

# Highly Selective Thiocyanate PVC Membrane Electrode based on Ni (II) Complex of 2-Acetyl Thiophene Thiosemicarbazone Schiff Base (NATS) as Ionophore

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**Abstract:** A highly selective PVC-membrane electrode based on the Nickel (II) complex of 2-acetylthiophene thiosemicarbazone schiff base  $[\text{Ni}(\text{L})_2]\text{Cl}_2$  was fabricated and tested as a membrane sensor towards  $\text{SCN}^-$  ions. The newly synthesized 2-acetylthiophene thiosemicarbazone ligand (L) was prepared with the help of 2-acetyl thiophene and thiosemicarbazide hydrochloride. Metal complex was synthesized based on this ligand with  $\text{NiCl}_2$ . The ligand and complex were characterized by the FT-IR, Elemental analysis,  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  spectral studies. Ni (II) complex of 2-acetylthiophene thiosemicarbazone was then used as a good sensing material for preparing thiocyanate ion selective PVC membrane sensor. The proposed potentiometric sensor showed a stable potential response to thiocyanate ion with Nernstian slope of  $-59.2 \pm 0.1 \text{ mV decade}^{-1}$  over a linear concentration range of  $1.0 \times 10^{-6}$  to  $1.0 \times 10^{-1}\text{M}$ . The response of the developed electrode was independent of pH in the range of 2.5–10.0. The sensor worked well with a short response time of  $\sim 10 \text{ s}$  and a lifetime of about 6 weeks. The proposed sensor finds application as an indicator electrode in the potentiometric titration of  $\text{SCN}^-$  with  $\text{Ag}^+$  ions and to determine the concentration of thiocyanate ion in water samples.

**Keywords:** Schiff base, Sensor, Ni-Complex, Thiocyanate ion, Ion selective electrode, PVC-membrane.

## INTRODUCTION

The thiocyanate ion exists at low concentration in serum, saliva and urine on digestion of some vegetables containing glucosinolates (cabbage, turnip, kale) or by consuming thiocyanate containing foods such as milk and cheese. It also finds many industrial applications and even not as toxic as cyanide, but it's harmful to aquatic life. However higher concentration of this ion arises from tobacco smoke [1], which leads to dizziness or unconsciousness in human body [2]. Therefore, an accurate, simple, and fast method for the analysis of thiocyanate is significant in medicine and in life sciences [3]. Various analytical methods to determine thiocyanate ion are spectrophotometry [4], chromatography [5], polarography [6], amperometry [7], potentiometric methods [8-12] and voltammetry methods [13]. Among the various methods, the ion selective electrodes (ISEs) are useful since it is rapid and less expensive method with

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high sensitivity[14-18]. The use of Schiff base ligands and their metal complexes have been reported mostly for the construction of sensors for various cationic species, but a fewer works is available for anionic sensors [19-22]. Recently, several SCN<sup>-</sup> ion-selective electrodes based on variety of ion carriers such as metalloporphyrins [23-24], metallophthalocyanines [25], cyclometallic amines[26], modified zeolites [27], Schiff base complexes [10, 28-29], and N-4 metal complexes [11, 30-31] have been reported. Among these reported ISEs, some electrode sensors have narrow linear range [32], narrow pH range [9, 33] and high detection limit [32] and some suffers by serious interference from anions viz. CN<sup>-</sup>[10, 34], Cl<sup>-</sup> [32] and SO<sub>4</sub><sup>2-</sup> [34].

*S. K. Srivastava and V. K. Gupta et. al. (1995) reported a PVC-based membrane sensor of 15-crown-5 for Pb(II) ion [35] and ISE based on dibenzo-24-crown-8 for Cs ions[36]. S. K. Srivastava and V. K. Gupta et. al.[37](1996) also developed a PVC-based membrane sensor of 2,2,2-cryptand, for Zn<sup>2+</sup> in a wide concentration range with a slope of 22.0 mV/decade. V. K. Gupta and L. P. Singh et. al. (2012) reported [38], Cu (II) selective sensor based on dimethyl 4, 4' (o-phenylene) bis (3-thioallophanate) in PVC matrix. This sensor exhibits linear response over the concentration range of  $9.8 \times 10^{-6}$  –  $1.0 \times 10^{-1}$  M. V. K. Gupta and B. Sethi et. al. (2013) have prepared a novel potentiometric Hg (II) sensor based on 5, 11, 17, 23-tetratert- butyl-25, 27-dihydroxy-26, 28-bis(O-methyl glycylicarbonylmethoxy) thiacalix [4]-arene as ionophore [39]. V. K. Gupta and S. Kumar et. al. (2014) have developed sensor for Cd(II) containing p-tert-butylcalix [6] arene (I) as an electroactive material [40]. V. K. Gupta and coworkers (2014) reported fluorescent chemosensor for Al(III) ion by using thiazole Schiff bases[41] and a nanosensor based on graphene oxide/silver nanoparticles for the determination of quercetin and morin[42]. H. K. Maleh and F. T. Javazmi et. al. (2015) presented a novel biosensor employing immobilized DNA on a pencil graphite electrode modified with polypyrrole/functionalized multiwalled carbon nanotubes for the determination of 6- mercaptopurine (6-MP)[43]. V. K. Gupta and H. K. Maleh et. al. (2015) have further developed a novel 8,9-dihydroxy-7-methyl-12H-benzothiazolo[2,3-b]quinazolin-12-one -ZnO/CNTs modified carbon paste electrode for the electrocatalytic determination of hydroxylamine (HX) in the presence of phenol (PL) and sulfite (ST) in waste water samples[44].*

In the present section, Nickel complex of 2-acetylthiophene thiosemicarbazone [Ni(II) (L)<sub>2</sub>] was incorporated as an ionophore. It shows better electrode response as compared to the previously reported thiocyanate ISEs based on various schiff based ionophores. This ISE shows a good detection limit, high selectivity and sensitivity, wide dynamic range and fast response time.

## EXPERIMENTAL

### Reagents and Apparatus

Chemicals of the highest purity available and of reagent grade were used. 2-acetylthiophene and thiosemicarbazide were purchased from Central Drug House (New Delhi). Plasticizers dibutylphthalate (DBP), dioctylphthalate (DOP), 2-nitrophenyloctyl ether (NPOE) and tri-n-butylphosphate (TNBP) were purchased from E. Merck (Germany). High molecular weight PVC powder, cation excluder MTOAC (methyltrioctyl-ammonium chloride) and metal salts were purchased from Sigma-Aldrich. Standard solutions of metal salts were prepared in double distilled deionized water. The % content of C, H, N and S were analyzed on a Vario Micro Cube elemental analyzer; Model Vario-III. <sup>1</sup>H and <sup>13</sup>C- NMR spectra were recorded on a Bruker NMR spectrophotometer with DMSO-D<sub>6</sub> as solvent. Chemical shift are recorded in ppm with tetramethylsilane (TMS) as reference. The FT-IR spectra were recorded on a Perkin Elmer spectrophotometer. A Perkin-Elmer Model 3100 atomic absorption spectrophotometer (AAS) with a graphite furnace was used.

### Syntheses of ligand (L) [45]

Ethanol solution of 2-acetyl thiophene (1.26g, 0.01mol) was added in hot ethanolic solution (20 mL) of thiosemicarbazide (0.91g, 0.01 mol) with constant stirring. 4 drops of acetic acid were also added to this mixture. The mixture was then refluxed at  $\sim 80$  °C for 2 hrs. On cooling, a light yellow coloured compound was separated out. It was then filtered, washed with 50% ethanol, and further dried and recrystallized from methanol (Fig. 1).

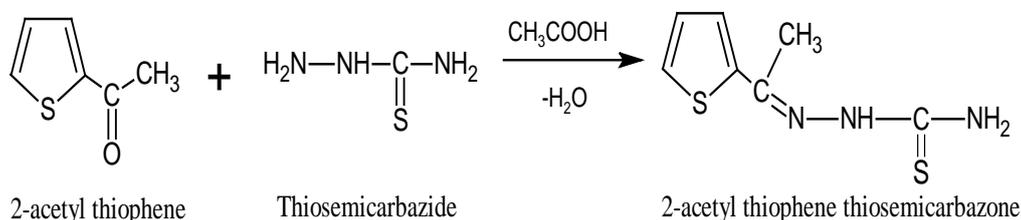


Figure 1: Scheme for the synthesis of 2-acetyl thiophene thiosemicarbazone (L).

**2-acetyl thiophene thiosemicarbazone ligand:** Yield (88.0%), M.P: 140 °C, Anal. calc. for (%) =  $C_6H_7N_3S_2$ : C, 42.18%; H, 4.55%; N, 21.09%; and Found (%): C, 40.66%; H, 3.49%; N, 22.15%; FT-IR (KBr)/  $cm^{-1}$ :  $\nu(NH_2)$  3407 (b),  $\nu(NH)$  3146 (b),  $\nu(C=N)$  1588,  $\nu(C=S)$  852;  $^1H$ NMR (DMSO- $D_6$ , 300 MHz):  $\delta$ / ppm= $\delta$ 3.39 (s,>NH);  $\delta$ 8.3 (s,  $H_2N-CS$ );  $\delta$ 10.35 (s,  $-HC=N-$ );  $\delta$ 2.28 (s,  $H_3C-C$ );  $\delta$ 7.43-7.58 (m, Ar-H).

### Synthesis of Ionophore Metal Complex $[Ni(L)_2]Cl_2$

A hot aqueous solution (20 mL) of nickel chloride (1.30g, 0.01 mol) was added dropwise to a hot ethanolic solution (20 mL 1:1 v/v) of 2-acetylthiophene thiosemicarbazone (3.98g, 0.02 mol) with constant stirring. The mixture was then set to reflux for about 9 hrs on a water bath at 75 to 80 °C. On cooling a green coloured precipitate was separated out. It was then filtered, washed several times with 50% ethanol, dried and were recrystallized (Fig. 2).

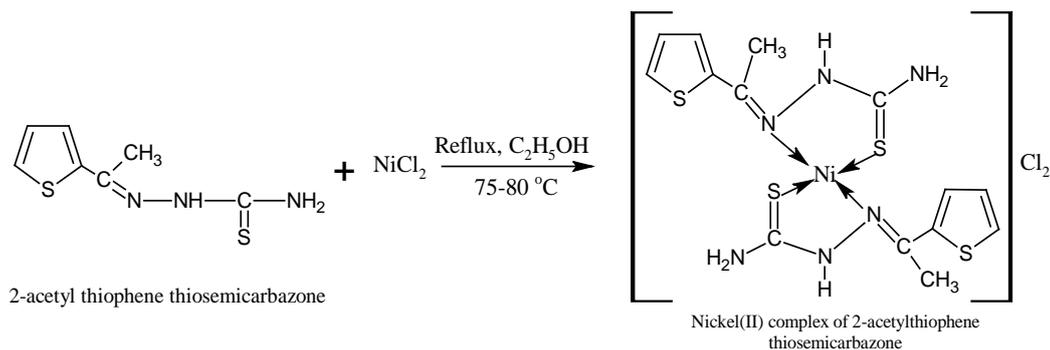


Figure 2: Scheme for the synthesis of Nickel(II) complex with 2-acetylthiophene thiosemicarbazone.

**Nickel(II) 2-acetylthiophene thiosemicarbazone complex:** Yield (90%), M.P.: 170 °C, Anal calc.for (%) =  $C_{12}H_{14}N_6S_4ZnCl_2$ : C,28.44; H,2.78; N,16.58; S,25.31; Found: (%): C,28.15; H,2.76; N,16.47; S,24.98; FT-IR(KBr)/  $cm^{-1}$ :  $\nu(NH_2)$  3447 (b), $\nu(NH)$  3284 (b),  $\nu(C=N)$  1508,  $\nu(C=S)$  851.  $^1H$  NMR (DMSO - $D_6$ ,  $\delta$ /ppm):  $\delta$ 4.1 (s,>NH);  $\delta$ 9.6 (s,  $-HC=N-$ );  $\delta$ 2.75 (s,  $H_3C-C$ );  $\delta$ 6.54-7.25 (m, Ar-H).

### Electrode Preparation

PVC membrane electrode was prepared by the method given by Craggs et. al. [46]. The membrane was prepared by taking the fixed mixture of PVC: plasticizer (TBP): Ionophore (NATS): Excluder (MTOAC) in the ratio 32: 63: 4: 1 (w/w %, in mg) as membrane contents. This mixture was dissolved in THF (10 mL)

vigorously and then poured into a glass dish. After some time, the solvent was evaporated and a sticky, oily mixture was obtained. Pyrex tubes of 5 mm internal diameter were dipped into this sticky mixture, hold for few seconds and then removed to obtain a transparent membrane (average thickness of 0.3 mm). Now fixed one end of these Pyrex tubes (from the membrane side) with the help of Araldite and then dried for 4 Hrs. These membrane glass tubes were then rinsed with water and filled with  $1.0 \times 10^{-2}$  M NaSCN solution for conditioning for 24 hrs.

### Potential Measurements and Calibration

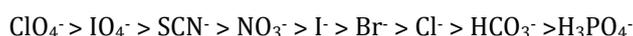
Electrode potentials were measured at constant temperature ( $25 \pm 0.05$  °C) with the help of digital pH/mV meter of ELICO model L1-10 and saturated calomel electrode (SCE) as reference electrode. Salt bridge was freshly prepared and used in conjugation. The following electrochemical cell set-up was used for the EMF measurements:

**Hg-Hg<sub>2</sub>Cl<sub>2</sub>, KCl (saturated) || sample solution ( $1.0 \times 10^{-2}$  M NaSCN) | PVC membrane | test solution || Hg-Hg<sub>2</sub>Cl<sub>2</sub>, KCl (saturated).**

## RESULTS AND DISCUSSION

### Influence of Membrane Composition and Response Characteristics

It is well known [47] that the sensitivity, linear range and selectivity of an electrode sensor depends not only on the nature of ionophore used, but also significantly affected by the membrane composition and the type of additives used [48-49]. The hydrophobic nature of the membrane prevents leaching of the sensing ion and plasticizer into the sample solution and thus extends the lifetime of the electrode. The chelating agent is hydrophobic and has the opposite polarity in ISE's, the ion-exchangers such as quaternary ammonium salts have been employed for the preparation of anion selective electrodes. The resulting ISEs usually display anion selectivity corresponding to the Hofmeister series [50-51].



Therefore, the influence of different membrane ingredients on potential were investigated by varying the amount of ionophore, amount and nature of the plasticizer and additives employed. The potential of each membrane electrode was measured in sodium thiocyanate solutions in the concentration range of  $1.0 \times 10^{-9}$  to  $1.0 \times 10^{-1}$  M. Then the potential responses of anions were plotted against the logarithm of anion concentration (Fig. 3). The best response was observed for the SCN<sup>-</sup> ion with the membrane no. 3 of following composition as reported in (Table 1): PVC 32%, TBP 63%, Ionophore 4%, and MTOAC 1%. From the potential response in Fig. 3, it is clear that the calibration curve slope was  $-59.2 \pm 0.1$  mV/decade in the linear range of  $1.0 \times 10^{-6}$  to  $1.0 \times 10^{-1}$  M SCN<sup>-</sup> concentration.

It was known that the best response and increased selectivity were usually observed with an ionophore/TOMAC ratio of nearly 4.0, which ensures enough mobility in the membrane composition. It is clear from Table 1, that TBP is used as a plasticizer to prepare the membrane for thiocyanate ion-selective electrode. It is also known that the amount of ionophore in PVC membrane also affect the Nernstian slope for any sensor electrode. It is obvious that on increasing the ionophore concentration from more than 2% (w/w) in membrane, the slope gets deteriorated with a narrow linear concentration range. Hence, a small amount of ionophore is only required for the preparation of electrode membrane [52]. It can be seen from (Table 1); that the most optimum ratio taken was PVC: TBP: Ionophore: MTOAC as 32: 63: 4: 1 (w/w %, in mg) which was used for further studies.

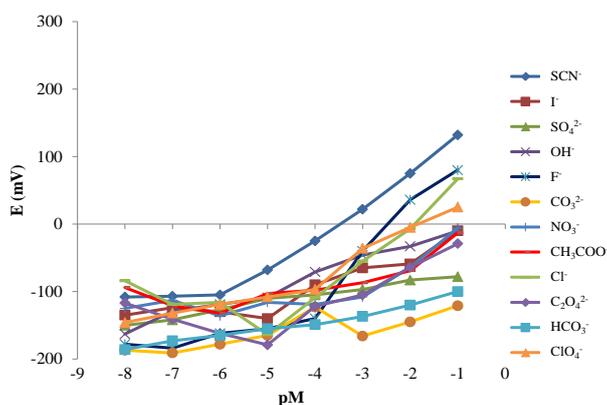


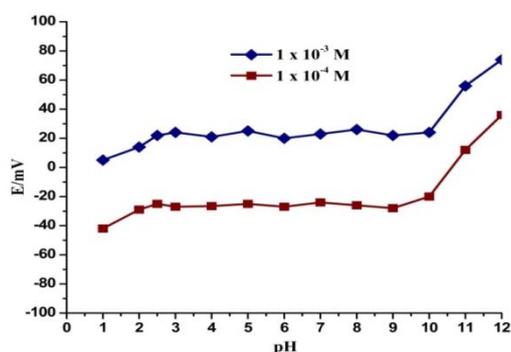
Figure 3: Potential response curve for different anions.

Table 1: Composition of PVC membrane of (NATS) and performance characteristics of SCN<sup>-</sup>-selective sensors based on them

S. No.	Composition of membranes (w/w %)				Linear range (M)	Slope (± mV/decade)
	NATS	PVC	MTOAC	Plasticizer		
1	2	33	5	-	$1.0 \times 10^{-6}$ to $1.0 \times 10^{-1}$	56.4
2	3	30	4	TBP, 63	$1.0 \times 10^{-5}$ to $1.0 \times 10^{-1}$	56.0
3	<b>1</b>	<b>32</b>	<b>4</b>	<b>TBP, 63</b>	<b><math>1.0 \times 10^{-6}</math> to <math>1.0 \times 10^{-1}</math></b>	<b>59.2</b>
4	4	33	3	NPOE, 60	$1.0 \times 10^{-4}$ to $1.0 \times 10^{-1}$	58.1
5	1	33	3	DBP, 63	$1.0 \times 10^{-5}$ to $1.0 \times 10^{-2}$	55.8
6	2	30	2	DOP, 66	$1.0 \times 10^{-5}$ to $1.0 \times 10^{-1}$	57.6
7	2	33	2	DOP, 63	$1.0 \times 10^{-7}$ to $1.0 \times 10^{-1}$	54.5

#### pH Effect

The effect of *pH* of the test solution on electrode response was examined at two thiocyanate concentrations over the *pH* range of 1.0–12.0 and typical results for  $1.0 \times 10^{-3}$  and  $1.0 \times 10^{-4}$  M SCN<sup>-</sup> are shown in Fig. 4. The *pH* was adjusted with dilute HNO<sub>3</sub> and NaOH solutions.

Figure 4: Effect of *pH* on Potential for the SCN<sup>-</sup> Selective Electrode

The results in Fig. 4 show that the present sensor is useful over the *pH* range of 2.5–10.0. Variations in the potential was observed at higher and lower *pH* values, which is due to the fact that electrode is responding to more than two ions, while at lower *pH* values this could be related to protonation of the ionophore in membrane.

### Non-Aqueous Effect

The effect of non-aqueous medium on electrode response was also investigated by using partially non-aqueous solutions as methanol-water, acetone-water and ethanol-water mixtures. It is illustrated from (Table 2) that the electrode worked well in partially non-aqueous medium of up to 20% (v/v), because the linear concentration range and slope remains unaffected. However, with non-aqueous content with more than 20%, both the slope and linear range was affected which may be due to leaching of ionophore at higher organic content.

Table 2: Effect of partially non-aqueous medium on SCN<sup>-</sup> selective sensor (sensor 3)

Non-aqueous content (v/v, %)	Working concentration range (M)	Slope (± 0.1mV/decade)
Methanol		
10	1.0×10 <sup>-6</sup> to 1.0×10 <sup>-1</sup>	59.2
20	1.0×10 <sup>-6</sup> to 1.0×10 <sup>-1</sup>	59.3
30	1.0×10 <sup>-6</sup> to 1.0×10 <sup>-1</sup>	59.4
Ethanol		
10	1.0×10 <sup>-6</sup> to 1.0×10 <sup>-1</sup>	59.1
20	1.0×10 <sup>-6</sup> to 1.0×10 <sup>-1</sup>	59.2
30	1.0×10 <sup>-6</sup> to 1.0×10 <sup>-1</sup>	59.3
Acetone		
10	1.0×10 <sup>-6</sup> to 1.0×10 <sup>-1</sup>	59.2
20	1.0×10 <sup>-6</sup> to 1.0×10 <sup>-1</sup>	59.2
30	1.0×10 <sup>-6</sup> to 1.0×10 <sup>-1</sup>	59.1

### Potentiometric Selectivity

The selectivity is one of the most important characteristics of any ISE sensor because it delineates the extent to which an ion-selective sensor can be used for the determination of analyte ion in presence of interfering ions[53-54].

Basically it is response of the electrode to the primary ion in presence of interfering ions in solution and is expressed as the selectivity coefficients ( $K_{ij}$ ).

Potentiometric selectivity coefficient values for thiocyanate sensor ( $K_{A,B}^{pot}$ ), were determined by the fixed interference method (FIM) [36], which describe the preference of the membrane for an interfering ion A<sup>-</sup> relative to SCN<sup>-</sup> ion. The selectivity coefficients of the proposed electrode for various anions are presented in (Table 3), which clearly indicates that the electrode is highly selective to SCN<sup>-</sup> over a number of other anions. The potential is measured with solution of constant interference  $a_B$ , and different primary ion activity  $a_A$ [55-56]. Potential values were plotted against the activity of primary ion and the values of  $a_A$  from the curve were used to calculate  $K_{A,B}^{pot}$  from the equation:

$$K_{A,B}^{pot} = \frac{a_A}{(a_B)^{z_A/z_B}} \quad (1)$$

Where both  $z_A$  and  $z_B$  have the same sign; positive or negative.

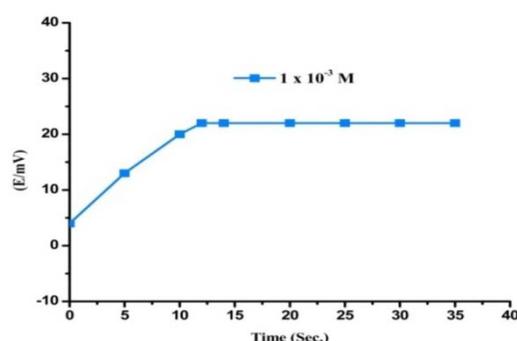
Selectivity coefficient values in (Table 3) shows that the ionophore 2-acetylthiophene thiosemicarbazone Ni(II) complex seems to have higher interaction with SCN<sup>-</sup> compared to the other anions.

Table 3: Selectivity coefficient values ( $K_{A,B}^{Pot}$ ) for  $SCN^-$  ion selective sensor by fixed interference method

S. No.	Interfering ion (B)	Selectivity coefficients ( $K_{A,B}^{Pot}$ )
1	$ClO_4^-$	0.6000
2	$I^-$	0.0850
3	$Cl^-$	0.0030
4	$CF_3COO^-$	0.0020
5	$HCO_3^-$	0.0024
6	$C_2O_4^{2-}$	0.0016
7	$SO_4^{2-}$	0.0005
8	$NO_3^-$	0.0082
9	$CH_3COO^-$	0.0024
10	$F^-$	0.0021
11	$SO_3^{2-}$	0.0008
12	$CN^-$	0.0007

### Response Time and Lifetime

Response time for an ISE is an important factor and it can be defined as the time required for attaining a stable potential after successive immersion of the electrode in a series of primary ion solutions of different concentration by 10-fold [57]. The optimum response time for the electrode to achieve constant potentials in  $1.0 \times 10^{-3} M$  NaSCN obtained was <12 sec. (Fig.5).

Figure 5: Effect of time on potential for  $SCN^-$  ISE.

The lifetime of the sensor electrode was also studied and it is about 6 weeks, during which there is no measurable divergence in potential was observed. Lifetime for any ISE depends on the distribution coefficient of the ionophore in membrane and the plasticizer. Contact time was also optimized for the present sensor which is another important property for an ISE to generate stable and reproducible potentials in a short time. It was noticed that a solution of  $1.0 \times 10^{-2} M$  concentration was appropriate with 24 hrs. contact time for the smooth functioning of electrode.

Table 4: Comparison of the potentiometric parameters of the proposed  $SCN^-$  sensor with the literature reported

Ionophore Name	Working concentration Range (M)	Slope (mV/decade of activity)	pH range	Response Time (s)	Ref.
5,10,15,20-tetrakis-(4-methoxyphenyl)-porphyrin Co(II)	$1.0 \times 10^{-5}$ - $1.0 \times 10^{-1}$	65.8	3.0 - 9.5	20	[58]
Zeolite ZSM-5	$1.0 \times 10^{-6}$ - $1.0 \times 10^{-1}$	58.9	2.0 - 10.1	10	[59]
1-benzyl-3-(4-nitrophenyl) thiourea	$1.0 \times 10^{-5}$ - $1.0 \times 10^{-2}$	59.2	6.0	<5	[60]
bis(N-3-methyl phenyl salicylidenaminato) Cu (II)	$1.0 \times 10^{-6}$ - $1.0 \times 10^{-1}$	59.3	4.0 - 10.0	9-21	[61]
N, N'-bis-(4-phenylazo salicylidene) o-phenylene diamine) Mn (II)	$1.0 \times 10^{-5}$ - $1.0 \times 10^{-1}$	58.1	4- 6	<17	[33]
Ni (II) 2-acetylthiophene thiosemicarbazone	$1.0 \times 10^{-6}$ - $1.0 \times 10^{-1}$	59.2	2.5 - 10.0	~ <12	This work

In Table 4, the proposed  $\text{SCN}^-$  electrode was compared with other reported  $\text{SCN}^-$  electrodes (Vlascici et al. 2006; Badri et al., 2011; Lee et al., 2014; Benvidiet al. 2014; Han et al., 2011). As can be seen from the table that the selectivity, linear range, response time and  $\text{pH}$  range of the proposed sensor is superior to most of the reported thiocyanate sensors.

## ANALYTICAL APPLICATIONS

### Potentiometric Titration of $\text{SCN}^-$ ions with $\text{AgNO}_3$ Solution

The optimized thiocyanate electrode was successfully applied as an indicator electrode for the potentiometric titration of 20 mL thiocyanate solution ( $1.0 \times 10^{-2}$  M) against the  $\text{AgNO}_3$  ( $1.0 \times 10^{-2}$  M) solution as titrant. Results for the titration are shown in Fig. 6, in which a sharp inflection point was observed at the end point to determine the concentration of thiocyanate ion in solution. The titration volume was measured at the inflection point of the titration curve.

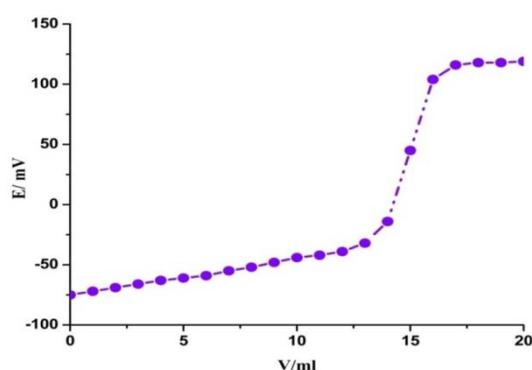


Figure 6: Potentiometric titration curve for 20 ml solution of  $\text{SCN}^-$  ( $1.0 \times 10^{-2}$  M) with  $\text{AgNO}_3$  ( $1.0 \times 10^{-2}$  M), using the proposed sensor in pH 3 sulfonic acid buffer (MES).

### Determination of $\text{SCN}^-$ in Real and Synthetic Samples

The PVC membrane based thiocyanate ion selective electrode was also used for the determination of  $\text{SCN}^-$  ion in some real and synthetic samples. The results obtained were also compared with those determined by the standard spectrophotometric method [62] and are summarized in Table 5. The results of analysis indicate good agreement between two methods.

Table 5: Determination of thiocyanate in real and synthetic samples

Thiocyanate Sample	Sensor found ( $\mu\text{g/ml}$ )	By spectrophotometry ( $\mu\text{g/ml}$ )
Tap Water	$2.5 \pm 0.2$	2.2
Yamuna River Water	$18.14 \pm 0.32$	18.5
Urine Sample (Smoker)	$7.8 \pm 0.5$	8.1
Milk Sample	$3.6 \pm 0.6$	3.3
Synthetic Sample	$20.6 \pm 0.2$	20.4

## CONCLUSIONS

In the present work, the thiocyanate electrochemical sensor was introduced based on Nickel (II) complex of 2-acetylthiophene thiosemicarbazone as an ionophore. The proposed electrode sensor was prepared by using a membrane with composition of 32% PVC, 63% TBP as solvent mediator, 4% MTOAC as anion excluder, and 1% ionophore. The electrode can be employed to determine the  $\text{SCN}^-$  ion in

solution within a concentration range  $1.0 \times 10^{-6}$  to  $1.0 \times 10^{-1}$  M. The proposed electrochemical sensor has been shown to have high degree of selectivity and relatively short response time. The sensor electrode was successfully applied as an indicator electrode to determine thiocyanate ion potentiometrically. The electrode was also used to determine thiocyanate content in real samples.

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### REFERENCES

- [1] Bliss, R. E., & O'connell, K. A. (1984). Problems with thiocyanate as an index of smoking status: A critical review with suggestions with improving the usefulness of biochemical measures in smoking cessation research. *Health Psychology*, 3(6), 563.-581.
- [2] Zhang, G., Li, B., Fan, J., & Feng, S. (1997). Determination of trace thiocyanate in body fluids by a kinetic fluorimetric method. *Talanta*, 44(7), 1141-1147.
- [3] Li, Q., Wei, W., & Liu, Q. (2000). Indirect determination of thiocyanate with ammonium sulfate and ethanol by extraction-flotation of copper. *Analyst*, 125(10), 1885-1888.
- [4] Van Staden, J. F., & Botha, A. (2000). Spectrophotometric determination of thiocyanate by sequential injection analysis. *Analytica chimica acta*, 403(1-2), 279-286.
- [5] Michigami, Y., Fujii, K., Ueda, K., & Yamamoto, Y. (1992). Determination of thiocyanate in human saliva and urine by ion chromatography. *Analyst*, 117(12), 1855-1858.
- [6] Lu G, Xu H and Jianyan L (1989) *Huaxue Fence* 25: 120.
- [7] Cox, J. A., Gray, T., & Kulkarni, K. R. (1988). Stable modified electrodes for flow-injection amperometry: application to the determination of thiocyanate. *Analytical Chemistry*, 60(17), 1710-1713.
- [8] Khorasani, J. H., Amini, M. K., Motaghi, H., Tangestaninejad, S., & Moghadam, M. (2002). Manganese porphyrin derivatives as ionophores for thiocyanate-selective electrodes: the influence of porphyrin substituents and additives on the response properties. *Sensors and Actuators B: Chemical*, 87(3), 448-456.
- [9] Abbaspour, A., Kamyabi, M. A., Esmaeilbeig, A. R., & Kia, R. (2002). Thiocyanate-selective electrode based on unsymmetrical benzoN4 nickel (II) macrocyclic complexes. *Talanta*, 57(5), 859-867.
- [10] LIM, S. M., JUNG, H. J., WON, H., MYUNG, N., & PAENG, K. J. (2002). Potentiometric Behavior of the Membrane Electrodes Based on the Model Compound of a Ni-Porphinoid. In *Analytical Sciences/Supplements Proceedings of IUPAC International Congress on Analytical Sciences 2001 (ICAS 2001)*, i1701-i1704.
- [11] Amini, M. K., Rafi, A., Ghaedi, M., Habibi, M. H., & Zohory, M. M. (2003). Bis (2-mercaptobenzoxazolato) mercury (II) and bis (2-pyridinethiolato) mercury (II) complexes as carriers for thiocyanate selective electrodes. *Microchemical journal*, 75(3), 143-150.

- [12] Shamsipur, M., Ershad, S., Samadi, N., Rezvani, A. R., & Haddadzadeh, H. (2005). The first use of a Rh (III) complex as a novel ionophore for thiocyanate-selective polymeric membrane electrodes. *Talanta*, 65(4), 991-997..
- [13] Kiryushov VN, Kopylova NS and Kletenik YB (1995) *Zavod. Lab.* 61: 8.
- [14] Hoseini, Z., & Nezamzadeh-Ejhieh, A. (2016). An oxalate selective electrode based on modified PVC-membrane with tetra-butylammonium—Clinoptilolite nanoparticles. *Materials Science and Engineering: C*, 60, 119-125.
- [15] Nezamzadeh-Ejhieh, A., & Nematollahi, Z. (2011). Surfactant modified zeolite carbon paste electrode (SMZ-CPE) as a nitrate selective electrode. *Electrochimica Acta*, 56(24), 8334-8341.
- [16] Ahmadpour-Mobarakeh, L., & Nezamzadeh-Ejhieh, A. (2015). A zeolite modified carbon paste electrode as useful sensor for voltammetric determination of acetaminophen. *Materials Science and Engineering: C*, 49, 493-499.
- [17] Mohan, C., Sharma, K., & Chandra, S. (2017). Cd (II) Ion-Selective Electrode Based on 2-Acetylthiophene Semicarbazone in Polymeric Membrane. *Analytical & Bioanalytical Electrochemistry*, 9(1), 35-46.
- [18] Mohan C, Sharma K and Kumari S (2017) *Der Pharma Chimica*. 9: 133-139.
- [19] Nezamzadeh-Ejhieh, A., & Badri, A. (2011). Perchlorate selective membrane electrode based on surfactant-modified zeolite Y nanocluster. *Anal Bioanal Electrochem*, 3, 565-568.
- [20] Nezamzadeh-Ejhieh, A., & Afshari, E. (2012). Modification of a PVC-membrane electrode by surfactant modified clinoptilolite zeolite towards potentiometric determination of sulfide. *Microporous and Mesoporous Materials*, 153, 267-274.
- [21] Hashemi S and Ejhieh AZ (2014) *Desalination and Water Treatment* 57: 3304-3314.
- [22] Mahdih H and Ejhieh AZ (2015) *Food chemistry* 172: 794-801.
- [23] Xie, Y., Zhang, F., Liu, P., Hao, F., & Luo, H. A. (2014). Catalytic oxidation of cyclohexane with dioxygen over boehmite supported trans-A2B2 type metalloporphyrins catalyst. *Journal of Molecular Catalysis A: Chemical*, 386, 95-100.
- [24] Penza, M., Rossi, R., Alvisi, M., Signore, M. A., Serra, E., Paolesse, R., & Di Natale, C. (2010). Metalloporphyrins-modified carbon nanotubes networked films-based chemical sensors for enhanced gas sensitivity. *Sensors and Actuators B: Chemical*, 144(2), 387-394.
- [25] Arıcan, D., Arıcı, M., Uğur, A. L., Erdoğan, A., & Koca, A. (2013). Effects of peripheral and nonperipheral substitution to the spectroscopic, electrochemical and spectroelectrochemical properties of metallophthalocyanines. *Electrochimica Acta*, 106, 541-555.
- [26] Sánchez-Pedreño, C., Ortuño, J. A., & Martínez, D. (1998). Anion selective polymeric membrane electrodes based on cyclopalladated amine complexes. *Talanta*, 47(2), 305-310.
- [27] Nezamzadeh-Ejhieh, A., & Badri, A. (2011). Surfactant modified ZSM-5 zeolite as an active component of membrane electrode towards thiocyanate. *Desalination*, 281, 248-256.
- [28] Li, Z. Q., Wu, Z. Y., Yuan, R., Ying, M., Shen, G. L., & Yu, R. Q. (1999). Thiocyanate-selective PVC membrane electrodes based on Mn (II) complex of N, N'-bis-(4-phenylazosalicylidene) o-phenylene diamine as a neutral carrier. *Electrochimica Acta*, 44(15), 2543-2548.
- [29] Sun, Z. Y., Yuan, R., Chai, Y. Q., Xu, L., Gan, X. X., & Xu, W. J. (2004). Study of a bis-furaldehyde Schiff base copper (II) complex as carrier for preparation of highly selective thiocyanate electrodes. *Analytical and bioanalytical chemistry*, 378(2), 490-494.

- [30] Ardakani, M. M., Ensafi, A. A., Niasari, M. S., & Chahooki, S. M. (2002). Selective thiocyanate poly (vinyl chloride) membrane based on a 1, 8-dibenzyl-1, 3, 6, 8, 10, 13-hexaazacyclotetradecane-Ni (II) perchlorate. *Analytica Chimica Acta*, 462(1), 25-30.
- [31] Poursaberi, T., Salavati-Niassari, M., Khodabakhsh, S., Hajiagha-Babaei, L., Shamsipur, M., Yousefi, M., & Ganjali, M. R. (2001). A selective membrane electrode for thiocyanate ion based on a copper-1, 8-dimethyl-1, 3, 6, 8, 10, 13-azacyclotetradecane complex as ionophore. *Analytical letters*, 34(15), 2621-2632.
- [32] Seguí, M. J., Lizondo-Sabater, J., Martínez-Mañez, R., Sancenón, F., & Soto, J. (2006). Linear polyamines as carriers in thiocyanate-selective membrane electrodes. *Talanta*, 68(4), 1182-1189.
- [33] Han, W. S., Hong, T. K., & Lee, Y. H. (2011). Thiocyanate Ion Selective Solid Contact Electrode Based on Mn Complex of N, N'-Bis-(4-Phenylazosalicylidene)-O-Phenylene Diamine Ionophore. *American Journal of Analytical Chemistry*, 2(06), 731.
- [34] Bühlmann, P., Yahya, L., & Enderes, R. (2004). Ion-selective electrodes for thiocyanate based on the dinuclear zinc (II) complex of a bis-N, O-bidentate Schiff base. *Electroanalysis: An International Journal Devoted to Fundamental and Practical Aspects of Electroanalysis*, 16(12), 973-978.
- [35] Srivastava SK, Gupta VK and Jain S (1995) *Analyst* 120: 495-498.
- [36] Srivastava, S. K., Gupta, V. K., Dwivedi, M. K., & Jain, S. (1995). Caesium PVC-crown (dibenzo-24-crown-8) based membrane sensor. In *Analytical Proceedings including Analytical Communications* (Vol. 32, No. 1, pp. 21-23). Royal Society of Chemistry.
- [37] Srivastava, S. K., Gupta, V. K., & Jain, S. (1996). PVC-based 2, 2, 2-cryptand sensor for zinc ions. *Analytical chemistry*, 68(7), 1272-1275.
- [38] Gupta, V. K., Singh, L. P., Singh, R., Upadhyay, N., Kaur, S. P., & Sethi, B. (2012). A novel copper (II) selective sensor based on dimethyl 4, 4'(o-phenylene) bis (3-thioallophanate) in PVC matrix. *Journal of Molecular Liquids*, 174, 11-16.
- [39] Gupta, V. K., Sethi, B., Sharma, R. A., Agarwal, S., & Bharti, A. (2013). Mercury selective potentiometric sensor based on low rim functionalized thiacalix [4]-arene as a cationic receptor. *Journal of Molecular Liquids*, 177, 114-118.
- [40] Gupta, V. K., Kumar, S., Singh, R., Singh, L. P., Shoora, S. K., & Sethi, B. (2014). Cadmium (II) ion sensing through p-tert-butyl calix [6] arene based potentiometric sensor. *Journal of Molecular Liquids*, 195, 65-68.
- [41] Gupta, V. K., Singh, A. K., & Kumawat, L. K. (2014). Thiazole Schiff base turn-on fluorescent chemosensor for Al<sup>3+</sup> ion. *Sensors and Actuators B: Chemical*, 195, 98-108.
- [42] Yola, M. L., Gupta, V. K., Eren, T., Şen, A. E., & Atar, N. (2014). A novel electro analytical nanosensor based on graphene oxide/silver nanoparticles for simultaneous determination of quercetin and morin. *Electrochimica Acta*, 120, 204-211.
- [43] Karimi-Maleh, H., Tahernejad-Javazmi, F., Atar, N., Yola, M. L., Gupta, V. K., & Ensafi, A. A. (2015). A novel DNA biosensor based on a pencil graphite electrode modified with polypyrrole/functionalized multiwalled carbon nanotubes for determination of 6-mercaptopurine anticancer drug. *Industrial & Engineering Chemistry Research*, 54(14), 3634-3639.

- [44] Gupta, V. K., Karimi-Maleh, H., & Sadegh, R. (2015). Simultaneous determination of hydroxylamine, phenol and sulfite in water and waste water samples using a voltammetric nanosensor. *Int. J. Electrochem. Sci*, 10, 303-316.
- [45] Mohan C, Sharma K and Kumari S (2015) International Journal of Chemical and Natural Science. 3: 312-319.
- [46] Craggs, A., Keil, L., Moody, G. J., & Thomas, J. D. R. (1975). An evaluation of solvent mediators for ion-selective electrode membranes based on calcium bis (dialkylphosphate) sensors trapped in poly (vinyl chloride) matrices. *Talanta*, 22(10-11), 907-910.
- [47] Bakker, E., Bühlmann, P., & Pretsch, E. (1997). Carrier-based ion-selective electrodes and bulk optodes. 1. General characteristics. *Chemical Reviews*, 97(8), 3083-3132.
- [48] Danesh-Khorasgani, M., & Nezamzadeh-Ejhieh, A. (2016). PVC-zeolite nanoparticle-surfactant anion exchanger membrane: preparation, characterization, and its application in development of ion-selective electrode for detection of sulfate. *Journal of Solid State Electrochemistry*, 20(10), 2827-2833.
- [49] Mahdavi, M., & Nezamzadeh-Ejhieh, A. (2017). An aluminum selective electrode via modification of PVC membrane by modified clinoptilolite nanoparticles with hexadecyltrimethyl ammonium bromide (HDTMA-Br) surfactant containing Arsenazo III. *Journal of colloid and interface science*, 494, 317-324.
- [50] Nezamzadeh-Ejhieh, A., & Mirzaeyan, E. (2013). Hexadecylpyridinium surfactant modified zeolite A as an active component of a polymeric membrane sulfite selective electrode. *Materials Science and Engineering: C*, 33(8), 4751-4758.
- [51] Naghash, A., & Nezamzadeh-Ejhieh, A. (2015). Comparison of the efficiency of modified clinoptilolite with HDTMA and HDP surfactants for the removal of phosphate in aqueous solutions. *Journal of Industrial and Engineering Chemistry*, 31, 185-191.
- [52] Bakker, E., Pretsch, E., & Bühlmann, P. (2000). Selectivity of potentiometric ion sensors. *Analytical chemistry*, 72(6), 1127-1133.
- [53] Nezamzadeh-Ejhieh, A., & Mirzaeyan, E. (2011). Oxalate membrane-selective electrode based on surfactant-modified zeolite. *Electrochimica Acta*, 56(22), 7749-7757.
- [54] Nezamzadeh-Ejhieh, A., & Badri, A. (2011). Application of surfactant modified zeolite membrane electrode towards potentiometric determination of perchlorate. *Journal of electroanalytical chemistry*, 660(1), 71-79.
- [55] Goyal, R. N., Gupta, V. K., & Chatterjee, S. (2010). Electrochemical investigations of corticosteroid isomers—testosterone and epitestosterone and their simultaneous determination in human urine. *Analytica chimica acta*, 657(2), 147-153.
- [56] Chandra, S., & Sarkar, A. (2013). Spectral, thermal and electrochemical investigation of carbohydrazone derived ionophore as Fe (III) ion selective electrode. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 107, 271-279.
- [57] Mousavi, M. F., Arvand-Barmchi, M., & Zanjanchi, M. A. (2001). Al (III)-Selective Electrode Based on Furil as Neutral Carrier. *Electroanalysis: An International Journal Devoted to Fundamental and Practical Aspects of Electroanalysis*, 13(13), 1125-1128.
- [58] Vlascici, D., Fagadar-Cosma, E., & Bizerea-Spiridon, O. (2006). A new composition for Co (II)-porphyrin-based membranes used in thiocyanate-selective electrodes. *Sensors*, 6(8), 892-900.

- [59] Badri, A., & Pouladsaz, P. (2011). Highly selective and sensitive thiocyanate PVC membrane electrodes based on modified Zeolite ZSM-5. *Int. J. Electrochem. Sci*, 6, 3178-3195.
- [60] Lee, K., Kang, D. H., Choe, J. E., Yun, M., You, J. M., Go, M. J., ... & Jeon, S. (2014). The Novel SCN-Ion-selective Electrode Based on the 1-Benzyl-3-(4-nitrophenyl) thio-urea Ionophore. *Bulletin of the Korean Chemical Society*, 35(11), 3175-3180.
- [61] Benvidi, A., Ghanbarzadeh, M. T., Dehghan, M., Mazloum-Ardakani, M., & Vafazadeh, R. (2014). Thiocyanate ion selective electrode based on bis (N-3-methylphenyl salicylidenaminato) copper (II) ionophore. *Chinese Chemical Letters*, 25(12), 1639-1642.
- [62] Whiston, T. G., & Cherry, G. W. (1962). The determination of thiocyanate in coal-carbonising plant effluents, sewage works influents and effluents and polluted waters. *Analyst*, 87(1039), 819-823.