



POTENTIOMETRIC STUDY FOR RAPID CONTINUOUS MONITORING OF TRACE LEVEL THIOCYANATE USING SOLID AND CONVENTIONAL TYPES PVC MEMBRANE SENSORS

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A comparative study using two different thiocyanate electrode designs was conducted; a solid type electrode (type A) and conventional liquid inner contact electrode (type B). The fabrication of these electrodes was based on Al (III) [4-(2-Pyridylazo) resorcinol] (Al/PAR) and Mg (II) phthalocyanine (MgPC) complexes as a charged carrier, aliquate 336S and TDMAC as ion exchangers in plasticized poly (vinyl chloride) membrane. Electrodes type (A) revealed significantly enhanced response towards SCN⁻ ions with displayed near-Nernstian slope of -53.7 - -55.8 mV decade⁻¹ over the concentration range 5.0x10⁻⁶-1.0x10⁻² mol L⁻¹ and a detection limit of 0.4-3.7 µg mL⁻¹. Type (B) sensors revealed near-Nernstian potential response to SCN⁻ with a slope of -45.9 - -62.4 mV decade⁻¹ over a linear range of 5.0x10⁻⁵-1.0x10⁻² mol L⁻¹ and a detection limit of 0.12-0.3 µg mL⁻¹. Membrane sensors based on (Al/PAR) and (MgPC) using the so called "fixed interference method" (FIM) exhibited a good selectivity over different anions which differ significantly from the classical Hofmeister series. All sensors were integrated in a flow system for continuous monitoring of thiocyanate under hydrodynamic mode of operation. The sensors revealed a frequency of ~ 54 samples h⁻¹. Application of the proposed sensors for SCN⁻ determination in biological fluid samples such as saliva collected from some non-smoker and smoker donors. Determination of cyanide content in electroplating wastewater samples after its conversion into thiocyanate was also applied. The results obtained from the proposed sensors were agreed with that obtained using the standard methods of thiocyanate and cyanide analysis.

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ion buffers^{10,11} or ion-exchange resins.¹² A carefully designed internal solution reduces trans-membrane concentration gradients through the partial exchange of primary ions by interfering ones on the inner membrane side.¹³ However, a significant drawbacks of these sensors are miniaturization and difficulty in use due to the presence of this internal filling solution. This requires avoiding leakage via alignment of the sensor in a vertical position, refilling the solution; moreover, there are problems with shape tailoring.

INTRODUCTION

Potentiometric ion-sensors have become a versatile instrument in chemical analysis because of their wide applications in different fields such as clinical diagnostics and environmental monitoring.¹⁻⁵ Ease of use, simplicity, ease of manipulation and no sample pre-treatment have replaced for long other wet analytical methods, because they offer high precision and rapidity, low cost, high selectivity and enhanced sensitivity over a wide linear range of concentrations. From all of the above, potentiometric sensors can be used as appropriate devices for process control.

Good analytical performances were noticed for conventional potentiometric sensors such as potential stability, short response time and high selectivity. On the other hand, low detection limit and lack of miniaturization were also noticed. Significant progress, concerning construction and analytical parameters of potentiometric sensors could be noticed in the last three decades.⁶⁻⁹ This goal has been achieved in potentiometric sensors having a liquid internal contact by reducing zero-current trans-membrane ion flux effects. For that, the primary ion activity in the internal filling solution is kept at a low level by using

A new trial regarding solution-free sensors was proposed, based on inclusion of additional layer between the membrane and support, called solid contact ion selective electrodes (SC-ISEs).¹⁴ The first reported SC-ISEs were commonly referred to as coated-wire electrodes (CWEs).¹⁵ In which, a sensing polymeric membrane is directly coated onto an electronic conductor. These sensors have a high potential drift due to the "blocked" interface between the sensing membrane and the electronic conductor.¹⁶ These initial detections soonheless led to dense research to introduce materials that facilitate the charge transfer at the interface between the ion conducting membrane and the electronic conductor "ion-to-electron transduction". The most promising "ion-to-electron transducers" introduced to date include conducting polymers¹⁷⁻²⁰ and different carbon structures such as carbon nanotubes,^{21, 22} graphene,²³⁻²⁵ and colloid-imprinted mesoporous carbon.²⁶

For biomedical analysis, relevant contributors to the potential at the membrane of sample interface are thiocyanate itself and interfering ions. For most applications, a solvent polymeric membrane is used. Perm-selectivity is a necessary condition for thiocyanate and is achieved by

incorporating cationic sites in the membrane, addition of an ion complexing agent or ionophore to the membrane. Many ionophores have been used for thiocyanate monitoring using solid contact potentiometric electrodes.²⁷⁻³² Although these sensors exhibit an anti-Hoffmeister selectivity order, they suffer from strong interference by I^- , CN^- , NO_2^- , IO_4^- , ClO_4^- , Br^- , and N_3^- . In addition, some of these sensors suffer from the disadvantages of limited range of the linear response, and a long response time.

In this work, a comparative study concerning slopes, detection limits, concentration ranges and selectivity for a potentiometric determination of SCN^- using ion selective membrane was made between two types of transducers: high double layer capacitance (Solid contact) e.g. graphite/graphene sensors type (A) and classical inner filling solution (Liquid contact) sensors type (B).

Herein, we present a novel potentiometric thiocyanate membrane sensors based on the Al(III) [4-(2-Pyridylazo)resorcinol] (Al/PAR) and Mg (II) phthalocyanine (MgPC) complexes as a charged carrier, aliquate 336S and TDMAC as ion exchangers in plasticized poly (vinyl chloride) membrane are described and developed. These sensors were used for thiocyanate determination in saliva and urine fluids, and for the determination of cyanide in waste-water and electroplating samples after conversion into thiocyanate.

EXPERIMENTAL

An Orion (Cambridge, MA, USA) Model 720/SA pH /mV meter was used for all potential measurements. Thiocyanate membrane sensor in conjunction with an Orion double-junction Ag /AgCl reference electrode (Model 90-20) filled with 10% (w/v) KNO_3 were used for cell construction. For pH measurements, Ross glass electrode (Orion 81-02) was used.

Continuous monitoring of SCN^- using flow system was carried out using a two-channel peristaltic pump (Ismatech Ms-REGLO) integrated with an Omnifit injection valve (Omnifit, Cambridge, UK) with a sample loop of 500 μ L volume. The potential readings were continuously recorded through the interface ADC 16 (Pico Tech, UK) and Pico Log software (version 5.07).

All UV/Vis measurements were conducted using spectrophotometer (Shimadzo, model 1601, Japan) under the recommended conditions of the standard method used for thiocyanate assessment.³³

4-(2- monosodium salt monohydrate (PAR), tri-dodecyl methyl ammonium chloride (TDMAC), high molecular weight poly (vinyl chloride) (PVC), graphene and *o*-nitrophenyloctyl ether (*o*-NPOE) were used as received from Fluka (Ronkonoma, NY). Tetrahydrofuran (THF) and Mg (II) phthalocyanine (MgPC) were purchased from Sigma (St. Louis, MO). Aliquat 336 was purchased from Acros. Aluminium potassium sulfate was purchased from (BDH chemicals Ltd). The buffer used in this work was 0.1 mol L^{-1} acetate buffer, pH 5.0.

Preparation of Al/PAR complex

Al/PAR ionophore (Figure 1) was prepared and structurally characterized using elemental and spectral analysis. To a solution containing 4-(2-pyridylazo)resorcinol monosodium salt monohydrate (PAR), (3.5 mmol) in 20 mL ethyl alcohol, $K[Al(SO_4)_2] \cdot 12H_2O$ (1.5 mmol) was added. A solid precipitate was immediately produced, stirred at room temperature for 30 min, collected by filtration and washed with de-ionized water. The crude precipitate was re-crystallized from ethanol to give fine dark red crystals.

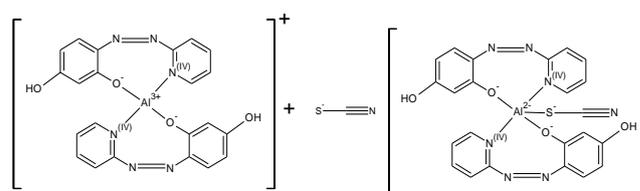


Figure 1. Chemical structure of Al (III)–PAR complex.

Sensor preparation and emf measurements

Liquid contact sensors were prepared as described previously.^{34, 35} A 2.0 mg portion of the ionophore was mixed with 126 mg of the plasticizer, 66 mg of PVC, 1.0 mg TDMAC and dissolved in 3 mL THF in a glass ring (2.2 cm diameter). The cocktail left to stand overnight for solvent evaporation at room temperature. The master membrane was sectioned with a cork borer (10 mm diameter) and glued using THF to PVC tubing (~3 cm length, 8 mm; internal diameter). The PVC tube was attached to a 1 mL micropipet tip. The blue tip was internally filled with 10^{-2} mol L^{-1} thiocyanate solution. Homemade Internal reference electrode Ag/AgCl (1.0 mm diameter) was immersed in the internal reference solution. The conditioning solution was 10^{-2} mol L^{-1} SCN^- solution for 12 h and was stored in the same solution when not in use.

Solid contact sensors were fabricated as described previously³⁶ and as shown in Figure 2. A solid electrical contact is made from graphene which is characterized with high double layer capacitance. The epoxy metal mixture, used as supporting conductor, was obtained by pressing out an equal amount of both components onto the enclosed mixing tray. These two equal parts were mixed well with a synthetic spatula until a paste is obtained with a homogeneous color. This resulting paste was then mixed with graphite powder 1:1 mass ratio, introduced to the electrode body which is made from polypropylene and a copper disk with diameter 5.5 mm welded to a copper wire and immersed inside the paste. The electrodes were left to dry in air for 24 h. A volume of 10 μ L of graphene solution (dissolved after sonication in THF) was applied onto the conductive layer. After dry, a volume of 20 μ L of the membrane cocktail is applied at once by drop casting above the graphene layer. The membranes were left to dry at ambient temperature for 2 h before use. These solid contact electrodes were conditioned in a 1.0×10^{-2} mol L^{-1} aqueous SCN^- solution for 2 h before using and were stored dry when not in use.

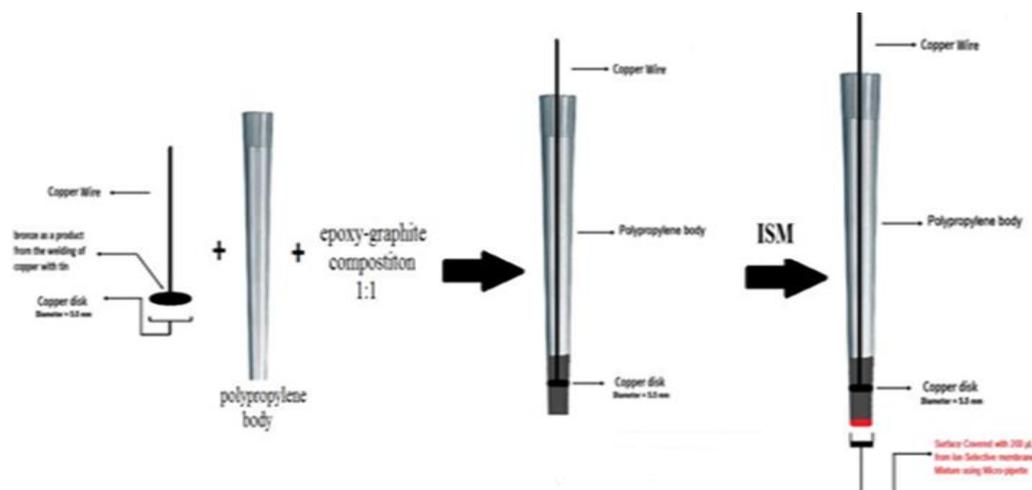


Figure 2. Fabrication of a SC-ISE high double layer capacitance based on epoxy-graphite composite.

Table 1. Potentiometric response characteristics of SCN^- membrane sensors type (A) and (B) in 0.1 mol L^{-1} acetate buffer pH (5.0).

Parameter	Sensors type (A)				Sensors type (B)			
	Sensor I	Sensor II	Sensor III	Sensor IV	Sensor I	Sensor II	Sensor III	Sensor IV
Slope, (mV decade^{-1})	-53.7 ± 0.6	-55.3 ± 0.9	-54.7 ± 1.5	-55.8 ± 0.95	-46.4 ± 1.1	-56.1 ± 1.7	-55.1 ± 0.78	-62.4 ± 0.5
Correlation coefficient, (r)	0.9998	0.9999	0.9998	0.99997	0.9988	0.9998	0.9996	0.9995
Linear range, mol L^{-1}	5.0×10^{-6} - 1.0×10^{-2}	5.0×10^{-5} - 1.0×10^{-2}	5.0×10^{-6} - 1.0×10^{-2}					
Detection limit, mol L^{-1}	1.45×10^{-6}	2.68×10^{-6}	7.56×10^{-6}	3.88×10^{-6}	5.0×10^{-6}	2.9×10^{-6}	5.3×10^{-6}	2.0×10^{-6}
Working range, (pH)	3.5 – 10.0	4.5-10.0	3.0 – 10.0	4.0 – 10.0	4.0 – 7.0	2.5 – 8.0	4.0 – 10.0	4.0 – 10.0
Response time, (s)	10	15	30	10	10	10	10	10
Life span, (week)	12	12	12	8	12	12	12	8
Intercept	-201.7	-148.2	-182.8	-233.4	-21.4	-46.0	-65.6	-110.8
Standard deviation $\sigma_v(\text{mv})$	0.6	0.9	1.5	0.95	1.1	1.7	0.78	0.5

The sensors were calibrated under a static mode of operation by transferring (0.5-1.0) mL aliquots of a 1.0×10^{-1} - $1.0 \times 10^{-4} \text{ mol L}^{-1}$ aqueous solution of SCN^- to a 25 mL beaker containing 10.0 mL of 0.1 mol L^{-1} acetate buffer of pH 5.0. The potential readings were recorded after stabilization to $\pm 1 \text{ mV}$.

Determination of SCN^- content in saliva

Different saliva samples were collected from cigarette smokers and non-smokers into polyethylene tubes. The samples were immediately centrifuged and stored at 4°C . A 1 mL aliquot of the sample was transferred into 10 mL measuring flask and diluted with 0.1 mol L^{-1} acetate buffer (pH= 5.0). The proposed sensor in conjunction with the reference electrode were immersed in the solution, and the potential readings were recorded after stabilization.

Cyanide determination

An aliquot of 10 mL of standard $1.0 \text{ mol L}^{-1} \text{CN}^-$ test solution was boiled for 30 min using a hot plate with 1.0 g potassium polysulfide, pH adjusted at 10 by ammonia solution to prevent formation of volatile HCN. The solution

was cooled, transferred into a 100 mL measuring flask and completed to the mark with 0.1 mol L^{-1} acetate buffer of pH 5.0. Further dilutions (1.0×10^{-2} - 1.0×10^{-4}) were made by the same buffer solution. The solutions were shaken well and (0.5-1.0) mL aliquots of a 1.0×10^{-1} - $1.0 \times 10^{-4} \text{ mol L}^{-1}$ of converted CN^- solution were transferred into a 25 mL beaker. The potential changes after each addition was recorded, and a calibration curve was constructed by plotting the potential reading against the concentration of cyanide ions.

RESULTS AND DISCUSSIONS

Characterization of Al/PAR complex

4-(2-Pyridylazo)resorcinol monosodium salt monohydrate (PAR) reacts with $\text{K}[\text{Al}(\text{SO}_4)_2] \cdot 12\text{H}_2\text{O}$ to form an orange complex. The precipitate was isolated and characterized by elemental analysis. Al/PAR, $\text{K}[\text{Al/PAR}]$, $\text{K}[\text{Al}(\text{C}_{11}\text{H}_7\text{N}_3\text{O}_2)_2] \cdot 2\text{H}_2\text{O}$; yield 80 %, orange, m.p. $>300^\circ\text{C}$. Anal.: Calcd. for $\text{K}[\text{Al}(\text{C}_{11}\text{H}_7\text{N}_3\text{O}_2)_2] \cdot 2\text{H}_2\text{O}$: C, 49.34; H 3.36; N 15.70. Found: C 46.25; H 3.58; N 14.88. The conductivity measurements showed a conductance value of $17.36 \mu\text{s cm}^{-1}$ indicating the non-electrolytic nature of the

complex. The IR spectra of both PAR and Al/PAR complex are shown in Figure S1. The IR spectrum of the free ligand displayed strong bands at 3419 cm^{-1} , 1491.8 cm^{-1} , 1325.5 cm^{-1} and 1213.4 cm^{-1} due to O-H, C=C, C-N and C-O. In the IR spectrum of Al/PAR, these bands are shifted to 3437.96 cm^{-1} , 1477.65 cm^{-1} , 1285.83 cm^{-1} and 1192.18 cm^{-1} , respectively. This confirms the complexation between Al^{3+} ion and the PAR ligand. Mass spectroscopy analysis with molecular weight 536.0 confirmed the formation of 2:1 complex as shown in Figure S2.

Performance characteristics of thiocyanate sensors

Development of new potentiometric ion-sensors with better designs is a prospering area of research. An improvement in detection limit is more likely by introduction of solid inner contact instead of the traditional internal filling solution of the membrane. This may ideally give rise to a more reliable and robust sensors.

We have designed and characterized these new sensors, a conventional and solid contact types for thiocyanate monitoring and then compared their properties in light of these considerations. The optimum membrane composition was 33.0 wt % PVC, 1.0 wt % sensing material, 66.0 wt % of the plasticizer and 0.5 wt % TDMAC as cation excluder in case of Al (III)-PAR complex and MgPC, whereas 33.0 wt % PVC, 1.0 wt % sensing material, 66.0 wt % of the plasticizer in case of aliquat and TDMAC ion exchangers. The response characteristics of thiocyanate sensors based on these ionophores were given in Table 1. Sensors based on Al(III)-PAR/TDMAC complex (sensor I) revealed a potentiometric response towards SCN^- ions with near-Nernstian slope of -53.7 ± 0.6 and -46.4 ± 1.1 mV decade^{-1} ($r^2 = 0.9998$ and 0.9988) and a detection limit of 1.45×10^{-6} and 5.0×10^{-6} mol L^{-1} for type (A) and (B) sensors, respectively. For sensors based on MgPC/TDMAC (sensor II) exhibited a Nernstian potentiometric slope of -55.3 ± 0.9 and -56.1 ± 1.7 mV decade^{-1} ($r^2 = 0.9999$ and 0.9998) with a detection limit of 2.7×10^{-6} and 2.9×10^{-6} mol L^{-1} for type (A) and (B) sensors, respectively. For sensor III based on aliquat exhibited a potentiometric response with near-Nernstian slope of -54.7 ± 1.5 and -55.1 ± 0.8 mV decade^{-1} ($r^2 = 0.9998$ and 0.9996) and a detection limit of 7.56×10^{-6} and 5.3×10^{-6} mol L^{-1} for type (A) and (B) sensors, respectively. Sensors based on TDMAC only (sensor IV) exhibited a potentiometric response towards SCN^- ions with near-Nernstian slope of -55.8 ± 0.9 and -62.4 ± 0.5 mV decade^{-1} ($r^2 = 0.9999$ and 0.9995) and a detection limit of 3.9×10^{-6} and 2.0×10^{-6} mol L^{-1} for type (A) and (B) respectively. Potentiometric responses of these sensors are shown in Figure 3.

The pH effect on the potentiometric response of the sensors was studied over the pH range of 2 to 11 at fixed concentrations of thiocyanate (1.0×10^{-3} and 1.0×10^{-2} mol L^{-1}). The pH of these solutions was adjusted by adding NaOH and/or HCl. The solid contact sensors exhibited wider pH range 3.5-10, 4.5-10, 3.5-10 and 4-10 for sensor I, II, III, and IV, respectively.

For conventional sensors, they were pH independent in the pH range 4.0-7.0, 2.5-8.0, 4.0-10, 5.0-9.0 and 4.0-7.0 for sensor I, II, III, IV and V, respectively. The potentials of all sensors considerably declined with negative drift at higher

pH values probably due to an increase of the OH^- competition with the SCN^- anion. The sensors were stored and conditioned in 10^{-2} mol L^{-1} SCN^- solution of pH 5.0. With all sensors examined, the detection limits, response times, linear ranges and calibration slopes were reproducible within $\pm 3\%$ of their original values over a period of at least 12 weeks for both sensors types.

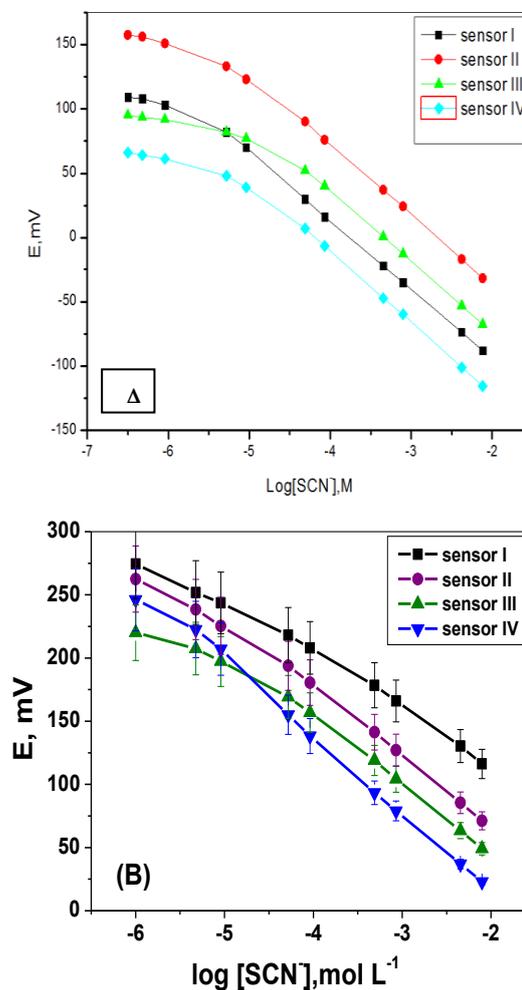


Figure 3. Calibration plot of thiocyanate sensors type (A) and type (B) I, II, III and IV; in 0.1 mol L^{-1} acetate buffer pH 5.0

One of the important features of the electrochemical sensor is the response time which can be evaluated by measuring the time required to achieve a steady-state potential within ± 0.2 mV of the final equilibrium value after successive immersion in a series of SCN^- solution, each having a 10-fold difference from low to high concentrations. The time required to achieve a steady potential response (± 3 mV) using the proposed sensors in 10^{-6} to 10^{-4} mol L^{-1} SCN^- solutions with a rapid 10-fold increase in concentration was < 20 s and < 10 s for sensors type (B) and type (A), respectively. Replicate calibrations for each sensor indicated low potential drift, long-term stability and negligible change in the response of the sensors.

Effect of foreign ions on thiocyanate sensors

Selectivity of the sensors was assessed by means of potentiometric selectivity coefficients ($K^{\text{POT}}_{\text{SCN},\text{J}}$), calculated by the fixed interference method (FIM).³⁷ The potential

measurements determined by using a solution contain a fixed activity of the interfering ion (10^{-3} mol L $^{-1}$) on acetate buffer pH 5.0 and varying the activity of the primary ion. The logarithmic values of $\log K^{\text{POT}}_{\text{SCN},\text{J}}$ were indicated in Table 2.

The selectivity order for type (A) sensors were illustrated as follow: For sensor I, the selectivity order as follow sensor

I revealed a selectivity pattern $\text{SCN}^- > \text{I}^- > \text{IO}_4^- > \text{S}_2\text{O}_3^{2-} > \text{NO}_3^- > \text{Br}^- > \text{NO}_2^- > \text{S}^{2-} > \text{CN}^- > \text{SO}_3^{2-} > \text{Cl}^- > \text{F}^- > \text{ClO}_4^- > \text{SO}_4^{2-}$, sensor II: $\text{SCN}^- > \text{IO}_4^- > \text{I}^- > \text{S}_2\text{O}_3^{2-} > \text{NO}_3^- > \text{CN}^- > \text{S}^{2-} > \text{Br}^- > \text{ClO}_4^- > \text{F}^- > \text{NO}_2^- > \text{SO}_3^{2-} > \text{Cl}^- > \text{SO}_4^{2-}$, sensor III: $\text{SCN}^- > \text{IO}_4^- > \text{I}^- > \text{S}_2\text{O}_3^{2-} > \text{NO}_3^- > \text{S}^{2-} > \text{CN}^- > \text{SO}_3^{2-} > \text{SO}_4^{2-} > \text{Br}^- > \text{ClO}_4^- > \text{NO}_2^- > \text{Cl}^- > \text{F}^-$ and sensor IV: $\text{SCN}^- > \text{I}^- > \text{IO}_4^- > \text{S}_2\text{O}_3^{2-} > \text{NO}_3^- > \text{CN}^- > \text{Br}^- > \text{SO}_3^{2-} > \text{NO}_2^- > \text{F}^- > \text{ClO}_4^- > \text{Cl}^- > \text{SO}_4^{2-} > \text{S}^{2-}$.

Table 2. Effect of foreign ions on SCN^- membrane sensors type (A) and (B) by using FIM.

Interfering anion	$\log K^{\text{POT}}_{\text{SCN}^-, \text{B}}$							
	Sensor type (A)				Sensor type (B)			
	Sensor I	Sensor II	Sensor III	Sensor IV	Sensor I	Sensor II	Sensor III	Sensor IV
SCN^-	0	0	0	0	0	0	0	0
Br^-	-2.34	-2.44	-2.27	-2.15	-1.66	-1.7	-1.8	-1.83
Cl^-	-2.84	-2.64	-2.36	-2.38	-1.66	-1.63	-1.77	-2.05
ClO_4^-	-2.93	-2.44	-2.24	-2.36	-1.11	-1.28	-1.35	-1.1
CN^-	-2.52	-2.16	-2.01	-1.95	-1.42	-1.5	-1.65	-1.88
F^-	-2.85	-2.50	-2.39	-2.29	-1.63	-1.74	-1.81	-2.16
I^-	-0.75	-0.68	-0.78	-0.67	-0.67	-0.6	-0.63	-0.5
NO_2^-	-2.41	-2.52	-2.25	-2.29	-1.53	-1.58	-1.7	-1.83
NO_3^-	-1.81	-1.71	-1.59	-1.72	-1.26	-1.36	-1.42	-1.38
S_2^{2-}	-2.46	-2.42	-1.91	-2.55	-2.16	-2.5	-2.1	-2.25
$\text{S}_2\text{O}_3^{2-}$	-1.55	-1.48	-1.19	-1.38	-1.43	-1.98	-1.59	-1.51
SO_3^{2-}	-2.62	-2.51	-2.08	-2.24	-2.22	-2.11	-1.89	-2.01
SO_4^{2-}	-2.94	-2.64	-2.18	-2.54	-2.54	-2.24	-2.07	-2.34
IO_4^-	-1.12	-0.50	-0.33	-0.73	-1.012	-0.73	-0.42	-0.62

Table 4. Determination of thiocyanate in saliva samples using type (A) sensors I, II, III and IV.

No. of smoked cigarettes Day $^{-1}$	Spectrophotometry* [Saliva- SCN^-] mol L $^{-1}$	Potentiometry* [Saliva- SCN^-] mol L $^{-1}$			
		Sensor I	Sensor II	Sensor III	Sensor V
0	8.59×10^{-5}	8.47×10^{-5}	8.9×10^{-5}	8.7×10^{-5}	8.49×10^{-5}
15 - 20	7.46×10^{-4}	7.2×10^{-4}	7.62×10^{-4}	7.5×10^{-4}	7.35×10^{-4}
20 - 25	9.34×10^{-3}	9.27×10^{-3}	9.5×10^{-3}	9.4×10^{-3}	9.3×10^{-3}

*Average of 5 measurements

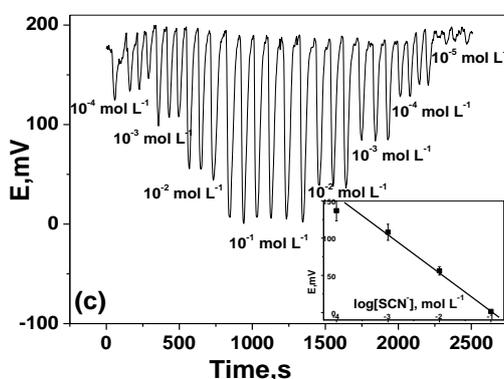
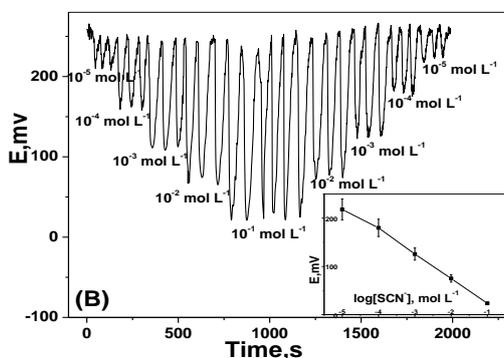
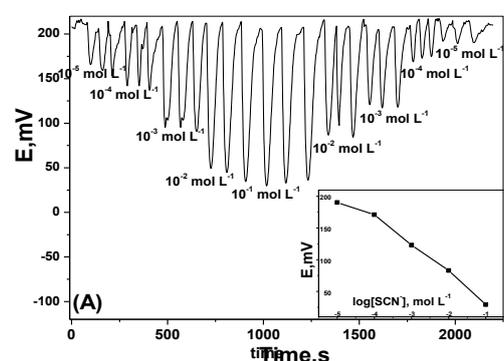
For Sensors type (B) they exhibited selectivity order as follow: sensor I revealed a selectivity pattern $\text{SCN}^- > \text{I}^- > \text{IO}_4^- > \text{ClO}_4^- > \text{NO}_3^- > \text{CN}^- > \text{S}_2\text{O}_3^{2-} > \text{NO}_2^- > \text{F}^- > \text{Cl}^- > \text{Br}^- > \text{S}^{2-} > \text{SO}_3^{2-} > \text{SO}_4^{2-}$, sensor II: $\text{SCN}^- > \text{I}^- > \text{IO}_4^- > \text{ClO}_4^- > \text{NO}_3^- > \text{CN}^- > \text{NO}_2^- > \text{Cl}^- > \text{Br}^- > \text{F}^- > \text{S}_2\text{O}_3^{2-} > \text{SO}_3^{2-} > \text{SO}_4^{2-} > \text{S}^{2-}$, sensor III: $\text{SCN}^- > \text{I}^- > \text{IO}_4^- > \text{ClO}_4^- > \text{NO}_3^- > \text{S}_2\text{O}_3^{2-} > \text{CN}^- > \text{NO}_2^- > \text{Cl}^- > \text{Br}^- > \text{F}^- > \text{SO}_3^{2-} > \text{SO}_4^{2-} > \text{S}^{2-}$ and sensor IV: $\text{SCN}^- > \text{I}^- > \text{IO}_4^- > \text{ClO}_4^- > \text{NO}_3^- > \text{S}_2\text{O}_3^{2-} > \text{NO}_2^- > \text{Br}^- > \text{CN}^- > \text{SO}_3^{2-} > \text{Cl}^- > \text{F}^- > \text{S}^{2-} > \text{SO}_4^{2-}$ and all the results are summarized in Table 2. As noticed from the results, sensor I exhibited better selectivity towards the lipophilic anions such as I^- , ClO_4^- , IO_4^- and NO_3^- than other sensors. Finally we can conclude that, the selectivity is mainly depending on the membrane composition but the electrode configuration has no observed effect on the selectivity pattern of all proposed sensors.

Hydrodynamic monitoring of thiocyanate

Flow-through analysis using potentiometric detectors showed high advantages such as low cost, simple instrumentation and automation. In addition, the transient nature of the signal in flow injection analysis is help to overcome the effects of interfering ions if the electrode's response to the target analyte is faster than those interfering ions.³⁸ A tubular-type detector incorporating Al (III)-PAR/TDMAC (sensor I), MgPC/TDMAC (sensor II) and Aliquat sensor (III) based membrane sensors were prepared and used under the hydrodynamic mode of operation for continuous SCN^- quantification. A triplicate transient peaks were obtained from the flow injection analysis system under optimal experimental conditions and are shown in Figures 4A, 4B and 4C.

Table 3. Potentiometric response characteristics of SCN⁻ membrane type (B) sensors I, II and III using FI operation.

Parameters	Sensor I	Sensor II	Sensor III
Slope	-46.5±0.2	-52.0±0.3	-53.3±0.1
Correlation coefficient, (<i>r</i>)	0.998	0.9999	0.9996
Linear range mol L ⁻¹	1.0 x 10 ⁻⁴ – 1.0 x 10 ⁻¹	1.0 x 10 ⁻⁴ – 1.0 x 10 ⁻¹	1.0 x 10 ⁻⁴ – 1.0 x 10 ⁻¹
Detection limit mol L ⁻¹	1.0 x 10 ⁻⁵	1.0 x 10 ⁻⁵	1.0 x 10 ⁻⁵
Life span (week)	12	12	12
Intercept	-14.7	-29	-41.5
Flow rate mL min ⁻¹ .	4.0	4.0	4.0

**Figure 4.** Transient potentiometric signals obtained in triplicate for sensor I (A), sensor II (B) and sensor III (C). Conditions: carrier solution, 0.1 mol L⁻¹ acetate buffer pH 5.0, flow rate 4.0 mLmin⁻¹; sample volume, 500 µL.

A linear relationship between the SCN⁻ concentrations and FIA signals was obtained over a concentration range of 1.0 x 10⁻⁵ to 1.0 x 10⁻¹ mol L⁻¹ using a 0.1 mol L⁻¹ acetate buffer, pH 5.0. The general analytical features recorded under optimum flow conditions are presented in Table 3. The slope of the calibration plot was near-Nernstian (-46.5, -52.0 and -53.3 mV decade⁻¹), the lower limit of detection was 1.0 x 10⁻⁵ mol L⁻¹, and the sampling frequencies were about 44, 54 and 44 samples per hour respectively.

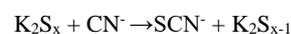
Thiocyanate determination in saliva

In the saliva of cigarette smokers, rhodanase enzyme catalyzes the detoxification reaction of hydrogen cyanide forming thiocyanate. The possibility of using the proposed sensors to measure SCN⁻ concentration in human saliva samples was examined. Table 4 indicates that the concentrations of saliva-SCN⁻ in the groups under study fairly agreed with data obtained by the standard spectrophotometric method.³⁹

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 1.1-5.2 compared with the tabulate value (6.39) at the 95 % confidence limit. 1

Cyanide determination in electroplating baths

Determination of cyanide ion after its conversion to thiocyanate ion using the potassium polysulfide treatment was investigated. Such a conversion is well-documented,⁴⁰ and occurs according to the following reaction:

**Table 5.** Potentiometric determination of cyanide in electroplating baths after conversion into thiocyanate using a thiocyanate PVC membrane type (B) sensor I, II and III.

ISE	Cyanide content (mol L ⁻¹)*			
	Batch		Flow	
	Waste-water	Electro-plating bath	Waste-water	Electro-plating bath
Sensor I	0.014	0.14	0.02	0.14
Sensor II	0.016	0.15	0.016	0.16
Sensor III	0.016	0.14	0.015	0.14
Cyanide sensor ^a	0.015	0.14	-	-

*Average of 5 measurements; ²Orion Cyanide solid state sensor

A linear calibration curve for CN⁻ ions (1.0 x 10⁻⁵-1.0x10⁻² mol L⁻¹) after conversion into SCN⁻ by a treatment with potassium polysulfide, followed by monitoring using the proposed sensors were obtained. The method was used for the potentiometric determination of free cyanide ions in industrial waste-water and electroplating samples obtained from an electroplating factory. These sensors are used under the hydrodynamic mode of operation for continuous monitoring of CN⁻ ions (1.0 x 10⁻⁴ - 1.0 x 10⁻¹ mol L⁻¹) after conversion into SCN⁻ using a 0.1mol L⁻¹ acetate buffer, pH 5.0 as a flow carrier. The obtained results agreed with data obtained using the solid state cyanide ion-selective electrode Table 5.

CONCLUSION

Two Types of potentiometric ISE (Solid type (A) and conventional type (B)) were studied to give a fast and simple method for determination of thiocyanate under static (manual) mode of operation and hydrodynamic (FIA) mode of operation for type (B). A new Al (III)–PAR complex was prepared and developed by using TDMAC as anionic additive. ISE type (A) improved the response of sensor I towards SCN^- ion with lower detection limit $1.45 \times 10^{-6} \text{ mol L}^{-1}$ and slope of $-53.7 \text{ mV decade}^{-1}$ while that of type (B) exhibit detection limit $5.0 \times 10^{-6} \text{ mol L}^{-1}$ and a Nernstian slope of $-46.4 \pm 1.1 \text{ mV decade}^{-1}$. So ISE type (A) can be preferred to use as a tool for low SCN^- concentration determination in biological fluids (saliva). ISE type (B) used for determination of CN^- ion in waste and electroplating.

REFERENCES

- Hassan, S. S. M., Kamel, A. H., Abd El-Naby, H., Flow-Through Potentiometric Sensors for Alizarin Red S Dye and Their Application for Aluminum Determination, *J. Chin. Chem. Soc.*, **2014**, *61*, 295. <https://doi.org/10.1002/jccs.201300293>
- Hassan, S. S. M., Kamel, A. H., Abd El-Naby, H., New potentiometric sensors based on selective recognition sites for determination of ephedrine in some pharmaceuticals and biological fluids, *Talanta*, **2013**, *103*, 330. doi: 10.1016/j.talanta.2012.10.067.
- Hassan, S. S. M., Sayour, H. E. M., Kamel, A. H., A simple-potentiometric method for determination of acid and alkaline phosphatase enzymes in biological fluids and dairy products using a nitrophenylphosphate plastic membrane sensor, *Anal. Chim. Acta*, **2009**, *640*, 75. <https://doi.org/10.1016/j.aca.2009.03.019>
- Kamel, A. H., New potentiometric transducer based on a Mn(II) [2-formylquinoline thiosemicarbazone] complex for static and hydrodynamic assessment of azides, *Talanta*, **2015**, *144*, 1085. DOI: [10.1016/j.talanta.2015.07.075](https://doi.org/10.1016/j.talanta.2015.07.075)
- van de Velde, L., d'Angremont, E., Olthuis, W., Solid contact potassium selective electrodes for biomedical applications - a review, *Talanta*, **2016**, *160*, 56. DOI: [10.1016/j.talanta.2016.06.050](https://doi.org/10.1016/j.talanta.2016.06.050)
- Zou, X. U., Cheong, J. H., Taitt, B. J., Bühlmann, P., Solid contact ion-selective electrodes with a well-controlled Co(II)/Co(III) redox buffer layer, *Anal. Chem.* **2013**, *85*(19), 9350-5., DOI: [10.1021/ac4022117](https://doi.org/10.1021/ac4022117)
- Michalska, A., All-Solid-State Ion Selective and All-Solid-State Reference Electrodes, *Electroanalysis*, **2012**, *24*, 1253. <https://doi.org/10.1002/elan.201200059>
- Kimmel, D. W., LeBlanc, G., Meschievitz, M. E., Cliffel, D. E., Electrochemical sensors and biosensors, *Anal. Chem.*, **2012**, *84*, 685. DOI: [10.1021/ac202878q](https://doi.org/10.1021/ac202878q)
- Tymecki, L., Glab, S., Koncki, R., Miniaturized, Planar Ion-selective Electrodes Fabricated by Means of Thick-film Technology, *Sensors*, **2006**, *6*, 390. doi: [10.3390/s6040390](https://doi.org/10.3390/s6040390)
- Sokalski, T., Ceresa, A., Zwickl, T., Pretsch, E., Large Improvement of the Lower Detection Limit of Ion-Selective Polymer Membrane Electrodes, *J. Am. Chem. Soc.*, **1997**, *119*, 11347. DOI: 10.1021/ja972932h
- Sokalski, T., Ceresa, A., Fibbioli, M., Zwickl, T., Bakker, E., Pretsch, E., Lowering the Detection Limit of Solvent Polymeric Ion-Selective Membrane Electrodes. 2. Influence of Composition of Sample and Internal Electrolyte Solution, *Anal. Chem.*, **1999**, *71*, 1210. DOI: 10.1021/ac9809332
- Qin, W., Zwickl, T., Pretsch, E., Improved Detection Limits and Unbiased Selectivity Coefficients Obtained by Using Ion-Exchange Resins in the Inner Reference Solution of Ion-Selective Polymeric Membrane Electrodes, *Anal. Chem.*, **2000**, *72*, 3236. DOI: 10.1021/ac000155p
- Ceresa, A., Radu, A., Peper, S., Bakker, E., Pretsch, E., Rational design of potentiometric trace level ion sensors. A Ag⁺-selective electrode with a 100 ppt detection limit, *Anal. Chem.*, **2002**, *74*, 4027. DOI: 10.1021/ac025548y
- Cadogan, A., Gao, Z., Lewenstam, A., Ivaska, A., Diamond, D., All-solid-state sodium-selective electrode based on a calixarene ionophore in a poly(vinyl chloride) membrane with a polypyrrole solid contact, *Anal. Chem.*, **1992**, *64*, 2496. DOI: 10.1021/ac00045a007
- Catrrall, R. W., Freiser, H., Coated wire ion-selective electrodes, *Anal. Chem.*, **1971**, *43*, 1905. DOI: 10.1021/ac60307a032
- Buck, R. P., Freiser, H. (Ed.), *Ion-Selective Electrodes in Analytical Chemistry*, Plenum, New York, **1980**, 58.
- Michalska, A., Optimizing the analytical performance and construction of ion-selective electrodes with conducting polymer-based ion-to-electron transducers, *Anal. Bioanal. Chem.*, **2006**, *384*, 391. DOI: 10.1007/s00216-005-0132-4
- Bobacka, J., Ivaska, A., Lewenstam, A., Potentiometric sensors based on poly(3,4-ethylenedioxythiophene) (PEDOT) doped with sulfonated calix[4]arene and calix[4]resorcarenes, *Electroanalysis*, **2002**, *15*, 366. DOI 10.1007/s10008-004-0597-7
- Mousavi, Z., Bobacka, J., Ivaska, A., Potentiometric Ag⁺ Sensors Based on Conducting Polymers: A Comparison between Poly(3,4 - ethylenedioxythiophene) and Polypyrrole Doped with Sulfonated Calixarenes, *Electroanalysis*, **2005**, *17*, 1609. <https://doi.org/10.1002/elan.200503269>
- Sutter, J., Radu, A., Peper, S., Bakker, E., Pretsch, E., Solid-contact polymeric membrane electrodes with detection limits in the subnanomolar range, *Anal. Chim. Acta.*, **2004**, *523*, 53. <https://doi.org/10.1016/j.aca.2004.07.016>
- Parra, E. J., Crespo, G. A., Riu, J., Ruiz, A., Rius, F. X., Ion-selective electrodes using multi-walled carbon nanotubes as ion-to-electron transducers for the detection of perchlorate., *Analyst*, **2009**, *134*, 1905. DOI: 10.1039/b908224g
- Rius-Ruiz, F. X., Crespo, G. A., Bejarano-Nosas, D., Blondeau, P., Riu, J., Rius, F. X., Disposable planar reference electrode based on carbon nanotubes and polyacrylate membrane, *Anal. Chem.*, **2011**, *83*, 8810. DOI: 10.1021/ac200627h
- Ping, J., Wang, Y., Wu, J., Ying, Y., Development of an all-solid-state potassium ion-selective electrode using graphene as the solid-contact transducer, *Electrochem. Commun.*, **2011**, *13*, 1529.
- Li, F., Ye, J., Zhou, M., Gan, S., Zhang, Q., Han, D., All-solid-state potassium-selective electrode using graphene as the solid contact, *Analyst*, **2012**, *137*, 618. DOI: 10.1039/C1AN15705A
- Jaworska, E., Lewandowski, W., Mieczkowski, J., Maksymiuk, K., Michalska, A., Critical assessment of graphene as ion-to-electron transducer for all-solid-state potentiometric sensors., *Talanta*, **2012**, *97*, 414. DOI: 10.1016/j.talanta.2012.04.054
- Hu, J., Zou, X. U., Stein, A., Bühlmann, P., Ion-Selective Electrodes with Colloid-Imprinted Mesoporous Carbon as Solid Contact, *Anal. Chem.*, **2014**, *86*, 7111. DOI: 10.1021/ac501633r
- Han, W., Hong, T., Lee, Y., Thiocyanate Ion Selective Solid Contact Electrode Based on Mn Complex of N,N'-Bis-(4-Phenylazosilylidene)-O-Phenylene Diamine Ionophore, *Am. J. Anal. Chem.*, **2011**, *2*, 731. DOI: 10.4236/ajac.2011.26084
- Vlascici, D., Pica, E. M., Fagadar-Cosma, E., Cosma, V., Bizerea, O., Thiocyanate and fluoride electrochemical sensors based on nanostructured metalloporphyrin systems, *J. Optoelectr. Adv. Mat.*, **2008**, *10*, 2303.

- ²⁹Vlascici, D., Fagadar-Cosma, E. and Bizerea-Spiridon, O., A New Composition for Co(II)-porphyrin-based Membranes Used in Thiocyanate-selective Electrodes, *Sensors*, **2006**, *6*, 892. <https://doi.org/10.3390/s6080892>
- ³⁰Shehab, O. R., Mansour, A. M., New thiocyanate potentiometric sensors based on sulfadimidine metal complexes: experimental and theoretical studies, *Biosen. Bioelect.*, **2014**, *57*, 77. DOI: 10.1016/j.bios.2014.01.051
- ³¹Arvand, M., Zanjanchi, M. A., Heydari, L., Voltammetric Oxidation of Potassium Thiocyanate using ErBa₂Cu₃O₇ Modified Glassy Carbon Electrode, *Sens. Act. B*, **2007**, *122*, 301.
- ³²Khorasan, J. H., Amin, M. K., Motagh, H., Tangestaninejad, S., Moghadam, M., Manganese porphyrin derivatives as ionophores for thiocyanate-selective electrodes: the influence of porphyrin substituents and additives on the response properties, *Sens. Act. B*, **2002**, *87*, 448. [https://doi.org/10.1016/S0925-4005\(02\)00294-0](https://doi.org/10.1016/S0925-4005(02)00294-0)
- ³³*Standard Methods for the Examination of Water and Wastewater*, 19th ed., American Public Health Association, Washington **1995**.
- ³⁴Kamel, A. H., Khalifa, M. E., Abd El-Maksoud, S. A., Elgendy, F. A., Selective sensors for potentiometric assessment of iodide based on anion recognition through copper(II) dipeptide derivative complex, *Eur. Chem. Bull.*, **2016**, *5*, 368. DOI: 10.17628/ECB.2016.5.368
- ³⁵Kamel, A. H., El-Naggar, A. M., Argig, A. A. A., Response characteristics of lead-selective membrane sensors based on a newly synthesized quinoxaline derivatives as neutral carrier ionophores, *Ionics*, **2017**, *23*, 3497. DOI <https://doi.org/10.1007/s11581-017-2141-7>
- ³⁶Cammann, K., Working with Ion-Selective Electrodes: Chemical Laboratory Practice, Springer-Verlag, Berlin, **1979**.
- ³⁷Umezawa, Y., Buhlmann, P., Umezawa, K., Tohda, K., Amemiya, S., Potentiometric selectivity coefficients of ion-selective electrodes part I. Inorganic cations (technical report), *Pure Appl. Chem.*, **2000**, *72*, 1851.
- ³⁸Cammann, K., Flow injection analysis with electrochemical detection, *Fres. Z., Anal. Chem.*, **1988**, 329, 691. DOI <https://doi.org/10.1007/BF00624777>
- ³⁹Hovinen, J., Lahti, M., Vilpo, J., Spectrophotometric Determination of Thiocyanate in Human Saliva, *J. Chem. Educ.*, **1999**, *76*, 1281. DOI: 10.1021/ed076p1281
- ⁴⁰Demirata, B., Apak, R., Asfar, H., Tor, I., Spectrophotometric determination of organic nitrogen by a modified Lassaigue method and its application to meat products and baby food., *J. AOAC*, **2002**, *85*, 971.

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