Construction of Uranyl Selective Electrode Based on Complex of Uranyl Ion with New Ligand Carboxybenzotriazole in PVC Matrix Membrane

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Abstract. In the present study uranyl selective electrodes in polyvinyl chloride (PVC) matrix membrane were prepared based on a complex of uranyl ion (UO₂⁺) with carboxybenzotriazole (CBT) as ligand. The effect of the nature of plasticizer in PVC matrix were evaluated using three different plasticizers, these are dibutyl phthalate (DBP), dioctyl phthalate (DOP) and bis(2-ethylhexyl) sebacate (BHS). The results of this study indicated that the best plasticizer could be used is the DBP, which may be attributed to its lowest viscosity value compared to DOP and BHS. The electrodes with DBP as plasticizer exhibits a Nernstian response with a slope of 28.0 mV/ decade, over a wide range of concentration from 3.0x10⁻⁵ to 6.0x10⁻² M and a detection limit of 4.0x10⁻⁶ M. It can be used in the pH range of 4.0-10.0 with a response time of less than 10 s for DBP and 25 s for both DOP and BHS. The effects of ions interferences on the electrode response were evaluated. The di- and tri-valent cations were found to interfere less than univalent cations, which was attributed to the high diffusion and the exchange rate between the univalent ions and the uranyl ion solution. The electrodes were characterized by Fourier Transform Infrared Spectroscopy (FTIR) and Scanning Electron microscopy (SEM). The results of the standard addition method were satisfactory with errors less than 7%. The developed electrode was found to be fast, sensitive and reliable indicated its potential use in measuring the uranyl ion concentration in the field.

1. Introduction

Uranium contamination can be introduced to the environment naturally from certain types of soils and rocks. Also, it can be introduced from mining, manufacturing activities, coal and other fuel combustion and nuclear power production. Therefore detection of uranyl ion percentages in water is inevitable due to its toxicity. Furthermore, measurement of uranium concentration is having a great importance in nuclear industries due to the application of metal fuel in nuclear reactors.
The presence of uranium in both water and soil environment and the limitations associated with measuring uranium by the reported techniques [1-4] create a need to develop a fast, sensitive and reliable method for uranium determination in various environmental samples. Ion- selective electrodes methods developed due to their unique advantages such as speed, sensitivity and ease of preparation. In literature, various ligands have been used to prepare uranyl ion selective sensors, such as 1-(4-carboxyphenyl)-1H-1, 2,3-triazole-4-carboxylicacid [5], crown ether [6], and bis(2-hydroxy acetophenone) ethylene diimine [7].

Uranyl ion selective electrodes were prepared using crown compounds in presence of different plasticizers by Nassory et al. [8], and have been tested for determination of uranyl ions in environmental water samples Tyagi et al. [9] have succeeded in preparation of uranyl ion selective electrode based on electro active p-tert-butyl-biscalix[4]arene, and have been used for analysis of tap and sea-water samples. The construction and reliability of uranyl membrane electrodes based on vastly available and affordable amino-(trimethyl)-phosphate were investigated by Badr et al. [10], and have been used in nuclear safeguards verification purposes. PVC membrane electrode for uranyl ion based on 2,2'-[1,2-Ethandiyl bis(nitroethyldiene)]bis(1-naphthalene) was prepared by Shamsipur et al. [11], and was successfully used to the recovery of uranyl ion in tap water. Uranyl selective electrode based on a membrane containing a complex of UO$_2$-bis[di-4-(1,1,3,3-tetramethylbutyl)phenyl phosphate] as an anion-exchanger and tri-tolyl phosphate as a mediator was prepared by Nassory [12], and used for titration of ammonium diuranate. Uranyl ion-imprinted polymers (IIP) resins were prepared by Metilda et al. [13] by dissolving stoichiometric amounts of uranyl nitrate and different ligands. These IIP resins were tested for the recovery of uranium from seawater samples [13].

There are various techniques have been used to determine uranyl ions concentration, such as determination of uranyl in sea water by spectrophotometric method [14,15], determination of uranyl adsorption onto poly(acrylamide-g-ethylenediaminetetraacetic acid) hydrogels in the presence of cadmium and lead by polarographic method [2]. The structural properties of UO$_2$ complex with macro cyclic ligands were studied by NMR [4].

In this study a uranyl selective electrodes using new ligand carboxybenzotriazole in PVC matrix along with different solvent mediators were prepared. These new ion selective electrodes could be used as a sensor, that provide a simple and sensitive method for uranyl determination in the presence of interfering metal ions in environmental water samples and uranium salts. Furthermore, electrode parameters such as pH, ion interferences, detection limit, response time and life time was evaluated.

2. Experimental

2.1. Apparatus

Potentiometric and pH measurements were carried out at room temperature (25.0 ± 0.1 °C) by a professional bench top TRANS MP3001 potentiometer. Potentiometric measurements were carried out using the fabricated sensor in conjugation with silver/silver chloride (Ag/AgCl) as a reference electrode (Orion, Beverly, MA, USA). Thermo Scientific Orion combination pH glass electrode was used for pH measurements. The potential measurements made with a constant moderate stirring at sensitivity of 0.1 mV. Construction of the electrode body and immobilization of uranyl complex in the PVC matrix membrane were done using a reported method by Craggs et al. [16]. A circular disk (10 mm in diameter) of the PVC membrane was attached to the end of Tygon tube using a concentrated PVC/ THF (tetrahydrofuran) solution as an adhesive. The other end of the Tygon tube was fixed into a glass tube in which silver wire coated with silver chloride was inserted, and then the tube was filled with 0.06 M UO$_2$ solution for uranyl electrode and 0.06 M CBT solution for CBT electrode. The electrodes were preconditioned by soaking them in 0.06 M of UO$_2$ or CBT solution for 60 min.

FTIR spectra were recorded using Shimadzu FTIR Affinity-1 spectrometer (Japan), at the range of 400-4000 cm$^{-1}$ with a resolution of 4 cm$^{-1}$. Scanning electron microscopy (SEM) measurements were viewed using F50 electron microscope (Netherland). Spectrophotometric measurements were recorded using a THERMO ELECTRON UVG-9423 Spectrophotometer (U.S.A).
2.2 Reagents and standard solutions
All chemicals were of analytical grade and used as received without further purification. Dioctyl phthalate 99% (DOP), Dibutyl phthalate 97% (DBP) and Bis (2-ethylhexyl sebacate) 97% (BHS) were obtained from ACROS Organics. Carboxybenzotriazole (CBT) was obtained from University of Colorado (Boulder, USA). Hydrochloric acid 37% (from Scharlau), sodium hydroxide (from LOBA chemie), tetrahydrofurane (THF) and N,N-Dimethyleformamide 99.5% (DMF) (from GCC, Cyprus), polyvinyl chloride (from Retest company, China), uranyl nitrate hexahydrate 98% (from RIEDEL-DE HAEN AG), tartaric acid 99.5% (from Sigma-Aldrich), ethylene di-amine tetra acetic acid (BDH, England) and arsenazo (III) 98% (from Fluka Chemie GmbH, Switzerland) were purchased and used in the processes of membranes preparation and evaluation. Analytical grade of nitrate salts of sodium, potassium, copper, barium, calcium cobalt, and lanthanum were used in ions interferences study.

2.3. Uranyl complex formation and membrane preparation
Uranyl-carboxybenzotriazole complex was prepared by dissolving 1.35 mmol CBT (0.22 g) in a mixture of 1 M NaOH (4 mL) and ethanol (4 mL). A 0.675 mmol of UO$_2$$(NO_3)_2$.6H$_2$O was dissolved in 5 mL HNO$_3$. The two solutions were mixed with stirring until a pale yellow complex precipitate was formed. The precipitated complex was filtered and dried at room temperature for 48 h. Then the dry complex was grounded in a mortar and sieved to particle sizes less than 90 µm. Membranes were prepared by dissolving 0.01, 0.02 or 0.4 g UO$_2$-CBT complex in a mixture of DMF (0.5 mL) and THF (5.5 mL), followed by adding a 0.4 mL plasticizer and 0.17 g PVC. The mixture was stirred until a clear homogeneous viscous state was obtained. The solution was poured into a glass ring (5 cm in diameter), and the ring was placed on a glass plate and covered with filter paper for 48 h for slow evaporation of the solvent.

2.4. Preparation of Standard Solutions
A stock standard solution of 0.06 M of uranyl nitrate (UO$_2$(NO$_3$)$_2$) was prepared freshly and daily with ultrapure water, then a working solutions of different concentrations ranged from 1x10$^{-5}$ to 6x10$^{-2}$ M were prepared by appropriate dilution with ultrapure water.

A 0.06 M stock solution of the following interfering ions (Na$^+$, K$^+$, Ba$^{2+}$, Ca$^{2+}$, Cu$^{2+}$, Cr$^{3+}$, and La$^{3+}$) was prepared using the following nitrate salts of these ions, then a working solutions of different concentrations ranged from 1x10$^{-5}$ to 6x10$^{-2}$ M were prepared by appropriate dilution with ultrapure water. A 0.1 M HCl solution and 0.1 M NaOH solution were prepared and used for pH adjustments. Tartaric acid (10%), EDTA (2.5%) and Arsenazo (III) (0.25 %) were prepared and used in the spectrophotometric study. All solutions were prepared using ultra-pure water obtained from water purification system (Aqua Max Ultra 370 series, Anyang, Korea) which provides water with resistivity of 18.2 ohm cm ($\Omega$.cm).

3. Results and discussion
3.1. Effect of the complex amount
Several uranyl electrodes were constructed based on a complex of uranyl ion with a new carboxybenzotriazole (CBT) ligand (the structure of CBT is shown in Figure 1).

The FTIR spectra of uranyl nitrate, CBT and UO$_2$-CBT complex are shown in Figure 2. The FTIR spectrum of CBT (Figure 2B) shows a sharp intense stretching vibrational band of N-H at 3450 cm$^{-1}$, a broad intense stretching vibrational band of O–H at 3200 cm$^{-1}$ and an intense stretching vibrational band of carboxyl group (C=O) in carboxylic acid at a band at 1700 cm$^{-1}$. The bending vibrational bands of N-H are shown at about 1500-1600 cm$^{-1}$ and the stretching vibrational bands of C-N are shown at about 1300-1450 cm$^{-1}$. The probable formation of uranyl-CBT complex has been investigated by FTIR (Figure 2). By comparing the major vibrational mode’s relative intensities and positions of free CBT spectrum (Figure 2B) with those of the uranyl-CBT complex spectrum (Figure 2C) one can observed that the vibrational band positioned at 1700 cm$^{-1}$ (C=O stretching mode, Figure 2C) is disappeared completely when the complex is formed.
Furthermore, Figure 2C showed a dramatic reduction of intensity and shifted to lower energy of the major bands allocated to U–O vibration at 800 and 940 cm$^{-1}$ and the band at 1025 cm$^{-1}$ was vanished completely. These results demonstrate the formation of the uranyl-CBT complex, by forming a bonding interaction between carboxyl group and the uranyl ion. In spectrum of the complex (Figure 2C), the broad and intense band positioned at 3300-3600 cm$^{-1}$ is allocated to O-H's stretching vibrations. The observed broadening of this band indicates the formation of an ice of water over the uranyl ion, through a hydrogen bonding. Figure 2C shows that the N-H stretching vibrational band of CBT in the region of 3300-3600 cm$^{-1}$ is unresolved, however the stretching vibrational band of aromatic C–H located just above 3000 cm$^{-1}$ designating the presence of CBT over the uranyl surface [17]. The intense band located at 1620 cm$^{-1}$ is allocated to OH$_2$ bending vibration (Figure 2C) [17]. In Figure 2C, the sharp and intense band located at about 1000 cm$^{-1}$ is assigned to O–U–O vibration. The weak vibrational band positioned at 1100 cm$^{-1}$ has been allocated to C–O–M stretching mode [18]. The other observed bands located at 850 cm$^{-1}$, and 1225 cm$^{-1}$ are allocated to C–C–N bending vibration, and O–C–N stretching vibration, respectively. From all these results of FTIR study, the formation of a uranyl-CBT complex is evident, and most probably this occur through bonding interaction between uranyl ion and the carboxyl group of CBT.
The morphology of the prepared membrane using the UO$_2$-CBT complex with and without conditioning has been assessed by scanning electron microscope, and images are shown in Figure 3.

![Figure 3(a)](image1)  ![Figure 3(b)](image2)

Figure 3. Scanning electron micrograph of UO$_2$-CBT complex (a) before conditioning, (b) after conditioning.

Figure 3 shows the scanning electron microscopy (SEM) image of the complex UO$_2$–CBT before and after conditioning with 0.06 M uranyl nitrate solution. Inspection of Figure 3a (before conditioning) reveals that the particles of the complex are formed in a regular spherical shape with an average of about 50 μm in diameter. In other hand, Figure 3b (after conditioning) shows that the formed particles look like a colloidal particles growing in a solution, this might take place due to a presence of excess of uranyl and nitrate ions that form ionic atmosphere surrounding the complex and create the formation of electric double layers. The image of the membrane that has been observed in this study is very similar to that observed by Coroian et al. [19] for a membrane that prepared using crown ether and used as potentiometric sensor for potassium ion.

The structure of CBT was found to be suitable to form metal complexes due to the presence of active sides [17,18]. Furthermore, the UO$_2$–CBT complex is extremely soluble in the membrane matrix and has a sufficient lipophilicity. These special properties of UO$_2$–CBT complex prevent leaching the complex from the membrane to the external solution. The membranes were prepared using different masses of UO$_2$–CBT complex (0.01 g, 0.02 g and 0.04 g) and di-butyl phthalate (DBP) as a plasticizer. The internal filling solution was 0.06 M UO$_2^{2+}$ for uranyl sensing electrodes and 0.06 M CBT solution for CBT sensing electrodes. The parameters of the prepared electrodes (named with number from 1 to 6) were calculated from the calibration curves and the results were summarized in Table 1.

All potentials were measured at room temperature, and the calibration curve was constructed for each electrode using uranyl standard solutions with a linear response ranged from 1.0 x 10$^{-5}$ to 6.0 x 10$^{-2}$ M. The calibration curves were prepared by plotting the potential in (mV) versus log concentration of uranyl. Electrode parameters including slopes, working concentrations, detection limit, and correlation coefficients were evaluated from the calibration curves. The detection limits for the electrodes calculated according to a reported literature [20] using the relation 18 mV/z (where, z is the charge) and given in Table 1.

The uranyl electrodes number 1, 2 and 3 (Table 1) were constructed and calibrated at different concentration of uranyl ion ranged from 1.0 x10$^{-5}$ to 6.0 x 10$^{-2}$ M. The potential measurements were made from low to high concentration range. The electrodes were kept in 0.06 M uranyl nitrate solution when it was not in use to avoid any damage due to evaporation of the plasticizer or a cracking of the membrane during drying by exposure to the atmosphere.
Table 1. Specific parameters of UO$_2$ and CBT electrodes using different quantities of the complex.

| Electrode No. | Type of electrode | Quantity of complex | Slope mV/decade | Linear response range /M | Detection limit /M |
|---------------|-------------------|---------------------|-----------------|--------------------------|-------------------|
| 1             | UO$_2$            | 0.01 g UO$_2$-CBT   | 18.6            | 2.0x10$^{-2}$ – 1x10$^{-3}$ | 3.0x10$^{-6}$     |
| 2             | UO$_2$            | 0.02 g UO$_2$-CBT   | 28.0            | 6.0x10$^{-2}$ – 3x10$^{-5}$ | 4.0x10$^{-6}$     |
| 3             | UO$_2$            | 0.04 g UO$_2$-CBT   | 21.0            | 6.0x10$^{-2}$ – 3x10$^{-5}$ | 7.0x10$^{-6}$     |
| 4             | CBT               | 0.01 g UO$_2$-CBT   | 35.0            | 6.0x10$^{-2}$ – 1x10$^{-5}$ | 2.0x10$^{-6}$     |
| 5             | CBT               | 0.02 g UO$_2$-CBT   | 29.9            | 2.0x10$^{-2}$ – 5x10$^{-5}$ | 2.0x10$^{-5}$     |
| 6             | CBT               | 0.04 g UO$_2$-CBT   | 22.9            | 6.0x10$^{-2}$ – 4x10$^{-5}$ | 2.0x10$^{-5}$     |

The listed results in Table 1 show slopes of 18.6, 28.0, and 21.0 mV/decade for electrodes number 1, 2, and 3, respectively, indicating that uranyl electrode number 2, which based on 0.02 g complex, gave the best results among the tested electrodes with a slope near to Nernstian slope of 28.0 mV/decade and having a detection limit of 4.0 $\times$ 10$^{-6}$ in a linear response range from 6.0 $\times$ 10$^{-2}$ to 3.0 $\times$ 10$^{-5}$ M. In addition, the calibration curves of CBT electrode number 5, which based on 0.02 g complex, gave the best results among the tested electrodes with a slope near to Nernstian slope of 29.9 mV/decade and having a detection limit of 2.0 $\times$ 10$^{-5}$ in a linear response range from 2.0 $\times$ 10$^{-2}$ to 5.0 $\times$ 10$^{-5}$ M. Therefore, for construction of UO$_2$ and CBT electrodes, the best mixing ratio of the complex, plasticizer, and PVC is found to be 0.02, 0.30, and 0.17 g, respectively. A typical calibration curve for UO$_2$ electrodes (electrode number 2) is shown in Figure 4.

Figure 4. A typical calibration curves of uranyl electrode based on DBP plasticizer. Membrane composition is complex-DBP (electrode number 2). Mass of the complex UO$_2$-CBT = 0.02 g.
3.2 Effect of the nature of plasticizer
In ion selective electrodes, the proper plasticizer that could be used in preparation of membranes should have desirable nature properties such as, low viscosity, low toxicity, low volatility, compatibility with the polymer, and low solubility in aqueous solution [21]. The nature of plasticizer influences the dielectric constant of the membrane phase, the mobility of the complex and state of ligand. The potentiometric response characteristics of membranes based on 0.02 g UO$_2$ complexes as an electroactive material and three types of plasticizers, these are dibutyl phthalate (DBP), dioctyl phthalate (DOP) and bis(2-ethylhexyl) sebacate (BHS) in PVC matrix were examined. The effects of the plasticizers were studied with respect to the values of slope, response time, linear working concentration range, life time and detection limit. Electrode parameters of uranyl electrodes based on different plasticizers were summarized in Table 2.

Table 2. Electrode parameters of uranyl electrodes based on different plasticizers.

| Membrane composition | Slope (mV/decade) | Linear response range (M) | Detection limit (M) | Response time (s) | Life time |
|----------------------|-------------------|--------------------------|---------------------|------------------|-----------|
| Complex +DBP         | 28.0              | $6.0 \times 10^{-2} - 3 \times 10^{-5}$ | $4.0 \times 10^{-6}$ | 10               | > 6 week  |
| Complex +DOP         | 23.5              | $4.0 \times 10^{-2} - 1.0 \times 10^{-5}$ | $1.0 \times 10^{-5}$ | 25               | -         |
| Complex +BHS         | 23.8              | $6.0 \times 10^{-2} - 1.0 \times 10^{-5}$ | $1.0 \times 10^{-5}$ | 25               | -         |

The data shown in Table 2 indicates that using DBP as plasticizer gave the best results among the tested plasticizers. It is believed that low viscosity of DBP (17 cP at 25 °C), which is less than the viscosity of the other two tested plasticizers (viscosity of DOP = 56 cP at 25 °C, and for BHS = 21.14 cP at 25 °C), seems to be a part from this good behavior of DBP, which make DBP the proper one among the tested plasticizers. The low viscosity of DBP provides a free mobility of the complex in the membrane and high compatibility of the complex with the DBP. Therefore, we have used the DBP as a proper plasticizer in other experiments.

3.3 Response and life time
Dynamic response time is very important factor for ion-selective electrodes. In this study the potential response time was recorded by changing the uranyl concentrations. The response time for electrode based on DBP plasticizer (electrode 2) at $10^{-6}$ M has found to be around 10 s while that for other tested electrodes based on DOP and BHS plasticizers have found to be around 25 s (Table 2), this designated to high viscosity of DOP and BHS relative to that of DBP which hinders the mobility of the complex and takes longer time for equilibrium. The life time for the electrode of uranyl based on DBP plasticizer has found to be around 6 weeks as shown in Figure 5. After 6 weeks, Figure 5 shows that the slopes become constant around 22 mV/decade this behavior indicates that the electrode can be used furthermore after 6 weeks.
3.4 Effect of pH of solution

The effect of pH on electrode response was studied for the prepared electrodes. The pH ranges for measuring uranyl nitrate solutions with concentrations of 1.0x10^{-3} M and 1.0x10^{-4} M were studied at pH range of 2-11. A shift and increase in potential were found at low pH due to hydrogen ions interference (Figure 6). Figure 6 shows better electrode response at higher pH. This result may be attributing to the increase in the negative charge on CBT surface as the pH increases which lead to a stronger interaction between the negatively charge CBT and uranyl ion. The observed small potential drift at higher pH value could be due to the formation of some hydroxyl complexes of UO_2^{2+} (Figure 6). The data that summarized in Table 3 shows that the UO_2 electrode worked properly at pH range from 4 to 11, while the CBT electrode worked properly at pH range of 6-10.

3.5 Selectivity coefficient

The selectivity coefficients have been evaluated using separated solution as recommended by Umezawa et al. [22]. The potential of the electrode is measured using two separate solutions, one containing uranyl ions (A) of activity a_A and charge z_A (in absence of B), the other solution containing the interfering species (B) with charge z_B when (a_A = a_B). The selectivity coefficient (K_{pot}) calculated using the method described by Umezawa et al. [22], using Eq. 1.

$$\log K_{pot}^{A,B} = \left[ \frac{(E_B - E_A) z_A F}{2.303RT} \right] + \left[ 1 - \frac{z_A}{z_B} \right] \log a_A$$

where E_A, E_B are the potential obtained by using solutions A and B (mV), z_A and z_B are the charges of A and B ions, a_A is the activity of A solution, T is the temperature in kelvin, R is the gas constant (8.314 joule/K.mole), and F is the Faraday constant (96500 coulombs). The slopes (in mV/decade) of tested electrodes calculated from the calibration curve (Eq. 1) and were summarized in Table 1 and 2.
Table 3. Values of the pH range for UO$_2$ and CBT electrode based on DBP plasticizer.

| Electrode | Membrane composition | [UO$_2$] = 1x10$^{-3}$ M | [UO$_2$] = 1x10$^{-4}$ M |
|-----------|----------------------|--------------------------|--------------------------|
| UO$_2$    | 0.02 g UO$_2$ + CBT  | 4.2 – 9.8                | 4.6 – 11.0               |
| CBT       | 0.02 g UO$_2$ + CBT  | 6.7 – 10.0               | 6.4 – 10.3               |

Table 4. Values of selectivity coefficients for interfering ions at different concentrations of uranyl ions using electrode based membrane composition of complex-DBP (electrode number 2). Mass of the complex UO$_2$-CBT = 0.02 g.

| Conc./ M | Cr(NO$_3$)$_3$ | La(NO$_3$)$_3$ | Ba(NO$_3$)$_2$ | Ca(NO$_3$)$_2$ | Cu(NO$_3$)$_2$ | NaNO$_3$ | KNO$_3$ |
|----------|----------------|----------------|----------------|----------------|----------------|-----------|---------|
| 1.0 x10$^{-5}$ | 0.347 | 1.260 | 16.700 | 1.270 | 0.410 | 2.68 x 10$^{-3}$ | 9.904 x 10$^{-5}$ |
| 1.0 x10$^{-4}$ | 0.451 | 0.580 | 4.350 | 0.400 | 0.440 | 1.88 x 10$^{-4}$ | 2.39 x 10$^{-4}$ |
| 1.0 x10$^{-3}$ | 0.577 | 0.260 | 1.100 | 0.140 | 0.460 | 1.17 x 10$^{-3}$ | 5.76 x 10$^{-3}$ |
| 1.0 x10$^{-2}$ | 0.752 | 0.120 | 0.290 | 0.050 | 0.490 | 84.02 | 1.42 x 10$^{-3}$ |
| 6.0 x 10$^{-2}$ | 0.918 | 0.060 | 0.110 | 0.020 | 0.540 | 10.74 | 4.90 x 10$^{-2}$ |

The results in Table 4 indicate no interferences for divalent and trivalent ions. However, the univalent ions, Na$^+$ and K$^+$, was found to interfere with the determination of uranyl designating the presence of a strong interaction between univalent ions and CBT, in which the stability constant of CBT with sodium and potassium is expected to be much higher than that of CBT with uranyl ion. Therefore, it is difficult to measure the uranyl ion in samples containing univalent ions. The interference of trivalent ions, La$^{3+}$ and Cr$^{3+}$, was found to depend on the electronic structure of the tested ions which determine the type of interaction with CBT. The results of this study show that the selectivity coefficients for the Cr$^{3+}$ ion increases from 0.374 to 0.918 as the concentration increases form 1.0x10$^{-5}$ M to 6x10$^{-2}$ M, an opposite behavior was found for La$^{3+}$ (Table 4). Figure 7 shows the variation of selectivity coefficient of La$^{3+}$ with log [La$^{3+}$]. Based on the results of this study the selectivity coefficients have found to be dependent on the type (charge) and concentration of interfering ions (Table 4).

3.6 Quantitative analysis

Standard addition method (SAM) was used to determine the concentration of uranyl ions in synthetic samples at three concentrations 1.0 x 10$^{-3}$, 1.0 x 10$^{-4}$ and 1.0 x 10$^{-5}$ M. 50 ml of a synthetic uranyl nitrate solution was used as unknown and the electrode used is based on electrode number 2. The results of standard addition method were summarized in Table 5.

Table 5. Results of standard addition method for three concentrations of synthetic uranyl solutions using UO$_2$ electrode based on DBP plasticizer (electrode number 2).

| Standard deviation | Percent recovery | Measured UO$_2$ concentration | Calculated UO$_2$ concentration/M |
|--------------------|-----------------|------------------------------|----------------------------------|
| ± 0.073            | 107%            | 1.07 x 10$^{-3}$             | 1.0 x 10$^{-3}$                  |
| ±0.070             | 100.8%          | 1.008 x 10$^{-4}$            | 1.0 x 10$^{-4}$                  |
| ±0.716             | 83%             | 0.83 x 10$^{-3}$             | 1.0 x 10$^{-5}$                  |
Satisfactory results of percent recovery were found at high concentration of uranyl ion (at $10^{-3}$ M and $10^{-4}$ M), while the percentage of recovery decreases to 83% at low concentration of uranyl ion ($10^{-5}$ M). This result is consistent with the fact that the concentration of uranyl ion at $10^{-5}$ M is located in the non-linear response range of the calibration curve. A typical plot for standard addition method for uranyl solution at concentration of $10^{-4}$ M is shown in Figure 8. Uranyl electrode based on DBP plasticizer (electrode 2) was used for uranyl ion determination in water samples taken from different sites. The experiments showed that the uranyl ion concentration cannot be detected in the samples because it is under the detection limit of the tested electrode. Also the water samples were checked for uranyl concentration by using UV-vis spectrophotometer method [23]. For a synthetic solution of $10^{-5}$ M uranyl nitrate, the percentage of recovery was found to be around 97%. Furthermore, uranyl concentrations in all tested water samples couldn’t be detected by spectrophotometric method because it’s under the detection limit ($3.5 \times 10^{-7}$ M).

![Graph 1](image1.png)

**Figure 7.** Variation of selectivity coefficient of UO$_2$ electrode with different concentration of lanthanum nitrate.

![Graph 2](image2.png)

**Figure 8.** Standard addition method for water sample UO$_2$ electrode (electrode number 2). Concentration of synthetic solution = $1.0 \times 10^{-4}$ M. $E$ = potential and $S$ = slope. ). Membrane composition is complex-DBP. Mass of the complex UO$_2$-CBT = 0.02 g.

4. Conclusion
In this study new uranyl selective electrochemical sensors in polyvinyl chloride (PVC) matrix membrane were prepared based on a complex of uranyl ion (UO$_2^+$) with carboxybenzotriazole (CBT) as ligand and have been successfully evaluated for uranyl ion determination is synthetic water samples. The best plasticizer could be used is in PVC matrix was found to be dibutyl phthalate (DBP). The electrodes with DBP as plasticizer exhibit a Nernstian response. The developed electrode exhibited short response time and it was found to be sensitive, selective and reliable indicated its potential use in measuring the uranyl ion concentration in the field. Also, it has a stable potential over a wide pH range and good stable shelf life for about six week using electrodes with DBP.

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