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Development of Thiocyanate-Selective Membrane Electrodes by the Sol–Gel Method

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To prepare thiocyanate-selective chemical sensors, a sol–gel-based matrix was employed as a host membrane for the encapsulation of a sensing material. Tricaprylylmethylammonium thiocyanate (Aliquat336-SCN) was used as the dissociated ion-exchanger type sensing ionophore. Both 3-isocyanatopropyl-triethoxysilane and 1,4-butanediol were used for appropriate precursor preparation. Under acidic conditions, the sol precursor slowly gelled to yield a film in which the thiocyanate ionophore, Aliquat336-SCN, was encapsulated. Electrochemical responses of the potentiometric sensors were compared to those of traditional poly(vinyl chloride) (PVC) membrane electrodes prepared using the same ionophore. On the 7th working day, the average response slope toward thiocyanate was approximately 56.3 mV decade^{-1} in the concentration range $10^{-4.5}$ M to 5×10^{-1} M at 20°C. Selectivity toward thiocyanate over lipophilic anions such as perchlorate and salicylate was considerably improved. The results exhibit a clear tendency that deviates from the Hofmeister selectivity pattern which would be observed in a membrane electrode made of Aliquat336-SCN type salt. The potentiometric selectivity coefficients, as measured in a 0.05 M 2-morpholinoethanesulfonic acid monohydrate buffer, pH 5.5, were $\log k^{pot}_{\text{thiocyanate, chloride}} = -2.3$, $\log k^{pot}_{\text{thiocyanate, salicylate}} = -0.6$, and $\log k^{pot}_{\text{thiocyanate, perchlorate}} = -0.1$. The optimized membrane sensors were employed for the flow-injection measurement of thiocyanate levels in saliva samples from both smokers and nonsmokers. The membrane sensors exhibited a fairly good correlation with the traditional colorimetric method (n = 23; sensors = 0.84 (colorimetric) + 0.13: $R^2 = 0.97$).

Keywords: Thiocyanate-selective electrode, Aliquat336-SCN, Sol–gel encapsulation, Saliva

1. INTRODUCTION

In various biological and environmental fields, thiocyanate has been demonstrated to be an interesting analyte. As a main metabolite of toxic cyanide, thiocyanate is found in human serum/saliva.

Rhodanase has been well known to catalyze this enzymatic detoxification pathway [1] and vegetables, seeds, and other causes such as exposure to tobacco can trigger such processes [2]. Indeed, thiocyanate levels in serum can range from 50 to 500 μM depending on smoking status and consumption [3,4]. Interesting data on thiocyanate levels in stratal waters have also been reported [5].

Thiocyanate is typically measured by the spectrophotometric method [6,7], which is based on the formation of red complex in an acidic medium upon the addition of an iron(III) salt. However, this well-established colorimetric method has inherent limitations, when applied to colored samples such as whole blood. On the other hand, approaches using ion chromatography have been established [8], despite shortcomings in the sensitivity of conventional conductivity detectors. Various high-performance liquid chromatography and gas chromatography - mass spectrometric tandem methods have also been reported [9].

Potentiometric membrane electrode systems have been implemented in many diagnostic analyzers, due to their low cost, simplicity, and ease of microfabrication [10,11]. Moreover, they are not affected by sample color or turbidity. Among different types of systems, several polymer membrane-based potentiometric sensors have been exploited in the analysis of anions [12,13]. Quaternary ammonium salts have been exploited as a suitable ionophore in conjunction with PVC and plasticizers such as 2-nitrophenyl octyl ether (NPOE). The applications of such sensors in blood thiocyanate measurements, however, can lead to considerable errors due to the presence of lipophilic anions such as salicylate or heparin [14]. This phenomenon is explained partly by the so-called Hofmeister selectivity pattern. In an effort to overcome the Hofmeister pattern-related limitations with ammonium salts, Meyerhoff’s group has assessed the feasibility of using a manganese(III) porphyrin to determine thiocyanate levels in saliva [15].

Here, we aimed to replace the traditional PVC membrane matrix with a lipophilic sol–gel-based polymer while employing a typical ion-exchanger type anion sensing material, Aliquat336-SCN. Previous reports can be referred to for the concrete sol–gel process [16]. The slow reaction process, including hydrolysis, condensation, and drying/aging at relatively low temperatures with host materials encapsulated inside has been analyzed in applications of photoelectronic and composite materials as well as biosensors [17]. These applications are closely related to the resulting gel’s biocompatibility, extensive porosity, and encapsulation capabilities for active species such as enzymes [18]. The encapsulation procedure was applied in the present study for the matrix of thiocyanate-sensitive potentiometric sensors. Their analytical behaviors were compared to those of PVC-based electrodes. A flow-injection analysis (FIA) was then performed in their application with saliva samples.

2. EXPERIMENTAL SECTION

2.1. Reagents and Apparatus:

High molecular PVC, 3-isocyanatopropyltriethoxysilane, Aliquat336, and 2-morpholino-ethanesulfonic acid monohydrate (MES) were obtained from Fluka (Ronkonkoma, NY). Aliquat336-SCN was prepared as follows [19]: 4 g of Aliquat336 was dissolved in 25 mL of a 3:1 (v/v) mixture of cyclohexane-2-propanol. A 0.25 M aqueous sodium thiocyanate solution was then employed for extraction (five times). Between each extraction, 7 mL of fresh 2-propanol was added to maintain the solvent composition. After repeated equilibrations, the organic solvents were removed using a rotary evaporator. The resulting product was washed twice with cyclohexane. The compounds, before and after extraction, were identified with a Scimitar series Varian 1000 FT-IR spectrophotometer. Tetrahydrofuran (THF) from Aldrich was purified over sodium, while 1,4-butanediol was employed as received with no further purification. A buffer solution of 0.05 M MES was prepared with sodium hydroxide and was used throughout the batch and flow-injection mode experiments. Deionized water of 18 MΩ·cm resistivity was used for the preparation of buffer and standard solutions.

2.2. Polymer Films and Electrodes:

1,4-butanediol and 3-isocyanatopropyltriethoxysilane (molar ratio NCO/OH = 1) were dissolved in THF. The mixture was refluxed for 24 h under a nitrogen atmosphere, which yielded viscous sol-state precursor (1,4-precursor). After solvent evaporation, the precursor was dissolved in N,N-dimethylformamide (DMF) with Aliquat336-SCN following the ratios listed in Table 1. Fifteen microliters of 0.072 M HCl were then added after 1 min. of vigorous shaking. Before the mixture started to solidify, it was briefly shaken and poured onto a PET boat (1.4 × 1.4 cm). The gel reaction proceeded at 40°C for 48 h to yield a transparent membrane in which Aliquat336-SCN was homogeneously encapsulated. To ensure thorough aging, it was further vacuum-dried at the same temperature for another 48 h. The polymerization and drying processes were performed in a Fisher Scientific oven (model 280A) with and without vacuum setting (48 mmHg), respectively. PVC-based membranes were cast following the previous report [15]. The PVC and gel films were cut into 5.5-mm-diameter disks with a no.2 cork cutter, which were mounted on top of electrode bodies (ISE-561, Phillips Glasblaserei Möller, Switzerland). An aqueous solution of 0.01 M NaSCN/0.1 M NaCl was employed as an internal solution. The remaining 1,4-precursor was refrigerated when not in use.

2.3. Batch Mode EMF Measurements:

Potentiometric measurements were carried out at an ambient temperature of 20(±2)°C using the setup: Ag/AgCl(s)/4 M KCl saturated with AgCl/0.05 M MES buffer, pH 5.5/sample solution/ion-selective membrane/internal solution/AgCl(s)/Ag. Electromotive forces were obtained between the working electrode and a Fisher double-junction reference electrode by using a computer with an 8-channel A/D converter (Kosentech, Korea) at 1 Hz. The setup was further employed to obtain the calibration curves and selectivity toward thiocyanate over other anionic species in the equilibrium mode. Static mode readings (mV) were taken 100 s after each anion addition to the MES buffer. The separate solution method [20] was employed to evaluate the selectivity coefficients, $k^{pot}_{thiocyanate/y}$ at 10 mM solutions of each sodium salt, where subscript ‘y’ denotes interfering ions.

2.4 Flow Injection Analysis (FIA) Mode data Acquisition:

Figure 1 describes the experimental setup for the FIA in which the PVC- or sol–gel-based membrane electrode acts as a detector. A wall-jet type flow-through cap was employed to fit the Philips electrode body. The sample and carrier streams were controlled using a Rheodyne four-way rotary Teflon valve (Model 7125) as well as a peristaltic pump (Ismatech SA, Zürich). The size of the sample loop (0.012 in. teflon tubing) was typically 60 µL. The same buffer used in the static mode was used as the carrier stream. The previously used reference electrode was connected to complete the circuit. Two hertz data acquisitions were carried out to observe delicate changes in the electromotive forces.

2.5 FIA and Colorimetric Measurements of Thiocyanate in Real Samples:

Saliva samples were kindly provided by 10 smokers and 10 nonsmokers at the Inje University and were further employed for the real sample measurement of thiocyanate. Five milliliters of each sample were placed in a centrifuge (Hanil Science Industrial Co., MICRO 17TR, Korea) and treated at 18,000 g for 10 min. [15]. This eases the manipulation of the supernatant by settling protein materials. For the flow-injection measurements described previously, the supernatants were diluted 20 times with 0.05M MES buffer, pH 5.5. A linear regression fit, ∆E (mV) vs. log [SCN], was obtained for thiocyanate standards and was further employed to determine thiocyanate levels for the diluted saliva samples. These diluted saliva samples were further used for the recovery study; three different amounts of thiocyanate standards were added to 1-mL aliquots. A correlation study was further carried out in conjunction with the reference method, UV-VIS spectrophotometry. Each mixture of 0.1 mL of supernatant and 0.1 mL of 0.77 M ferric nitrate in 4 M nitric acid was diluted with deionized water (3.5 mL) prior to absorbance measurements at 460 nm with a Mega-V600 spectrophotometer. (Scinco Inc., Seoul, Korea).

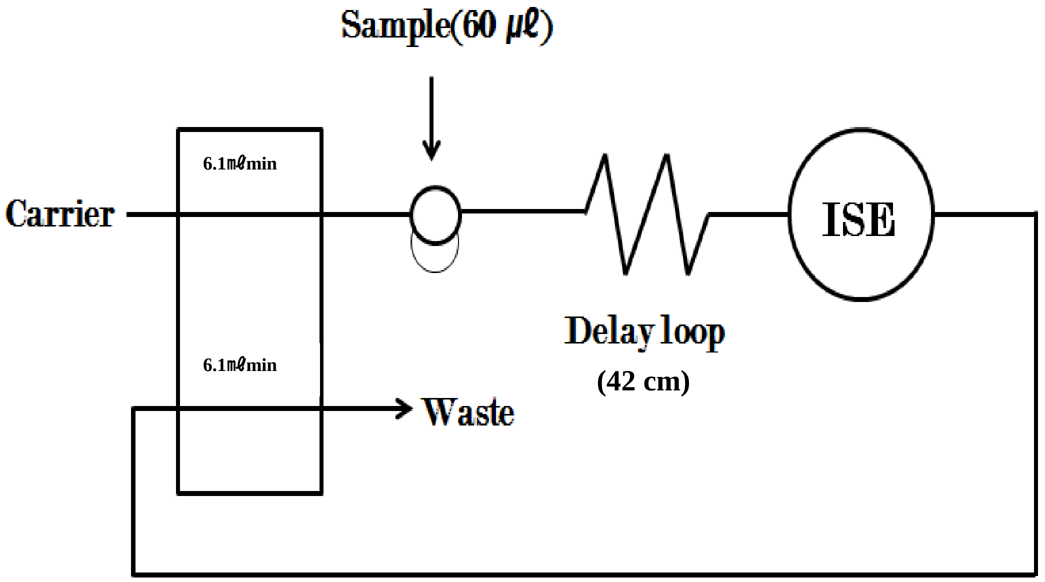

Figure 1. Schematic of FIA equipped with the thiocyanate-selective electrode as a detector

3. RESULTS AND DISCUSSION

Although previously reported precursors such as tetraethylorthosilicate (TEOS) and tetramethylorthosilicate (TMOS) were able to undergo a sol–gel reaction [21], the resulting inorganic/glassy membranes were too brittle to be placed on top of electrode bodies such as a Phillips electrode body, ISE561 that used in this study. In addition, they seem to be inadequate to encapsulate most lipophilic ionophores. In this report, the 1,4-precursor, based organic and inorganic moieties, was found to overcome these obstacles, resulting in an appropriate host for Aliquat336 salts. Related precursors were identified by their FTIR and 1H NMR spectra [16]. Characteristic sharp bands of thiocyanate appeared near 2053 cm^{-1} and 749 cm^{-1} in the extracted product, Aliquat336-SCN (Figure 2) [22].

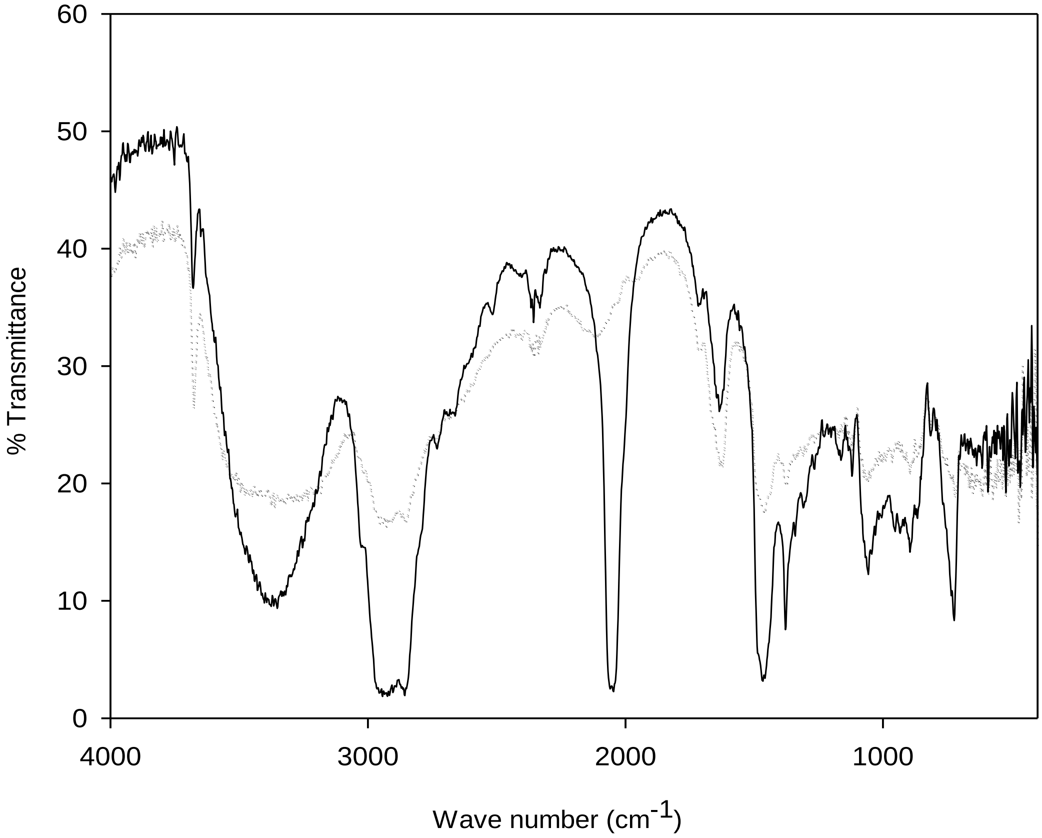

Figure 2. IR spectra of Aliquat336-Cl, before (----) and after (—) sodium thiocyanate treatment

Initially, the previously reported sol–gel polymerization procedure was employed for the new ionophore, Aliquat336-SCN [16]. It was possible to polymerize the sol-state precursor by using a mildly acidic catalyst (0.072 M HCl), instead of metal hydroxides or fluoride catalysts [23]. In addition, the use of small amounts of HCl (e.g., 15 µL) rendered enough time to add both tributylphosphate (TBP) and our ionophore, Aliquat336-SCN. TBP, which was selected out of more than 90 plasticizers,

helped our gel membranes stay more flexible without cracking. It was also quite compatible with the ionophore candidate Aliquat336-SCN. Enhanced compatibility was confirmed by the transparency of the membrane, as well as homogeneity without leakage of components. Other plasticizers such as NPOE, a typical plasticizer for PVC, resulted in either turbidity or segregation. Polymerization was performed at 40°C. Although a hotter reaction condition would be preferred for the hydrolysis and condensation reactions to proceed quickly, this may cause the resulting gel to crack easily. In addition, aging of the resulting gel membranes was required for the water and ethanol condensation reactions to complete. In the present work, the membranes were simply set to dry for another 48 h at a pressure of 48 mmHg (40°C) for the aging step. ^{29}Si magic-angle spinning (MAS) NMR and solid-state ^{1}H NMR spectra of similar membranes can be found elsewhere [16].

Electrochemical responses were tested using the resulting membranes, which had a thickness and density of 0.15 mm and 1.24 g/cm^3, respectively. Gel membranes prepared in different ionophore/matrix ratios (G1 to G3 in Table 1) had different characteristics. The G1 membranes, without any plasticizer, exhibited less flexibility. However, all other membranes including the PVC one were cut with the cork cutter relatively easily, allowing the membranes to be implemented readily on Philips electrode bodies. Calibration curves were plotted using the membranes in Table 1. Among different anions, G2, G3 and P1-based membrane sensors gave comparable responses toward thiocyanate in the range of 0-500 mM (Figure 3). Of the sol–gel membranes, G1 had a gentler slope and poorer physical robustness. This led us to use the aforementioned plasticizer, TBP. Higher amounts of TBP resulted in a slightly improved slope. However, membranes with TBP contents higher than that of G3 did not show further advantages in response behavior, and instead became overly soft. Therefore, electrodes based on G3 and P1 were tested throughout the following studies. In the batch mode, both membrane electrodes showed an almost similar and consistent response behavior even after 7 working days, with 56.3 mV decade^{-1} (average of three determinations) in the concentration range $10^{-4.5}$ to 5×10^{-1} M at 20°C. The G3 matrix-based electrode also gave a slightly lower detection limit of 6.3×10^{-3} mM.

Table 1. Formulation of the sol–gel- and PVC-based membranes

membrane ID*	Aliquat336-SCN (mg)	Plasticizer (mg)	Matrix (mg)	solvent
G1	10.5	TBP 0.0	95.2	0.4 mL DMF
G2	10.5	TBP 5.6	95.2	0.4 mL DMF
G3	10.5	TBP 55.4	95.2	0.4 mL DMF
P1	10.5	NPOE 108.6	50.0	1.0 mL THF

* P- and G- denote PVC-and gel-based membrane electrodes, respectively.

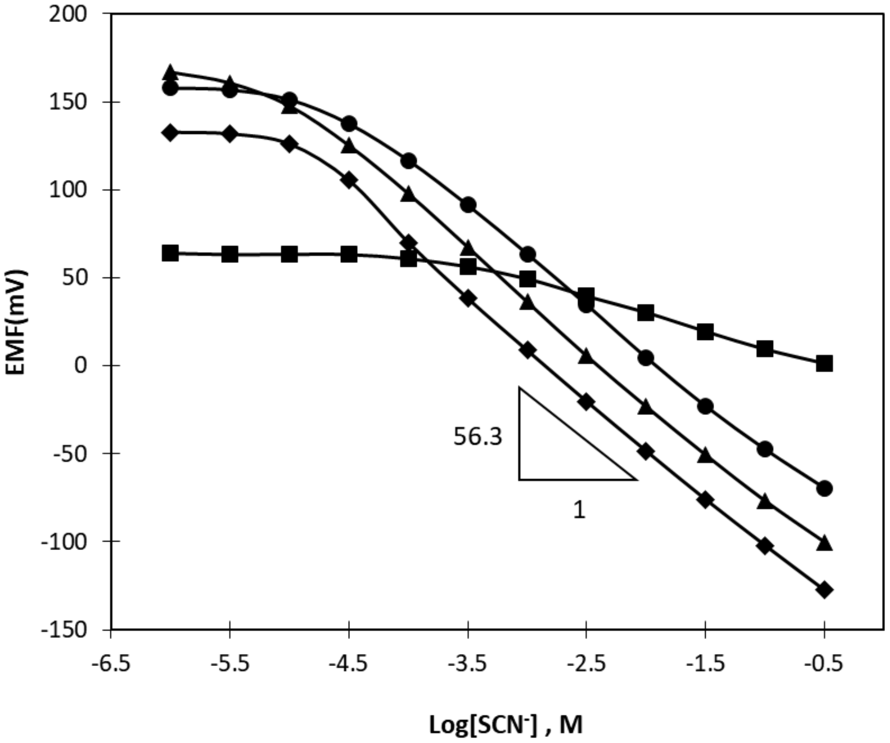

Figure 3. Calibration curves of electrodes prepared with (◆) P1; (■) G1; (●) G2; (▲) G3.

The equilibrium selectivity coefficients of the Aliquat336-SCN-based gel- and PVC-membrane electrodes for different anionic species relative to thiocyanate are listed in Table 2. The coefficients were evaluated in a pH 5.5 MES buffer at an anionic concentration of 10 mM. Although the gel membranes showed comparable selectivities toward thiocyanate over hydrophilic anions such as acetate, they exhibited significantly improved behavior over less hydrophilic anions such as salicylate and perchlorate, deviating from the Hofmeister pattern which was observed in the PVC electrode (P1). Notably, the gel membranes exhibited a selectivity improvement over salicylate of more than 2.5 times that of the PVC membrane. More interestingly, G3-based electrodes gave greater response toward thiocyanate than periodate or perchlorate.

Nonequilibrium FIA responses to thiocyanate for both G3 and P1 were obtained prior to real sample applications. In the case of G3 (see Figure 4A), the calibration slope toward thiocyanate (~50 mV decade^{-1}) seemed to be somewhat lower than that observed in the previous equilibrium mode (~56 mV decade^{-1}). Relative standard deviation (RSD) was lower than 1.0% for 1 mM sodium thiocyanate (5 replicates for both G3 and P1). Higher selectivity of the gel electrode toward thiocyanate over lipophilic anions was confirmed in the kinetic mode. Indeed, mV toward 50 mM sodium thiocyanate standards with added salicylate (0 - 2 mM) exhibited minimal differences (Figure 4A2) when compared to that of the PVC-based membrane electrodes (Figure 4B2). In addition, the lower detection limit for G3 membranes is more clearly seen in the FIA chart.

Table 2. Equilibrium potentiometric selectivity coefficients* (log $k^{pot}_{thiocyanate/y}$) and overall anion responses (mV)** of Aliquat336-SCN-based electrodes made of PVC- and gel- based membranes (average of three determinations).

Anion	G1**	G2*	G3*	P1*
acetate	-11.8	-1.9	-2.9	-2.8
Cl^-	-12.9	-1.4	-2.3	-2.6
Br^-	-19.5	-1.0	-1.7	-1.8
NO_2^-	-25.7	-0.8	-1.4	-1.6
NO_3^-	-31.8	-0.6	-1.0	-1.4
I^-	-26.5	-0.4	-0.7	-0.4
Salicylate	-30.4	-0.4	-0.6	-0.2
SCN^-	-47.1	0.0	0.0	0.0
IO_4^-	-18.7	-1.0	-1.2	0.6
ClO_4^-	-35.4	0.0	-0.1	1.3

Prior to real sample measurements using saliva, potentiometric selectivity coefficients were further evaluated in the FIA mode by the matched potential method [20]. An electrode constructed with G3 (Table 1) was implemented in the same FIA arrangement at thiocyanate levels of 0.5 mM and 1.0 mM (as opposed to 10 mM as in the equilibrium mode), and selectivity toward thiocyanate over several anions was obtained. As shown in Table 3, the two different measurement methods (separate solution method in batch mode and matched potential method in FIA) did not reveal identical results, despite being of comparable tendency. However, noting that the FIA measurement is a kinetic method, this behavior may not be so unusual because of the difference in measurement concentrations and transient response behaviors toward different anions [15]. To ensure the presence/absence of a matrix effect, a recovery study was carried out. One milliliter aliquots were filled with several supernatants, and then spiked with a different amount of sodium thiocyanate (n = 3). The resulting increase in concentration was determined by the potentiometric FIA method using the gel membrane. Table 4 indicates that the gel membrane-based electrode could be implemented for further use in FIA mode, without serious concern over the matrix effect.

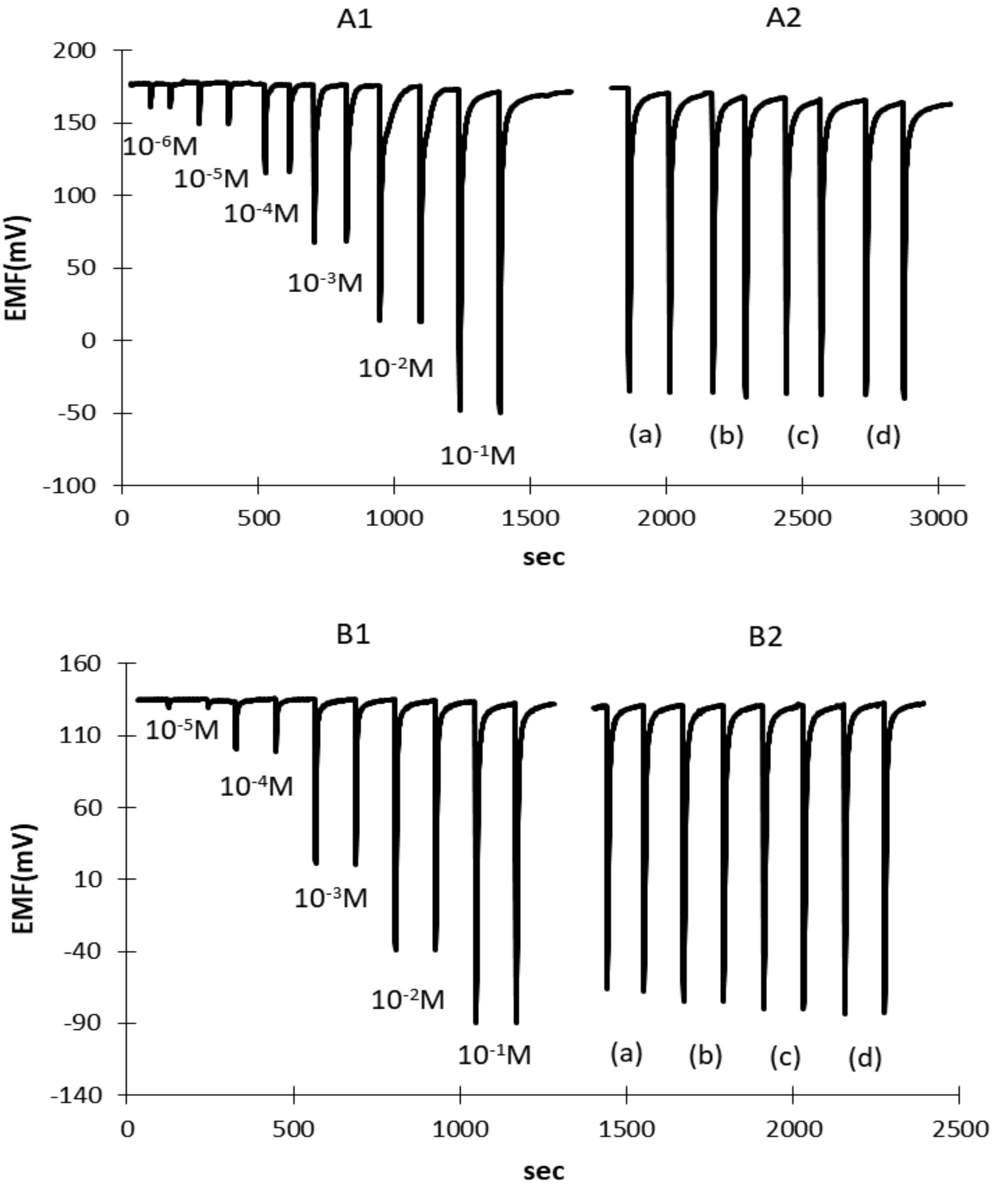

Figure 4. (A1) FIA chart for double injections of sodium thiocyanate standard solutions with a typical gel membrane (G3) electrode detector; (A2) FIA chart for double injections of 50 mM sodium thiocyanate with (a) 0, (b) 0.5, (c) 1, and (d) 2 mM sodium salicylate. (B1, B2) FIA chart obtained with a typical PVC membrane (P1) electrode detector. Procedures are the same as for G3.

Supernatants of 20 different saliva samples (20 times diluted with 0.05 M MES buffer, pH 5.5) were first evaluated in terms of thiocyanate in the FIA mode. The resulting data were compared with those from the colorimetric reference method (Figure 5, including additional data from three spiked saliva pools.). Although the raw data may need to be corrected before implementation in real instruments, they showed a fairly good correlation (R^2 = 0.97, slope = 0.84). The average values of thiocyanate present in the two classes of subjects (smokers = 0.86 mM, n = 10 ; nonsmokers = 0.33 mM, n = 10) were also comparable to previously reported thiocyanate levels (smokers = 1.32 mM and nonsmokers = 0.46 mM, mean values obtained by the reference procedure) [24] despite potential differences in the amount the subjects smoke and other elements such as diet.

Table 3. Non-equilibrium FIA mode potentiometric selectivity coefficients (log $k^{pot}_{thiocyanate/y}$) evaluated by the matched potential method.

Anion	0.5 mM	1.0 mM*
acetate	-2.3	-3.0
Cl^-	-1.9	-2.4
Br^-	-1.3	-1.7
NO_2^-	-0.8	-1.4
NO_3^-	-0.6	-1.1
I^-	-0.5	-1.0
salicylate	-0.5	-1.0
SCN^-	0.0	0.0
IO_4^-	-0.9	-1.1
ClO_4^-	-0.2	-0.5

Table 4. Recovery data for thiocyanate spiked to a pooled saliva as measured by the FIA-membrane electrode system*

added (mM)	found (mM)	% recovered
0.0	0.061	-
0.051	0.111	98.04
0.054	0.114	98.15
0.056	0.118	101.79

*average of two determinations

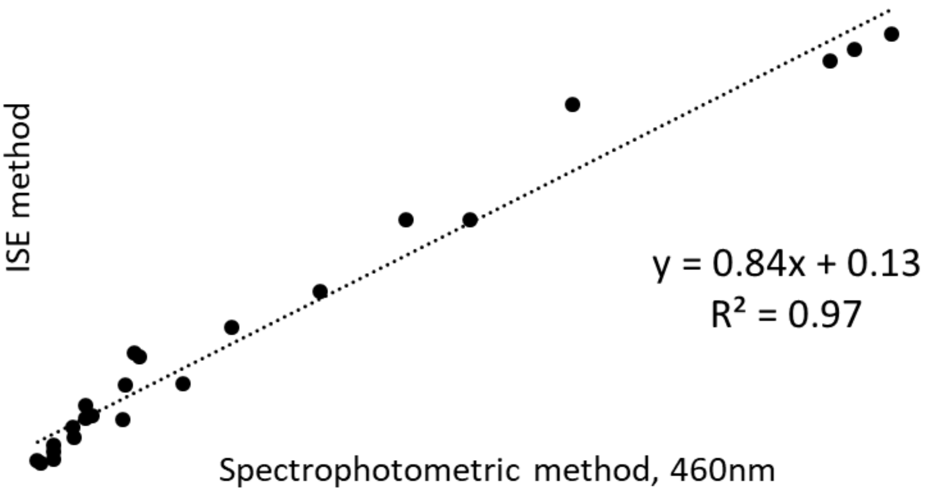

Figure 5. Correlation between the new FIA method and the colorimetric method by a Scinco spectrophotometer

The reasoning behind why the gel membranes exhibit better selectivity toward more hydrophilic anions seems to relate to the chemical properties of the membranes themselves. Like gels synthesized by TEOS, which are known to be relatively hydrophilic, our organic–inorganic precursor-based membranes might also be less lipophilic than PVC-based ones. During hydrolysis of the sol–gel process, some portion of terminal alkoxides may generate unreacted hydroxyl moieties resulting in hydrogen bonding with aqueous adsorbates at the membrane surface. In addition, the gel matrix has urethane (NHCOO) and silicate (Si–O–Si) functional groups, enhancing its hydrophilicity. However, despite the lower lipophilicity of the gel membranes, their three-dimensional structure supports the highly lipophilic quaternary ammonium salt. The plasticizer (TBP) seems to give physical flexibility to the membrane as well as mobility to our ion sensing species, Aliquat336-SCN.

Although the sol–gel encapsulation method seems to be broadly applicable in chemical sensors, there are limitations. For example, commercially available chloride ionophores (Fluka selectophore 24901 and 24894) are either insoluble in DMF or not compatible with the gel. These limitations make it challenging to apply the sol–gel concept to various ionophores. Efforts aimed at overcoming these obstacles are being implemented currently.

4. CONCLUSIONS

A potentiometric thiocyanate-sensitive membrane with encapsulated Aliquat336-SCN was developed by the sol–gel method. The resulting hybrid gel-based electrode exhibited a comparable response slope and improved selectivity toward thiocyanate, when compared to a traditional PVC-based membrane electrode with the same ionophore. The electrode system was successfully implemented in FIA mode to analyze thiocyanate levels in human saliva samples.

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