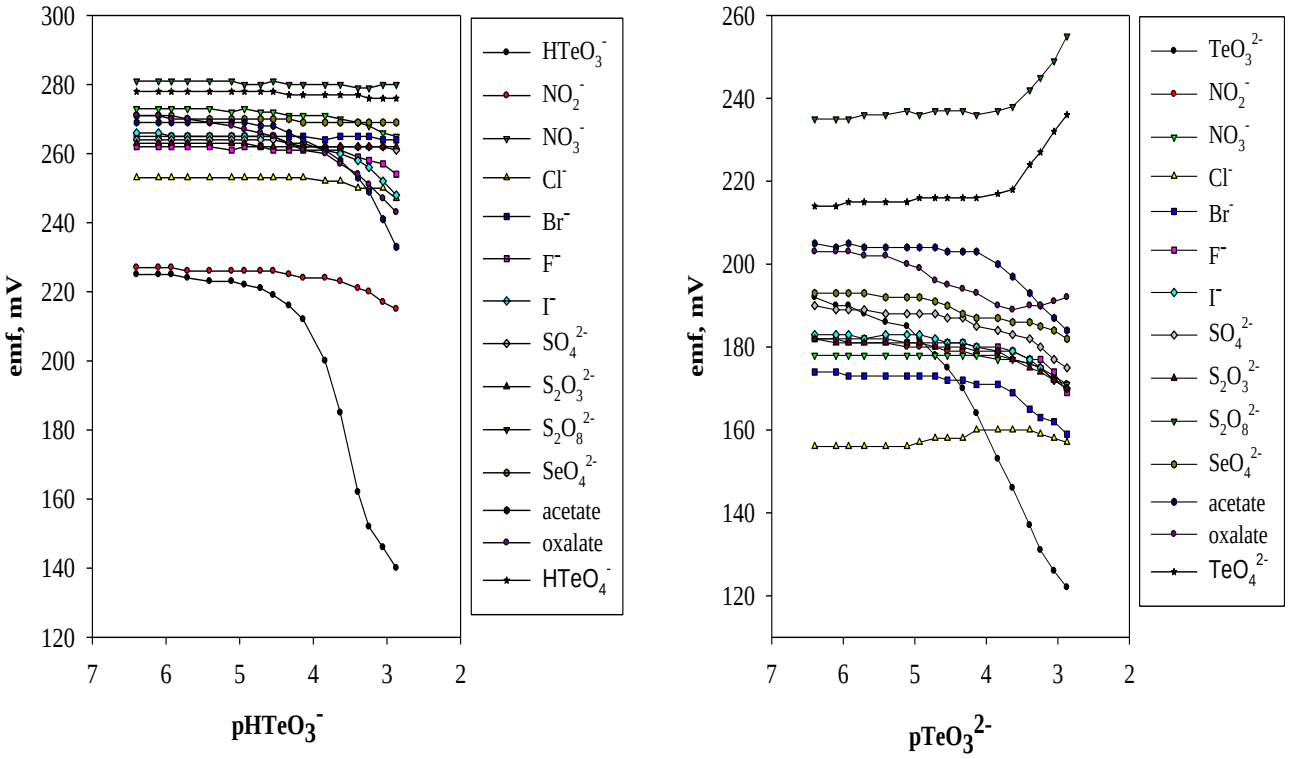

Figure 10. Potentiometric response of FephenD$_2$ CMCPE towards various interfering anions at pH 4.63 and 9.10.

3.3. Potentiometric determination of tellurite ion in real samples

Real samples containing tellurite exhibit toxicity of varying degrees as a result of the accumulation of this toxic reagent in the kidneys, heart, liver, spleen, bone, and lung. If the concentration exceeds threshold value, it could induce the degeneracy of the liver and kidneys. For these reasons, tellurite content in biological and environmental samples must be controlled and reduced.

In order to assess the suitability of the proposed tellurite sensors for real applications, our present method was applied for the determination of tellurite content in different real samples such as waste water, human serum, tellurite culture media, tellurite/tellurate mixture and synthetic tellurite/cefotaxime samples by applying standard addition method. Collective results are given in Table 4 and compared with the spectrophotometric method [15]. From the results, it is evidence that tellurite sensors are very useful potentiometric electrodes for a micro-determination of tellurite in pure, environmental and biological samples over a concentration range 0.04431-106.78 µg/mL.

3.3.1. Determination of tellurite in industrial waste water

Tellurite is required in a number of important industrial applications, especially in glass manufacture, so there is a need for determination of its ions in waste water. Table 4 shows results

obtained from determination of tellurite in waste water spiked with known amount of tellurite. The waste water samples were collected from a glass manufacturing factory that is known to contain a wide range of interfering pollutants. As can be seen from the results, that in all cases there is a satisfactory agreement between the taken and found amounts (recovery ranges 97.37-102.57%).

3.3.2. Determination of tellurite in human serum

Tellurite is a toxic substance and has 10-times greater toxicity than tellurate, which may lead to serious human health problems on exposure to its ions. Therefore, the proposed sensors were subjected to analysis of tellurite in human serum. From the results indicated in Table 4, the sensors show high recovery ranged from (93.55-103.28%) for determination of tellurite in human serum samples spiked with definite amounts of tellurite (less than its threshold value).

3.3.3. Determination of tellurite in tellurite culture media

Tellurite has been used for 80 years for the selection and isolation of several pathogens, where tellurite allow the growth of certain bacteria but partially or completely inhibited the growth of others. Therefore, tellurite is wide applicable in preparation of biological culture media. The amount of tellurite in media was measured by the proposed sensors. It is clear from the results given in Table 4 that the recovery values are high and reproducible which ranges from 96.17-103.27%.

3.3.4. Determination of tellurite in synthetic tellurite/cefotaxime samples

Since tellurite is toxic to most microorganisms, sub lethal tellurite concentrations were used to strengthen the effect of several antibiotics. It was reported that tellurite at nmol/L or mmol/L concentrations can increase the toxicity of defined antibacterials. For this reason, tellurite and cefotaxime act synergistically against *E. coli* bacteria. The proposed sensors were applied for testing an assay of synthetic tellurite-cefotaxime samples (2×10^{-7} mol/L of tellurite) by applying double standard additions method. As can be observed from Table 4, the sensors were successfully used for the determination tellurite in synthetic samples with recovery ranges from 98.85-106.3%.

3.3.5. Determination of tellurite in tellurite/tellurate mixture

It is widely accepted that tellurite and tellurate are the most mobile and bio-geochemically important forms of tellurium. It is, thus, important to test whether the proposed sensors have the ability to specify between these two different chemical forms. It was found that the sensors under investigation can be successfully used for the determination of the concentration of tellurite in presence of tellurate without any interference from tellurate. The percent of recovery ranged from 97.27 to106.9% (Table 4). The solutions were prepared by mixing equimolar amounts of tellurite and tellurate solutions and pH was adjusted with buffer.

3.3.6. Determination of tellurate

This method has been used for indirect determination of tellurate samples by converting tellurate to tellurite by heating with conc. HCl. The reduced tellurate was successfully determined by the proposed sensor (FebipyD$_2$ CMCPE) after adjusting the pH at 4.99 by NH_4OH (1:1). The resulting recovery ranges from 97.22-98.74% with good RSD% values.

Table 4. Determination of tellurite in pure solutions and real samples using tellurite CMCPEs by applying standard additions method.

Sample	FephenD$_2$ CMCPE							
	pH 4.63				pH 9.10			
	Taken	Found	Recovery%	RSD%	Taken	Found	Recovery %	RSD%
	µg/mL				µg/mL			
Pure solutions								
	22.15	21.80	98.41	2.30	22.15	20.96	94.62	2.49
	11.07	10.86	98.10	2.11	66.47	65.64	98.75	3.16
Spiked waste water								
	88.63	88.59	99.95	2.18	4.43	4.40	99.32	2.89
	66.47	65.47	98.50	0.25	11.08	11.36	102.53	0.60
Spiked human serum								
	1.11	1.07	96.39	1.89	1.11	1.14	102.71	2.00
	2.22	2.16	97.30	2.45	2.22	2.26	101.82	3.24
Tellurite culture media								
	24.77	23.82	96.16	0.91	24.50	23.64	96.49	1.31
	70.79	70.59	99.72	0.45	69.97	70.91	101.31	4.5*
	105.29	108.09	102.65	2.78	105.29	106.73	101.37	2.97
Synthetic tellurite/cefotaxime								
	44.31×10^{-3}	44.01×10^{-3}	99.32	1.62	44.31×10^{-3}	47.13×10^{-3}	106.36	2.00
Tellurite/tellurate mixture								
	22.15	22.90	103.38	1.98	2.22	2.16	97.29	1.69
	17.72	17.47	98.58	1.15	11.07	10.83	97.83	1.64
	FebipyD$_2$ CMCPE							
Sample	pH 4.99				pH 9.25			
Pure solutions								
	22.15	21.40	96.61	2.69	22.15	21.71	98.01	3.07
	11.07	10.92	98.64	0.987	66.47	61.71	92.83	1.59
Spiked waste water								
	66.47	67.51	101.56	1.53	22.15	21.57	97.38	1.78
Spiked human serum								
	1.11	1.15	103.60	1.59	1.11	1.14	102.70	0.72
	2.22	2.19	98.64	1.53	2.22	2.07	93.24	0.72
Tellurite culture media								
	24.92	24.78	99.44	1.33	24.50	25.30	103.27	2.56
	71.13	72.96	102.50	0.375	70.00	67.31	96.16	2.25
	106.78	106.89	100.10	0.24	105.60	103.85	98.35	2.80
Synthetic tellurite-cefotaxime								
	44.31×10^{-3}	43.80×10^{-3}	98.85	2.15	44.31×10^{-3}	45.11×10^{-3}	101.81	2.67
Tellurite/tellurate mixture								
	22.15	21.52	97.15	2.32	22.15	21.69	97.90	2.09
	66.47	66.45	99.96	1.13	44.31	47.37	106.90	3.10
Reduced tellurate								
	22.15	21.54	97.24	1.05	---	---	---	---
	66.47	65.63	98.74	1.76	---	---	---	---

RSD: Relative Standard Addition (three determinations)

3.3.7. Statistical Treatment of Results

The F values were calculated [64] and found to be less than the tabulated F value (19.0) where v_1 = 2 and v_2 = 2 at 95% confidence level. t-test [64] was also performed at 99.9% confidence level (tabulated t = 4.604), the results are shown in Table 5. Therefore, it can be concluded that the proposed

sensors does not exhibit significant differences in comparison with the published method. This reflects the accuracy and precision of the method under investigation.

Table 5. Statistical treatment of data obtained for the determination of tellurite anion applying the standard addition method in comparison with spectrophotometric method.

	Spectrophotometric method	X±S.E	RSD	F value	t value
FephenD$_2$ at pH 4.63					
Pure solutions	101.93±0.51	98.09±1.19	2.11	5.44	2.95
Synthetic tellurite-cefotaxime	103.32±0.59	99.32±0.92	1.62	1.08	3.64
Spiked human serum	105.04±1.23	97.35±1.37	2.45	1.25	4.16
Tellurite culture media	101.55±1.18	102.65±1.64	2.77	1.94	0.54
Spiked waste water	103.91±0.59	99.93±1.26	2.18	4.56	2.85
FephenD$_2$ at pH 9.10					
Pure solutions	101.93±0.51	98.72±1.81	3.16	12.50	1.707
Synthetic tellurite-cefotaxime	103.32±0.59	106.37±1.22	2.00	4.317	2.24
Spiked human serum	105.04±1.23	102.70±1.19	2.00	1.51	1.366
Tellurite culture media	101.55±1.18	101.37±1.73	2.97	2.168	0.085
Spiked waste water	103.91±0.59	102.57±0.35	0.60	2.76	1.94
FebipyD$_2$ at pH 4.99					
Pure solutions	101.93±0.51	98.61±0.56	0.98	1.21	4.36
Synthetic tellurite-cefotaxime	103.32±0.59	98.85±1.22	2.15	4.32	3.28
Spiked human serum	105.04±1.23	103.29±0.95	1.59	1.67	1.12
Tellurite culture media	101.55±1.18	99.41±0.83	1.33	2.00	1.48
Spiked waste water	103.91±0.59	101.56±0.90	1.53	2.32	2.18
FebipyD$_2$ at pH 9.25					
Pure solutions	101.93±0.51	97.84±1.59	2.83	9.78	2.43
Synthetic tellurite-cefotaxime	103.32±0.59	101.82±1.56	2.67	7.07	0.89
Spiked human serum	105.04±1.23	102.42±0.42	0.72	8.44	2.01
Tellurite culture media	101.55±1.18	98.35±1.59	2.80	1.82	1.62
Spiked waste water	103.91±0.59	97.37±1.00	1.78	2.89	--

X±S.E: recovery±standard error.

4. CONCLUSIONS

In this work, a chemically modified carbon paste electrodes have been constructed and successfully utilized in the determination and speciation of tellurite in real and environmental samples. The electrodes had wide working concentration range (1.92×10^{-5} – 1.00×10^{-2} mol/L), low detection limit (1.42×10^{-5} mol/L) and short response time (less than 20 seconds). The sensor can also distinguish between monovalent and divalent anions. Based on these results, we conclude that the proposed electrode can be used in the trace analysis of tellurite in real and environmental samples with detection limits well below the lethal concentrations according to the Occupational Safety and Health Administration.

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