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Development of a highly selective and sensitive sulfate—polymeric membrane sensor based on Nickel(II)–dioxime complex as neutral carrier

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ABSTRACT

A novel sulfate–poly(vinyl chloride) (PVC) membrane based on nickel complex of 3,8-dimethyl-5,6-benzo-4,7-diazadece-3,7-diene-2,9-dione (dioxime) was prepared and used as a sensor for sulfate ions in solution. The proposed sensor revealed an excellent linear response towards SO_4^{2-} ion in the concentration range of 5.0×10^{-7} to 1.0×10^{-2} M with an anionic slope of -30 ± 0.2 mV per decade. The potentiometric behavior of the sensor was independent of the pH of the solution in the range of 4.5–7.5. The fabricated sensor showed an outstanding reproducibility, fast response time, and with a low detection limit as 3×10^{-7} M. The interference of hydrophobic inorganic anions was very low in comparison with the conventional ion-exchanger-based electrodes, as shown by the selectivity coefficients determined by the separate solution method. The sensor also was used successfully as an indicator electrode in the potentiometric titration of sulfate with barium ions and in quantification and quality assessment of sulfate in some pharmaceutical formulations.

Keywords: Sulfate ion-selective sensor; Dioxime; PVC membrane; Potentiometric titration; Pharmaceutical formulations

1. Introduction

The quick determination of minute quantities of ionic species by ion selective electrode in a wide variety of real samples, as well as the growing interest in the host guest chemistry of anions [1] widens the areas of applications. For instance, ion exchange electrodes are successfully applied for the estimation of sea and brackish waters and also for treating industrial effluents. Furthermore, they are efficient tools for the evaluation or separation of food and pharmaceutical products containing ionic species as well as the manufacture of basic chemical products.

The selectivity of such kind of electrodes is introduced by the receptor molecules (or ionic carrier) which are generally immobilized in a polymeric membrane matrix, often consisting of high molecular weight poly(vinyl chloride) (PVC) mixed with a plasticizer. The receptor molecule attributes selectivity to the sensor by its strong and selective interactions with the target analyte.

Ion selective electrodes (ISEs) technique showed great advantages such as fast and ease of preparation and procedures, wide dynamic range often spanning about five decades of ion concentration, low cost, no sample destruction, and short response time. These characteristics have inevitably led to detect several ionic species [2–5], and the list of available sensors has grown substantially over the past decades. These wide

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uses of ISEs in routine chemical analysis have been accompanied by a search for ionophores that can chemically recognize specific ions and offer either new or improved selectivities for different ions.

Among different anions, the recognition of strongly hydrophilic anions such as SO_4^{2-} by potentiometric methods has shown to be quite difficult [6]. Thus, despite the urgent need for selective potentiometric determination of minute amounts sulfate ion in many chemicals, pharmaceutical, environmental, and industrial samples, only a few reports on the preparation of SO_4^{2-} ion-selective electrodes are available in the literature [7–10]. None of the solid state sulfate ion-selective electrodes has reported to be satisfactory, due to the lack of adequate selectivity [4]. Furthermore, the design of a selective ligand for its selective recognition has been a challenging subject because of the low lipophilicity of sulfate ion [11–15].

Recently, new sulfate ion-selective sensor based on a bis-thiourea, [10,16] a derivative of imidazole [11], cytosine [17], and guanidinium ion [4,18], as well as different and macrocyclic polyamines [19–21] possessing high enough lipophilicity and specific host–guest interactions with sulfate ion, has recently shown to be promising for this purpose. Although, these electrodes show a close Nernstian behavior over a relatively wide concentration range, they suffer from rather strong interferences from other anions such as $NO_2^-, NO_3^-, Br^-, I^-, ClO_4^-$ and SCN^- [11,12,22].

Due to vital importance of sulfate determination in chemical, pharmaceutical, environmental, and industrial analyses, we are interested in fabrication of a new PVC-based membrane sensor for sulfate ion monitoring in solutions. Due to its enhanced conductivity, this new sensor presents very large current response from electroactive substrates. We report here a highly selective PVC membrane sulfate ion-selective electrode based on nickel complex of 3,8-dimethyl-5,6-benzo-4,7-diazadece-3,7-diene-2,9-dione (dioxime) as an excellent ionic carrier (Fig. 1).

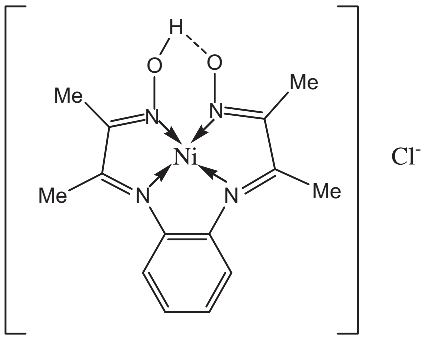

Fig. 1. Structure of Ni–dioxime (complex).

2. Experimental

2.1. Reagents and materials

All chemicals were of analytical grade. Dioctyl phthalate (DOP), dioctyl sebacate (DOS), tetrahydrofuran (THF), and high relative molecular weight PVC were purchased from Aldrich Chemical Company and used as received. Potassium salts of all anions used (all from Merck) were of the highest available purity and used without any further purification except vacuum drying over P_2O_5; deionized water was used throughout the experimental work. The chelating agent H_2L (Dioxime) was synthesized and purified as described elsewhere [23]. The chloro–nickel complex of this ligand [Ni(HL)]Cl was prepared by direct reaction of equal quantities of the ligand and $NiCl_2$ solution of concentration 1×10^{-2} M. The red precipitate was filtered, washed, dried at room temperature, and incorporated as electroactive material in the formation of the selective membrane sensitive to sulfate ions.

2.2. Electrode preparation

The used procedure to prepare the PVC membrane was to mix thoroughly 190 mg of powdered PVC, 350 mg of plasticizer DOP or DOS, and 10 mg of the elctroactive [Ni(HL)]Cl. Then, the mixture was dissolved in 5 ml of THF. The resulting clear mixture was evaporated slowly until an oily concentrated mixture was obtained. A thick disk (0.1 mm) was cut from the transparent membrane and glued to PVC tube as previously described [24]. The tube was then filled with the internal solution (1.0×10^{-3} M K_2SO_4). The electrode was finally conditioned for 24 h by soaking in a 1.0×10^{-3} M potassium sulfate solution until a stable potential value was obtained according to the widely accepted practice. A silver–silver chloride electrode was used as an internal reference electrode.

2.3. Characterization tools

Carbon, hydrogen, and nitrogen were determined using JEOL JMS-AX500 elemental analyzer. FTIR spectra of both the ligand before and after complexation with Ni were collected by Varian 3100 FT-IR Excalibur Series instrument. The UV–visible absorption spectrum of the prepared Ni–dimethylglyozimate was carried out using Jasco UV–visible spectrophotometer (Model V530, Japan).

2.4. The electromotive force (emf) measurements

All emf measurements were carried out with the following assembly:

(1) Ag–AgCl | KCl (3 M) internal solution, 1.0×10^{-3} M K_2SO_4 PVC membrane test solution | Ag–AgCl;

(2) All potentiometric measurements were made at 25 ± 1˚C with an Orion digital pH/mV using PVC-Ni-3, 8-dimethyl-1,5,6-benzo-4,7-diazadece-3, 7-diene-2, 9-dione (dioxime) sulfate membrane sensor in conjunction with an Orion double junction Ag/AgCl reference electrode (model 90-02) filled with 10% w/v KNO_3 in the outer compartment. An Orion combination pH electrode (model 91-02) was used for all pH adjustment.

3. Results and discussion

3.1. Characterization of the newly synthesized Ni–dioxime complex

The composition of the prepared red Ni–dioxime sulfate complex was confirmed via elemental analysis and electric spectra. The data of the elemental analysis of both chelating agent and its corresponding Ni–dioxime complex is presented in Table 1. The consistency between calculated and experimental values of the elemental analysis gives an indication that the used preparation procedure is successful and the formation of $[Ni(H_2L)]Cl$ complex is expected.

The UV–visible absorption spectrum of the prepared Ni-dimethylglyozimate is presented in Fig. 2. It is similar to that previously reported for Ni-dimethylglyozimate [25]. For further confirmation, FTIR spectra of both the ligand before and after complexation with Ni were recorded and presented in Fig. 3. It was noticed that $\gamma C_{N}^{=}$ (1,629 cm^{-1}) in the FTIR spectra of the ligand was shifted to lower wave number (1,449 cm^{-1}) in the complex spectra. Furthermore, a new band at 519 cm^{-1} respective for Ni–N bond was observed in addition to two new bands at 1,240 and 1,100 cm^{-1} which can be assigned to the cyclic skeleton of the complex. Since the FTIR spectra of the prepared membrane was evaluated after soaking in 1 mM K_2SO_4 solution, the prepared complex was performed using $NiSO_4$ and the resulted precipitate was measured by IR; the spectra give new band at 1,050 cm^{-1} indicating the presence of sulfate group in the prepared complex.

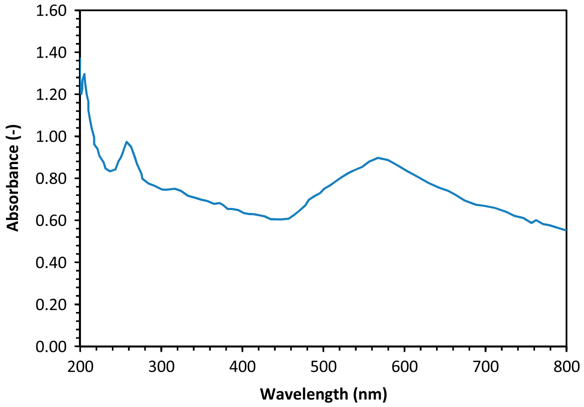

Fig. 2. UV–visible absorption spectrum of Ni–dimethylglyozimate.

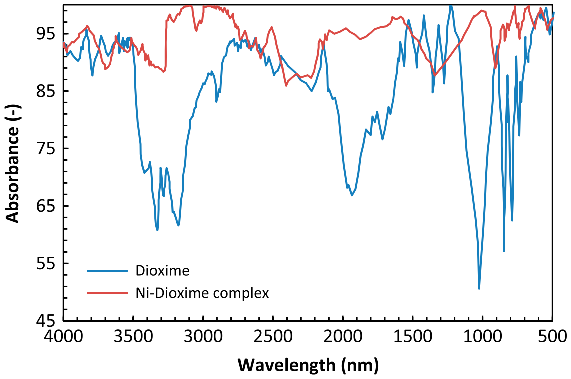

Fig. 3. FTIR spectra of the Ni–dioxime complex (after soaking in K_2SO_4 solution) and dioxime.

Table 1
Elemental analysis of ligand and Ni–dioxime

	Dioxime		Ni–dioxime complex	
Element (%)	Calculated	Experimental	Calculated	Experimental
C	61.29	61.29	44.7	43.8
H	6.78	6.78	4.81	4.64
N	20.47	20.47	15.9	17.29

3.2. Characterization of the membrane electrode

Various membrane compositions have been investigated with different plasticizers (DOP and DOS) during this study. Among the tested different membrane compositions, membrane with composition 1% [Ni(HL)]Cl ionic carrier, 33% PVC, and 66% plasticizer (DOP or DOS) offers the best sensitivity as well as the widest linear range, with a Nernstian slope of about −30 mV per decade as illustrated in Fig. 4. It is immediately obvious that the nature and amount of the additives (DOP or DOS) did not influence the performance characteristics of the membrane sensor significantly. It can be seen that the two sensors prepared showed a linear potentiometric response over a wide concentration range of 5×10^{-7}– 1×10^{-2} M sulfate ions concentration with a slope of −30.04 mV per decade of sulfate ions and a correlation coefficient of 0.9998. The slopes of the calibration graphs are Nernstian compared with the sub-Nernstian or over-Nernstian slopes given by some other sensors [26–28].

The linear range of the sensor response for SO_4^{2-} is about five decades of concentration which is 1–2 decades greater than those reported for some other sulfate ions electrodes.

The limits of detection, defined as the concentration of sulfate ions obtained when extrapolating the linear calibration region to the baseline potential, are given in Table 2. As can be seen, the sensor showed detection limits of (0.288 ppm) which are better than those of most other sulfate sensor. The limits of detection obtained in this work are several orders of magnitude below the sulfate concentration in pharmaceutical samples [18,29].

The influence of the concentration of internal solution on the potential response of the SO_4^{2-} ion-selective sensor was studied. The K_2SO_4 concentration was changed from 1.0×10^{-7} to 1.0×10^{-2} M and the emf was recorded. It is seen that the variation of the concentration of the internal potassium sulfate solution does not cause any significant difference in the potential response, except for an expected change in the intercept of the resulting Nernstian plots. A 1.0×10^{-3} M concentration of the reference solution is quite appropriate for smooth functioning of the sensor system.

Table 2
Performance characteristics of the Ni–dioxime–PVC sulfate membrane sensor

Slope (mV/decade)	− 30.3
Liner concentration range (M)	5×10^{-7} to 10^{-2}
Lower limit of detection (M)	3×10^{-7}
Response time (s)	< 1
Range (pH)	4. –7.5
Intercept (mV)	710
Correlation coefficient (*r*)	0.999

The pH sensitivity of the proposed electrode was examined by obtaining the potential responses of the membrane electrode in 1.0×10^{-3} and 1.0×10^{-4} M sulfate solution at pH 2–9, and the results are shown in Fig. 5. As seen, the most sensitive potential response is obtained at a pH range 4–7.5. At pH values lower than 4, the sensor seems to respond to proton significantly while at higher pH values, the ionic carrier has presumably a low tendency for sulfate ions.

As shown in Fig. 6, the time for the electrode to reach 90% of the steady response was <15 s and no change is normally observed up to 5 min. Potential was monitored periodically at fixed concentration and standard deviation of 10 identical measurements was 2.0 mV. In terms of the life of the PVC membrane sensor, the response stability was observed for over more than 6 months.

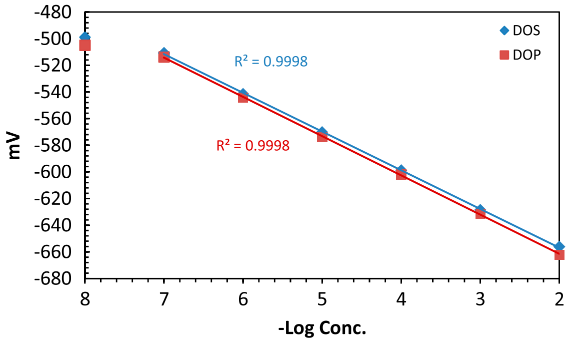

Fig. 4. Potentiometric response curves for the sensor with different plasticizers.

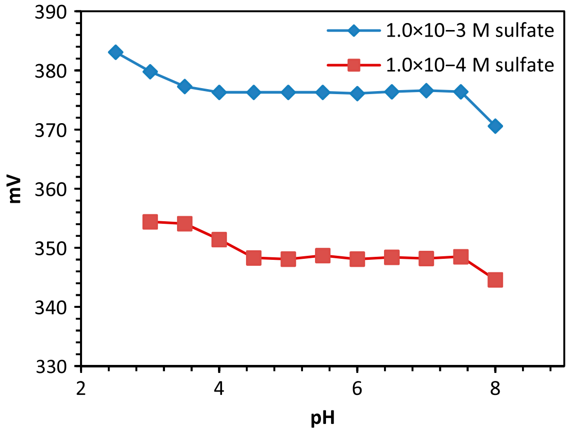

Fig. 5. Effect of pH on the potential response of the proposed sulfate sensor selective electrode.

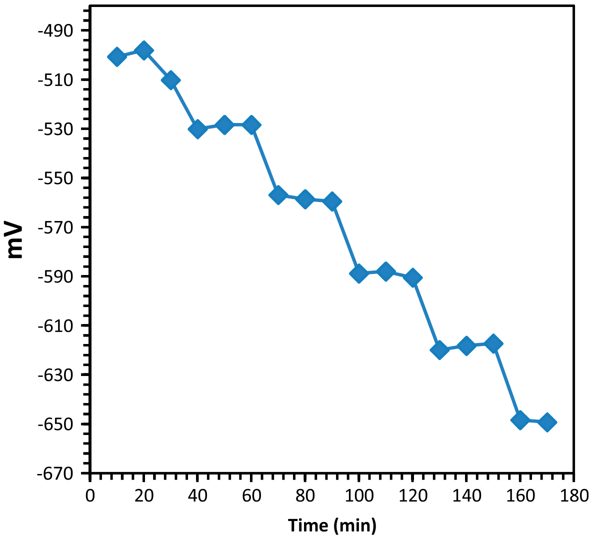

Fig. 6. Dynamic response time of Ni–dioxime complex membrane electrode for step changes concentration of sulfate from 1×10^{-7} to 10^{-2} M.

The potentiometric selectivity coefficients K_{ij}^{pot} describing the preference by the PVC membrane incorporating the ionic carrier for an interfering ion *j*, relative to sulfate ion *i*, were determined by the separate solution method (SSM), which is recommended by IUPAC, 2000 [30]. In this method, the selectivity coefficients of sulfate sensor were evaluated graphically at fixed concentration of sulfate ion and interferant as shown in Fig. 7. According to the data in Table 3, excellent selectivity coefficients in the order of 10^{-3} and lower are obtained for a large number of inorganic and organic anions indicating insignificant interfering effect of these anions on the sulfate ion determination by the proposed membrane sensor.

Table 3
Selectivity coefficients for Ni–dioxime PVC–sulfate membrane sensor

Interferent, *j*	$K^{\mathrm{Pot}}_{\mathrm{SO_4^{2-}}j}$
$\mathrm{I^-}$	2.71×10^{-3}
$\mathrm{Cl^-}$	8.57×10^{-4}
$\mathrm{IO_4^-}$	7.35×10^{-4}
$\mathrm{ClO_4^-}$	1.99×10^{-4}
$\mathrm{BrO_3^-}$	1.07×10^{-3}
$\mathrm{B_4O_7^-}$	2.15×10^{-3}
$\mathrm{SO_3^{2-}}$	8.51×10^{-3}
$\mathrm{S_2O_3^{2-}}$	5.84×10^{-3}
$\mathrm{CO_3^{2-}CO_3{}^{2-}}$	7.94×10^{-3}
$\mathrm{HCO_3^-}$	4.64×10^{-4}
$\mathrm{NO_2^-}$	1.35×10^{-4}
$\mathrm{NO_3^-}$	5.01×10^{-4}
$\mathrm{SCN^-}$	2.92×10^{-4}
$\mathrm{HPO_4^-}$	4.29×10^{-3}
$\mathrm{CH_3COO^-}$	1.16×10^{-3}

Typical selectivity pattern for these series of anions showed by the electrode was as follows:

$$\mathrm{SO_4^{2-} > SO_3^{2-} > CO_3^{2-} > S_2O_3^{2-} > HPO_4^{2-} > B_4O_7^{2-}}$$
$$\mathrm{> CH_3COO^- > BrO_3^- > Cl^- > IO_4^- > NO_3^- > HCO_3^-}$$
$$\mathrm{> SCN^- > NO_2^- > ClO_4^-}$$

In Table 4, the selectivity coefficients of proposed sensor were compared with those reported previously [10–12,23,26,31–34]. Noteworthy, this is just a gross relative comparison, since the selectivity data have been reported using different experimental method. The table clearly indicates a tremendous enhancement in selectivity behavior of the PVC membrane sensor proposed in this work.

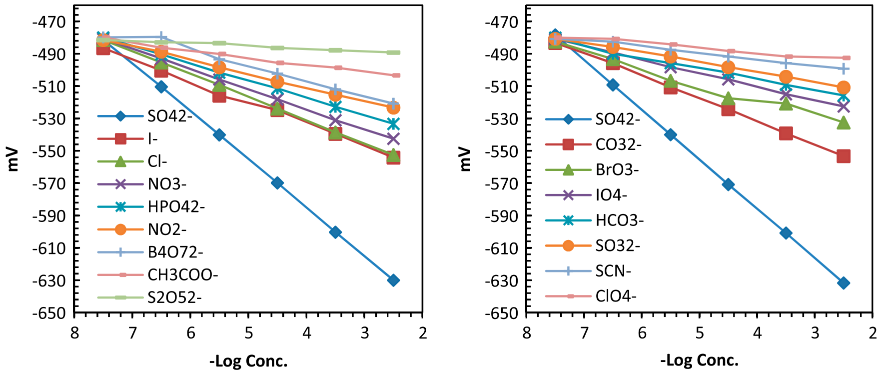

Fig. 7. Potential response of sulfate–PVC membrane sensor based on Ni–dioxime complex for various ions.

Table 4
Comparison among the selectivity coefficients of different prepared sensors

Anions	Ref [10, 26]	Ref [11]	Ref [12]	Ref [23]	Ref [31]	Ref [32]	Ref [33]	Ref [34]	This work
Br	12.6	7.9	2.5×10^2	7.9×10^{-3}	1.0×10^{-3}	1.0×10^{-1}	3.2×10^{-3}	6.9×10^{-3}	–
CO_3^{2-}	–	–	7.9	3.3×10^{-3}	1.0×10^{-3}	–	6.3×10^{-3}	4.0×10^{-3}	7.94×10^{-3}
Cl^-	7.9×10^{-1}	1.1×10^{-1}	6.3×1	5.8×10^{-3}	–	3.0×10^{-1}	4.0×10^{-3}	4.9×10^{-3}	8.57×10^{-4}
CN^-	–	–	–	3.5×10^{-4}	1.0×10^{-3}	–	1.5×10^{-2}	4.0×10^{-3}	–
I^-	–	–	$2.5 \times 10^{-}7$	2.7×10^{-4}	1.0×10^{-3}	–	1.6×10^{-2}	8.0×10^{-3}	2.7×10^{-3}
NO_3^-	4.0×101	1.2×10^2	2.0×10^4	3.4×10^{-3}	–	3.3	6.2×10^{-3}	5.0×10^{-3}	5.01×10^{-4}
NO_2^-	4	2	–	7.2×10^{-2}	5×10^{-1}	–	1.0×10^{-2}	9.9×10^{-4}	1.35×10^{-4}
SO_3^{2-}	5.0×10^{-1}	–	–	8.7×10^{-3}	1.0×10^{-3}	–	1.2×10^{-3}	7.9×10^{-2}	8.51×10^{-3}
SCN^-	8.0×10^2	–	–	3.4×10^4	1.0×10^{-3}	1.0×10^2	7.9×10^{-2}	1.0×10^{-4}	2.98×10^{-4}
ClO_4^-	–	–	2.5×10^{10}	3.6×10^{-4}	–	–	3.1×10^{-2}	4.0×10^{-3}	1.99×10^{-4}
CH_3COO^-	–	–	–	–	–	–	6.3×10^{-3}	3.1×10^{-3}	1.16×10^{-3}
HPO_4^{2-}	–	–	–	–	–	–	–	–	4.29×10^{-3}

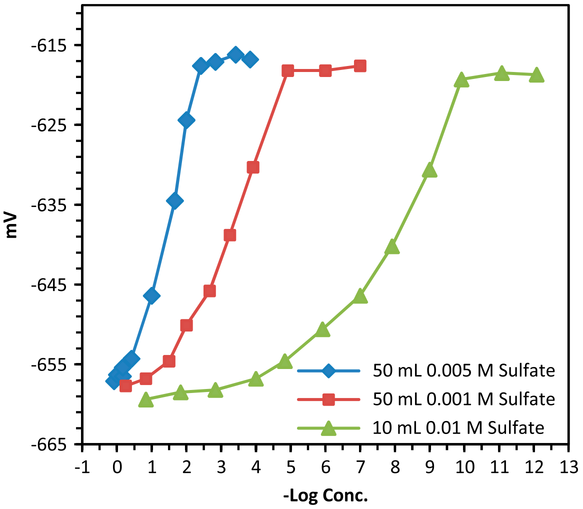

Fig. 8. Potentiometric titration curves for different concentrations of sulfate solution, 1.0×10^{-2} M of Ba^{2+} (barium nitrate).

3.3. Analytical application

The proposed membrane sensor was found to perform well under laboratory conditions. It is successfully used as an indicator electrode in the titration of sulfate ion solution (1.0×10^{-2}, 1.0×10^{-3} and 5.0×10^{-3} M) with Ba^{2+} ion (1.0×10^{-2} M) and vice versa. The results of both titrations are shown in Fig. 8. It illustrates that the amount of SO_4^{2-} or Ba^{2+} ions can be accurately determined with the proposed sensor.

The sensor was also applied for the determination of sulfate concentration in some pharmaceutical products using direct potentiometry, for instance, Neomycine tablets, Visceralgin tablets, and also streptomycin powder injection. The sulfate was determined in these three drugs using the proposed sensor. The results are favorably compared to the conventional turbidimetry method as a standard method (Table 5).

Table 5
Determination of sulfate in some pharmaceutical formalization using potentiomtric method & turbidimetrey method

	Potentiometry		Turbidimetry	
Sample *(sources)*	Conc. (mg/L)	Recovery (%)	Conc. (mg/L)	Recovery (%)
Visceralgine *(Sedico Pharmaceutical Co.)*	2.9 ± 0.3	96.60	3.1 ± 0.4	103.30
Streptomycine *(Nile Co. for Pharmaceutical & Chemical Industry)*	394.3 ± 0.4	99.50	395 ± 0.5	99.70
Neomycine *(Memphis Co. for Pharmaceutical & Chemical Industry)*	94.9 ± 0.2	97.80	95.5 ± 0.3	98.40

4. Conclusion

A highly selective and sensitive sulfate–PVC membrane based on nickel complex of 3,8-dimethyl-5,6-benzo-4,7-diazadece-3,7-diene-2,9-dione (dioxime) was successfully synthesized. Various membrane compositions have been investigated with different plasticizers (DOP and DOS) during this study. However, it was confirmed that the nature and amount of the additives (DOP or DOS) did not influence the characteristics of the membrane sensor significantly. The prepared membrane showed an outstanding reproducibility and fast response time towards SO_4^{2-} ion in the concentration range of 5.0×10^{-7} to 1.0×10^{-2} M with an anionic slope of -30 ± 0.2 mV per decade along with as low detection limit as 3×10^{-7} M. Furthermore, it was noticed that the potentiometric behavior of this sensor is independent of the pH of the solution in the range of 4.5–7.5. The selectivity coefficients determined by the SSM revealed that the interference of hydrophobic inorganic anions was very low in comparison with the conventional ion-exchanger-based electrodes. The sensor also was applied fruitfully in the potentiometric titration of sulfate with barium ions and in quantification and quality assessment of sulfate in some pharmaceutical formulations.

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