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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.

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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, dialkylmonothio-phosphinic 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-trimethylpentyl) monothio-phosphinic 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.

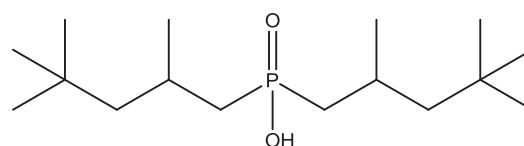
2.2. Reagents and chemicals

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 adipate (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.

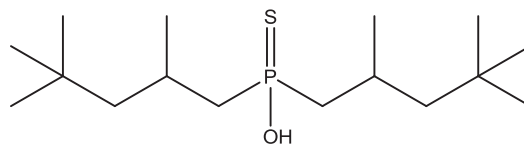
2.3. Preparation of membrane electrodes

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



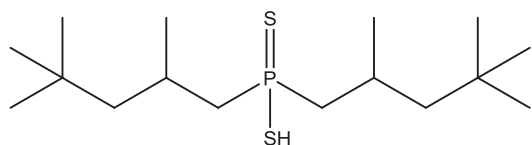
Bis(2,4,4 trimethylpentyl) phosphinic acid

Cyanex 272 (L1)



Bis(2,4,4,-trimethylpentyl) monothio-phosphinic acid

Cyanex 302 (L2)



Bis(2,4,4,-trimethylpentyl) dithiophosphinic acid

Cyanex 301 (L3)

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

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