PVC membrane based potentiometric sensor for uranyl ion using thenoyl trifluoro acetone as ionophore

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Received 30 December 2003; revised 13 April 2004

Uranyl ion selective electrode based on thenoyl trifluoro acetone (TTA) incorporated into a polyvinyl chloride (PVC) membrane has been developed where dibutyl phthalate and sodium tetraphenyl borate have been used as plasticizer and anion excluder respectively. The PVC membrane containing the active ionophore, TTA, and the other ingredients has been directly cast on a graphite electrode. The electrode shows near Nernstian response to UO22+ in the concentration range of 10^-10^⁻^1 mol. L^-1 with an average slope of 30 mV/decade. Alkali and alkaline earth metal ions do not interfere with the determination of uranyl ion. Interference of transition metal ions and Th (IV) is eliminated with EDTA.

IPC Code: In. C7. G01N 27/00

Measurement of uranium concentration is of great importance in nuclear industry due to the application of the element as a fuel in nuclear reactors. It is necessary to monitor the concentration of uranium at various stages of preparation of uranium dioxide fuel pellets and also in the environmental safety assessment related to the nuclear industry. There are several analytical methods commonly used for the measurement of uranium concentration in solution. Depending on the sample matrix and the concentration of uranium, various methods such as spectrophotometry, spectrofluorimetry, potentiometry etc. are used. The potentiometric sensors based on the PVC membrane impregnated with active ionophore have the specific advantage of simplicity, selectivity, speed and cost effectiveness. There are many applications of PVC based membrane electrodes for the determination of different metal ions including UO2²⁺ (ref S 12-15). Most of the electrodes used for the determination of uranium are based on the ionophores of organophosphorus derivative. They show near Nernstian response in the concentration range of 10^{-1}-10^{-5} mol. L^{-1}. In the present study, the chelating β-diketone TTA has been used as the sensing ionophore in a PVC membrane for the potentiometric determination of UO₂²⁺ in solution where a near Nernstian response was obtained for the cation in the concentration range 10^{-1} - 10^{-6} mol. L^{-1}.

Experimental

All reagents used were of analytical grade and deionized water was used for the preparation of all solutions.

Solutions of transition metals were prepared by dissolving weighed quantities of metal chlorides (S D Fine Chemicals, India) in dilute acids. The solutions were standardized by complexometric titration with EDTA using xylene orange as the metallochromic indicator. Uranium solution was prepared by dissolving weighed amount of uranium pellets in dil. nitric acid.

Polyvinyl chloride (PVC) of high molecular weight, dibutyl phthalate (DBP) and sodium tetraphenyl borate (NaTPB) were obtained from E. Merck, Germany.

All the potential measurements were made at room temperature using a digital pH meter (Toshniwal, India, model CL 46) operating in the mV mode. Saturated calomel electrode was used as reference electrode for the potential measurements with the membrane electrode. A combination electrode was used for pH measurements. The ionic strength was maintained using 0.1 M KNO₃.

Preparation of membrane electrode

A graphite electrode (10 mm long, 5 mm dia.) was prepared from spectroscopic grade graphite rod. The rod was fixed with epoxy resin to a glass tube 5 cm long and of appropriate diameter. A copper wire was fixed to the closed end of the electrode using soldering element. The free end of the wire was fitted to an adapter suitable for connecting to the pH meter for measurement of potential. The working surface was polished with fine emery paper. The electrode surface was washed thoroughly with water, methanol and tetrahydrofuran (THF) and dried in air.

A mixture of TTA, DBP and NaTPB in a desired ratio was dissolved in 3 ml of THF. The clear solution
was allowed to stand and evaporate slowly until an oily concentrate was formed. The clean graphite electrode was dipped in the concentrated solution for about a minute so that a nontransparent coating was formed. The electrode was removed from the mixture and allowed to dry at room temperature for 10 - 12 hours. The electrode, after complete drying, was conditioned by equilibrating with 0.1 M solution of uranyl nitrate for two days. This was absolutely necessary for obtaining stable and reproducible potential values.

Results and discussion

The normal procedure for preparing the PVC based cation selective membrane is to prepare a mixture of PVC, ionophore, a plasticizer and anion excluder in a small volume of THF. The membrane is cast on a glass plate by the slow evaporation of THF solution. The membrane is then removed from the glass plate and fixed to a glass or teflon tube. The tube is filled with appropriate internal solution and the contact is established through a conducting wire. Unlike the conventional method of preparation of the membrane electrode as described above, the electrode used in the present study was prepared by casting the membrane directly on the graphite electrode surface as described by Armini et al. There is no internal solution and the external contact to the measuring instrument was made from a direct connection with the graphite electrode. This type of electrode is simple and easy to construct. The lifetime is sufficiently long and the results are reproducible.

The choice of TTA as the ionophore is based on its strong complexing ability (log $K_{uranyl} = 18.4$) and the facilitated transport of UO$_2^{2+}$ using TTA as carrier. The performance of the electrode was tested at various membrane compositions and under different experimental conditions. The optimum membrane composition for the best electrode performance was arrived at by trial with different compositions of the constituents. Each ingredient in the membrane has its specific role to play. The ionophore is responsible for the complexation of uranyl ion and the electrode response due to the difference in the concentration of UO$_2^{2+}$ between the solution and the solid electrode; DBP acts as a plasticizer and sodium tetraphenylborate as an anion excluder. The effect of the variation in the amount of TTA was studied keeping the composition of PVC, DBP and NaTPB constant. The actual amount of ionophore was decided on the basis of the performance of the membrane electrode. In practice, 11.0 mg of ionophore was found to give a reproducible linear response in the range of $10^{-3}$-10$^{-6}$ mol. L$^{-1}$ of uranium. The amount of PVC was varied to change the thickness of the membrane coating. This variation did not significantly affect the electrode performance. However, if the amount of PVC was too low, the membrane became soft and brittle and at higher PVC concentration the electrode response was slow. The optimum concentration of PVC used was found to be 120 mg in 2.0 ml solution of THF. The optimum amount of DBP for the same volume was 2.0 drops (which is about 96 mg). At lower DBP content, proper membrane coating could not be obtained and at higher values, the electrode response was poor. The anion excluder, NaTPB, had significant influence on the measured potential values. In the absence of NaTPB, the variation of the measured potential was non-linear and there was pronounced deviation from linearity particularly at the extreme ends of the concentration axis (i.e., at low and high concentrations).

The pH had significant influence on the potential measurement. At lower pH, there was interference from hydrogen ion and at higher pH, uranyl ion formed hydroxo complex and was precipitated. The results show that the optimum pH range of operation was 3.2 - 4.6. A pH of 4.0 was, therefore, chosen for all measurements.

The electrode showed a near Nernstian response for the uranyl ion concentration in the range of $10^{-3}$-10$^{-6}$ mol.L$^{-1}$ with an average slope of 30.0 mV/decade. The response time, which is the time taken for the potential to stabilize to ± 2 mV, was 25-30s. Although the solid contact electrodes are often criticized for their poor response and stability, the response of this electrode was quick and the lifetime was reasonably long. It is desirable that the performance of any ion selective selective electrode should be checked preferably every time before using it for any analytical work. For the present electrode, it was found that the measured e.m.f. for a uranyl solution of given concentration was reproducible within ± 2 mV anytime during the experiment. There was no significant variation in the calibration and response of the electrode over a period of 30 days. The e.m.f. values were reproducible within ± 5.0 mV of the initial values and there was no significant change in the slope of the Nernst plot. This suggests a longer electrode life and a stable electrode performance. The limit of detection
defined as the concentration of uranyl ion obtained when extrapolating the linear region of the standard calibration curve to the base line is $5 \times 10^{-7}$ mol. L$^{-1}$. This is much lower than the detection limit usually obtained in the membrane based potentiometric sensors. The performance of the electrode was found to be superior in many respects to those reported in the literature.$^{12,15}$ The operating range of the electrode is $10^{-1} - 10^{6}$ mol. L$^{-1}$, whereas the other ion selective electrodes generally operate in the range of $10^{-1} - 10^{5}$ mol. L$^{-1}$. The response time is quicker and the detection limit is lower. The best performance of the electrode could be obtained if it was stored by dipping in $10^{-1}$ mol. L$^{-1}$ uranyl ion solution.

Selectivity

It is seldom possible to choose an ionophore, which is completely selective for a metal ion whose concentration is to be measured. Interferences from various cations are common in most of the membrane electrodes. The interfering cations in the matrix get absorbed into the membrane phase and compete with the analyte (uranyl) ion for occupying the coordination sites of the ionophore. The anions on the other hand, tend to leach out the complexed metal ion from the membrane by forming soluble anionic complexes. The presence of anion excluder NaTPB in the membrane, however, helps to minimize the interferences from anions like fluoride and EDTA.

The reduced form of Eisenman’s equation$^{13}$ is often used to calculate the selectivity coefficient. A more simplified form of the equation$^{16}$ as given below was used to calculate the selectivity coefficients of mono, di and trivalent cations.

$$K = \frac{[UO_2^{2+}]}{[A^{n+}]} \times 10^{n}$$

The potential measured by the mixed solution method with constant concentration of uranyl ion ($10^{-3}$ mol. L$^{-1}$) and varying concentration of interfering ion from $10^{-4} - 10^{-1}$ mol. L$^{-1}$ was used to evaluate the selectivity coefficients from the above equation.

### Table 1 — Selectivity coefficients of cations and anions

<table>
<thead>
<tr>
<th>Ion</th>
<th>$K$</th>
<th>Ion</th>
<th>$K$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$^+$</td>
<td>0.4</td>
<td>Cu$^{2+}$</td>
<td>1.0</td>
</tr>
<tr>
<td>K$^+$</td>
<td>0.6</td>
<td>Fe$^{3+}$</td>
<td>0.16</td>
</tr>
<tr>
<td>Ca$^{2+}$</td>
<td>0.2</td>
<td>Th$^{4+}$</td>
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</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>0.02</td>
<td>EDTA</td>
<td>0.0045</td>
</tr>
<tr>
<td>Pb$^{2+}$</td>
<td>0.1</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* In the presence of EDTA

Table 1 summarizes the selectivity coefficient of different cations calculated from the potential measurements of $10^{-3}$ mol. L$^{-1}$ solutions of uranyl and various interfering ions. The values of selectivity coefficients of different ions were calculated using the above equation. It is seen from Table 1 that the alkali and alkaline earth metal ions do not interfere in the determination of uranyl ion while Fe$^{3+}$, Th (IV) and Cu$^{2+}$ interfered seriously. The interference of Fe$^{3+}$ and Th (IV) could be eliminated using EDTA as masking agent but that of Cu$^{2+}$ could only be reduced partially. These metal ions form stable anionic complexes with EDTA, which are rejected by the membrane. The stability constants for the EDTA complexes of the transition metal ions are very high. The log $K$ values of Cu$^{2+}$, Al$^{3+}$, Fe$^{3+}$ and Th (IV) are 18.8, 16.1, 25.1 and 23.2 respectively.$^{17}$ Thus, the presence of EDTA in the experimental solution enables the determination of uranium even in the presence of transition metal ions and thorium. This is reflected in their selectivity coefficient values (Table 1). Uranium forms a weak complex with EDTA at pH ≤ 4 (log $K$ = 7.4). Consequently, the addition of EDTA did not affect the measurement of the uranyl ion concentration significantly.

Table 2 gives the results of the analysis of synthetic mixtures of UO$_2^{2+}$ and other metal ions using EDTA as the masking agent. The values obtained by this method are in good agreement with those obtained by fluorimetric method.

### Table 2 — Analysis of synthetic samples and comparison with fluorimetric analysis. Interfering ions: $10^{-3}$ mol. L$^{-1}$ each.

<table>
<thead>
<tr>
<th>No.</th>
<th>Matrix</th>
<th>Present method</th>
<th>Fluorimetry</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>Ca$^{2+}$; Mg$^{2+}$; Fe$^{3+}$; Th$^{4+}$</td>
<td>94.2</td>
<td>94.7</td>
</tr>
<tr>
<td>2</td>
<td>Na$^+$; K$^+$</td>
<td>94.4</td>
<td>94.5</td>
</tr>
<tr>
<td>3</td>
<td>Fe$^{3+}$; Th$^{4+}$</td>
<td>94.0</td>
<td>94.3</td>
</tr>
<tr>
<td>4</td>
<td>Cu$^{2+}$</td>
<td>93.3</td>
<td>94.5</td>
</tr>
</tbody>
</table>

* Values in the presence of EDTA

References