

# Selective Separation of Uranium (VI) ion From Different Media Using Chloromethylated Polystyrene Polymer Modified with Zincon

Adel M. El-Menshawy \*and Fathi K.A.wad\*\*

\**Department of Chemistry, Faculty of Science, Mansoura University, Mansoura, Egypt*

\*\* *Department of Chemistry, Faculty of Science at Suez, Suez canal University, Egypt*

E-mail address: [awadpoll@yahoo.com](mailto:awadpoll@yahoo.com)

**Summary:** Chloromethylated polystyrene polymer modified with 2- carboxy-2-hydroxy-5-sulfo-formazyl-benzene (Zincon) has been developed, for the selective separation and/or preconcentration of Uranium ion. The resulting modified resin was characterized using elemental analysis and infrared spectra. Batch and column techniques were applied in this work. The newly modified resin quantitatively sorbs uranium ion at pH 3-5 when the flow rate is 15 mL min<sup>-1</sup>. The sorption capacity was 0.690 mmol g<sup>-1</sup> of the resin for Uranium ion, while the preconcentration factor was 250. The lower detection limit was 1 ng mL<sup>-1</sup> and its desorption was effective with 5 mL of 0.5 mol L<sup>-1</sup> HCl or HNO<sub>3</sub> prior to detection spectrophotometry. The modified resin was highly ion-selective in nature even in the presence of large concentrations of electrolyte or organic media, with removal ability for Uranium ion. The developed modified resin was tested for its utility with synthetic, real and certified ore samples. The shows method R.S.D. values of < 2% reflecting the accuracy and reproducibility of data using the newly modified resin.

## Introduction

The intense current interest in uranium arises from its known toxicity and the possibility of human exposure to it. Severe exposure to uranium compound can cause acute renal failure; uranium is also known to induce minor damage to the liver <sup>(1)</sup>. In many instances, the low concentrations of uranium undetected and the presence of high levels of potentially interfering matrix constituents preclude its direct determination. As a result, various separation and preconcentration tools are often employed prior to analysis <sup>(2)</sup>. Liquid-liquid extraction procedures are mostly used for separation of uranium <sup>(3-5)</sup>. However, such treatment is relatively expensive <sup>(6)</sup>. Solid phase extraction (SPE) is experienced with several major advantages over the classical liquid-liquid extraction technique. Some of these advantages include; 1) fast, simple and direct application in very small sample amounts (micro liter volumes) without any loss; 2) no waste generation as practiced in the liquid-liquid extraction method, 3) low risk of contamination, and 4) time and cost saving.

SPE is based upon modification of a solid support for separation of metal ions from complex matrices. Two methodologies are adopted for preparation of the solid phase. One is based upon the physical adherence of a suitable reagent on the solid support, while, the second one

involves binding of a chelating ligand to the support material. Various solid phase extraction methods were developed using different types of solid supports such as activated carbon, naphthalene, benzophenone, octadecyl bonded silica membrane disks and polymeric resins, etc. for separation, pre-concentration, and recovery of uranium<sup>(7-8)</sup>. The solid phases modified using 4,4-bis-[bis-(2-ethyl-hexyl)-carbamoyl]-2-oxo-butyl]-phosphinic acid<sup>(8)</sup>, succinic acid<sup>(9)</sup>, o-vanillinsemicarbazone<sup>(10)</sup>, pyrogallol<sup>(11)</sup>, calixarene-o-vanillin semicarbazone<sup>(12)</sup>, N,N,N',N'-tetrahexylmalonamide<sup>(13)</sup>, as sorbents were prepared by chemical interaction with the support. Such a process involved tedious chemical reactions. Some of these methods had pre-concentration factors less than 150 and lower sorption capacity<sup>(9-15)</sup>. Accordingly; we are hardly trying to find a new modified resin could overcome these difficulties. In this work, a new type of modified polymer is prepared by reacting 2- carboxyl-2-hydroxy-5-sulfo-formazyl-benzene(Zincon) with chloromethylated polystyrene polymer and its sorption behavior toward Uranium(VI) ion has been investigated in batch and column modes.. The procedure has been successfully applied for separation and preconcentration of Uranium(VI) ion from natural water and certified Uranium ores.

## Experimental

### *Reagents*

Commercial chloromethyl poly (styrene)-copolymer with divinyl benzene (CMPS - polymer) (MP-500A; Bayer Co., Germany); 2% DVB; specific surface area (BET) is  $66 \text{ m}^2\text{gram}^{-1}$  and  $46 \text{ meq Cl gram}^{-1}$  resin was used. 2- carboxyl-2-hydroxy-5- sulfo- formazyl- benzene (Zincon), cetyltrimethyl ammonium bromide (CTAB) and a stock solution of Uranium (VI) ( $1000 \mu\text{g mL}^{-1}$ ) was prepared by dissolving appropriate amounts of uranyl acetate (Aldrich, USA) in deionized water. Arsenazo III (Fluka, Buchs, Switzerland), 0.1% (w/v) was prepared by dissolving 0.1 gram of the reagent in 100 ml of deionized water. Uranium (VI) ion purchased from the Canadian Certified Reference Material Project (CRMP) and kindly supplied by the Atomic Energy Authority, Cairo, Egypt

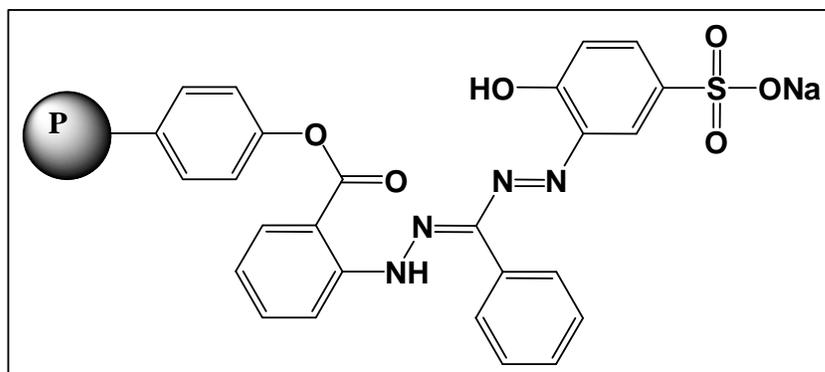
### *Equipment*

The reaction was followed up in all experiments with the aid of FT-IR spectroscopic analysis. Potentiometric measurements were performed using a Metrohm E53b potentiograph equipped with a 665 DOSIMAT (Metrohm, Herisau, Switzerland). The combined glass electrode was standardized before and checked after each titration with buffer solutions produced by FISHER (New Jersey, USA). All titrations were carried out at temperatures from 28 to 40°C and ionic strengths from  $0.04$  to  $0.12 \text{ mol L}^{-1}$  KCl. The temperatures were adjusted by circulating water

from an ultra thermostate (Kottermann 4130, Germany) through the annular space of double-walled pyrex titration cell of 100 mL-capacity. Alkali was added from the Dosimat and the content of the titration vessel was stirred magnetically. A Perkin-Elmer Model 2380 atomic absorption spectrometer (USA) was used. The IR spectra were carried out using Mattson 5000 FTIR spectrometer in the range of 4000–200  $\text{cm}^{-1}$  applying KBr disc technique. UV-visible absorption spectrometric measurements were performed on a Unicam 2001 UV-VIS spectrophotometer using a 1-cm quartz cell. The pH values were measured using a pH-meter (Hanna-Instruments, 8519, Italy) with an expanded scale with an accuracy of  $\pm 0.01$  and it was first standardized with 0.05  $\text{molL}^{-1}$  potassium hydrogen phthalate (pH 4.01) and a standard pH tablet (9.2) at 25 °C.

#### ***Preparation of Z- polymer***

In a 100 ml round bottom flask, 1 g of chloromethylated poly(styrene) polymer was soaked for three days in 25 mL of chloroform as swelling medium. To the swollen polymer 0.5 g Zincon, 0.1 gram CTAB and 5 mL of 30% aqueous solution of sodium carbonate were added. The reaction mixture was refluxed on a water bath and stirred magnetically for 10 hrs, then cooling. The modified polymeric product was filtered off, washed thoroughly with acetic acid, methanol, distilled water, acetone and finally diethyl ether. The polymeric product (Z-P) was dried at 40°C overnight and characterized by means of FTIR spectroscopic, thermal and electronic measurements. The suggested structure of the prepared Z-P is shown in Scheme 1.



*scheme 1. the CMPS polymer modified with Zincon (Z- polymer)*

#### **Investigation for the optimal conditions of the modified resin**

##### ***Batch method***

A sample solution (100 mL) containing a known concentration of the studied metal ion (100  $\mu\text{g/mL}$ ) was transferred to a glass stoppered bottle (250 mL) and after adjusting its pH to the

optimum value, 100 mg of Z-polymer was added. The mixture was shaken for 30 min with a mechanical stirrer. After filtration, the modified resin was washed with double distilled water, and the sorbed metal ion was eluted with 5 ml of  $0.5 \text{ mol L}^{-1}$  HCl and the resulting solution was adjusted to a final volume of 100 mL and determined spectrophotometrically using the Arsenazo III method <sup>(16)</sup>.

#### ***Column method***

Z-polymer (1.00 g) was first swollen for 24 hrs, packed in a glass column of (4 x 10 cm), treated with  $1 \text{ mol L}^{-1}$  HCl (20 ml) at the optimum flow rate and washed with double distilled water until the modified polymer become free from acid. A 100 mL of  $100 \mu\text{g/mL}$  metal ion solution buffered at the optimum pH, was passed through the column at optimum flow rate. After this sorption step, the column was washed with 100 mL of double distilled water to remove any uncomplexed metal ion from polymer bed. The stripping of the metal from the Z-polymer was carried out by suitable eluting agent like HCl and  $\text{HNO}_3$  solution. The eluted solution was collected in a 100 mL calibrated flask and analyzed spectrophotometrically as usual.

#### ***Determination of sorption capacity***

The sorption capacity of the resin for the studied metal ion was determined by shaking the solution containing excess metal ion with 50 mg of the resin under optimum conditions. The maximum sorption capacity for Uranium (VI) ion with Z-polymer is  $0.69 \text{ mmol gram}^{-1}$ .

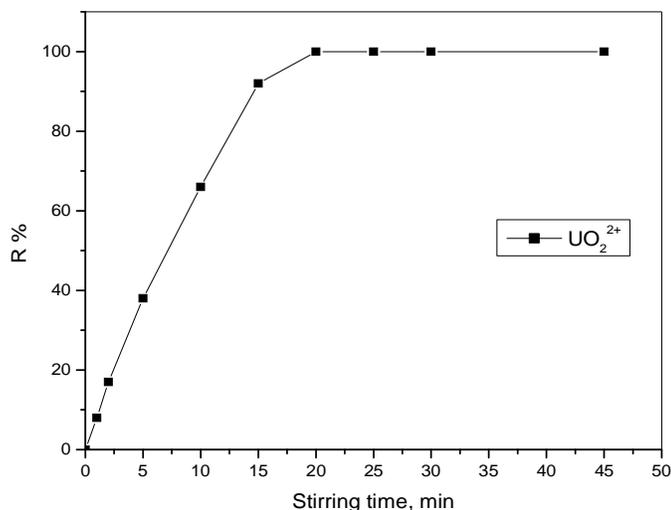
#### ***Effect of amount of resin***

The amount of Z-polymer is an important parameter that affects the recovery of metal ion. The quantitative sorption is not obtained by the smaller amount of Z-polymer than the optimum amount. On the other hand, the excess amount of Z-polymer also prevents the elution of the quantitative sorbed metal ion by a small volume of eluent. For this reason, the used amount of Z-polymer was optimized. To test the Z-polymer amount for quantitative sorption of Uranium (VI) ion, different amounts of Z-polymer from 10 to 1000 mg were used. Quantitative recoveries of Uranium (VI) ion was obtained in the range of 50 –500 mg of the Z-polymer. Thus 50 mg of polymer has been used for subsequent experiments.

#### ***Stirring time***

To determine the rate of sorption of metal ion on Z-polymer, batch experiments were elaborated by shaking the solution containing the ion with 50 mg of the modified resin at room temperature ( $25^\circ\text{C}$ ). Aliquots of 1 ml solution were taken out for analysis at pre-determined

intervals. The concentration of metal ion in the supernatant solution was determined and the amount of metal ion sorbed on the Z- polymer was calculated by mass balance. The sorption half-time ( $t_{1/2}$ ) defined, as the time needed to reach 50% of the total sorption capacity was estimated from Fig. 1. From the data obtained, it was observed that, the maximum sorption of Uranium (VI) ion with Z- polymer reached its equilibrium time after about 20 min. However, the time required for 50% sorption of Uranium (VI) ion was 8 min for Z- polymer.



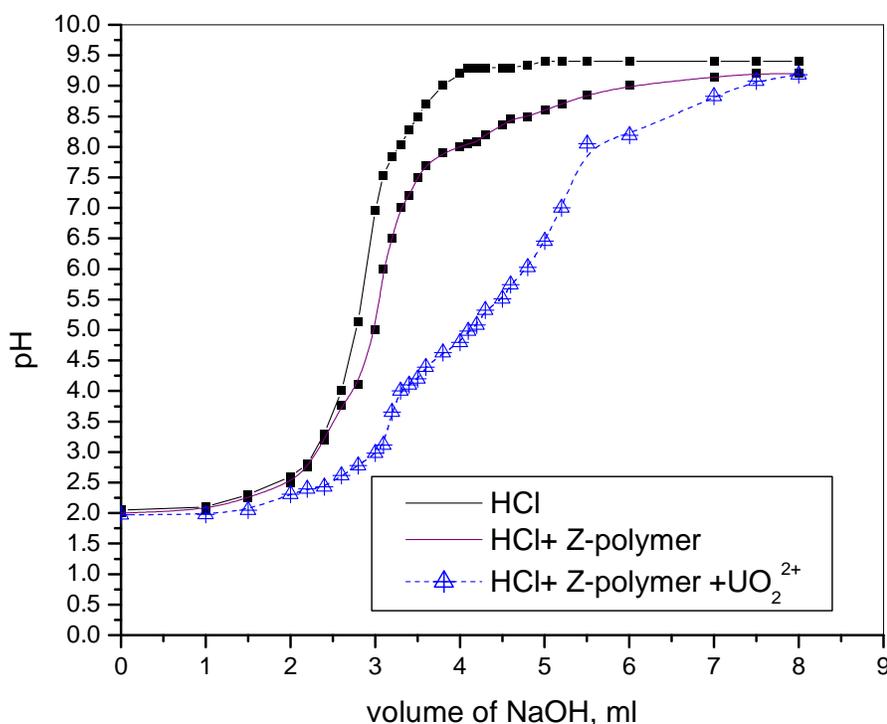
**Fig. 1** Effect of stirring time on the recovery% of Uranium (VI) ion using 50 mg Z- polymer and pH = 3 at 25°C.

### Results and discussion

In order to verify the presence of the active functional groups of zincon in the functionalized polymer, the spectra of the CMPS-polymer and Z-polymer were observed. The IR spectra of CMPS-polymer exhibited a characteristic band at  $701\text{ cm}^{-1}$  which may be attributed to C-Cl band and show also the presence of a broad band attributed to OH stretching at  $3400\text{ cm}^{-1}$  due to the presence of water molecules. Upon modification of CMPS-polymer with zincon (scheme 1), there are additional bands at 3600- 3500, 3160, 1708, 1655, 1630 and  $1050\text{ cm}^{-1}$  corresponding to OH-phenolic, NH, N=N, C=N and  $\text{CH}_2\text{-O}$  bands, respectively. Also, the sharp decrease in the intensity of the band located at  $701\text{ cm}^{-1}$ , may be due to the formation of a new band at  $1050\text{ cm}^{-1}$  and the presence of the phenolic OH was taken as an evidence to the progress of the reaction through ester link<sup>(17)</sup>. Metal-Z-polymer was confirmed by: 1) the shift in C=O and N=N bands to lower wave number by  $20 - 30\text{ cm}^{-1}$  and  $20\text{ cm}^{-1}$ ,

respectively; and 2) the absence of OH- phenolic and NH bands. This behavior indicates that the ligand reacted in the enol- form with Uranium (VI) ion.

The C, H and N content in the Z-polymer estimated by elemental analysis (Calcd. %): C =58.9 (60.2%), H = 4.1 (4.0 %), N = 9.0 (9.7 %)] indicating the formation of Z-polymer. The modification was carried out by 92%. The nitrogen content was measured in Z-polymer which was absent in CMPS- polymer. The shifts observed in pH readings of the titration curve (Fig. 2) for Z- polymer with Uranium (VI) ion than the Z- polymer was taken as a support for the interaction of Z-polymer with Uranium (VI) ion *via* liberation of hydrogen ions. Water regain values were measured by recording the difference in weight of the modified resins after drying at (100 °C) for 48 hours. The water regains values found to be 0.30 g.g<sup>-1</sup> for Z-polymer. Comparison of these values with that of CMPS- polymer itself (0.12 g.g<sup>-1</sup>) indicates appreciable improvement of the sorption capacity of the modified resin

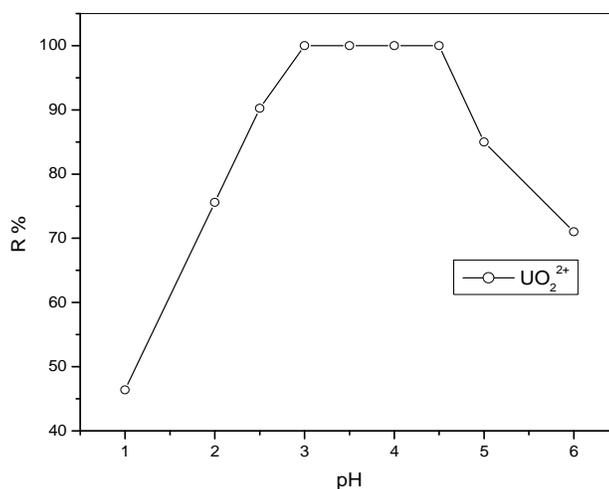


**Fig. 2:** The pH metric titrations of HCl, [HCl + Z- polymer] and [HCl + Z- polymer + Uranium (VI) ion] against 0.0052 mol L<sup>-1</sup> NaOH

### Batch technique

#### *Effect of pH*

The effect of pH on the sorption of the studied metal ion has been investigated in the pH range 1–6 by batch equilibrium experiments. The experiment was elaborated by shaking the solution containing the ion with the modified resin of variable acidity for sufficient equilibrium time. The pH was adjusted using suitable buffer solutions. From data represented in Figure. 3, it could be concluded that, the maximum sorption efficiency of Z-polymer for Uranium (VI) ion was achieved in the pH range 3 –4.5. For subsequent experiments the working media is adjusted pH to 3 for sorption of Uranium (VI) ion. These low pH values are generally preferred for analyzing real samples, such as biological and geological samples which are generally acidic. In addition, these conditions prevent the precipitation of metal hydroxides.



**Fig. 3:** Effect of pH on the recovery % of Uranium (VI) ion at 50 mg modified resin and stirring time 30 min at 25°C

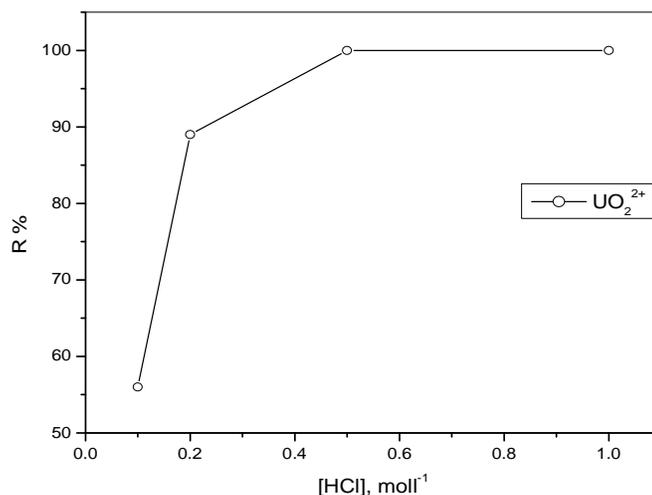
### ***Resin stability***

The modified polymer (50 mg) was shaken with 100 mL of acid (1- 6 mol L<sup>-1</sup> HCl) or electrolytes (0.001-1 mol L<sup>-1</sup> NaCl, KCl and NaNO<sub>3</sub>) and /or organic solvents (ethanol, acetone and chloroform) solutions for 24 hrs, filtered then was washed with doubly distilled water. After air drying, various elemental constituents were investigated. It was found that, there was no change in its composition, which suggests a robust and stable nature of the Z-polymer. The exchange capacity of Uranium (VI) ion on the Z- polymer was subjected to several sorption and desorption (batch) operations. The Z- polymer (50 mg) was stirred with 100 ml of 20 mg L<sup>-1</sup> solution of Uranium (VI) ion for 1 h at room temperature. The Z-polymer was separated and Uranium (VI) ion was desorbed using 5 mL of 0.5 mol L<sup>-1</sup> HCl. It was found that, the sorption capacity after 50 cycles for Uranium (VI) ion varied by less than 2%. Therefore, repeated use

of the Z-polymer is feasible. The capacity of the Z- polymer stored for more than 1 year under ambient conditions has been found to be practically unchanged.

### *Choice of eluent*

Choice of the most effective eluent for the quantitative stripping of the sorbed metal ion on Z-polymer is of special interest. The metal sorbed on the Z-polymer can be eluted with acid solutions (hydrochloric, nitric and sulphuric acid) into the aqueous phase. Other approach was the use of complexing agents such as potassium thiocyanate and EDTA for elution of the sorbed metal ion. Literatures survey showed that, the technique used for determining the concentration of the analyte may be negatively affected by the presence of a complex organic matrix that causes severe suppression of analyte signal. Therefore, the use of acid solution is analytically preferred. Data obtained in (Fig 4.) indicated that,  $0.5 \text{ mol L}^{-1}$  of all acids could afford quantitative elution of Uranium (VI) ion from the Z-polymer. Subsequent elution of metal ion was carried out with hydrochloric acid solution taking the advantage that, chloride ion is an acceptable matrix for both AAS and spectrophotometric determination of metal ion.



**Fig. 4:** Effect of HCl concentration (5 ml) on the recovery of Uranium (VI) ion –Z- polymer = 50 mg; stirring time = 5 min at 25°C.

### *Effect of diverse ions*

The effect of diverse ions which usually accompany Uranium (VI) in its ores (alkaline and alkaline earth elements,  $\text{Al}^{3+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{TiO}^{2+}$ ,  $\text{Th}^{4+}$  and  $\text{Zr}^{4+}$ ) on the recovery of Uranium from aqueous solutions has been investigated. From this 100 mL solution containing  $5 \mu\text{g mL}^{-1}$  Uranium (VI) ion and other ions  $50 \mu\text{g mL}^{-1}$  for each,

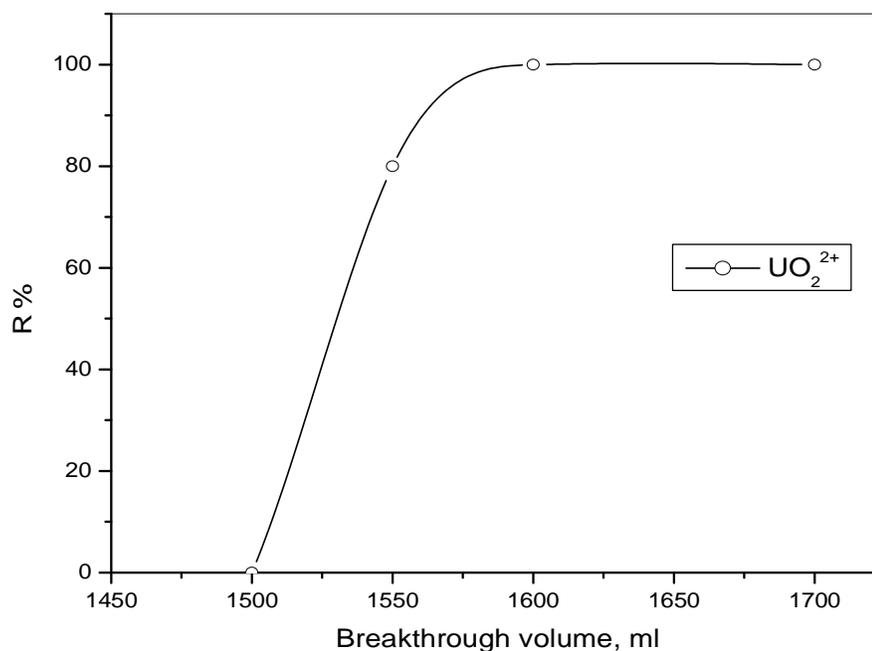
buffered and equilibrated with the Z- polymer at pH 3. Uranium (VI) retained on the resin was eluted and analyzed. The concentration of foreign ions was determined in the mother liquor by AAS. Diethylene triamine penta acetic acid trisodium salt (Na<sub>3</sub>DTPA) was used to suppress the sorption of Cu<sup>2+</sup>, Th<sup>4+</sup>, Fe<sup>3+</sup>, Zr<sup>4+</sup> and TiO<sup>2+</sup> with the Z- polymer as shown in (Table 1) [19].

**Table1.** Influence of interfering cations and anions on recovery percentage of 10 µg ml<sup>-1</sup> UO<sub>2</sub><sup>2+</sup> ion using 50 mg of Z-polymer and shaking for 30 min at 25°C

Interfering ion	Concentration µg ml <sup>-1</sup>	UO <sub>2</sub> <sup>2+</sup> (R %)
K <sup>+</sup>	200	99.6
Mg <sup>+</sup>	200	98.8
Ca <sup>2+</sup>	200	99.0
NH <sub>4</sub> <sup>+</sup>	200	99.5
Acetate	200	100.0
Oxalate	200	65.2
Citrate	200	54.6
Tartrate	200	60.2
Thiourea	200	80.6
SO <sub>4</sub> <sup>2-</sup>	200	99.4
NO <sub>3</sub> <sup>-</sup>	200	99.8
Cl <sup>-</sup>	200	100.0
SCN <sup>-</sup>	200	100.0
F <sup>-</sup>	200	98.9
S <sub>2</sub> O <sub>3</sub> <sup>2-</sup>	200	98.4
EDTA	200	97.6

### ***Breakthrough capacity***

The breakthrough capacity was used to evaluate the amount of metal ion sorbed per gram on the Z-polymer under the optimum operating conditions <sup>(21)</sup>. In order to obtain a breakthrough volume; a glass column (4 x 10 cm) was packed with 1.0g of the Z-polymer. 100 µg ml<sup>-1</sup> of uranium solution buffered at pH 3.0 was passed through the column with a flow rate 5 ml min<sup>-1</sup>. The effluent received after an elapsed time of 5 minutes was fractionized into 5 ml portions and UO<sub>2</sub><sup>2+</sup> ion was determined as usual. The breakthrough volume presented in *Fig. 5* indicates that, the column is exhausted with (160 mg g<sup>-1</sup>) 1600 ml of Uranium (VI) ion.



**Fig. 5:** Breakthrough curve for Uranium (VI) ion with flow rate  $5 \text{ mL min}^{-1}$  at  $25^\circ\text{C}$ .

#### ***Column reuse***

To test the long-term stability of the column containing Z-polymer, it was subjected to successive sorption and desorption cycles by passing a metal ion solution through it at the optimum flow rate. The sorbed metal ion is then desorbed from the Z-polymer by appropriate eluent. The procedure was carried out several times. The stability of the column was assessed by monitoring the change in the recoveries of the sorbed metal ions. Results of fifty sorption /desorption cycles indicated that, the recovery% decreased by 2 –3 % for Uranium (VI) ion, which reflect the good stability of the organic ligand on the Z-polymer.

#### ***Lower limit of metal ion detection***

The lowest concentration of metal ion of interest below which quantitative sorption of the metal ion by the modified resin is not perceptibly seen was investigated using Uranium(VI) ion solution in the concentration range ( $10^{-4}$  to  $10^{-2} \mu\text{g mL}^{-1}$ ) passed through the resin bed at a flow rate  $5 \text{ mL min}^{-1}$ . The limit of detection (LOD) value is  $1 \text{ ng mL}^{-1}$ , shows the high sensitivity of the developed Z- polymer in preconcentration trace analyte down to  $\text{ng mL}^{-1}$  level without any analyte loss.

#### **Analytical application**

**Selective separation of uranium ion from other metal ions:** Due to the association of Uranium (VI) ion with many metal ions, it is crucial to separate uranium from these metal ions. The proposed Z-polymer was found to be effective for such a selective separation. At pH 3.0 the Z- polymer selectively takes up Uranium (VI) ion from an aqueous solution containing a group of metal ions which usually accompany it in its ores when the column procedure is used. The interfering  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Bi}^{3+}$ ,  $\text{Al}^{3+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Be}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Zn}^{2+}$  ions are not retained. The concentration of foreign ions was determined in the mother liquor by Atomic absorption Spectrophotometer (AAS).  $\text{Cu}^{2+}$ ,  $\text{Th}^{4+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Zr}^{4+}$  and  $\text{Ti}^{4+}$  ions are not retained on the presence of Diethylene triamine penta acetic acid trisodium salt ( $\text{Na}_3\text{DTPA}$ ). For eluting Uranium (VI) ion from the resin using 5 mL of 0.5 mol L HCl as an eluent. The amount of Uranium (VI) ion recovered was then determined as usual. Table 2 shows the results of the separation of Uranium (VI) ion from other metal ions

**Table 2.** Separation of  $20 \mu\text{g}\cdot\text{mL}^{-1}$  of Uranium (VI) ion from other metal ions at pH 3.0 in presence of foreign ion (column method).

<b>Metal ion</b>	<b>Uranium found (<math>\mu\text{g mL}^{-1}</math>)</b>	<b>Recovery %</b>	<b>R.S.D</b>
( $\text{Cu}^{2+}$ ) <sup>a</sup>	19.96	99.00	0.25
( $\text{Cu}^{2+} + \text{Fe}^{3+}$ ) <sup>a</sup>	19.85	99.25	1.20
( $\text{Co}^{2+}$ )	20.00	100.00	0.05
( $\text{Ni}^{2+}$ )	20.00	100.00	0.03
( $\text{Co}^{2+} + \text{Ni}^{2+}$ )	20.00	100.00	0.08
( $\text{Pb}^{2+}$ )	19.98	99.90	0.22
( $\text{Th}^{4+}$ ) <sup>a</sup>	19.96	99.80	0.16
( $\text{Zr}^{4+}$ ) <sup>a</sup>	19.92	99.60	0.26
( $\text{Ca}^{2+}$ )	19.99	99.95	0.13
( $\text{Ti}^{4+}$ ) <sup>a</sup>	19.98	99.90	0.15
( $\text{Fe}^{3+} + \text{Al}^{3+} + \text{Co}^{2+}$ ) <sup>a</sup>	20.00	100.00	0.06

<sup>a</sup> In the presence of 2 mL of 0.01 mol. L<sup>-1</sup> DTPA.

(Conditions: flow rate = 5 mL min<sup>-1</sup>, volume of sample = 100 ml, number of measured values, n = 5 at 27°C)

***Selective separation of uranium ion from sea water***

Because no standard reference material for seawater was available, the precision and accuracy of the method was tested by spiking the samples. The results show that, the recoveries are reasonable for trace analysis; in the range of 98- 101% and the recovery of the total uranium ion in the seawater samples were also good. No systematic error was observed. The efficiency of the separating and preconcentration system was high.

***Selective separation of uranium ion from certified ores***

A weighed amount of the certified ore (150- 250 mg) was digested with 10 mL aqua regia and heated to near dryness. Then the sample was heated with 5 mL of concentrated sulfuric acid for 30 minutes. The solution was then diluted and neutralized with NaOH, evaporated, and the remaining solid was ignited at 800 -850°C for short time (5-10 minutes). Sulfates were converted to the corresponding oxides under these conditions. These oxides were boiled with concentrated nitric acid to near dryness, cooled, and diluted with doubly distilled water in a 100-mL calibrated flask. After adjusting the pH of the ore solution and suitable masking agents were added. Then, the solution was passed through the column under optimum conditions. For eluting Uranium (VI) ion from the Z- polymer using 5 mL of 0.5 mol L<sup>-1</sup> HCl as an eluent. The amount of UO<sub>2</sub><sup>2+</sup> ion recovered, determined as usual and the results of analysis are listed in Table 3.

**Table 3.** Recovery % of UO<sub>2</sub><sup>2+</sup> ion from Certified Ores<sup>a</sup> using Z-polymer (column method), (Conditions: flow rate = 5 ml min<sup>-1</sup>, n = 5 at 27°C)

<i>UO<sub>2</sub><sup>2+</sup> ion %</i>					
<i>Ore number</i>	<i>Certificate composition %</i>	<i>Certified %</i>	<i>Found %</i>	<i>Recovery %</i>	<i>R.S.D.</i>
1- BL <sub>2a</sub>	SiO <sub>2</sub> (59.12), Al(6.60), Fe(4.75), Ca(4.06), Na(3.42), Mg(1.50), S(0.36), K(0.33), Pb(0.09)	0.430	0.429	99.76	0.16
2- DH <sub>1a</sub>	SiO <sub>2</sub> (79.75), Fe(5.17), S(4.82), Al(3.44), K(1.43), Mg(0.07), C(0.05), Ca(0.04), Na(0.04)	0.263	0.262	99.62	0.20

<sup>a</sup> Purchased from the Canadian Certified Reference Material Project (CRMP) and kindly supplied by the Atomic Energy Authority, Cairo, Egypt

*R.S.D.* Abbreviated to the relative standard deviation which equal  $\frac{s.100}{\bar{X}}$  where,  $\bar{x}$  is the experimental average and S is the standard deviation.

### Conclusion

It has been demonstrated that the Z-polymer is suitable for trace enrichment of Uranium (VI) ion. The methodology described offers a simple and fast means for selective sorption and preconcentration of metal ions. The elution step does not involve the use of organic solvents as other procedures do. In comparison with other modified resins, the main advantages of Z-polymer were: 1) higher preconcentration factor; 2) higher sorption capacity; 3) low matrix effect; and 4) good precision. Results obtained showed that, Z-polymer can quantitatively sorb very low concentrations of the uranium ion. Beside its stability in strongly acidic medium, the Z-polymer could be recycled for many hundred cycles without any change in its sorption properties. The short loading time ( $t_{1/2}$ ) of Z-polymer is another advantage. The Z-polymer has been demonstrated to be suitable for preconcentration of metal ions in samples with complicated and variable matrices like seawater and certified ores. From the economic point of view, the sorption capacity of Z-polymer, after its versatile use for more than a year and store under ambient conditions, has been found to be practically unchanged.

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