A Novel Poly(vinyl chloride) Matrix Membrane Sensor for Batch and Flow-Injection Determinations of Thiocyanate, Cyanide and Some Metal Ions

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A poly(vinyl chloride) matrix membrane sensor for the selective determination of thiocyanate has been developed based on the use of copper(II)-2-(5-bromo-2-pyridylazo)-5-diethylaminophenol complex (Cu-PADAP) as a novel charged carrier, and *o*-nitrophenyloctyl ether (*o*-NPOE) as a solvent mediator. The sensor displays a significantly enhanced response towards SCN⁻ ions over the concentration range 7.0×10^{-6} to 1.0×10^{-2} mol L⁻¹ with a detection limit of 5.6×10^{-6} mol L⁻¹ and a calibration slope of -57.5 ± 0.5 mV decade⁻¹. The sensor exhibits a long life-span, long-term stability, high reproducibility, and a fast response time. The selectivity coefficients of some anions were calculated using the separate solutions method, and found to be in the following order: SCN⁻ > ClO₄⁻ > I⁻ > Sal⁻ > NO₂⁻ > Br⁻ > NO₃⁻ = CH₃COO⁻ > Cl⁻ > SO₄²⁻ = PO₄³⁻. The effects of the pH and ionic membrane additives (*e.g.* tridodecylmethylammonium chloride, TDMAC and potassium tetrakis[bis(3,5-trifluoromethyl)phenyl] borate, KTFPB) were examined. The sensor was used for the determination of SCN⁻ ions in saliva and urine samples collected from some smoker and non-smoker donors. The developed sensor was also applied to determine the cyanide content in electroplating waste water samples after its conversion into thiocyanate. The application of the sensor to monitor the potentiometric titration of Ag⁺ and Hg²⁺ using SCN⁻ resulted in sharp inflection breaks at the equivalent points. The data obtained using the proposed sensor correlate very well with results collected using the standard methods of thiocyanate, cyanide and metal analysis.

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Introduction

The thiocyanate anion possesses numerous industrial and biological applications, and is a potent inhibitor of iodide transport in humans.¹ Thiocyanate is also the end product of the detoxification of cyanide compounds, and is excreted in urine, saliva and sweat. The thiocyanate content in human saliva is considered to be a biomarker for the identification of nonsmokers and smokers. Human plasma levels are 2–3 mg L⁻¹ in nonsmokers and 9–12 mg L⁻¹ in smokers.² Chronically elevated levels of thiocyanate in body fluids are known to be toxic and correlate with local goiter, vertigo, and unconsciousness.³ On the other hand, thiocyanate containing waste discharged into rivers is harmful to aquatic life due to its degradation to cyanide in the presence of oxidants. Therefore, a simple, rapid, reproducible, and high-throughput determination of the SCN⁻ concentration at low levels in body fluids, water and diverse industrial samples is highly demanded. Various methods, such as spectrometry,⁴ spectrofluorometry,⁵ Raman spectroscopy,⁶ capillary zone electrophoresis,⁷ gas chromatography,⁸ ion chromatography,⁹ photokinetic voltammetry,¹⁰ and amperometry¹¹ have been reported for thiocyanate determination. Most of these methods are time consuming and involve the use of sophisticated high-cost equipment.

Potentiometric sensors offer simple, cost effective, selective

and sensitive techniques for chemical analysis. Anion-selective membrane sensors based on the use of ion exchangers such as lipophilic quaternary ammonium or phosphonium salts, display the classical Hofmeister selectivity sequence: (ClO₄⁻ > SCN⁻ > I⁻ > NO₃⁻ > Br⁻ > NO₂⁻ > Cl⁻ > SO₄²⁻). In this case the membrane selectivity is controlled only by the free energy of ion hydration^{12,13} and the sensors respond more to highly lipophilic anion. Polymer membrane sensors incorporating lipophilic organo-metallic compounds or metal-ligand complexes show potentiometric selectivity patterns that deviate significantly from the Hofmeister sequence.^{14–18} Various anion carriers have been reported for the development of thiocyanate membrane sensors, including organo silver,¹⁹ nickel,²⁰ copper,²¹ mercury,²² zinc,²³ cadmium,²⁴ manganese,²⁵ and palladium²⁶ complexes. Metal porphyrin,²⁷ metallophthalocyanine,²⁸ metal azamacrocyclic,²⁹ and calixarene³⁰ derivatives have also been used. Some of these sensors suffer from the disadvantages of poor selectivity, limited range of the linear response, and a long response time.

Herein, we present a novel potentiometric thiocyanate membrane sensor based on the Cu(II)-2-(5-bromo-2-pyridylazo)-5-diethylaminophenol complex as a charged carrier. The selectivity behavior, response mechanism, response time, and signal stability were evaluated, and found to be superior than most of those previously described. The sensor is satisfactorily used for batch and flow-injection analysis of thiocyanate in biological fluids. The sensor is also utilized for the determination of cyanide in waste-water samples after conversion into thiocyanate. Potentiometric titrations of some metal ions with SCN⁻ are successfully followed using the proposed sensor.

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Experimental

Equipment

All potential measurements were made at $25 \pm 1^\circ\text{C}$ with an Orion (Cambridge, MA) Model 720/SA pH/mV meter using the proposed thiocyanate membrane sensor in conjunction with an Orion Ag/AgCl double-junction reference electrode (Model 90-20) filled with 10% (w/v) KNO_3 . A combination Ross glass electrode (Orion 81-02) was used for pH measurements. A computer-controlled spectrophotometer (Jenway, Model 1601) was used for spectrophotometric measurements.

A flow-injection manifold utilized for the analysis of SCN^- consisted of a two-channel peristaltic pump (Ismatech Ms-REGLO), polyethylene tubing (0.71 mm i.d.), and an Omnifit injection valve (Omnifit, Cambridge, UK) with a sample loop of 100 μL volume. The potential signals were recorded using a home-made high input-impedance 8-channel box connected to a PC through the interface ADC 16 (Pico Tech, UK) and Pico Log software (Ver. 5.07).

Reagents

2-[5-Bromo-2-pyridylazo-5-diethylaminophenol] (Br-PADAP), tridodecylmethylammonium chloride (TDMAC), potassium tetrakis[bis(3,5-trifluoromethyl)phenyl] borate (KTFPB), high molecular weight poly(vinyl chloride) (PVC), and *o*-nitrophenyloctyl ether (*o*-NPOE) were used as received from Fluka (Ronkonoma, NY). Tetrahydrofuran (THF) and 2-morpholinoethanesulfonic acid (MES) were purchased from Sigma (St. Louis, MO). The buffer used in this work was 0.05 mol L^{-1} MES buffer of pH 5.

Preparation of Cu-PADAP complex

Cu-PADAP ionophore (Fig. 1) was prepared and structurally characterized using elemental analysis and spectral data according to literature procedures.³¹ To a solution containing 2-[5-bromo-2-pyridylazo-5-diethylaminophenol] (5-Br-PADAP) (1.7 mmol) in 20 mL of ethyl alcohol, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (2.4 mmol) was added. A solid precipitate was immediately produced, stirred at room temperature for 30 min, collected by filtration and washed with deionized water. The crude precipitate was recrystallized from ethanol to give fine violet crystals.

Membrane preparation and EMF measurements

Thiocyanate PVC membrane sensors were prepared as described previously.^{32,33} A 2-mg portion of Cu-PADAP complex was thoroughly mixed with 126 mg of *o*-NPOE, 67 mg of PVC and 3 mL of THF in a glass Petri dish (3 cm diameter) covered with a filter paper and left to stand overnight to allow slow evaporation of THF at room temperature. The master membrane was sectioned with a cork borer (10 mm diameter) and glued to PVC tubing (~3 cm length; 8 mm i.d.) using THF. The sensor body consisted of a 5-ml pipette tip attached to PVC tubing. The internal reference solution was a mixture of equal volumes of 1.0×10^{-2} mol L^{-1} KSCN and 1.0×10^{-2} mol L^{-1} KCl. Ag/AgCl wire (1.0 mm diameter) was immersed in an internal reference solution. The sensor was conditioned by soaking in a 1.0×10^{-2} mol L^{-1} aqueous KSCN solution overnight, and was stored in the same solution when not in use. The sensor was calibrated under a static mode of operation by transferring 1.0 mL aliquots of a 1.0×10^{-2} – 1.0×10^{-6} mol L^{-1} aqueous solution of SCN^- to a 20-mL beaker containing 9.0 mL of 0.05 mol L^{-1} MES buffer of pH 5. The sensor was immersed in the buffer solution in conjunction with a double-junction Ag/AgCl reference electrode. The potential readings were

Fig. 1 Chemical structures of the Cu-PADAP complex.

recorded after stabilization to ± 1 mV and the emf was plotted as a function of the logarithm $[\text{SCN}^-]$ concentration.

Flow-injection setup

Tubular sensors were constructed according to literature procedures.³⁴ A casting membrane solution of the sensor was prepared by dissolving 67 mg of PVC in 3 mL of THF, followed by the addition of 126 mg of *o*-NPOE and 2 mg of Cu-PADAP complex. The casting solution was deposited, using a micro dropper, onto a hole (3 mm wide $\times$ 5 mm length) made in the middle of a 5-cm Tygon tube (ALKEM, P/N A003494). The casting process was repeated 3 times at 2 min intervals. The tube was inserted and sealed with Araldite into a pipette tip. The tubular sensor was inserted into the flow-injection system and 0.05 mol L^{-1} MES buffer of pH 5 was used as a carrier solution at a flow rate of 3 mL min^{-1} . The tubular sensor was located at a distance of about 30 cm from the injection valve and at a distance of about 20 cm from the waste container. An Orion Ag/AgCl double-junction reference electrode was placed in the waste reservoir downstream from the working sensor. The detector was calibrated at 25°C by the injection of thiocyanate samples through a loop of 100 μL volume in the carrier stream.

Determination of SCN^- in saliva and urine

Samples of saliva and urine were collected from cigarette smokers (10 persons each) and non-smokers into polyethylene tubes. The samples were immediately centrifuged and stored at 4°C . A 1.0-mL aliquot of the sample was transferred into a 10-mL measuring flask and diluted with 0.05 mol L^{-1} MES buffer of pH 5. For batch analysis, the thiocyanate sensor and double-junction Ag/AgCl reference electrode were immersed in the same solution, and the potential readings were recorded.

For flow-injection analysis (FIA), successive 100 μL aliquots of the standard SCN^- solution and the unknown thiocyanate test samples were injected into a flowing stream of 0.05 mol L^{-1} MES buffer of pH 5. A typical FIA calibration plot was made by plotting the potential change against the logarithm $[\text{SCN}^-]$ concentration. The obtained calibration curve was used for subsequent determinations of SCN^- in unknown samples.

Potentiometric determination of cyanide

An aliquot of 5 mL of standard 1.0×10^{-6} to 1.0×10^{-2} mol L^{-1} CN^- test solutions was successively added to 20 mL beakers containing 5 mL aliquots of 1.0×10^{-6} to 1.0×10^{-2} mol L^{-1} ammonium polysulfide. The solution was boiled for 15 min using a hot plate, cooled and transferred into a 10-mL measuring flask and completed to the mark with 0.05 mol L^{-1} MES buffer of pH 5. The solution was shaken well and transferred to a 100-mL beaker. A thiocyanate sensor in conjunction with a

double-junction Ag/AgCl reference electrode was immersed into the test solution. The potential changes after each addition were recorded, and a calibration curve was constructed by plotting the potential reading against the logarithm of the cyanide concentration.

Results and Discussion

Potentiometric characteristics of thiocyanate membrane sensors

The reaction of copper(II) with 5-Br-PADAP in an acidic medium of pH 3.2 gave a charged complex^{31,35} with the composition $[\text{Cu(II)R(R-H)}]^+$ (Fig. 1). The complex was prepared, characterized, dispersed in a plasticized polymeric membrane and used as a potentiometric sensor for thiocyanate. A conventional poly(vinyl chloride) matrix membrane sensor based on the Cu-PADAP complex as an ionophore and plasticized with *o*-nitrophenyloctyl ether (NPOE) was prepared and tested under static- and flow-injection modes of operation (FIA). The composition of the membrane was 64.6 wt% plasticizer, 1.0 wt% Cu-PADAP complex, and 34.4 wt% PVC.

Fig. 2 Potentiometric response of Cu-PADAP (■), Cu-PADAP + TDMAC (●), and Cu-PADAP + TFPB (▲) based membrane sensors toward SCN^- in a 0.05 mol L^{-1} MES buffer, pH 5.

At pH 5, the sensor displayed a linear response toward SCN^- over the concentration range 7.0×10^{-6} to $1.0 \times 10^{-2} \text{ mol L}^{-1}$, a detection limit of $5.6 \times 10^{-6} \text{ mol L}^{-1}$, and a near-Nernstian potentiometric response of $-57.5 \pm 0.5 \text{ mV decade}^{-1}$ of thiocyanate (Fig. 2).

A Cu-PADAP based sensor with a membrane containing cationic additive (*i.e.* 30 mol% TDMAC relative to the ionophore) showed an enhancement of the potentiometric response characteristics. This membrane electrode exhibited a slope of $-61.1 \pm 0.8 \text{ mV decade}^{-1}$, a linear dynamic range of 5.6×10^{-6} to $1.0 \times 10^{-2} \text{ mol L}^{-1}$, and a detection limit of $3.1 \times 10^{-6} \text{ mol L}^{-1}$. Surprisingly, the incorporation of an anionic additive (*i.e.* 30 mol% TFPB⁻ relative to the ionophore) in the membrane of a Cu-PADAP based sensor deteriorated the potentiometric response. The calibration slope, detection limit and linear response range observed in this case were $-49.0 \pm 0.2 \text{ mV decade}^{-1}$, $1.0 \times 10^{-5} \text{ mol L}^{-1}$ and 3.0×10^{-5} to $1.0 \times 10^{-2} \text{ mol L}^{-1}$, respectively. The obtained results are given in Table 1.

The potentiometric selectivity coefficients ($K_{\text{SCN}^-}^{\text{pot}}$) of thiocyanate sensors based on the Cu-PADAP complex in a PVC membrane plasticized with *o*-nitrophenyloctyl ether (*o*-NPOE) with and without anionic and cationic additives were evaluated using the separate solutions method,^{36,37} with EMF values measured in 0.1 M salt solutions and theoretical slope values. Although, the calibration slopes of most interfering ions measured with anionic additive containing membranes were sub-Nernstian, the theoretical slope values were used instead for calculating their selectivity coefficients. The practical analytical selectivity was also illustrated graphically (Fig. 3). This normalization allows a comparison of the obtained selectivity data with those previously reported. This approach was recommended and similarly used with non-Nernstian responding anions.³⁸

The selectivity of a thiocyanate sensor based on the use of a plasticized membrane electrode containing only TDMAC as an ion-exchanger was also examined for a comparison. The response for all ions was Nernstian; the calculated potentiometric selectivity coefficients are summarized in Table 2. The selectivity coefficients of a Cu-PADAP membrane sensor without membrane additives were in the order: $\text{SCN}^- > \text{ClO}_4^- > \text{I}^- > \text{Sal}^- > \text{NO}_2^- > \text{Br}^- > \text{NO}_3^- = \text{CH}_3\text{COO}^- > \text{Cl}^- > \text{SO}_4^{2-} = \text{PO}_4^{3-}$. Membrane electrodes doped with anionic sites (*e.g.* KTFPB 30 mol%) exhibited almost the same selectivity order of membranes containing no additives with a slight improvement of the potentiometric selectivity towards the thiocyanate anion,

Table 1 Potentiometric response characteristics of thiocyanate PVC membrane sensors based on Cu-PADAP, with and without anionic and cationic additives

Parameter	Cu-PADAP	Cu-PADAP + 30 mol% TDMAC	Cu-PADAP + 30 mol% TFPB
Slope/ mV decade^{-1} ^a	-57.5 ± 0.5	-61.1 ± 0.8	-49.0 ± 0.2
Correlation coefficient, <i>r</i>	-0.9994	-0.9997	-0.9996
Intercept/ mV^a	66.8	52.9	66
Linear range/ mol L^{-1} ^a	$7.0 \times 10^{-6} - 1.0 \times 10^{-2}$	$5.6 \times 10^{-6} - 1.0 \times 10^{-2}$	$3.0 \times 10^{-5} - 1.0 \times 10^{-2}$
Detection limit/ mol L^{-1} ^a	5.6×10^{-6}	3.1×10^{-6}	1.0×10^{-5}
Working range (pH)	3.2 – 8	3 – 8.5	5.0
Response time/s	< 10	< 10	< 10
Precision, %	1.1	0.8	1.2
Accuracy, %	0.5	1.2	0.6
Reproducibility/ mV	1.3	1.6	1.5
Between-day-variability (C_{vis} , %)	0.9	0.7	1
Relative standard deviation, %	1.1	0.9	1.9

a. Average of six determinations.

Fig. 3 Potential responses of: (A) Cu-PADAP based membrane sensor, (B) Cu-PADAP + TDMAC based membrane sensor, (C) Cu-PADAP + TFPB based membrane sensor towards various anions: PO_4^{3-} (■); SO_4^{2-} (●); Cl^- (▲); acetate^- (▼); Br^- (◆); I^- (+); NO_2^- (×); salicylate^- (*); NO_3^- (-); ClO_4^- (⌋); SCN^- (□).

Table 2 Selectivity coefficients ($K_{\text{SCN},J}^{\text{pot}}$) of thiocyanate PVC membrane sensors based on Cu-PADAP, Cu-PADAP + TFPB, Cu-PADAP + TDMAC, and TDMAC

Interferant, J	$\log K_{\text{SCN},J}^{\text{pot}}$			
	Cu-PADAP	Cu-PADAP + 30 mol% TFPB	Cu-PADAP + 30 mol% TDMAC	TDMAC
I^-	< -2.7	< -2.9	-0.7	0
NO_3^-	< -4.0	< -4.3	-1.9	-1.2
NO_2^-	< -3.7	< -3.4	< -2.8	-2.6
ClO_4^-	< -2.2	< -2.7	0.8	+1.9
Cl^-	< -4.2	< -4.5	< -3.9	-3.3
PO_4^{3-}	< -4.3	< -4.5	< -4.2	-3.9
Br^-	< -3.8	< -4.0	< -2.8	-2.1
CH_3COO^-	< -4.0	< -4.2	< -3.9	-3.3
Salicylate^-	< -3.5	< -3.8	+0.7	+1.2
SO_4^{2-}	< -4.3	< -5.0	< -4.2	-3.6

a. < Sign was used in the case of anions that did not respond in a Nernstian fashion.

compared with membrane sensors prepared without an anionic additive site. An improvement was obtained over perchlorate, iodide, nitrate, and bromide (*i.e.* the lipophilic anions), whereas no improvement was obtained over nitrite. This selectivity order clearly differs from the classical Hofmeister pattern. It is well known that PVC contains an anionic impurity that works well as a charged ionophore with small concentrations of ionic sites; similar effects were obtained with metalloporphyrins.

However, Cu-PADAP based membrane sensors doped with TDMAC as a cationic additive and membrane sensors incorporating only TDMAC displayed a selectivity pattern in the order: $\text{ClO}_4^- > \text{Sal}^- > \text{SCN}^- > \text{I}^- > \text{NO}_3^- > \text{NO}_2^- = \text{Br}^- > \text{CH}_3\text{COO}^- = \text{Cl}^- > \text{SO}_4^{2-} = \text{PO}_4^{3-}$, which is almost identical to the Hofmeister pattern. The improvement of the potentiometric selectivity by the addition of anionic sites and the relative deterioration of the selectivity by the incorporation of cationic sites supports the charged-carrier mechanism of the Cu-PADAP ionophore.^{39,40} Membranes containing charged ionophores, but

no ionic sites do exhibit anionic responses, but their selectivity can be improved by the use of anionic sites.

The observed selectivity behavior is due to the mode of interaction between the electroactive species in the membrane and the analyte anions in the aqueous test solution. For the classical ion-exchange membrane sensors (Cu-PADAP based membrane doped with TDMAC and that containing TDMAC only) where a Hofmeister pattern was displayed, the hydration energy or hydrophilicity of the anions plays a dominant role for the transfer of the anions across the organic/water membrane interface. However, membranes containing Cu-PADAP with/without TFPB exhibited a strong coordination affinity between the ionophore and some anions, leading to a non-Hofmeister selectivity sequence.

The effect of the pH on the response of the sensor was studied over the pH range of 2 to 11 at fixed concentrations of thiocyanate (1.0×10^{-4} and 1.0×10^{-3} mol L⁻¹). The pH of these solutions was altered by adding KOH and/or HCl. The potential response of the Cu-PADAP membrane-based sensor was pH independent in the pH range 3.5 – 8, as shown in Fig. 4. At approximately pH > 8, the potential decreased, probably due to an increase of the OH⁻ competition with the SCN⁻ anion.

The response time of the Cu-PADAP sensor was evaluated by measuring the time required to achieve a steady-state potential (within ± 0.2 mV). A response time of less than 10 s was obtained for all thiocyanate solutions in the linear calibration range. The stability and reproducibility of the response of the sensors were also tested. The potential readings remained constant for ~10 min (drift < 0.5 mV). The potential readings of the sensor for 6 identical measurements over a period of 2 months showed variations of not more than ± 1.3 mV. The reproducibility of the calibration slope was within ± 1.5 mV decade⁻¹ over a period of 2 months ($n = 6$).

A comparison of the selectivity coefficient values of the present sensor with some of those previously described is shown in Table 3. It can be seen that the present sensor offered better selectivity in the presence of I^- , NO_3^- , NO_2^- , Cl^- , and Br^- ,^{20,21,24,28} as well as ClO_4^- ,^{20,21,24,28,29} SO_4^{2-} ,^{20,23,24,28} and PO_4^{3-} .^{21,23} The linear response range was slightly better than some of those previously suggested.^{19,33}

Table 3 Selectivity coefficient data of some thiocyanate potentiometric membrane sensors

Ionophore	Selectivity, $-\log K_{\text{SCN,J}}^{\text{rel}}$	Ref.
1,8-Dibenzyl-1,3,6,8,10,13-hexaazacyclotetradecane-Ni(II)-perchlorate	NO_2^- , 2.04; salicylate $^-$, 1.4; Br^- , 1.6; SO_4^{2-} , 1.3; acetate $^-$, 1.3; NO_3^- , 1.2; I^- , 1.0; ClO_4^- , 2.3; Cl^- , 0.5	20
Bis-[N-(2-hydroxyethyl)salicylamino]-copper(II)	ClO_4^- , 1.9; I^- , 2.3; salicylate $^-$, 2.4; Br^- , 2.7; NO_2^- , -2.9; Cl^- , 3.0; NO_3^- , 3.2; H_2PO_4^- , 3.4; SO_4^{2-} , 3.5	21
Butane-2,3-dione-bis(salicylhydrazonato)-zinc(II) complex	Cl^- , 4.1; Br^- , 3.3; NO_3^- , 3.0; SO_4^{2-} , 4.1; NO_2^- , 3.1; PO_4^{3-} , 4.2; acetate $^-$, 4.2; salicylate $^-$, 3.2; HPO_4^{2-} , 4.0	23
Cadmium-Schiff's base complex	Acetate $^-$, 4.6; ClO_4^- , 2.04; NO_3^- , 2.1; salicylate $^-$, 1.8; NO_2^- , 2.4; SO_4^{2-} , 2.2; I^- , 1.5; Cl^- , 2.01; Br^- , 2.1	24
Nickel(II)-1,4,8,11,15,18,22,25-octabutoxyphthalocyanine	ClO_4^- , 2.04; Cl^- , 3.09; Br^- , 2.6; I^- , 2.39; acetate $^-$, 3.4; NO_3^- , 2.4; SO_4^{2-} , 3.02; NO_2^- , 3.0	28
Nickel(II)-azamacrocyclic complex	Cl^- , 3.3; Br^- , 3.1; I^- , 1.6; SO_4^{2-} , 3.4; NO_2^- , 2.5; NO_3^- , 2.6; ClO_4^- , 2.1; salicylate $^-$, 2.8	29
Cu-PADAP complex	I^- , 2.7; NO_3^- , 4.0; NO_2^- , 3.7; ClO_4^- , 2.2; Cl^- , 4.2; PO_4^{3-} , 4.3; Br^- , 3.8; acetate $^-$, 4.0; salicylate $^-$, 3.5; SO_4^{2-} , 4.3	This work

Fig. 4 Effect of the pH on the potentiometric response of a Cu-PADAP based membrane sensor.

Fig. 5 Typical flow-injection potentiometric peaks obtained using the Cu-PADAP based membrane sensor towards thiocyanate.

Flow-injection measurements

A tubular-type detector incorporating a Cu-PADAP based membrane sensor was prepared and used under the hydrodynamic mode of operation for continuous SCN^- quantification. A linear relationship between the SCN^- concentrations and FIA signals was obtained over a concentration range of 1.0×10^{-5} to 1.0×10^{-2} mol L^{-1} using a 0.05 mol L^{-1} MES buffer, pH 5 (Fig. 5). The optimum flow rate was 3 mL min^{-1} . The slope of the calibration plot was near-Nernstian (-55.9 ± 0.2 mV decade $^{-1}$). The lower limit of detection was 5.8×10^{-6} mol L^{-1} and the sampling frequency was about 50 samples per hour.

Determination of thiocyanate in urine and saliva

A chemical test to distinguish smokers and non-smokers is important in many epidemiological studies.⁴⁰ Experimental results have shown that the urinary and salivary SCN^- concentrations were higher for smokers than for non-smokers. Thus, the adequate degree of SCN^- selectivity exhibited by Cu-PADAP based sensors make them potentially useful for monitoring the SCN^- concentration levels in biological samples. The feasibility of using the proposed sensor to measure the thiocyanate concentration in human urine and saliva samples was examined. Samples were collected from various donors of age ranging from 25 to 65 years. Five donor groups (10 persons each) were tested: non-smokers (group I), smokers (1–5 cigarettes per day) (group II), smokers (6–10 cigarettes per

day) (group III), and smokers (more than 20 cigarettes per day) (group IV). Table 4 indicates that the concentrations of saliva- SCN^- and urine- SCN^- in non cigarette smokers were 0.41–0.58 and 0.09–0.18 mmol L^{-1} , respectively. These results fairly agreed with data obtained by other authors using a spectrophotometric technique,^{41,42} and are in good agreement with results obtained by the reference spectrophotometric method (Table 4). The *F*-test showed no significant difference at the 95% confidence level between the mean and the variance of the potentiometric and spectrophotometric set of results. The calculated *F*-values ($n = 5$) were found to be in the range 0.9–5.1 compared with the tabulated value (6.39) at the 95% confidence limit.

Determination of cyanide ions

Determination of cyanide ion after its conversion to thiocyanate ion using the ammonium polysulfide treatment was investigated. Such a conversion is well-documented, and occurs according to the following reaction:⁴³

Table 4 Potentiometric determination of thiocyanate in some saliva and urine samples using a thiocyanate PVC membrane sensor based on Cu-PADAP and the standard spectrophotometric method⁴¹

Test smoker group	Spectrophotometry ⁴¹ /mmol L ⁻¹		Potentiometry/mmole L ⁻¹			
			Batch		FIA	
	Saliva	Urine	Saliva	Urine	Saliva	Urine
(I)	(0.41 – 0.51) ± 0.2	(0.10 – 0.15) ± 0.1	(0.40 – 0.58) ± 0.1	(0.09 – 0.17) ± 0.2	(0.42 – 0.55) ± 0.3	(0.11 – 0.18) ± 0.2
(II)	(0.61 – 0.72) ± 0.3	(0.31 – 0.35) ± 0.3	(0.60 – 0.75) ± 0.2	(0.29 – 0.32) ± 0.1	(0.59 – 0.69) ± 0.1	(0.30 – 0.35) ± 0.4
(III)	(1.97 – 2.10) ± 0.1	(1.51 – 1.62) ± 0.2	(1.89 – 2.20) ± 0.4	(1.50 – 1.61) ± 0.4	(1.93 – 2.18) ± 0.3	(1.49 – 1.62) ± 0.3
(IV)	(3.91 – 4.21) ± 0.3	(2.35 – 2.46) ± 0.4	(4.40 – 4.71) ± 0.2	(2.51 – 2.72) ± 0.3	(4.45 – 4.71) ± 0.5	(2.44 – 2.53) ± 0.2

Fig. 6 Typical potentiometric titration plots using the Cu-PADAP based membrane sensor and $1.0 \times 10^{-2} \text{ mol L}^{-1} \text{ SCN}^-$ titrant. (A) 5 (■) and 10 (●) mL of $1.0 \times 10^{-3} \text{ mol L}^{-1} \text{ Hg}^{2+}$ solutions, (B) 5 (●) and 10 (■) mL of $1.0 \times 10^{-3} \text{ mol L}^{-1} \text{ Ag}^+$ solutions, (C) a mixture of 5 mL + 5 mL of $1.0 \times 10^{-3} \text{ mol L}^{-1} \text{ Hg}^{2+}$ and Ag^+ solutions.

A linear calibration curve for CN^- ions ($1.0 \times 10^{-5} - 1.0 \times 10^{-2} \text{ mol L}^{-1}$) after conversion into SCN^- by a treatment with ammonium polysulfide solution, followed by monitoring using a Cu-PADAP based membrane sensor was obtained. The method was used for the potentiometric determination of free cyanide ions in industrial waste-water samples obtained from an electroplating factory. The obtained results ($55 - 105 \text{ mg L}^{-1}$) agreed well with data obtained using the solid state cyanide ion-selective electrode (Table 5).

Potentiometric titration of metal ions

The thiocyanate sensor based on Cu-PADAP was used as an indicator electrode for monitoring the titration of silver and mercury metal ions and their binary mixtures using a standard thiocyanate solution. The obtained titration curves showed sharp inflection breaks ($\sim 100 \text{ mV}$) at 1:1 and 2:1 reactions for SCN^-/Ag^+ and $\text{SCN}^-/\text{Hg}^{2+}$, respectively. For the titration of a binary mixture ($\text{Ag}^+ + \text{Hg}^{2+}$), two sharp successive inflection breaks at the equivalent points of both metals were obtained. Typical potentiometric titration curves are shown in Fig. 6.

Conclusions

A Cu-PADAP based PVC membrane sensor was prepared and used for the thiocyanate measurement. The sensor was utilized for manual and FIA monitoring of SCN^- . Under the static mode

Table 5 Potentiometric determination of cyanide in electroplating baths after conversion into thiocyanate using a thiocyanate PVC membrane sensor based on Cu-PADAP

Sample	Cyanide content/mg L ^{-1a}	
	Cu-PADAP sensor	Solid state cyanide sensor
1	55.9 ± 0.3	61.2 ± 0.6
2	98.2 ± 0.6	103.1 ± 0.4
3	105.4 ± 0.8	114.2 ± 0.6

a. Average of 5 measurements.

of operation, the sensor displayed high selectivity in the presence of many anionic species, a wide dynamic response range (7.0×10^{-6} to $1.0 \times 10^{-2} \text{ mol L}^{-1}$), a low detection limit ($5.6 \times 10^{-6} \text{ mol L}^{-1}$), good sensitivity ($-57.5 \pm 0.5 \text{ mV decade}^{-1}$) and a rapid response (10 s). Under the hydrodynamic mode of operation, the sensor exhibited a near-Nernstian slope of $-55.9 \pm 0.1 \text{ mV decade}^{-1}$ over a concentration range of $1.0 \times 10^{-5} - 1.0 \times 10^{-2} \text{ mol L}^{-1} \text{ SCN}^-$. These characteristics enabled accurate measurements of as low as $0.2 \mu\text{g mL}^{-1}$ thiocyanate in the saliva and urine of cigarette smokers and non-smokers. Cyanide after conversion into thiocyanate and some metal ions were also accurately measured.

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