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Cyanex based uranyl sensitive polymeric membrane electrodes

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ABSTRACT

Novel uranyl selective polymeric membrane electrodes were prepared using three different low-cost and commercially available Cyanex extractants namely, bis(2,4,4-trimethylpentyl) phosphinic acid [L1], bis (2,4,4-trimethylpentyl) monothiophosphinic acid [L2] and bis(2,4,4-trimethylpentyl) dithiophosphinic acid [L3]. Optimization and performance characteristics of the developed Cyanex based polymer membrane electrodes were determined. The influence of membrane composition (e.g., amount and type of ionic sites, as well as type of plasticizer) on potentiometric responses of the prepared membrane electrodes was studied. Optimized Cyanex-based membrane electrodes exhibited Nernstian responses for UO_2^{2+} ion over wide concentration ranges with fast response times. The optimized membrane electrodes based on L1, L2 and L3 exhibited Nernstian responses towards uranyl ion with slopes of 29.4, 28.0 and 29.3 mV decade^{-1} respectively. The optimized membrane electrodes based on L1–L3 showed detection limits of 8.3×10^{-5}, 3.0×10^{-5} and 3.3×10^{-6} mol L^{-1} respectively. The selectivity studies showed that the optimized membrane electrodes exhibited high selectivity towards UO_2^{2+} ion over large number of other cations. Membrane electrodes based on L3 exhibited superior potentiometric response characteristics compared to those based on L1 and L2 (e.g., widest linear range and lowest detection limit). The analytical utility of uranyl membrane electrodes formulated with Cyanex extractant L3 was demonstrated by the analysis of uranyl ion in different real samples for nuclear safeguards verification purposes. The results obtained using direct potentiometry and flow-injection methods were compared with those measured using the standard UV–visible and inductively coupled plasma spectroscopic methods.

1. Introduction

Uranium is the most commonly radioactive element used as nuclear fuel in fission reactors. There is a special interest for U(VI) analysis in nuclear industry, particularly in fuel manufacturing and processing. Uranium dioxide is used in the preparation of fuel pellets for nuclear power reactors. Several steps are necessary in this process (e.g., leaching from ores, purification by ion-exchange/solvent extraction, precipitation and reduction). Monitoring of uranium concentration in such process is essential [1]. Furthermore, there is a considerable interest in on-site environmental monitoring of uranium. Thus, the determination of uranium ion on a routine basis in nuclear fuel manufacturing or for the immediate detection of sudden uranium contamination is necessary in environmental safety assessment related to nuclear industry [2]. Moreover, continuous monitoring of uranium in wash streams coming out from nuclear reactors is essential to avoid nuclear contaminations [3].

Several characteristics are highly desirable in analytical methods which are intended for uranium determination such as wide concentration range, ability of measurement in colored or turbid solutions, high sensitivity, fast analysis time, simplicity, adequate accuracy and precision, as well as cost-effectiveness. Electroanalytical techniques appear to be the most appropriate for direct determination of many ions and are currently used in routine analysis in many fields (e.g., clinical and environmental) [4–14].

Chemical sensors, especially carrier-based polymer membrane electrodes, are convenient for this purpose and are suitable for use in routine analysis and field applications owing to their portable instrumentation character and low power requirements [15–25]. Moreover, membrane electrodes have the advantages of measuring uranium concentration over several orders of magnitude and are suitable for flow-through techniques. The above advantages make membrane electrodes suitable for real-time monitoring of clean-up studies, process streams and nuclear safeguards.

Although a large number of uranyl ionophores have been developed so far [26–42], synthesis of many of these ionophores

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involves complicated synthetic and purification procedures, which could limit their analytical applications [26,29,42,43]. Moreover, some of those uranyl-selective ionophores are commercially available, however, at very high cost even for few milligram quantities [29]. Recently, we developed a uranyl membrane electrode based on a low-cost and commercially available amino (trimethyl)phosphate and its performance characteristics were found to be comparable to membrane electrodes based on high cost uranyl ionophores or those involve complicated synthetic and purification procedures [44]. Herein, we extend our strategy of using low-cost and commercially available extractants for the development of membrane electrodes for uranyl ions. Over the last few decades, great efforts were made towards synthesis of novel extractants and chelating exchangers capable of improving efficiency and selectivity of a number of separation processes for a wide range of chemical species [45–47]. Some of such compounds have been used as ionophores in polymeric membrane electrodes. For instance, uranyl selective electrodes based on uranyl extractants such as di-2-ethylhexyl phosphate [33], tri-2-ethylhexyl phosphate [34] and trioctylphosphine oxide [27] have been reported. Some of those electrodes, however, exhibited high detection limits or suffer from strong interferences.

Cyanex extractants (e.g., dialkylphosphinic, dialkylmonothiophosphinic and dialkyldithiophosphinic derivatives) are commercially available at low cost and have been successfully applied for recovery and separation of metal ions from acidic solutions [48–51]. For example, Cyanex 272 (bis(2,4,4-trimethylpentyl) phosphinic acid) [52–53], Cyanex 302 (bis(2,4,4-trimehylpentyl) monothiophosphinic acid) [54–55] and Cyanex 301 (bis(2,4,4-trimethylpentyl) dithiophosphinic acid) [56–57] have been utilized in the extraction of UO_2^{2+} from aqueous acidic solutions. Although Cyanex extractants have been extensively used in extraction of uranium, to the best of our knowledge there is no report on using Cyanex extractants in the construction of polymer membrane electrodes for UO_2^{2+} ions.

In this study, three Cyanex extractants were examined as novel ionophores in polymeric membrane electrodes for uranyl ions. Characterization and applications of such sensors in the determination of uranyl ion in real samples collected from some Egyptian nuclear facilities and other locations for safeguards verification purposes are presented.

2. Material and methods

2.1. Apparatus

All potentiometric measurements were made at ambient temperature with eight-channel electrode-computer interface (Nico2000 Ltd., UK) controlled by Nico-2000 software. A double junction Ag/AgCl reference electrode (Sentek, UK) was used for all mV measurements and combination glass electrode (Sentek, UK) was used for all pH measurements. UV–visible spectrometer (Thermo Evolution 300, England) and inductively coupled plasma optical emission spectrometer (ICP-OES) (Thermo iCAP6500, England) were used for spectrometric uranium measurements. The flow injection analysis (FIA) system consisted of a two-channel (Ismatech MS-REGLO model) peristaltic pump, polyethylene tubing and a medium-pressure 6-port injection valve (model V540, CLUZEAU INFO LABO, France) with a sample loop of 100 μL volume.

2.2. Reagents and chemicals

High molecular weight poly(vinyl chloride) (PVC), 1-chloronaphthalene (CN) and selectphore grade tetrahydrofuran (THF) were obtained from Sigma-Aldrich (Milwaukee, WI, USA). *o*-Nitrophenyl octyl ether (*o*-NPOE), dioctyl sebacate (DOS), tris(2-ethylhexyl)phosphate (TEHP), potassium tetrakis(4-chlorophenyl) borate (KTpClPB) and tridodecyl methyl ammonium chloride (TDMACl) were obtained from Fluka (Milwaukee, WI, USA). Dioctyl adiapate (DOA) and dioctylphthalate (DOP) were obtained from Merck (Germany). Uranyl nitrate hexahydrate was obtained from Spectrum Chemicals (USA) and used as received. Uranium ICP standard, (1000 mg L^{-1} U) in 3% HNO_3, was obtained from Ricca Chemical (USA). Cyanex 272, Cyanex 301 and Cyanex 302, were supplied by Cytec Inc. (Canada) and used as received (see Fig. 1 for chemical structure). Arsenazo-III was obtained from Sigma-Aldrich (Milwaukee, WI, USA). All metal solutions examined in the selectivity experiments were prepared from nitrate salts of high purity. All solutions were prepared in doubly distilled water. All other chemicals were of analytical reagent grade unless stated otherwise.

2.3. Preparation of membrane electrodes

Polymer membrane electrodes were prepared according to the literature procedures [58]. Membrane cocktails were prepared by dissolving appropriate amounts of ionophores, different plasticizers, PVC and various mole percentages of KTpClPB (relative to the ionophore weight) in ~2 mL of THF (see Tables 1 and 2 for membrane compositions). A homogeneous mixture was obtained after complete dissolution of all membrane components. Then the mixture was poured into a 22 mm i.d. glass ring placed onto a glass plate. The glass ring was covered with a filter paper till complete evaporation of THF and formation of a transparent membrane (average thickness of ~0.2 mm). Smaller discs of ~5 mm diameter were cut out from this

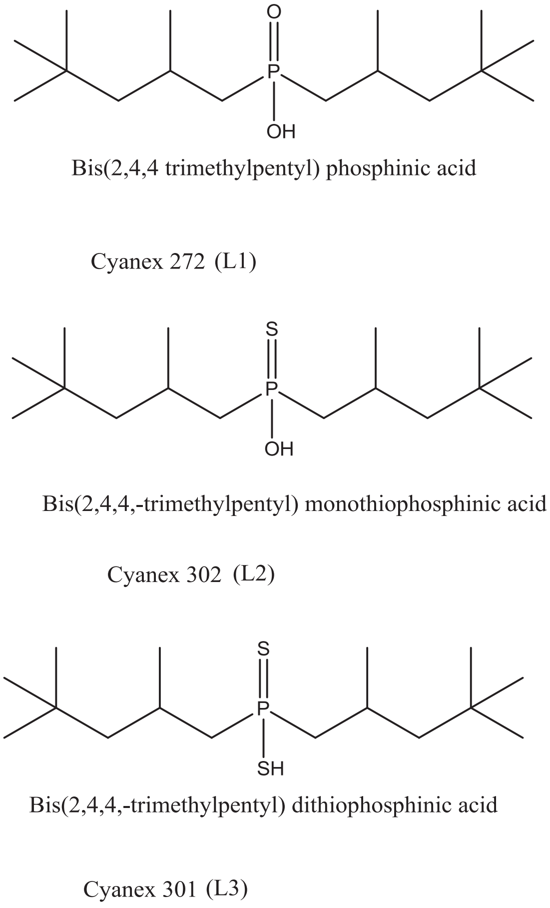

Fig. 1. Chemical structure of the Cyanex ionophores L1–L3.

master membrane with a cork borer and glued to the distal end of a PVC tube (8 mm diameter and 3 cm length) using THF. The sensor body consisted of 1-mL pipette tip attached to the PVC tube. An internal filling solution composed of an equal volume of 10^{-3} mol L^{-1} uranyl nitrate and sodium chloride solutions was used. Ag/AgCl wire (0.3 mm diameter) was used as an inner reference electrode.

Potentiometric responses of the prepared membrane electrodes were determined by recording cell potential as a function of uranyl concentration at ambient temperature. The cell potential was recorded at a constant stirring when stabilized to ± 0.2 mV, and emf was plotted as a function of logarithm $[UO_2^{2+}]$ concentration. A double junction Ag/AgCl reference electrode was utilized in all measurements.

Table 1
Effect of the plasticizer type on the response of Cyanex based membrane electrodes towards uranyl ions.

Membrane Electrode	**Membrane composition** [a]		**Slope (mV decade^{-1})**
	Ionophore	**Plasticizer**	
A1	L1	DOS	18.2
A2	L1	DOA	18.0
A3	L1	NPOE	17.7
A4	L1	DOP	13.7
A5	L1	TEHP	42.2
A6	L1	CN	[b]
B1	L2	DOA	18.7
B2	L2	TEHP	12.6
B3	L2	DOP	14.5
B4	L2	DOS	12.6
B5	L2	CN	[b]
B6	L2	NPOE	[b]
C1	L3	DOA	49.5
C2	L3	TEHP	43.6
C3	L3	DOP	96.6
C4	L3	DOS	102.0
C5	L3	CN	10.2
C6	L3	NPOE	[b]

[a] All membranes were prepared using 2 PVC: 1 plasticizer weight ratio and 1 wt% ionophore.

[b] No response was obtained.

2.4. *Effect of pH and dynamic response times*

The effect of pH was tested by measuring the cell potential over a wide pH range (1.5–9.0) in solutions containing UO_2^{2+} ions. The pH of the sample solution was changed by adding small aliquots of concentrated nitric acid or sodium hydroxide solutions as required. The corresponding mV readings were recorded after each addition and plotted as function of pH of the sample solution.

Dynamic response times of the prepared membrane electrodes were measured in constantly stirred solutions of varying UO_2^{2+} concentrations. The relation between mV readings and time was then plotted.

2.5. *Evaluation of potentiometric selectivity*

The modified separate solution method was used for calculations of unbiased selectivity coefficients following the literature procedure [59]. The potentiometric selectivity coefficients were calculated using the cell EMF values obtained by extrapolating the Nernstian response region to 1 M for both interfering cation and uranyl ion. Selectivity coefficient values ($K^{pot}_{UO_2^{2+},j}$) were calculated using Eq. (1) [59],

$$K^{pot}_{UO_2^{2+},j} = \exp\left(\frac{z_{UO_2^{2+}} F(E^0_j - E^0_{UO_2^{2+}})}{RT}\right) \tag{1}$$

where $E^0_{UO_2^{2+}}$, E^0_j are the potential values of uranyl and interfering ions at 1 M, respectively. $z_{UO_2^{2+}}$ is the charge of the uranyl ion. *R*, *T* and *F* have their regular meanings. It should be mentioned that selectivity coefficients were calculated as described above, if Nernstian responses were obtained for the primary and the interfering cation. Maximal limiting potentiometric selectivity coefficients of cations that induced very little or sub-Nernstian responses are calculated according to the literature recommendations [59]. If the primary ion

Table 2
Effect of addition of ionic sites on the response characteristics of uranyl membrane electrodes based on Cyanex ionophores.

Membrane electrode	**Membrane composition**			**Slope (mVdecade^{-1})**	**Linear range (mol L^{-1})**	**Detection limit (mol L^{-1})**
	Ionophore (wt%)	**KTpClPB (mol%)**[a]	**TDMACl (mol%)**[a]			
A7	L1(1)	25	0	29.4	5.3×10^{-4}–1.0×10^{-1}	8.3×10^{-5}
A8	L1(1)	50	0	28.9	5.3×10^{-4}–1.0×10^{-1}	2.3×10^{-4}
A9	L1(1)	75	0	27.4	5.3×10^{-4}–1.0×10^{-1}	4.2×10^{-4}
A10	L1(1)	100	0	24.71	5.3×10^{-4}–1.0×10^{-1}	2.8×10^{-4}
A11[b]	L1(1)	0	20	−62.5	5.3×10^{-4}–1.0×10^{-1}	2.9×10^{-4}
B7	L2 (1)	25	0	28.0	5.5×10^{-5}–1.0×10^{-1}	3.0×10^{-5}
B8	L2 (1)	50	0	26.6	5.3×10^{-4}–1.0×10^{-1}	2.5×10^{-4}
B9	L2 (1)	75	0	26.5	5.3×10^{-4}–1.0×10^{-1}	1.8×10^{-4}
B10	L2 (1)	100	0	25.0	5.3×10^{-4}–1.0×10^{-1}	1.0×10^{-4}
B11[b]	L2 (1)	0	20	−64.3	5.3×10^{-4}–1.0×10^{-1}	3.1×10^{-4}
C7	L3 (1)	25	0	29.3	5.0×10^{-6}–1.0×0^{-1}	3.3×10^{-6}
C8	L3 (1)	50	0	23.5	5.5×10^{-5}–1.0×10^{-1}	4.0×10^{-5}
C9	L3 (1)	75	0	25.2	5.5×10^{-5}–1.0×10^{-1}	5.3×10^{-5}
C10	L3 (1)	100	0	22.7	5.5×10^{-5}–1.0×10^{-1}	4.0×10^{-5}
C11[a]	L3 (1)	0	20	−60.2	5.3×10^{-4}–1.0×10^{-1}	3.8×10^{-4}
C12	L3 (2)	25	0	27.8	5.5×10^{-5}–1.0×0^{-1}	3.5×10^{-5}
C13	L3 (3)	25	0	26.8	5.0×10^{-6}–1.0×0^{-1}	1.3×10^{-5}
D1[c]	0	1 wt%	0	59.4	5.0×10^{-3}–1.0×10^{-1}	2.5×10^{-3}
D2[d]	0	1 wt%	0	46.7	5.0×10^{-3}–1.0×10^{-1}	5.0×10^{-3}

[a] Relative to ionophore.

[b] Anionic response for nitrate (uranyl counter ion).

[c] Ionophore free membrane was prepared using 1 wt% of KTpClPB and formulated with DOS (b) or DOA (c) respectively.

[d] Ionophore free membrane was prepared using 1 wt% of KTpClPB and formulated with DOS (b) or DOA (c) respectively.

response was not Nernstian, theoretical slopes were used in calculation of the selectivity coefficients. No correction was made for the slight changes in the liquid junction potential as a function of increasing cation concentrations.

2.6. Flow injection set-up

Flow Injection set-up and the tubular sensor used therein were constructed according to the literature procedures [60,61]. Casting solution for such electrode was prepared by dissolving 1.0 wt% L3, 65.7 wt% DOA, 32.8 wt% PVC and 25 mol% of KTpClPB (relative to L3) in ~1 mL of THF. The casting solution was deposited using a micro dropper into a hole (3 mm wide × 5 mm length) made in the middle of a 5 cm Tygon tube. After each casting the THF was allowed to evaporate. This casting process was repeated five times. The final ISE tube was allowed to dry completely for an additional 1 h. The tube was then inserted into a pipette tip which was sealed in place to prevent leakage of the internal reference solution. The electrode assembly was completed by filling the tip with a sufficient filling solution to cover the tubular electrode and the internal Ag/AgCl reference electrode. The tubular sensor was inserted into the flow injection system and 0.001 mol L^{-1} HNO_3, pH 3, was used as a carrier solution at a flow rate of 3.5 mL min^{-1}. The tubular electrode was placed at a distance of about 30 cm from the injection valve and at a distance about 20 cm from the waste container. A double junction Ag/AgCl reference electrode was placed downstream. The tubular electrode was calibrated at 25 °C under hydrodynamic mode of operation by injection of uranyl standard solutions through a valve loop of about 100 μL volume. After the baseline was reached the potential signals were recorded using the data acquisition system described above.

2.7. Spectrometric determination of uranium contents in real samples

Spectrometric analysis of uranium was performed using both UV–Visible and ICP-OES spectrometers. The standard Arsenazo III UV–Visible method based on the formation of colored complexes (λ_{max} of 650 nm) was used for determination of uranium [62]. In case of ICP measurements, the ICP-OES was adjusted at 385.4 nm and was allowed to warm up for about 30 min with the continuous aspiration of deionized water and UO_2^{2+} standards.

Experimental work using uranyl nitrate hexahydrate was carried out in the safeguards destructive analysis laboratory (KMP-I) at the Egyptian Nuclear and Radiological Regulatory Authority (ENRRA).

3. Results and discussion

The electrochemical performance characteristics of the prepared membrane electrodes were systematically evaluated according to International Union of Pure and Applied Chemistry (IUPAC) recommendations [63] and results obtained are summarized below.

3.1. Effect of membrane composition

Potentiometric responses of polymeric membrane electrodes are significantly affected by nature and amount of membrane components [64]. To study the influence of membrane compositions (e.g. plasticizer and type of ionic-additives) on the potentiometric responses, several membranes with various compositions were prepared using three different ionophores namely, Cyanex 272 (L1), Cyanex 302 (L2) and Cyanex 301 (L3) (see membrane compositions depicted in Tables 1 and 2). In all investigations, a plasticizer to polymer ratio of nearly 2:1 was used since films with such composition have optimum physical properties and to ensure relatively high mobility of their constituents [65].

Plasticizer is a very important constituent of polymer membrane electrode and strongly affects most potentiometric response characteristics such as detection limits [66], sensitivity and more importantly selectivity [67]. The type of plasticizer controls to much extent the dielectric constants (ε) of the membrane phase, which strongly affects ion–ionophore interactions, as well as partition of ions between aqueous and membrane phases. The effect of the plasticizer type on the performance of UO_2^{2+} membrane electrodes based on L1–L3 was initially screened by measuring the potentiometric responses towards UO_2^{2+} of membrane electrodes formulated with 1 wt% ionophore and different plasticizers (see data depicted in Table 1). Variety of plasticizers having a wide range of dielectric constant (*o*-NPOE; $\varepsilon = 23.9$, TEHP; $\varepsilon = 10$, DOP; $\varepsilon = 7$, DOA; $\varepsilon = 4.13$, DOS; $\varepsilon = 3.9$ and CN) were tested. As shown in Table 1, among all studied plasticizers, membrane electrodes formulated with DOS and based on L1 exhibited the best performance (e.g., closest to Nernstian response, signal stability). However, membrane electrodes formulated with DOA exhibited the best performance in case of L2 and L3 based membrane electrodes (Table 1). It is plausible that DOA and DOS as low dielectric constant plasticizers provide more appropriate conditions for the incorporation of uranyl ion into the membrane phase prior to its coordination with the ionophore due to a synergism between lipophilicity and polarity [41]. It was also found that membrane electrodes A1, B1 and C1 (formulated with DOS in case of L1 and with DOA in case of L2 or L3) exhibited widest linear ranges and smallest detection limits (data not shown). Therefore, DOS (in case of L1) and DOA (in case of L2 or L3) were selected as plasticizers of choice for further investigations. It could be also noticed in Table 1, that all membrane electrodes formulated without exogenous ionic additives exhibited either sub-Nernstian or super-Nernstian responses.

It is well-known that nature and amount of lipophilic ionic additives greatly improve response characteristics of carrier-based membrane electrodes [68–70]. Therefore, we investigated the effect of addition of different mol% of KTpClPB (relative to the ionophore) on the response characteristics of membrane electrodes based on L1–L3 ionophores. As depicted in Table 2, membrane electrodes prepared with added lipophilic anionic sites, such as KTpClPB, exhibited greatly improved potentiometric response characteristics (e.g., slope, linear range and selectivity). Optimal additive concentrations which resulted in the best performance for uranyl membrane electrodes based on L1–L3 was reached at about 25 mol% KTpClPB (relative to the ionophore) (Table 2). However, further increase in the mol% of KTpClPB (up to 100 mol% with respect to the ionophore) deteriorates the response characteristics. Table 2, also indicates that optimized membrane electrodes A7, B7 and C7 based on L1–L3 exhibited linear ranges of 5.3×10^{-4}–1.0×10^{-1}, 5.5×10^{-5}–1.0×10^{-1} and 5.0×10^{-6}–1.0×0^{-1} mol L^{-1} with Nernstian slopes of 29.4, 28.0 and 29.3 mV $decade^{-1}$, respectively. It can be also noticed that optimized membrane electrodes based on L3 (C7) exhibited the best detection limit and widest linear range compared to those based on L1 or L2 (see data in Table 2).

Fig. 2 shows the effect of different mol% of KTpClPB (relative to the ionophore) on the potentiometric responses of polymer membrane electrodes based on L3 as a representative example for the UO_2^{2+} ionophores used in this study. As shown in this figure polymer membrane electrodes prepared using L3 and formulated with 25 mol% KTpClPB exhibited optimal response characteristics (e.g., slope, linear range and detection limits) compared to membrane electrodes formulated without anionic additives or those formulated with higher than 25 mol% KTpClPB. It was also found that the addition of cationic sites in the form of TDMACl resulted in an anionic response rather than cationic (Table 2). The enhancement of potentiometric response

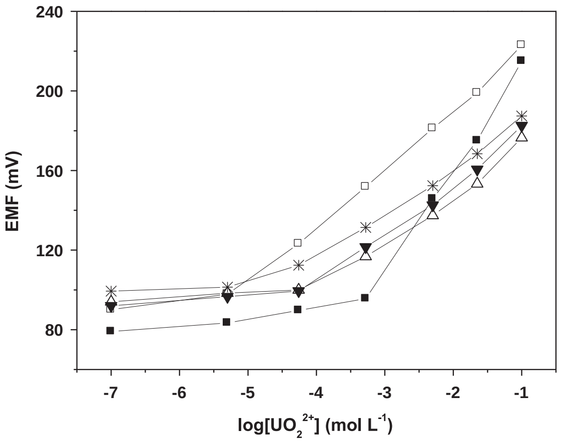

Fig. 2. Potential response of UO_2^{2+} membrane electrodes based on L3 and doped with mol% of KTpClPB (relative to L3); 0 mol% (■), 25 mol% (□), 50 mol% (Δ), 75 mol % (▾), and 100 mol% (*).

by addition of anionic sites and the anionic response observed upon addition of cationic sites suggested that these ionophores operate via a neutral carrier mechanism (see below). It should be noted that the cationic response observed for membranes formulated without added anionic sites (see data in Table 1) are likely due to the presence of trace anionic impurities within the PVC polymer matrix [71]. The p*K*a of –SH group in Cyanex 301 is 2.6 [72], which indicates that it is highly possible that this group in unionized in the membrane phase and consequently this ionophore could work as a neutral carrier. This notation is strongly supported by the neutral carrier mechanism suggested above based on the additive study.

In order to study the effect of the ionophore's amount on the performance characteristics of membrane electrodes, ionophore L3 was selected as a representative example of the Cyanex extractants. The amount of L3 was changed from 1% (2 mg) to 3% (6 mg) (see data in Table 2), while maintaining the same amounts of PVC, plasticizer (DOA) and mol% of additives. It was found that increasing L3 concentration in the membrane phase did not enhance the performance of membrane electrodes. Moreover, a shift in the lower detection limits to slightly higher concentrations was observed upon increasing the amount of L3 (Table 2). Therefore, 1 wt% (2 mg) ionophore was chosen for further investigations. The lower detection limit of polymer membrane electrodes is controlled by the flux of primary ions to the membrane sample solution interface [64]. The local concentration of primary ion at the interface controls the lower detection limits. It is possible that high ionophore concentration in the membrane phase could increase the uranyl flux to the interface and thus shifts the lower detection limit to higher concentrations. Several reports in the literature indicated the dependence of the potentiometric response of some carrier-based cation selective membrane electrodes on the amount of ionophore in the membrane phase [73–75,44].

The effect of the concentration of the internal solution on the potentiometric responses of the optimized membrane electrode (C7) was also investigated in the concentration range of 10^{-2} to 10^{-4} mol L^{-1} of $UO_2(NO_3)_2 \cdot 6H_2O$. It was found that the variation in the internal solution concentration causes no significant difference in the response characteristics (data not shown).

3.2. *Potentiometric selectivity*

Ionophores play a key role in controlling selectivity of membrane electrodes. Selectivity of polymer membrane electrode is controlled by binding constant between ions and ionophore, as well as partition coefficient of ions between aqueous and membrane phase [40]. The cationic responses of the optimized membrane electrodes

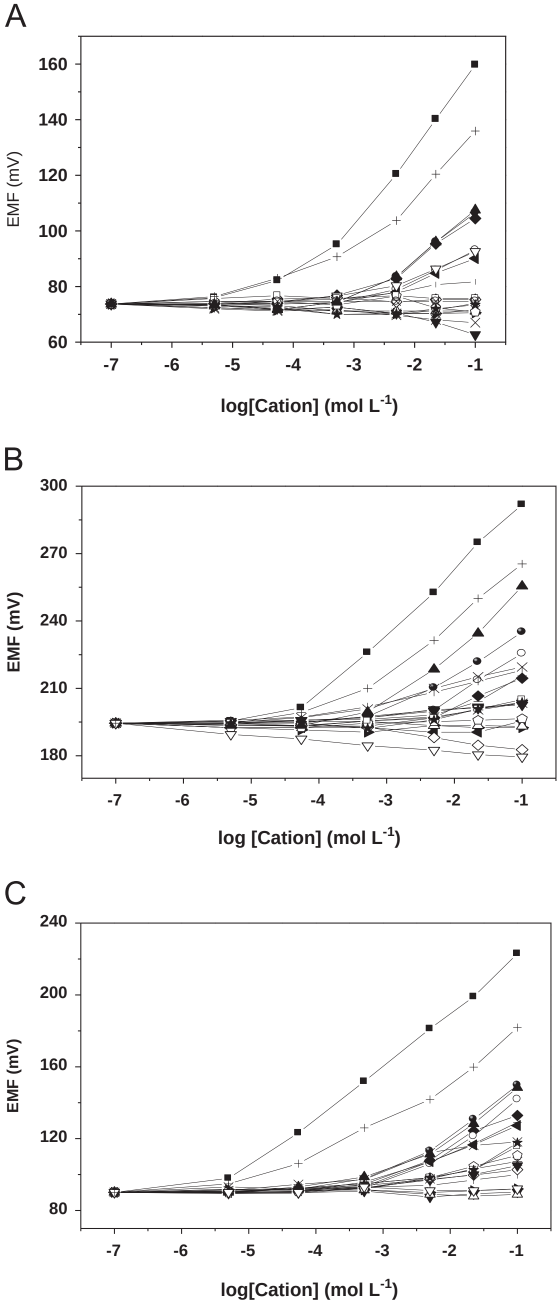

Fig. 3. Potentiometric responses of optimized membrane electrodes (A7) (A), (B7) (B), and (C7) (C) towards various cations; UO_2^{2+}(■), Na^+(◆), K^+(●), Cs^+(¤), Li^+(◂), NH_4^+(–), Mg^{2+}(►), Sr^{2+}(▾), Zn^{2+}(Δ), Pb^{2+}(×), Cu^{2+}(|), Co^{3+}(◇), Ca^{2+}(▾), Cd^{2+}(ж), Ba^{2+}(⌂), Ni^{2+}(□), Cr^{3+}(⁎), Fe^{3+}(▴), Al^{3+}(Ø), and Th^{4+}(+).

(A7, B7 and C7) based on L1–L3 towards various cations are shown in Fig. 3, and their corresponding selectivity coefficients are presented graphically in Fig. 4. As shown optimized electrodes (A7, B7 and C7) exhibit relatively better selectivity coefficients for UO_2^{2+} ion over a large number of monovalent, divalent, trivalent and tetravalent cations. Such membrane electrodes exhibited selectivity sequence of a non-Hofmeister type: $UO_2^{2+} > Th^{4+} > K^+ > Fe^{3+} > Cs^+ > Na^+ > NH_4^+ > Sr^{2+}$. This indicates a preferred interaction between Cyanex ionophores and UO_2^{2+} in comparison with other cations. Although Th^{4+} causes some interference, the developed membrane electrodes are more selective for UO_2^{2+} compared to Th^{4+}. It could be noticed in Fig. 4, that uranyl membrane electrodes based on L3 (C7) exhibited the best selectivity compared to those based on L1 (A7) and L2 (B7). Therefore L3 based membrane

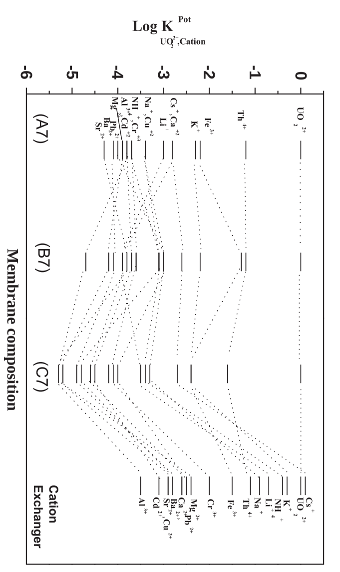

Fig. 4. Selectivity coefficients ($\log K^{pot}_{UO_2^{2+},j}$) of optimized electrodes based on Cyanex ionophores and obtained using modified SSM.

electrode (C7) was utilized in analytical application both in batch and FIA modes. The high uranyl ion selectivity observed for L3 based membrane electrodes, compared to that of L1 and L2 membrane electrodes, could be explained by the presence of sulfhydryl group (–SH) in case of L3. Thiol (–SH) group could enhance binding stability and affinitiy of L3 towards uranyl ions. Such enhancement in binding constant is expected to improve the potentiometric selectivity of L3 based membrane electrodes towards uranyl ions [76]. It has been previously shown, that ligands containing sulfhydryl group form complexes with high stability constants with U(IV) ions ($\log K_{Stab.} \sim 8$) [76]. More recently, stable uranyl(VI) complexes possessing unsupported unidentate thiolate ligands were characterized and isolated [77], which indicates the possible formation of similar complexes in case of L3. Study of the complexation of Cyanex extracts and uranyl ion is underway in our laboratory and attempts will be make to isolate single crystals for X-ray analysis.

It was established that the ratio of lipophilic additive to ionophore in the membrane that results in optimal selectivity for primary ion over interfering ions depends on the charge of the primary ion, interfering ions, ionophore, and additive, as well as ion:ionophore stoichiometries for both primary and interfering ions [78]. A quantitative model has been developed and can be used to predict the nature of ion–ionophore complexation based on the effect of ionic additives on potentiometric selectivity [79–80]. Application of this model to the studies described in this work was performed to predict a possible stoichiometry of ion-ionophore complexes. The model predicts that highest selectivity for uranyl ion relative to divalent interfering cations could be achieved at 25 mol% KTpClPB for 1:1 uranyl-ionophore and 1:1 divalent cations-ionophore [79]. On the other hand, optimal selectivity for uranyl over monovalent interfering cations could be achieved at 40 mol% KTpClPB for a 1:1 uranyl-ionophore and 1:1 monovalent cations-ionophore [79]. Data shown in Table 3 revealed that highest selectivity for UO_2^{2+} is achieved at 25 mol % KTpClPB. Therefore, it is concluded that the binding probably involves 1:1 uranly-ionophore complex.

The potentiometric selectivity coefficients, ($K^{pot}_{UO_2^{2+},j}$), of all uranyl membrane electrodes prepared in this study are depicted in Table 3. As can be seen optimal amount of ionic sites was reached at 25 mol% relative to the ionophore (A7, B7 and C7), and optimized membrane electrodes exhibited a relatively high selectivity for UO_2^{2+} ion compared to other membrane compositions. The selectivity coefficients depicted in Table 3 clearly indicate that the prepared uranyl membrane electrodes were fairly selective for UO_2^{2+} over different tested cations. Selectivity coefficients of ion-exchanger based membrane electrodes (i.e. ionophore free membrane electrodes) are also included for comparison purposes. As can be seen in Tables 2 and 3 such membrane electrodes exhibited narrow working ranges, high detection limits and poor selectivity compared to Cyanex based membrane electrodes, which indicates the ionophoric effect of Cyanex extractants. It can be also noted that membrane electrodes doped with optimal amount of borate

Table 3
Potentiometric selectivity coefficients ($\log K^{pot}_{UO_2^{2+},j}$) of uranyl membrane electrodes based on L1–L3.

Cation	Membrane electrode															
	A1	A7	A8	A9	A10	B1	B7	B8	B9	B10	C1	C7	C8	C9	C10	D1	D2
Li^+	< −3.4	< −3.0	< −2.0	< −0.8	< −0.4	< −3.4	< −3.9	< −3.7	< −4.0	< −3.5	< −3.8	< −3.5	< −2.3	< −1.1	< −0.4	< −0.7	< −0.7
Na^+	< −2.8	< −2.4	< −1.8	< −1.9	< −1.0	< −3.8	< −3.0	< −2.9	< −3.0	< −2.3	< −3.1	< −3.3	< −2.8	< −1.1	< −0.9	< −0.9	< −0.9
K^+	< −2.4	< −2.3	< −1.4	< −1.1	< −0.1	< −3.3	< −2.2	< −1.2	< −3.0	< 0.2	−2.1	< −2.4	< −1.3	< −1.2	< −0.6	< −0.2	< −0.4
Cs^+	< −3.2	< −2.9	< −1.8	< −0.2	< −0.1	−3.1	< −2.6	< −1.2	< −0.1	< 0.3	−2.3	< −2.7	< −2.3	< −0.6	< −0.2	< 0.3	< 0.1
NH_4^+	< −3.6	< −3.7	< −1.6	< −0.3	< −0.4	< −3.2	< −3.1	< −1.6	< −0.8	< −0.7	< −2.8	< −3.4	< −2.1	< −1.3	< −0.6	< −0.5	< −0.3
Mg^{2+}	< −2.6	< −2.9	< −2.9	< −2.3	< −2.3	< −3.7	< −4.2	< −3.3	< −3.9	< −3.7	< −4.7	< −5.2	< −3.5	< −3.7	< −3.3	< −2.2	< −2.4
Ca^{2+}	< −2.9	< −2.8	< −2.8	< −1.8	< −2.1	< −3.7	< −3.8	< −3.1	< −3.3	< −3.2	< −3.8	< −4.6	< −2.8	< −3.8	< −3.4	< −2.7	< −2.6
Sr^{2+}	< −3.4	< −4.3	< −3.7	< −2.4	< −2.4	< −3.9	< −3.7	< −3.5	< −3.7	< −3.6	−3.5	< −5.2	< −2.9	< −3.5	< −3.1	< −2.1	< −2.9
Ba^{2+}	< −3.0	< −4.1	< −3.6	< −2.5	< −2.4	< −3.7	< −4.1	< −3.1	< −3.1	< −2.9	< −3.8	< −4.9	< −3.5	< −3.6	< −3.2	< −2.7	< −2.8
Ni^{2+}	< −3.4	< −3.7	< −3.2	< −3.1	< −2.9	< −3.5	< −3.6	< −3.5	< −3.6	< −3.1	< −3.8	< −4.2	< −3.4	< −3.7	< −3.3	< −2.9	< −3.0
Co^{2+}	< −3.2	< −3.7	< −3.4	< −3.0	< −3.0	< −3.8	< −4.7	< −3.7	< −3.6	< −3.6	−2.2	< −4.9	< −3.3	< −4.0	< −3.6	< −2.5	< −2.6
Cu^{2+}	< −3.3	< −3.4	< −3.1	< −2.8	< −3.0	< −4.0	< −3.1	< −2.9	< −2.9	< −2.4	< −3.4	< −4.8	< −2.7	< −3.1	< −2.6	< −2.8	< −2.9
Cd^{2+}	< −3.9	< −3.8	< −2.7	< −2.4	< −3.0	< −3.6	< −3.7	< −3.5	< −3.9	< −3.6	< −3.9	< −4.5	< −2.8	< −3.3	< −2.9	< −2.5	< −3.1
Zn^{2+}	< −3.9	< −3.9	< −3.0	< −2.5	< −2.8	< −3.6	< −4.2	< −3.6	< −3.3	< −3.2	< −3.6	< −5.3	< −3.2	< −3.7	< −3.3	< −2.6	< −3.1
Pb^{2+}	< −3.0	< −4.0	< −3.6	< −1.5	< −1.2	< −4.0	< −3.1	< −2.9	< −3.1	< −2.9	< −3.3	< −4.0	< −2.5	< −3.0	< −2.6	< −1.7	< −2.5
Al^{3+}	< −3.2	< −3.8	< −3.4	< −3.1	< −3.0	< −4.5	< −4.7	< −3.3	< −4.0	< −3.7	< −3.8	< −5.2	< −4.5	< −3.8	< −3.4	< −2.9	< −3.2
Cr^{3+}	< −3.3	< −3.7	−2.6	−1.8	−1.7	< −4.0	< −3.6	< −3.3	< −2.9	< −2.6	< −3.9	< −4.1	< −2.9	< −2.9	< −2.5	< −2.2	< −2.0
Th^{4+}	< 0.6	< −1.2	< −0.7	< −0.6	< −0.5	< −0.3	< −1.3	< −1.3	< −1.6	< −0.9	< −0.2	< −1.6	< −0.9	< −1.1	< −0.9	< −1.5	< −1.1
Fe^{3+}	−1.8	−2.2	−2.1	−1.6	−1.7	1.66	< −1.2	< −1.8	< −1.2	< −0.6	< −1.2	< −2.4	< −1.2	< −1.5	< −0.7	< −1.8	< −1.5

exhibit remarkably high selectivity in comparison with ionophore-free membrane electrodes (D1 and D2) and of membrane electrodes formulated without anionic sites (A1, B1 and C1). Enhancement of selectivity by addition of anionic sites indicates that Cyanex ionophores operate via the neutral mechanism [43]. This notion was further supported by the observed anionic responses of membrane electrodes doped with 20 mol% TDMAC relative to the ionophore weight (A11, B11 and C11).

3.3. Dynamic response times

The response time was calculated based on the average time required for the optimal UO_2^{2+} membrane electrode to reach a potentiometric response within ±1 mV of its final equilibrium value [81], after successive increase in UO_2^{2+} ion concentration by about 10-fold. As shown in Fig. 5, optimized membrane electrodes A7, B7 and C7 responded to uranyl ions with response times of 26, 35 and 20 s, respectively, for concentrations higher than 10^{-4} M. This indicates a fast binding kinetics between uranyl ion and Cyanex extractants which should enable the utilization of Cyanex based membrane electrodes in a flow injection set-up.

3.4. Lifetime of optimized membrane electrodes

The loss of membrane components due to chemical processes at the membrane sample interface is the main cause for the limited lifetime of neutral carrier-based ISEs [82]. The relative lifetime of the optimized electrodes (A7, B7 and C7) was studied by periodically recalibrating the sensors in standard UO_2^{2+} solutions and calculating slopes of uranyl responses and detection limits. It was found that the potentiometric response characteristics (e.g., slopes and detection limits) of the optimized membrane electrodes did not change significantly over a period of 10 weeks. After this period, the slopes became smaller and the detection limits shifted to higher concentrations.

3.5. Effect of pH

Hydrogen ions are known to affect performance of ISEs. Thus, it was necessary to determine the working pH range in which the response of the sensor is not disturbed by H^+ ions. pH dependence of the potentiometric responses of Cyanex based membrane sensors was tested using two different concentrations of uranyl (10^{-2} and 10^{-3} mol L^{-1}) over a wide pH range. It was found that the uranyl responses of the developed membrane electrodes did not change in the pH range 2.1–3.7, 2.1–3.7 and 2.2–3.7 for membrane electrodes (A7), (B7) and (C7), respectively. Fig. 6 shows the pH response of C7 membrane electrode as a representative example for the optimized membrane electrodes based on Cyanex ionophores. The observed drift at high pH values might be due to formation of hydroxo complexes of uranyl ion in solution and gradual increase of $[OH^-]$ ions, which causes a decrease in the potential. At low pH values, the deviations occur due to hydrogen ion contribution to the potentiometric response of the sensor, and the electrodes started to respond to H_3O^+ ions along with the UO_2^{2+} ions, leading to an increase in the potential.

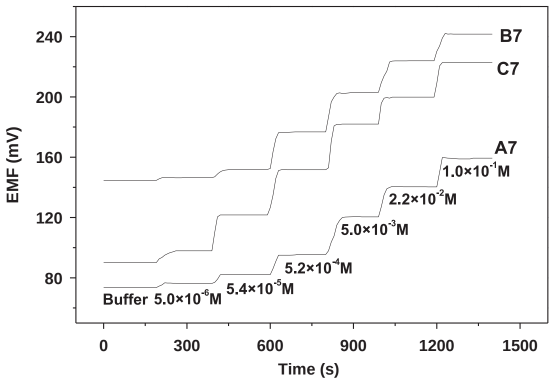

Fig. 5. Dynamic response times of optimized Cyanex based membrane electrodes (A7), (B7), and (C7) towards different concentration levels of UO_2^{2+}.

3.6. Flow injection

A flow injection analysis using ion-selective electrode offers several advantages (e.g., low cost, simple instrumentation, wide linear response, etc.). Therefore, FIA has been well-recognized over the past two decades for the determination of a variety of metal ions [83–84] including UO_2^{2+} [21]. Moreover, the transient nature of the signal in flow-injection analysis may help to overcome the effects of interfering ions if the electrode's response to these ions is slower than that to the target analyte [85].

A tubular-type detector incorporating L3 based membrane sensor (C7) was prepared and used under hydrodynamic mode of operation for continuous UO_2^{2+} quantification. Fig. 7 showed the triplicate peaks from the proposed FIA system obtained under optimal experimental conditions using electrode (C7) for varying concentrations of UO_2^{2+}. A linear relationship between UO_2^{2+} concentrations and FIA signals was obtained over a concentration

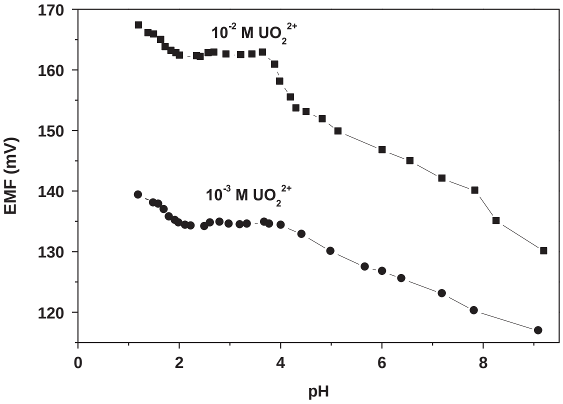

Fig. 6. Effect of pH on the potentiometric responses of the optimized membrane electrode (C7) at two concentration levels of UO_2^{2+} ions.

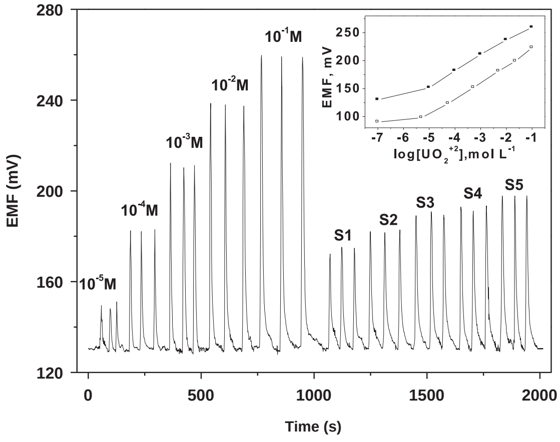

Fig. 7. Typical flow-injection potentiometric responses obtained using optimized membrane electrode (C7) towards UO_2^{2+}. Inset shows the potentiometric responses of optimized membrane electrode (C7) towards of UO_2^{2+} in static mode (□), and FIA mode (■).

Table 4
Comparison of the selectivity coefficients of $UO_2{}^{2+}$ polymer membrane electrode based on Cyanex 301 and some of the reported uranyl polymer membrane electrodes.

Ionophore	Selectivity, $K^{pot}_{UO_2{}^{2+},j}$	References
Tris(2-ethylhexyl)phosphate	Fe^{3+} −0.14, V^{4+} −0.92, Ca^{2+} −0.06, Li^{+} −0.95, Ni^{2+} −1.1, Cd^{2+} −1.1, Pb^{2+} −1.3, Co^{2+} −1.4, Th^{4+} −2.14	34
o-(1,2-Dihydro-2-oxo-1-pyridyl)-*N*,*N*, *N*/,*N*/-bis (tetramethyl) uronium hexafluorophosphate	Fe^{3+} −0.05, Th^{4+} −0.48, Y^{3+} −0.92, Ca^{2+} −2.50, Mg^{2+} −2.95, Cu^{2+} −2.49, Co^{2+} −2.58	34
Tertatolyl-*o*-xylylenediphosphine dioxide	Fe^{3+} 4.86, Ni^{2+} 4.1, Ca^{2+} 3.77, K^{+} 3.30,Cu^{2+} 3.84	43
Calixarene I	Fe^{3+} 1.02, Th^{+4} 0.15, Al^{3+} 0.38, Cu^{2+} 0.55, Ca^{2+} −2.1, Mg^{2+} −2.1, K^{+} −2.0,Na^{+} −2.2,	36
N,*N*/-Diheptyl-*N*,*N*/, 6,6-tetramethyl-4,8-dioxaundecane diamide (ETH 295)	Ag^{+} −2.50, Li^{+} −3.20, Na^{+} −3.60, Pb^{2+} −3.70,Cu^{2+} −4.00, Ca^{2+} −4.10	29
o-methyldihexylphosphine oxide *O*′-hexyl-2-ethylphosphoric acid	Fe^{3+} −1.67, Mn^{2+} −1.7, Sr^{2+} −2.16, Al^{3+} −2.40, Ni^{2+} −2.5, Co^{2+} −2.59, K^{+} −3.15, Ba^{2+} −3.16, Ca^{2+} −3.22, Cu^{2+} −3.48	35
2-Hydroxyacetophenone oxime thiourea trioxine resin	Fe^{3+} −0.65, Al^{3+} −0.63, Cu^{2+} −0.60, Ca^{2+} −0.49	27
1,18-Diaza-3,4;15,16-dibenzo-5,8,11,14,21,24-hexaoxacyclohexaeicosane-2,17-dione	Fe^{3+} −1.4, La^{3+} −2.1, Cu^{2+} −1.9, Ni^{2+} −1.9, Co^{2+} −2.8, Sr^{2+} −1.2, Cs^{+} −4.0	30
Cyanex 301 (bis(2,4,4-trimethylpentyl) dithiophosphinic acid)	$Th^{4+} < -1.6$, $Al^{3+} < -5.2$, $Fe^{3+} < -2.4$, $K^{+} < -2.4$, $Cs^{+} < -2.7$, $NH_4{}^{+} < -3.4$, $Li^{+} < -3.5$, $Ca^{2+} < -4.6$, $Cu^{2+} < -4.8$, $Co^{2+} < 4.9$, $Sr^{2+} < 5.2$, $Cd^{2+} < 4.5$	This work

Table 5
Determination of $UO_2{}^{2+}$ contents in real samples using standard methods and the developed uranyl membrane electrode.

Sample ID	Concentration (mg L^{-1})			
	Spectrophotometry		Potentiometry	
	ICP	UV	ISE	FIA
S1	9.7 ± 0.1	10.8 ± 0.1	14.2 ± 0.5	13.2 ± 1.6
S2	29.3 ± 0.9	28.6 ± 0.2	30.7 ± 0.2	26.5 ± 0.6
S3	51.9 ± 0.3	50.3 ± 0.6	49.9 ± 0.3	49.7 ± 0.9
S4	59.7 ± 0.1	60.0 ± 0.3	58.5 ± 0.3	60.5 ± 0.9
S5	100.3 ± 1.2	98.5 ± 0.8	101.1 ± 0.5	94.9 ± 0.5

range of 1.0×10^{-5} to 1.0×10^{-1} mol L^{-1} using 0.001 mol L^{-1} HNO_3, pH 3 as a carrier at a flow rate of 3.5 ml min^{-1}. The slope of the calibration plot under FIA mode was near-Nernstian (27.1 mV $decade^{-1}$) and the lower limit of detection was found to be 5.2×10^{-6} mol L^{-1}. A shift of the detection limit to a slightly higher concentration is observed relative to static mode as shown in the inset of Fig. 7. The calibration graph obtained in FIA was utilized in the analysis of real uranyl samples as discussed below.

3.7. *Comparison with some of the reported polymer membrane electrodes*

The potentiometric selectivity coefficients of the optimized polymer membrane electrode based on Cyanex 301 (C7) and some of the previously developed $UO_2{}^{2+}$ polymer membrane electrodes based on various ionophores are depicted in Table 4. As can be seen in this table polymer membrane electrodes based on L3 exhibited selectivity coefficients that are comparable to or better than some the previously reported $UO_2{}^{2+}$ membrane electrodes.

4. Analytical applications

Nuclear safeguards are applied to verify that nuclear material held by States is not diverted from peaceful purposes. There are many analytical techniques used in the verification activities. Those techniques should provide accurate and independent measurements, which could be provided by potentiometric sensors.

The analytical utility of the optimized membrane electrode (C7) was tested by the determination of $UO_2{}^{2+}$ content in different real samples collected from some of the Egyptian nuclear facilities and other locations for safeguards verification purposes. The $UO_2{}^{2+}$ content obtained from three replicate measurements for manual and FIA techniques was found to be in satisfactory agreement with that obtained by both ICP-OES and UV–Visible spectrometric techniques (Table 5). No significant difference was found by applying *F*-test at 95% confidence level between mean and variance of the potentiometric and the spectrophotometric set of results indicating good accuracy and precision. The calculated *F* was found to have an average value of 10.9 for the tested samples compared with a tabulated value of 19.2 at 95% confidence limit.

5. Conclusions

Cyanex extractants were utilized to develop $UO_2{}^{2+}$ sensitive and selective polymer membrane electrodes. The influences of membrane composition, pH and foreign cations were investigated. The best performance was obtained with a membrane composition of 32.8 wt% PVC, 65.7 wt% DOA, 25 mol% KTpClPB (relative to ionophore) and 1 wt% L3. Such optimized membrane electrode exhibited a wide linear concentration range of 5.0×10^{-6} to 1.0×0^{-1} mol L^{-1} and showed fast response times. Moreover, the optimized membrane electrode exhibited enhanced response towards uranyl ion over a wide range of other cations. Optimal uranyl selectivity can be achieved by addition of 25 mol% lipophilic anionic sites, while addition of cationic sites results in anionic response. This observation suggests that Cyanex extractants work via a neutral-carrier mechanism within polymeric membranes. The developed $UO_2{}^{2+}$ membrane electrode was applied for manual and FIA monitoring of $UO_2{}^{2+}$ in different real samples for nuclear safeguards verification purposes.

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