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The first use of a Rh(III) complex as a novel ionophore for thiocyanate-selective polymeric membrane electrodes

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Abstract

The feasibility of a newly synthesized Rh(III) complex, Rh[(trpy)(bpy)Cl]$(PF_6)_2$, as a novel ionophore for the preparation of anion-selective polymeric membrane electrodes was tested. The ionophore exhibited anti-Hofmeister behavior with enhanced potentiometric selectivity toward thiocyanate ion compared to other anions. The influence of some experimental parameters such as membrane composition, nature and amount of plasticizer and additive and concentration of internal solution on the potential response of the SCN^- sensor were investigated. The electrode exhibits a Nernstian response for SCN^- over a wide concentration range (1.0×10^{-5} to 1.0×10^{-1} M) with a slope -58.7 ± 0.5 mV per decade and a detection limit of 4.0×10^{-6} M (0.23 ppm). It could be used in a pH range of 3.0–8.0 and has a fast response time of about 15 s. The proposed sensor was used for the determination of thiocyanate ions in real samples such as urine and saliva of smokers and nonsmokers and, as an indicator electrode, in potentiometric titrations of SCN^- ion.

Keywords: SCN^--selective electrode; PVC-membrane; Rh[(trpy)(bpy)Cl]$(PF_6)_2$; Potentiometry

1. Introduction

Because of their widespread analytical applications in physiology, process control and environmental analysis, the ionophore-based ion-selective electrodes (ISEs) have been established as one of the most important groups of chemical sensors [1–3]. Thus, in the past two decades, there has been a growing interest in search for ionophores that can chemically recognize specific cations and anions and offer either new or improved selectivities for different ions [4–7].

Classical membrane electrodes for anions are based on quaternary ammonium and phosphoium salts and usually exhibit the Hofmeister pattern with the largest selectivity to lipophilic anions [8]. Recently, much attention has been focused on new ion carriers possessing an anti-Hoffmeister selectivity sequence in preparation of anion-selective electrodes. Generally, the antiHofmeister anion selectivity is achieved in the case of membrane electrodes doped with an organometallic complex, via specific anion coordination with the central metal ion of the complex; of course, for such a coordination process, the structure of the complex-forming carrier plays an important role in the final selectivity characteristics of the resulting electrode [9].

Thiocyanate is present as a normal constituent in mammalian tissues and body fluids [10]. The tyrostatic effect of the thiocyanate, brought about by inhibiting iodine transport in the thyroid, is well known [11]. Moreover, thiocyanate is present in human body as a metabolic degradation product of sulfur containing compounds in tobacco. It is a detoxication product of cyanide, and its content is higher in the body fluids of smokers [12,13]. Thus, due to the critical importance of selective thiocyanate determination, especially in food, biological and water samples [14], there are several reports on

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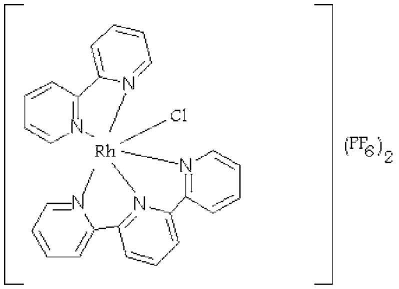
SCN^--selective electrodes based on a variety of ionophores. These ionophores include (octabromotetraporphyrinato) manganese(III) chloride [15], nickel phthalocyanine [16], Co(II) and Mn(II) phthalocyanine [17]. Mn(II) complex of *N*,*N*′-bis-(4-phenlyazasalicylidine)*o*-phenyldiamine [18], dibutyltin dihalides [19], a cadmium-Schiff's base complex [20], a Ni(II)-azamacrocycle complex [21], manganese tetraphenylporphyrin derivatives [22] and Ni(II) complexes with some unsymmetrical benzo N_4 macrocycles [23].

We have been recently involved in the preparation of PVC-membrane electrodes for selective determination of SCN^- [15,20,21], I_3^- [24,25], Br^- [26], I^- [27], ClO_4^- [28], NO_2^- [29], HPO_4^{2-} [30] and SO_4^{2-} [31,32]. In this paper, we report the first use of a rhodium(III) complex, $[Rh(trpy)(bpy)Cl](PF_6)_2$, as a suitable ionophore for the preparation of a highly selective PVC-membrane electrode.



$[Rh(trpy)(bpy)Cl](PF_6)_2$

2. Experimental

2.1. Reagents

Reagent-grade dibutyl phthalate (DBP), acetophenone (AP), nitrophenyl octyl ether (NPOE), hexadecyltrimethylammonium bromide (HDTMAB), cetyltrimethylammonium bromide (CTMAB), high relative molecular weight PVC and tetrahydrofuran (THF), were purchased from Merck and used as received. The sodium salts of anions used (all from Merck) were of the highest purity available and used without any further purification expect for vacuum drying over P_2O_5.

2.2. Preparation of $Rh(trpy)Cl_3$

To 150 ml of absolute ethanol in a 250 ml round-bottom flask was added 792 mg (3 mmol) of $RbCl_3 \cdot 3H_2O$ and 700 mg (3 mmol) of 2,2′,2″-terpyridine (trpy). The mixture was heated at reflux for 3 h while vigorous magnetic stirring was maintained. After this time, the reaction was cooled to room temperature, and the resulting fine brown powder was filtered from the reddish yellow solution. The product was washed with 3 ml × 30 ml portions of absolute ethanol followed by 3 × 30 ml portions of ether and air-dried. The yield was 1.062 g (80%).

2.3. Preparation of $[Rh(trpy)(bpy)Cl](PF_6)_2$

$Rh(trpy)Cl_3$ (880 mg, 2 mmol) and 2,2′-bipyridine (bpy, 390 mg, 2.5 mmol) were heated at reflux for 6 h in 150 ml of 4:1 (v/v) water ethanol containing excess amount of LiCl. After the reduction of reaction solvent volume was to half in a rotary evaporator, an aqueous solution saturated in NH_4PF_6 was added so that a deep yellow solid was precipitated out. The solid product was then collected on a frit and washed with cold water and ether. For further purification, the solid was re-dissolved in acetonitrile and precipitated by ether diffusion. The yield was 1.390 g (85%). ^1H NMR in DMSO-d_6 (ppm): 9.06 (1H, doublet), 8.75 (3H, multiplet), 7.79 (1H, triplet), 7.57 (2H, triplet), 7.17 (1H, triplet), 6.88 (1H, triplet), 5.79 (1H, doublet). Elemental analysis for $C_{25}H_{19}ClF_{12}N_5P_2Rh$ (calculated): C, 36.89% (36.72%); H, 2.35% (2.32%); N, 8.64% (8.57%). λ_{max} in DMF: 486 nm ($\varepsilon = 31\ M^{-1}\ cm^{-1}$).

2.4. Preparation of electrode

The general procedure to prepare the PVC membrane was to mix thoroughly 30 mg of powdered PVC and 2.0 mg additive HDTMAB with 65 mg of NPOE as solvent mediator in 5 ml THF. To this mixture was added 3 mg of ionophore $[Rh(trpy)(bpy)Cl](PF_6)_2$, which was already dissolved in 2 ml of acetone, and the solution was mixed well. The resulting mixture was transferred into a glass dish of 2 cm diameter. The solvent was evaporated slowly until an oily concentrated mixture was obtained. A polyethylene tube of 5 mm diameter on top was dipped into the mixture for about 10 s so that a transparent membrane of about 0.3 mm thickness was formed. After removing the tube from the mixture, it was kept at room temperature for about 1 h. The tube was then filled with an internal filling solution (1.0×10^{-3} M SCN^-). The electrode was finally conditioned for 12 h by soaking in 1.0×10^{-2} M solution of sodium thiocyanate. A silver/silver chloride electrode was used as an internal reference electrode.

2.5. Emf measurements

All emf measurements were carried out with the following cell assembly:

$$\begin{aligned}&\text{Ag–AgCl}\ |\text{KCl(3 M)}|\ \text{internal solution},\ 1.0\times10^{-3}\\&\quad \text{M SCN}^-\ |\text{PVC membrane}|\ \text{test solution}\\&\quad \left|\text{Hg–Hg}_2\text{Cl}_2,\ \text{KCl(stated)}\right|\end{aligned}$$

A metrohm ion analyzer pH/mV meter was used for potential measurement at 25.0 ± 0.1 °C. Activities were calculated according to the Debye–Hückel procedure [33].

3. Results and discussion

3.1. Preliminary potentiometric studies and UV–vis spectra

Preliminary experiments revealed that the plasticized PVC-based membrane electrodes containing the ionophore generate stable potential responses in solutions containing thiocyanate, after conditioning for about 12 h in 1.0×10^{-2} M NaSCN solution. The membrane demonstrated a remarkable selectivity for thiocyanate over most common inorganic and organic anions. The preferential response of the ionophore used towards SCN^- is believed to be associated with the coordination of thiocyanate with the metal center in the complex $[Rh(trpy)(bpy)Cl](PF_6)_2$, and it is the relative affinity of the SCN^- as a suitable ligand for Rh(III) that dictates the observed selectivity pattern of the electrodes. With UV–vis spectra, as illustrated in Fig. 1, it is possible to distinguish the interaction between the central Rh(III) ion and thiocyanate. As seen from Fig. 1, the addition of SCN^- to the solution resulted in distinct decreases of the absorption signals of the ionophore at 329.2 and 340.5 nm, while shifting the ionophore signal at 355.8–358.3 nm with some increased intensity. Such spectral changes could be due to the axial coordination of SCN^- to Rh(III) in $[Rh(trpy)(bpy)Cl](PF_6)_2$.

In order to obtain more information about the stoichiometry and stability of the resulting complex between ionophore and thiocyanate ion, A 5.0×10^{-5} M solution of $[Rh(trpy)(bpy)Cl](PF_6)_2$ in acetonitrile was titrated with a concentrated solution of SCN^- (1.0×10^{-3} M) and the resulting spectra are shown in Fig. 2. As is obvious the absorption bands of ionophore at >260 nm are increased in the expense of the decreased intensity of its absorptions at <250 nm, via a distinct isosbestic point at 254.5 nm, upon titration with thicynate ion, indicating the formation of a relatively stable complex between the two species. It should be noted that the addition of excess amount of other anions resulted in negligible change in the absorption bands of the ionophore, revealing its selective behavior towards thiocyanate ion over other anionic species. The corresponding absorbance-mole ratio plot obtained at 311 nm revealed a pronounced inflection point at a thiocyanate-to-ionophore ratio of about 1, indicating the formation of a 1:1 adduct between the two species in solution. This could possibly happened via the replacement of chloride with thiocyanate in the Rh(III) complex. The binding constant of the resulting adduct, evaluated from computer fitting of the absorbance-mole ratio data, was found to be $\log K_f = 4.18 \pm 0.03$.

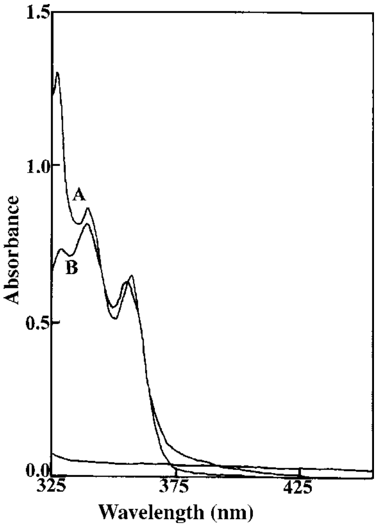


Fig. 1. UV–vis absorption spectra of 1.2×10^{-4} M acetonitrile solution of in the absence (A) and presence of 1.0×10^{-2} M thiocyanate (B).

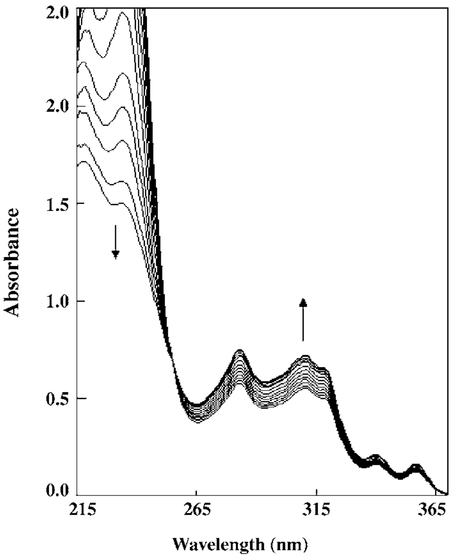


Fig. 2. Spectrophotometric titration of a 5.0×10^{-5} M of $[Rh(trpy)(bpy)Cl](PF_6)_2$ with a 1.0×10^{-3} M solution of SCN^- in acetonitrile. The corresponding $[SCN]/[[Rh(trpy)(bpy)Cl](PF_6)_2]$ mole ratios from low to high values are: 0.0, 0.1, 0.2, 0.5, 0.7, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5 and 5.0.

At the same time, the effects of other anions such as I^-, CN^- and $ClO_4{}^-$ on the spectrum of the carrier was investigated and no detectable changes in the corresponding UV–vis spectra were noted. Thus, the anti-Hofmeister behavior of the electrode can be explained by the specific interaction between the central Rh(III) and thiocyanate ion.

3.2. Effect of membrane composition

Besides the critical role of the nature of the ion carrier in preparing membrane-selective sensors, some other important features of the PVC membrane are known to significantly influence the sensitivity, linearity range and selectivity of ion-selective electrodes. These include the amount of ionophore, the nature of solvent mediator, the plasticizer/PVC ratio and, especially, the nature of additives used [16–19,27,28,34–37]. Thus, different aspects of membrane preparation based on the $[Rh(trpy)(bpy)Cl](PF_6)_2$ for SCN^- ion were optimized and the results are summarized in Table 1. As seen, the sensitivity

Table 1
Optimization of membrane ingredients for SCN^- electrode

Membrane number	Composition (%)				Slope (mV/decade)
	PVC	Plasticizer	Rhodium complex	Additive	
1	30	NPOE, 60	–	–	–
2	33	NPOE, 66	1	–	−43.2
3	33	NPOE, 65	3	–	−45.5
4	30	NPOE, 65	5	–	−44.0
5	30	NPOE, 65	3	2, HDTMAB	−58.7
6	30	NPOE, 65	3	2, CTMAB	−54.5
7	30	DBP, 65	3	2, HDTMAB	−51.0
8	30	AP, 65	3	2, HDTMAB	−22.0
9	30	NPOE, 65	3	2, NaTPB	−36.0

of electrode response increases with increasing ionophore content from 1 to 3%. Further addition of ionophore to 5% will, however, result in diminished response of the electrode, most probably due to some inhomogeneities and possible saturation of the membrane [38].

As is obvious from Table 1, among three different plasticizers used, NPOE resulted in the best response. It should be noted that the nature of plasticizer influences both the dielectric constant of the membrane and the mobility of ionophore and its complex with SCN^- [34].

The optimization of premselectivity of membrane sensors is known to be dependent on the incorporation of additional membrane components. In fact, it has been demonstrated that the presence of lipophilic charged additives improves the potentiometric behavior of ion selective electrodes not only by reducing the ohmic resistance [38,39] and improving the response behavior and selectivity [40,41] but also, in cases where the extraction capability of the ionophore is poor, by enhancing the sensitivity of the membrane electrode [42]. Moreover, the additives may catalyze the exchange kinetics at the sample-membrane interface [40]. The data given in Table 1 revealed that, in the absence of a proper additive, the sensitivity of the PVC membrane based on $[Rh(trpy)(bpy)Cl](PF_6)_2$ is quite low (Nos. 2–4). However, the presence of 2% HDTMAB, as a suitable lipophilic additive, will improve the sensitivity of the PVC membrane considerably (No. 5). In order to investigate the fact that the Rh(III) complex used behaves whether as a neutral or a charged ionophore, the influence of NaTPB as an ionic additive on the response characteristics of the proposed electrode was also studied and the results are also included in Table 1 (No. 9). As is obvious, in the presence of NaTPB as additive, the slope of the potential response of the membrane electrode has been diminished to 36.0 mV/decade, in a narrow linear range of 1.0×10^{-3} to 1.0×10^{-1} M. Thus, it seems more likely that the $[Rh(trpy)(bpy)Cl](PF_6)_2$ complex behaves as a neutral ionophore in the membrane electrode proposed.

Thus, based on the results obtained on the optimization of the membrane composition, the membrane 5 with the optimized composition of NPOE:PVC:$[Rh(trpy)(bpy)Cl](PF_6)_2$:HDTMAB percent ratio of 65:30:3:2 was selected for the preparation the polymeric membrane electrode for thiocyanate ion. It is interesting to note that, in the absence of ionophore, the electrode showed a negligible response slope.

3.3. Effect of internal reference solution

The concentration of the internal solution (NaSCN) in the electrode was changed from 1.0×10^{-2} to 1.0×10^{-4} M and the emf-$pSCN^-$ plots were obtained. It was found that the variation of the concentration of the internal NaSCN solution did not cause any significant difference in potential response except for an expected change in the intercept of the resulting plots. A 1.0×10^{-3} M concentration of internal reference solution is quite appropriate for smooth functioning of the electrode system.

3.4. Calibration plot

The emf response of the proposed SCN^- sensors based on $Rh(trpy)(bpy)Cl](PF_6)_2$, prepared under optimal membrane

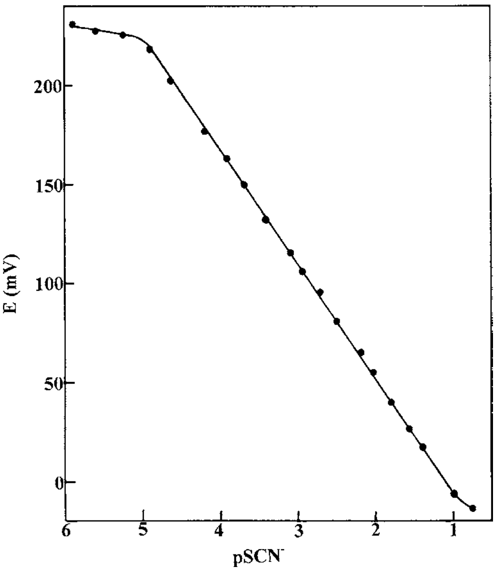


Fig. 3. Potential response of the proposed electrode.

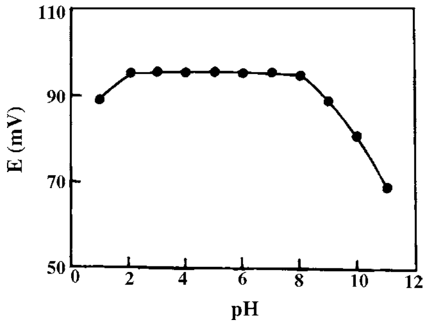


Fig. 4. Effect of pH of the test solution on the potential response of the SCN^--selective electrode.

ingredients, indicates a linear range from 1.0×10^{-5} to 1.0×10^{-1} M (Fig. 3). The slope of calibration plots was −58.7 ± 0.5 mV per decade. The limit of detection, as determined from the intersection of the two extrapolated segments of the calibration plot, was 4.0×10^{-6} M.

3.5. *Effect of pH*

The influence of pH of the test solution (1.0×10^{-3} M thiocyanate) on the potential response of the membrane sensor was tested in the pH range 3.0–11.0 (adjusted with either HCl or NaOH) and the results are shown in Fig. 4. As seen, the membrane electrode can be suitably used in the pH range 3.0–8.0. However, drastic potential changes are observed at higher and lower pH values. This is most probably due to the simultaneous response of the electrode to SCN^- and OH^-, at $pH > 8$, and some ionophore protonation and consequent diminished responsivity to SCN^- and/or simultaneous response to thiocyanate and chloride ions, at $pH < 3$.

3.6. *Response time*

Dynamic response time is an important factor for any ion-selective electrode. In this study, the practical response time of the electrode was recorded by using solutions with different SCN^- concentrations, from 1.0×10^{-5} to 1.0×10^{-1} M. It was found that the electrode reaches the equilibrium response in a short time of about 15 s. This is most probably due to the fast exchange kinetics of association-dissociation of SCN^- ion with the central metal of ionophore at the test solution-membrane interface.

3.7. *Lifetime*

Lifetime studies are based on monitoring the change in electrodes slope and linear response range with time. After 12 weeks, very slight gradual decrease in slopes was observed. It should be noted that, during these 12 weeks, the electrode was in daily use for about 1 h, and then it was washed with water, dried and kept aside for the next day's use.

3.8. *Selectivity*

The influence of interfering ions on the response behavior of ion-selective membrane electrodes is usually described in terms of selectivity coefficients. Potentiometric selectivity coefficient values for the present sensors were determined by the match potential method [43]. Based on this method, specified amounts of thicyanate ion (A) (in the range of 1.0×10^{-4} to 1.0×10^{-2} M) were added to a reference solution (1.0×10^{-5} M) and the potential was measured. In a separate experiment, the interfering anions (B) (in the range of 1.0×10^{-3} to 1.0×10^{-1} M) were successively added to an identical reference solution until the measured potential matched that obtained before by adding the thiocyanate ions. The matched potential method selectivity coefficients, $K_{A,B}^{Pot}$, is then given by the resulting primary ion to interfering ion activity (concentration) ratio, $K_{A,B}^{Pot} = a_A/a_B$. The results are summarized in Table 2. It is seen that the electrode is very selective to thiocyanate ion and the observed selectivity pattern for the proposed sensors significantly differs from the so-called Hofmeister selectivity sequence (i.e. selectivity based solely on lipophilicity of anions) [8].

In Table 2, the selectivity coefficients for diverse anions of the proposed electrode are also compared with the corresponding values reported during recent years for electrodes based on different metal ion complexes as SCN^- ion carriers, including (octabromotetraphenylporphyrinateto) manganese(III) chloride [15], nickel phthalocyanine [16], Co(II) and Mn(II) phthalocyanine [17], Mn(II) complex of *N*,*N*′-bis-(4-phenylazasalicylidine)*o*-phenyldiamine [18], dibutyltin dihalides [18], a cadmium-Schiff's base complex [20], a Ni(II)-azamacrocycle complex [21], manganese tetraphenylporphyrin derivatives [22] and Ni(II) complexes with some unsymmetrical benzo N_4 macrocycles [23]. It should be noted that, this is just a gross relative comparison, since the selectivity coefficients have been reported using different experimental methods.

As is seen from Table 2, the ionophore used in this work shows selectivities somewhat similar, in many cases, or even superior, in some cases, to the potentiometric thiocyanate sensors prepared previously. Meanwhile, in terms of wide linear ranges, low detection limits short response times and fully Nernstian slopes the proposed electrode is advantageous over many previously reported SCN^- selective membrane electrodes.

3.9. *Analytical applications*

The high degree of thiocyanate selectivity exhibited by the electrodes $[Rh(trpy)(bpy)Cl](PF_6)_2$ electrodes makes it potentially useful for monitoring low concentration levels of thiocyanate in biological samples. Experimental results have shown that the urinary and salivary thiocyanate concentration is higher for smokers than nonsmokers, so that thiocyanate has historically been monitored as an assessment of the effectiveness of cigarette smoking cession program. Thus,

Table 2
Selectivity coefficients for different thiocyanate ion-selective electrodes

Interfering ion	$\log K^{\mathrm{Pot}}_{\mathrm{A,B}}$									
	This work (MPM)	Ref. [15] (FIM)	Ref. [16] (SSM)	Ref. [17] (SSM)	Ref. [18] (SSM)	Ref. [19] (SSM)	Ref. [20] (MPM)	Ref. [21] (MPM)	Ref. [22] (SSM)	Ref. [23] (FIM)
F^-	−4.7	−3.7	−2.7	–	–	–	−3.6	−4.5	−3.4	−2.3
Cl^-	−4.0	−3.1	−2.5	−3.0	−4.8	–	−3.0	−4.4	−3.9	−3.1
Br^-	−3.4	−2.7	−2.2	−2.4	−4.0	−0.2	−3.2	−4.1	−2.9	−2.4
I^-	−3.9	−2.3	−1.3	−2.2	−1.3	−0.1	−2.5	−2.6	−2.5	−1.1
NO_2^-	−4.8	−3.2	−4.4	–	−3.1	–	−3.4	−2.5	−3.9	−2.7
NO_3^-	−5.0	−3.7	−2.7	–	–	−0.4	−3.1	−3.6	−2.9	−2.2
ClO_4^-	−2.2	−2.5	−0.4	−0.4	−1.4	−0.1	−3.0	−3.1	−1.3	−0.4
IO_3^-	−3.3	–	–	–	–	–	−3.8	−3.1	–	–
SO_3^{2-}	−4.7	–	–	–	–	–	–	–	–	–
SO_4^{2-}	−4.8	−4.7	−4.3	–	–	–	−3.3	−4.4	−5.3	−4.1
$S_2O_3^{2-}$	−4.2	–	–	–	–	–	–	–	–	−3.5

FIM: fixed interference method, MPM: matched potential method, SSM: separate solution method.

Table 3
Determination of thiocyanate in different samples

Sample	SCN^- (mmol l^{-1})[a]	
	Proposed method	Colorimetric method
Nonsmoker urine	0.24 ± 0.05	0.25 ± 0.05
Smoker urine	0.75 ± 0.05	0.76 ± 0.08
Nonsmoker saliva	0.58 ± 0.06	0.56 ± 0.05
Smoker saliva	1.69 ± 0.04	1.71 ± 0.07

[a] Mean value ± standard deviation (three determinations).

experiments were carried out to determine the feasibility of using the proposed electrode to measure thicyanate in urine and saliva samples. The samples were first diluted 1:10 and adjusted to pH 5.0 with phosphoric acid and potassium hydroxide solutions. The calibration plots, obtained under the same experimental conditions, were employed to evaluate the thiocyanate contents of the samples.

Table 3 lists thiocyanate concentration in human urine and saliva measured by the proposed electrodes as well as the colorimetric results [44,45]. As shown, there is a fair agreement between the values obtained by the electrode and the colorimetric methods.

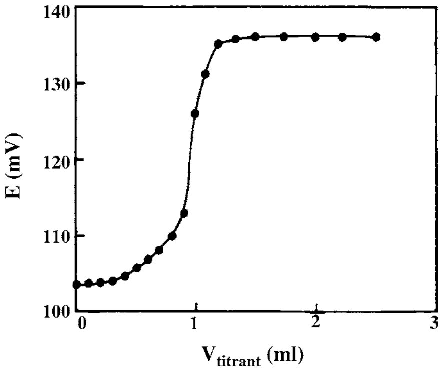


Fig. 5. Potentiometric titration curve of 10.0 ml 1.0 × 10^{-3} M SCN^- with 1.0 × 10^{-2} M of Ag^+, using the proposed SCN^--selective sensor as an indicator electrode.

The electrode was also successfully applied as an indicator electrode for the potentiometric titration of silver ion with thiocyanate solution, and the amount of Ag^+ ion was accurately determined and the resulting well defined titration curve (Fig. 5).

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