A new nano-composite modified carbon paste electrode as a high performance potentiometric sensor for nanomolar Tl(I) determination

Hasan Bagheri [a,*], Abbas Afkhami [b], Ali Shirzadmehr [b], Hosein Khoshsafar [b]

[a] Chemical Injuries Research Center, Baqiyatallah University of Medical Sciences, Tehran, Iran
[b] Faculty of Chemistry, Bu-Ali Sina University, Hamedan, Iran

ABSTRACT

In the present study, a novel nano-composite potentiometric sensor for the determination trace amounts of Tl(I) was prepared containing the room temperature ionic liquid, 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide, as the conducting binder, and multi-walled carbon nanotubes, TiO$_2$ nanoparticles, graphite powder and also tri-aza dibenzosulfoxide macrocyclic ligand as efficient ionophore. For investigation of the ion-to-electron transducing ability of multi-walled carbon nanotubes, ionic liquid and TiO$_2$ nanoparticles on the electrode surface, the electrochemical impedance spectroscopy measurements were done. Under the optimized experimental conditions, the suggested potentiometric Tl(I) sensor exhibited an excellent Nernstian slope of 59.31 mV decade^{-1}, with rapid response time (5 s) and a linear calibration curve that ranged from 8.50×10^{-9} to 1.00×10^{-2} M was obtained with a detection limit of 5.50×10^{-9} M.

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1. Introduction

The monitoring of hazardous elements in environmental samples can provide important information concerning pollution, since they are usually released in the environment from anthropogenic sources, such as agricultural and industrial activities [1]. Among many targeted systems, the detection of heavy metal ions is of particular interest due to their environmental and biological toxicities [2–8]. In recent years, the monitoring and evaluation of thallium have received increasing attention, from both nutritional and toxicological points of view. Thallium is one of the hazardous elements, and it is regarded as one of the most toxic of the heavy metals, causing both chronic and acute poisoning. Because of its toxicity, Tl was included in the list of 129 so called "priority pollutants" by the US Environmental Protection Agency [9]. It is extremely toxic to humans, plants and animals and plays no role in their metabolisms. Soluble univalent thallium compounds, e.g. thallium(I) sulfate, nitrate, acetate and carbonate are very toxic because they are easily absorbed into the human body by skin contact or ingestion [10]. The estimated lethal dose in humans is 8–12 μg g^{-1} [11]. Tl(I) is highly toxic to the biosphere several orders of magnitude higher than mercury, cadmium, lead and copper [9]. For example, the toxicity of thallium is even more than that of mercury; in enzymes and protoplasm, the thallium ion replaces potassium to their close ionic radii. Also, Tl causes gastrointestinal irritation and disorders of the nervous system after exposure for relatively short times. In the long term, this has the potential to cause effects such as changes in blood chemistry, damage to liver, kidney, intestinal, and testicular tissue, and hair loss [12]. It is therefore important to develop the simple, selective, sensitive, efficient and eco-friendly methods for the determination trace levels of Tl(I) in environmental, food and biological samples. Various instrumental techniques have been employed for the determination of traces of Tl species in different real samples, including spectrophotometry [13], neutron activation [14], inductively coupled plasma atomic emission spectrometry (ICP-AES) [15], flame atomic absorption spectrometry (F-AAS) [16] and inductively coupled plasma mass spectrometry [17]. However, these techniques are too expensive and are not available in most analytical laboratories or need time consuming procedures. So, the development of convenient and direct methods for the assay of thallium in different real samples is an urgent need. Electrochemical sensors have been widely used to determine various species due to their high sensitivity and desirable selectivity in their responses [18–33]. Among these sensors, potentiometric carbon paste electrodes (CPEs), due to the ease of their construction, easy renewability of the surface, inexpensive techniques, chemical inertness, robustness, stability of response, low ohmic resistance, no need of internal solution and compatibility with various types of modifiers, have been widely used as suitable tools for the determination of the various species. Further, modification can improve the surface state of the electrode, which may lead to a significant increase of the target signals [24–29]. The ion-sensing properties of potentiometric CPEs largely depend on the nature of the employed sensing material [25–27]. Nowadays, research activities are related to optimize rational design of both ionophores and matrixes targeted to particular applications. At the same time, the

* Corresponding author. Tel./fax: +98 218284251.
E-mail addresses: h.bagheri@srbiau.ac.ir, h.bagheri82@gmail.com (H. Bagheri).

researches for novel matrices became the subject of increasing interest. Since the discovery of multiwalled carbon nanotubes (MWCNTs) by Iijima [34], these materials have attracted enormous interest because of their novel structure, narrow distribution size, highly accessible surface area, low resistance and high stability. Electrochemical sensors based on MWCNTs represent a new and interesting alternative for the quantification of different analytes. It has been concluded that introduction of MWCNTs into a carbon paste improves the electric conductivity as well as the mechanical properties of the original paste matrix. In addition, MWCNTs have a role to enhance the hydrophobicity of the surface, which leads to a more stable potential signal by removing the undesirable water layer from the interface [35]. In the past years, as a new "green" media, room temperature ionic liquids (RTILs) have emerged as a frontier and novel area of research because of their excellent chemical and physical properties such as high chemical and thermal stability, ionic nature, good extraction ability, ion-exchange properties, low equilibrium vapor pressure, high conductivity and wide electrochemical windows [27]. Recently, RTILs have been proposed to be very interesting and efficient pasting binders in place of non-conductive organic binders for the preparation of carbon composite electrodes [24–27]. At present, nanometer materials have become more and more important as solid matrices due to their special properties. The modification of the electrodes with nanoparticles has been the focus of recent attention owing to improvement of the response signal, increased sensitivity, decreased detection limit, and better reproducibility. TiO$_2$ nanoparticles have a wide range of technological applications due to their excellent physical and chemical properties "non-toxicity, excellent chemical and photochemical stability, large surface area, good biocompatible, high mechanical strength and fast electron transfer ability" [28]. Due to the fact that, TiO$_2$ nanoparticles have a bigger surface area compared to the bulk of them and relatively good electrical conductivity, they can help in decreasing the detection limit of the target analyte. Also, they provide more active sites at the electrode surface and improve the stability of the electrode. Because of these properties, we can use them for the preparation of modified electrodes [28].

In this study, we report on the use of novel sensing materials that act as a matrix and ionophore for improving response of sensor. The novel potentiometric sensor based on MWCNTs, TiO$_2$ nanoparticles, 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl) imide, as the conductive binder, graphite powder and 7, 10, 13-triaza-1-sulfoxo-4, 16-dioxa-20, 24-dimethyl-2,3;17,18-dibenzo cyclooctadecane-6, 14-dione (TSD) a macrocycle ligand "Scheme 1" as an efficient ionophore was fabricated for the determination of Tl(I). It was expected that replacing paraffin oil with IL, in preparation of carbon paste, would enhance the sensor response. Also, MWCNTs, TiO$_2$ nanoparticles and TSD in the electrode composition could amplify the signal significantly. Moreover, the sensor could also be renewed easily by mechanical polishing whenever needed.
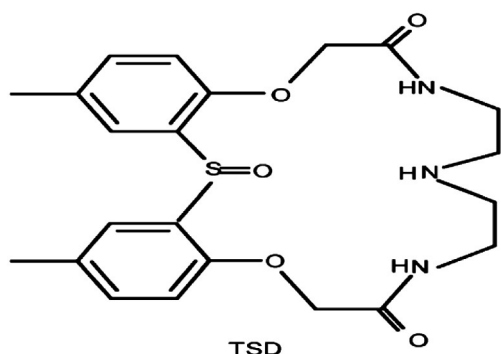
Scheme 1. Structure of TSD.

2. Experimental

2.1. Apparatus

The constructed Tl(I) selective carbon paste electrode, as the working electrode, and a single junction saturated Ag/AgCl, as the reference electrode (Azar electrode, Iran), were placed in a glass cell and used for the potentiometric measurements. Both the electrodes were connected to a digital milli-voltmeter (HIOKI 3256.50, Japan). Electrochemical impedance spectroscopy (EIS) was performed in an analytical system, with Autolab PGSTAT 302N (Netherlands). A Metrohm pH-meter (CRISON GLP 22, Swiss) with a combined glass electrode was used for pH controlling, and a Heidolph type of (MR 2000, Germany) stirrer was used for stirring the solutions. Scanning electron microscopy (SEM) was performed to survey the electrode surface (SEM-EDX, XL30, Philips Netherland). A Shimadzu model AA-670 atomic absorption spectrometer with GFA-4B graphite furnace atomizer was used.

2.2. Reagents and materials

The graphite powder with a <50 µm particle size (Merck, Darmstadt, www.merck.de), 2.2 g cm^{-3} density and about 200–300 g L^{-1} bulk density, V_{total} 0.35 cm^3 g^{-1} and S$_{BET}$ 4.5 m^2 g^{-1}, and high-purity paraffin oil (Aldrich, USA) were used for the preparation of the carbon pastes. The ionic liquid 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl) imide, ([BMP]Tf$_2$N), and chloride and nitrate salts of the cations were purchased from Merck (Darmstadt, www.merck.de). MWCNTs with outer diameter: 5–20 nm; inner diameter: 2–6 nm; length: 1–10 µm; apparent density: 150–350 g/cm^3 and with 95% purity were purchased from Plasmachem GmbH (Germany, www.plasmachem.com). Distilled deionized water was used throughout all experiments. TSD as a macrocycle ligand was synthesized and purified according to literature [36].

2.3. Pretreatment of MWCNTs

In order to eliminate graphitic nanoparticles, amorphous carbon, and metallic impurities, and/or for improvement of the electron transfer properties and/or to allow further functionalization, the pretreatment of the MWCNTs is usually necessary [37,38]. The pretreatment consists in exposing the MWCNTs to an acidic solution of sulfuric, nitric or hydrochloric acid, or mixture of these acids at room temperature, under refluxing or under sonication for different times [38,39]. The MWCNTs were purified according to the literature [25] as follows: about 500 mg of MWCNT was heated at 400 °C using an air flow of 12 mL min^{-1} for 1 h. To eliminate metal oxide catalysts, the heated processed amount of MWCNTs was dispersed in 60 mL of 6.0 mol L^{-1} HCl for 4 h under ultrasonic agitation; filtered on a Whatman No. 42 filter paper and washed until the pH of the solution was neutral; and finally, dried.

2.4. Preparation of TiO$_2$ nanoparticles

TiO$_2$ nanoparticles were prepared according to the literature [40] as follow: 1.5 mL TiCl$_4$ was slowly added drop wise into 15 mL ethanol at room temperature. A light yellow solution was obtained and gelatinized for one day to form sol–gel. Then, the sol–gel solution was vaporized at 80 °C until a dry-gel was obtained. The dry-gel precursor was calcined at 450 °C for 1 h to form TiO$_2$ powders with an anatase structure.

2.5. Preparation of working electrodes

The general procedure to prepare the carbon nanotube paste electrode was as follows: Different amounts of the ionophore along with an appropriate amount of graphite powder, ionic liquid, TiO$_2$ nanoparticles and MWCNTs were thoroughly mixed. The resulting mixture was transferred into an insulin syringe with an internal diameter of 2.5 mm and a height of 3 cm as an electrode body. After homogenization

Table 1
Optimization of the carbon paste compositions.

Electrode no	Binder	Ionophore	Graphite powder	MWCNTs	Nano-TiO$_2$	Slope mV/decade
1	30%–paraffin	0.0%	70%	0.0%	0.0%	19.72 ± 0.12
2	30%–paraffin	10%	60%	0.0%	0.0%	38.91 ± 0.31
3	30%–paraffin	13%	57%	0.0%	0.0%	41.32 ± 0.21
4	30%–paraffin	14%	56%	0.0%	0.0%	40.86 ± 0.13
5	30%–[BMP]Tf$_2$N	13%	57%	0.0%	0.0%	44.72 ± 0.13
6	30%–[BMP]Tf$_2$N	13%	52%	5.0%	0.0%	48.32 ± 0.22
7	30%–[BMP]Tf$_2$N	13%	47%	10%	0.0%	53.91 ± 0.31
8	30%–[BMP]Tf$_2$N	13%	56%	15%	0.0%	53.37 ± 0.31
9	**30%–[BMP]Tf$_2$N**	**13%**	**40%**	**10%**	**7.0%**	**59.31 ± 0.31**
10	30%–[BMP]Tf$_2$N	13%	39%	10%	8.0%	59.11 ± 0.10

The bold data is related to composition of modified electrode.

of the mixture, the paste was carefully packed into the tube tip to avoid possible air gaps, which often enhance the electrode resistance. A copper wire was inserted into the opposite end of the electrode to establish electrical contact. The external surface of the carbon paste was smoothed with soft paper. A new surface was produced by scraping out the old surface and replacing the new paste. Finally, the electrodes were conditioned for 24 h by soaking it in a 1.00×10^{-3} mol L^{-1} Tl(I) nitrate solution.

3. Results and discussion

The results obtained from some experimental works revealed that the performance of Tl(I) carbon paste potentiometric sensor can be highly improved by using [BMP]Tf$_2$N, MWCNTs and TiO$_2$ nanoparticles. In preliminary experiments, we found that the carbon nanotube paste electrodes containing ionophore, generated stable potentials in solutions containing the analyte ions, after a conditioning in a 1.00×10^{-3} mol L^{-1} Tl(I) nitrate solution. The sensor revealed remarkable selectivity for Tl(I) relative to more common metal ions. This is likely due to the high selectivity of the functionalized sensing material for Tl(I) ions over other metal ions as well as the rapid exchange kinetics of the resulting complex. Furthermore, the potentiometric responses of the modified CPE towards target metal ions were studied in terms of selectivity coefficients, response time, Nernstian slope, linear range, and response stability which are important characterization of the ion selective electrodes.

3.1. Electrode composition and modification

It is well known that the sensitivity, linear dynamic range and selectivity obtained for a given potentiometric sensor depend significantly on the composition of the sensor [19–33]. Thus, it is necessary to investigate the influence of paste composition on the potential responses of the modified CPEs. For this reason, several electrodes with different compositions were fabricated and investigated in this study. Unmodified CPE was prepared by mixing 70% of graphite powder with 30% of paraffin oil with a mortar and pestle. Modified pastes were prepared in a similar fashion, except that the graphite powder was mixed with a desired weight of TSD, MWCNTs, [BMP]Tf$_2$N and TiO$_2$ nanoparticles to get different compositions as shown in Table 1. According to this table, the electrode composed of 30% BMIM-PF$_6$, 13% ionophore, 40% graphite powder, 10% MWCNT, and 7% TiO$_2$ nanoparticles (no. 9) was found to be optimal for the Tl(I) electrode. This new nanocomposite was selected for further examinations. As it can be seen from Table 1, using RTILs instead of paraffin oil in the carbon paste yields more efficient extraction of Tl(I) into the CPE. This is probably due to the much higher dielectric constant, high ionic conductivity and good electrochemical and thermal stability of RTIL, and they may be a better binder compared to paraffin oil. Using MWCNTs in the carbon paste improves the conductivity and, therefore, conversion of the chemical signal to an electrical one. Carbon nanotubes have many properties that make them ideal as components in electrical circuits, including their unique dimensions and their unusual current conduction mechanism [27,37–39]. By increasing the conductivity, the dynamic working range and response time of the sensor improve. If the transduction property of the sensor increases, the potential response of the sensor improves to Nernstian values. Also, application of TiO$_2$ nanoparticles in the composition of the carbon paste can also improve the response of the electrode due to the large surface area and relatively good conductivity [28].

3.2. The surface morphologies of prepared CPEs

Fig. 1 shows SEM images for bare CPE and modified CPE with nanomaterials. As can be seen at a surface of CPE (Fig. 1a), the layer of irregularly flakes of graphite powder was present and isolated with each
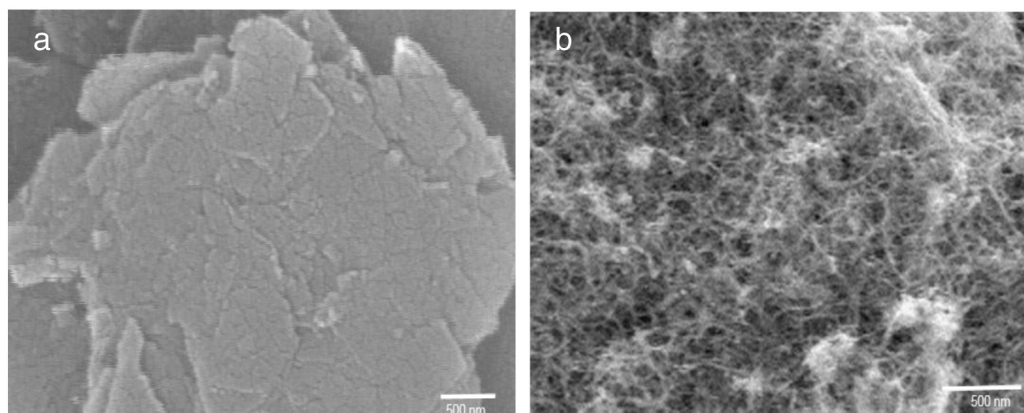

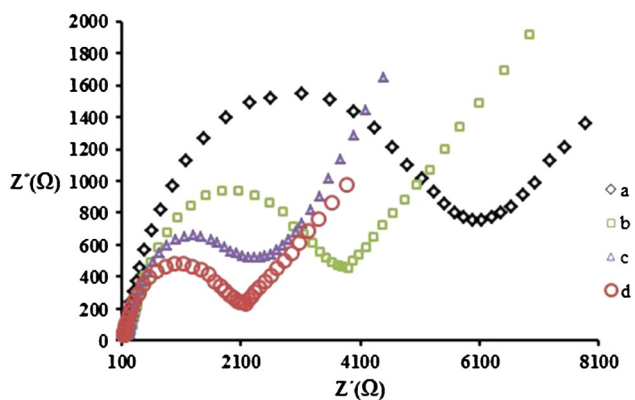**Fig. 1.** SEM images for bare CPE (a) and suggested modified CPE (b).

Fig. 2. Impedance plots for different electrodes in $Fe(CN)_6^{3-/4-}$ containing 0.1 M KNO_3: (a) bare-CPE, (b) modified-CPE with MWCNTs, (c) modified-CPE with MWCNTs and TiO_2 nano-particles, and (d) modified-CPE with MWCNTs and TiO_2 nano-particles and RTIL.

other. After the modification of the CPE with MWCNTs and TiO_2 nano-particles, it can be seen that nano-materials were distributed on the surface of electrode with a special three dimensional structure (Fig. 1b). Significant improvements in the surface structure of modified CPE are observed.

3.3. EIS study of prepared potentiometric sensors

EIS is a powerful technique to study the conductivity properties of the modified sensor surface. For investigation of the effects of MWCNTs, TiO_2 nano-particles and RTIL on the conductivity property of the prepared potentiometric sensor surface, EIS measurements were done. The semicircle diameter of the Nyquist plot reflects the electron transfer resistance (Rct). Nyquist diagrams of $[Fe(CN)_6]^{3-/4-}$ solution containing 0.1 M KNO_3 at different electrodes (bare CPE and modified CPEs) are shown in Fig. 2. According to this figure, curve a represents impedance spectrum at bare CPE. Impedance spectra at modified CPEs with MWCNTs, MWCNTs and TiO_2 nanoparticles and MWCNTs, TiO_2 nanoparticles and RTIL were presented in Fig. 2. As can be seen from this figure, the semicircle diameter decreases from curve a to d. So, semicircle diameter comparison of these curves clearly shows that charge transfer resistance decreased by adding 10% MWCNTs and 7% TiO_2 nanoparticles into the paste and also by using RTIL as conducting binder instead of paraffin oil. By increasing the conductivity, the dynamic working range, sensitivity and response time of the sensor were improved. If the transduction property of the sensor increases, the potential response of the sensor improves to Nernstian values.
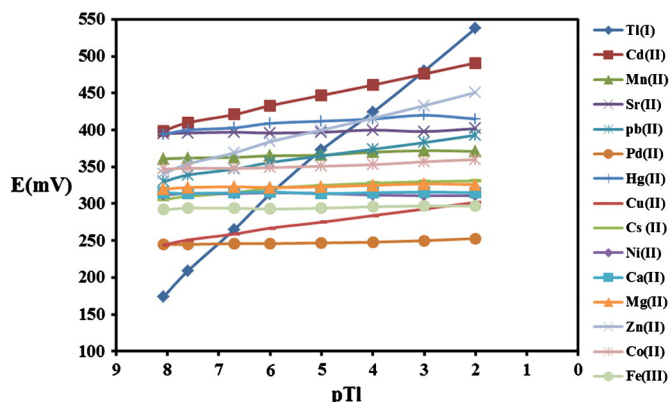

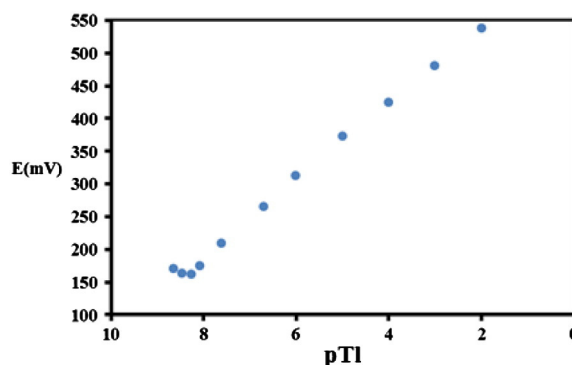**Fig. 3.** Schematic diagram of modified CPE response to various cations (electrode No. 9).

Fig. 4. Calibration curve of the Tl^+ modified CPE (electrode No. 9).

3.4. Emf measurements

The electrochemical cell can be represented as follows:
Ag, AgCl, KCl (3 mol L^{-1}) | sample solution | working electrode
Calibration graph was drawn by plotting the potential, E, versus the logarithm of the ion concentration. All measurements were carried out at 25 °C.

3.5. Response of the electrode to various cations

In preliminary experiments, the optimal modified Tl(I) carbon paste sensor (Table 1, No. 9) was tested for wide variety of metal ions, including alkali, alkaline earth, transition, and heavy metal ions. The potentials obtained for the most sensitive modified CPE based on the TSD ligand are shown in (Fig. 3). The Tl(I) selective electrode exhibited linear response to the logarithm of the concentration of Tl(I) ions within the concentration range 8.50×10^{-9} to 1.00×10^{-2} mol L^{-1} of Tl(I) with a Nernstian slope of 59.31 ± 0.10 mV decade^{-1} at 25 ± 1 °C.

3.6. Measuring range and detection limit

Linear curve fitting using IUPAC method was used for the determination of ISE characteristics. The electrode showed a linear response with the calibration equation of $y = 59.31x + 661.12$ and a correlation coefficient of $r = 0.998$ to the concentration of Tl(I) ion in the range 8.50×10^{-9} to 1.00×10^{-2} mol L^{-1} (Fig. 3). The slope of the sensor was 59.31 ± 0.10 mV decade^{-1}. The standard deviation for ten replicates was 0.1 mV. By extrapolating the linear parts of the Tl(I) modified CPE calibration curve, detection limit can be calculated. In this work, the detection limit for the determination of Tl(I) by the proposed sensor was 5.50×10^{-9} mol L^{-1}, which was calculated by extrapolating the two segments of the calibration curve in Fig. 4.
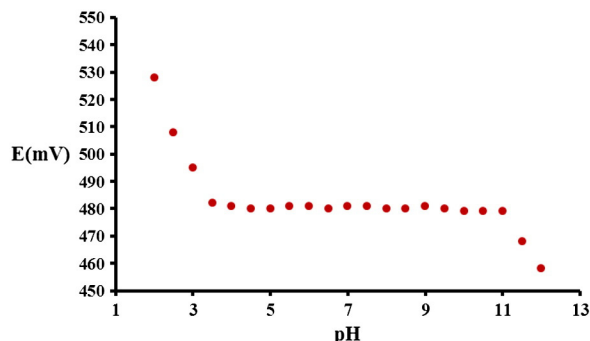

Fig. 5. Effect of pH on the potential response of the suggested thallium(I) CPE.

Table 2
Selectivity coefficient (K_{ij}) for various interfering cations for Tl(I) selective carbon paste electrode.

Interference (j)	$K_{Tl,j}$ [41]	[42]	[43]	[44]	[45]	This work (MPM)
Pb^{2+}	5.62×10^{-4}	–	3.09×10^{-4}	4.57×10^{-4}	7.94×10^{-4}	3.31×10^{-4}
Mg^{2+}	2.75×10^{-4}	1.00×10^{-5}	1.12×10^{-4}	3.16×10^{-3}	3.31×10^{-4}	9.13×10^{-6}
Fe^{2+}	–	–	2.00×10^{-4}	4.27×10^{-3}	–	1.19×10^{-4}
Mn^{2+}	–	–	–	–	–	4.64×10^{-4}
Al^{3+}	–	–	1.23×10^{-4}	–	1.91×10^{-5}	2.71×10^{-5}
Sr^{2+}	2.34×10^{-4}	–	7.94×10^{-5}	7.94×10^{-3}	2.34×10^{-4}	2.34×10^{-5}
Cr^{3+}	–	–	2.63×10^{-4}	–	9.77×10^{-5}	4.47×10^{-5}
Cu^{2+}	4.89×10^{-4}	–	1.62×10^{-4}	2.69×10^{-3}	5.13×10^{-4}	4.14×10^{-5}
Ni^{2+}	4.07×10^{-5}	–	7.59×10^{-5}	2.88×10^{-3}	5.62×10^{-5}	3.43×10^{-5}
Ca^{2+}	1.62×10^{-4}	–	1.58×10^{-4}	1.51×10^{-3}	3.16×10^{-4}	2.11×10^{-4}
Ba^{2+}	2.00×10^{-4}	–	6.03×10^{-5}	2.19×10^{-3}	–	1.57×10^{-4}
Hg^{2+}	3.31×10^{-4}	–	3.98×10^{-4}	8.32×10^{-1}	5.50×10^{-4}	3.19×10^{-4}
Zn^{2+}	1.41×10^{-4}	–	1.02×10^{-4}	2.82×10^{-2}	2.23×10^{-4}	2.53×10^{-3}
Na^{+}	4.57×10^{-4}	1.00×10^{-4}	3.98×10^{-5}	7.94×10^{-4}	5.75×10^{-4}	1.24×10^{-5}
Cs^{+}	1.25×10^{-1}	2.00×10^{-1}	4.67×10^{-2}	6.31×10^{-3}	–	8.92×10^{-3}
K^{+}	9.77×10^{-3}	1.00×10^{-3}	1.58×10^{-4}	4.90×10^{-2}	8.71×10^{-3}	7.56×10^{-5}
Cd^{2+}	5.25×10^{-5}	–	1.23×10^{-4}	1.12×10^{-1}	6.92×10^{-5}	1.34×10^{-4}
Co^{2+}	4.47×10^{-5}	–	2.63×10^{-5}	7.76×10^{-2}	3.89×10^{-5}	2.57×10^{-5}
Fe^{3+}	–	–	–	–	–	1.84×10^{-5}
Ag^{+}	2.51×10^{-2}	3.16×10^{-4}	3.16×10^{-3}	4.37×10^{-2}	3.16×10^{-2}	3.48×10^{-4}
La^{3+}	–	–	1.66×10^{-4}	–	–	7.73×10^{-5}
NH_4^{+}	5.50×10^{-3}	–	6.31×10^{-5}	7.94×10^{-2}	7.08×10^{-3}	7.61×10^{-6}

3.7. pH dependence

The most important factor in the functioning of most ion selective electrodes is the pH value of the test solution. The influence of the pH of the solution on the response of the suggested electrodes was studied on 1.00×10^{-3} mol L^{-1} Tl(I) ion having different pH values. The pH varied from 2.0 to 12.0 by addition of dilute solutions of HCl or NaOH. The potential variation as a function of pH is plotted in Fig. 5. The composition of the electrode was kept constant during all experiments. The results obtained indicate the working range of the suggested electrode to be between pH 3.5 and 11.0. The increase in potential below the pH value of 3.5 could be attributed to the partial protonation of TSD. Moreover, above pH 11.0 the measured potential decreased, due to the effect of the hydroxyl ion.

3.8. Response time of the electrode

The response time of ion selective electrodes is an important factor for any analytical application. In the case of all electrodes, the average response time was defined as the required time for the electrodes to reach a cell potential of 90% of the final equilibrium values after successive immersions in a series of solutions each having a ten-fold concentration difference. The response time of the electrode was evaluated (according to IUPAC definition) by measuring the time required to achieve a 90% value of steady potential for a thallium solution. A response time of about 5 s was obtained for this electrode.

3.9. Selectivity of the electrode

An important characteristic of an ion selective electrode is its response to the primary ion in the presence of other ions in solution, which is expressed in terms of the potentiometric selectivity coefficient. The potentiometric selectivity coefficients of the suggested modified Tl(I) sensor were evaluated by the matched potential method (MPM) [23]. The resulting values of the selectivity coefficients are given in Table 2. According to this table, all interfering cations applied in this study would not affect the selectivity of the suggested sensor, and have a very small value of selectivity coefficient in most cases compared with the previously reported electrodes for Tl(I) determination. It was concluded that this sensor displays significantly high selectivity for Tl(I) ions.

3.10. Life time of the electrode

An important factor of the ion selective electrodes is lifetime of the sensor that is generally evaluated in these methods. After this time the slope of the sensor decreases, and the detection limit increases. The lifetime of the suggested nano-composite Tl(I)-selective sensor was evaluated for a period of 20 weeks by periodically recalibrating the potentiometric response to Tl(I) ion in a series of standard Tl(I) solutions. The obtained results showed that the proposed sensor can be used for at least 18 weeks. After this time, a slight gradual decrease in the slope from 59.31 to 58.86 mV decade^{-1} is observed.

Table 3
Comparison of the proposed Tl(I) selective electrode with the some previously reported electrodes.

DL (mol L^{-1})	Linear range (mol L^{-1})	Slope (mV decade^{-1})	Life time (weeks)	Ref.
5.50×10^{-9}	8.50×10^{-9}–1.00×10^{-2}	59.31	18	Proposed electrode
3.20×10^{-6}	1.00×10^{-5}–1.00×10^{-1}	56.00	4–6	[41]
3.00×10^{-7}	1.00×10^{-6}–1.00×10^{-2}	55.00	N. R	[42]
7.10×10^{-7}	1.00×10^{-6}–1.00×10^{1}	59.00	12	[43]
5.60×10^{-6}	1.00×10^{-5}–1.00×10^{-1}	56.90	N. R	[44]
1.58×10^{-7}	2.23×10^{-6}–1.00×10^{-1}	58.20	16	[45]

N. R = not reported

Table 4
Determination of Tl(I) recovery by the suggested electrode in the different water samples (mol L^{-1}).

Samples	Tl(I) added	Tl(I) found[a]	Recovery (%)	Tl(I) found by GFAAS
Tap water	2.00×10^{-7}	$1.95 \times 10^{-7}(\pm 0.11)$	97.5	1.99×10^{-7}
	2.50×10^{-6}	$2.46 \times 10^{-6}(\pm 0.21)$	98.4	2.48×10^{-6}
Well water	2.00×10^{-7}	$1.97 \times 10^{-7}(\pm 0.23)$	98.5	1.98×10^{-7}
	2.50×10^{-6}	$2.48 \times 10^{-6}(\pm 0.22)$	99.2	2.49×10^{-6}
Rain water	2.00×10^{-7}	$1.93 \times 10^{-7}(\pm 0.13)$	96.5	1.95×10^{-7}
	2.50×10^{-6}	$2.47 \times 10^{-6}(\pm 0.32)$	98.8	2.48×10^{-6}
River water	2.00×10^{-7}	$1.93 \times 10^{-7}(\pm 0.24)$	96.5	1.99×10^{-7}
	2.50×10^{-6}	$2.45 \times 10^{-6}(\pm 0.12)$	98.0	2.48×10^{-6}

[a] Average of four replicate measurements.

3.11. Precision and accuracy of the method

The precision of the suggested Tl(I) sensor was evaluated by carrying out an analysis using standard working solutions, the same sensors, and the same conditions. The RSD of <1% was observed for 10 measurements. The results indicate that the method is capable of producing results with high precision. Also, the accuracy was expressed in terms of percentage of absolute errors obtained in the measurement of known concentrations. The obtained results are within the acceptable range of <1%.

3.12. Comparison study

In Table 3, some important characteristics of the proposed electrode are compared with the corresponding values previously reported for Tl(I)-selective electrodes based on different modifiers [41–45]. The obtained results suggest that the prepared nanocomposite is a promising material which possesses the advantages in comparison with other suggested electrodes in potentiometric detecting analyte ions with detection limit in the range of nanomolar, high selectivity and a long-term usage possibility. Also, the ease of preparation and surface regeneration of the modified electrode, and reproducibility of the potentiometric responses make the proposed modified electrode in question very useful for accurate determination of the Tl(I) ions in various real samples.

3.13. Analytical applications

The new Tl(I) selective sensor was successfully applied to obtain recoveries of Tl(I) in water samples [tap water, well water, rain water and river water] taken from our research laboratory in Bu-Ali Sina University, Hamedan, Iran and from Hamedan Industerial Zone, Iran. The samples were filtered before analysis through a 0.45 μm membrane filter and then the pH value was adjusted at 7.0 with 0.01–0.10 mol L^{-1} HCl and/or NaOH. The analysis was performed by the standard addition technique. The results are given in Table 4. According to the results, the obtained results are comparable with those obtained by graphite furnace atomic absorption spectrometer (GFAAS). Thus the sensor provides a good alternative for the determination of Tl(I) in water samples.

4. Conclusions

In this study, a new nano-composite potentiometric sensor for the determination of trace amounts of Tl(I) ion based on graphite powder, TSD ligand as an efficient ionophore, MWCNTs, TiO$_2$ nanoparticles, and [BMP]Tf$_2$N, as conductive binder, was successfully fabricated. The suggested sensor displays an excellent Nernstian response of 59.31 ± 0.10 mV decade^{-1} and a wide concentration range from 8.50×10^{-9} to 1.00×10^{-2} mol L^{-1}, provides a low detection limit of 5.50×10^{-9} mol L^{-1}, shows a long life time (18 weeks), and exhibits excellent selectivity from several cations. These values are better or very similar than those previously published ones in the bibliography for other Tl(I) potentiometric sensors. The sensor could be successfully applied for the determination of Tl(I) in water samples.

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