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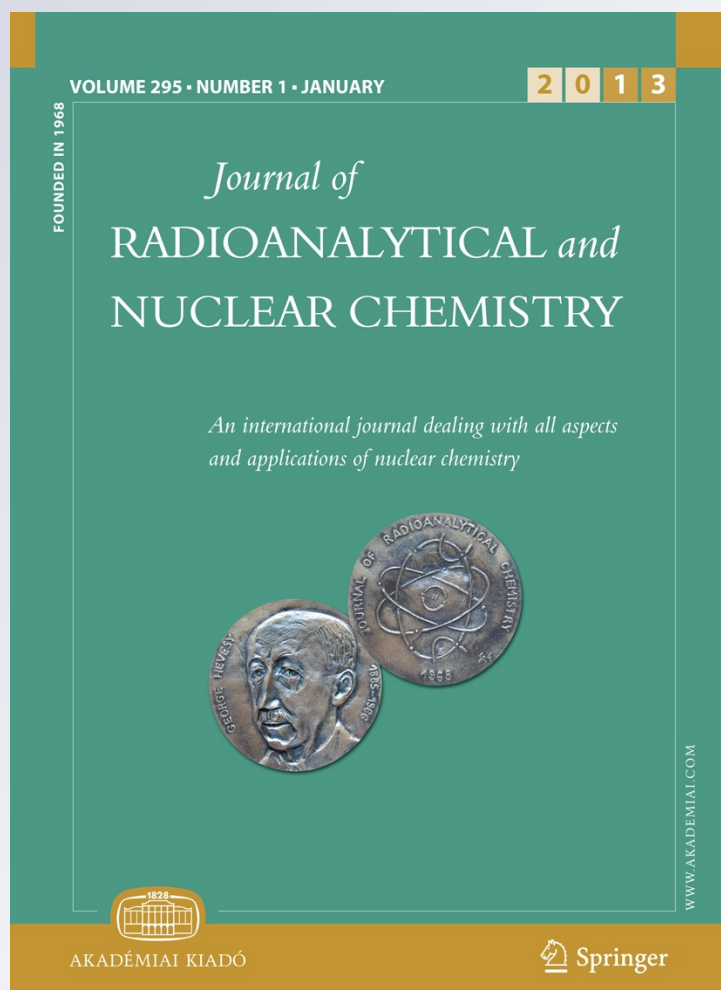
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# Enhanced chromatographic separation of cobalt and uranyl ions using tin (IV) antimonate column from aqueous solution

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**Abstract** The effect of electric field on tin (IV) antimonate column bed to separate cobalt and uranium was investigated. Separation was carried out from nitrate solution and ionic strength of 0.6. Variation of applied potential, time and pH were investigated. Ion mobilities at pH 1 are calculated and given to be  $5.5 \times 10^{-4}$  and  $2.73 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  for cobalt and uranyl ion respectively. Number of theoretical plate heights were calculated from the breakthrough curve and given to be 354 and 210 for cobalt and uranyl ions, respectively. Diffusion coefficient were calculated according to Nernst equation and found to be of  $7.6 \times 10^{-6}$  and  $3.5 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$  for cobalt and uranyl ions, respectively. Also, breakthrough capacities were calculated and found to be 0.7 mmol  $\text{g}^{-1}$  for cobalt ion and 0.4 mmol  $\text{g}^{-1}$  for uranyl ion, respectively.

**Keywords** Electrophoretic separation · Ion separation · Theoretical plate height · Ionic mobility

## Introduction

Separation of uranium and fission products is playing a key role in nuclear fuel cycle [1]. Recovery of these elements is very important for their limited resources and their environmental hazardous [2]. Solid phase extraction became necessary in recent years due to the advantages over other methods like solvent extraction, precipitation, and complexation [3, 4]. Chromatographic column techniques have been extensively studied for metal ion separation [5]. Ion exchange materials like hydrous oxide [6], activated carbon

[7], silica gel [8] and zeolite [9] were also studied for ion separation. Sequential separation of thorium and uranium was studied using Merrifield chloromethylated (MCM) resin with octyl(phenyl)-*N,N*-diisobutylcarbamoyl-methylphosphine oxide (CMPO). The resin shows sorption capacity of 0.96 mM  $\text{g}^{-1}$  for uranium [10]. Tin (IV) antimonate is one of the most radiation, thermal, and acid resistance among other ion exchange materials used in nuclear waste remediation [11].

Separation of uranium and transition metal ions by capillary electrophoresis utilizing complexing agent from aqueous solution were studied [12]. Electrokinetic remediation for uranium removal from aqueous solution was studied. The time required for uranium remediation is found to be 34 days to remove 98 % out of  $2.5 \times 10^{-10} \text{ g}$  initial uranium concentration [13].

The goal of this research was to explore a simple, efficient and economic method for the removal of cobalt and uranyl metal ions from simulated radioactive waste. The authors tried to overcome the complication of the electrophoresis and the time consuming of the column chromatographic method. To achieve this goal the electric potential was applied to a simple column bed matrix. The effect of applied potential and pH to tin (IV) antimonate fixed column bed were investigated for cobalt and uranyl ion separation. Tin (IV) antimonate matrix was used as fixed column bed and the break-through curves were studied. The kinetic parameters as well as ionic mobility were calculated for the ions under investigation.

## Experimental

All chemicals used were of analytical grade and used without further purification. Uranyl nitrate hexahydrate

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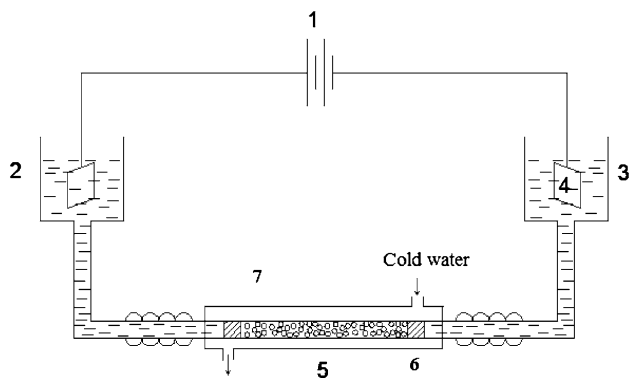
$\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  is obtained from M&Y Dagenham, England. Nitric acid of A.R grade is received from Merck, Germany. Cobalt nitrate hexahydrate  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  is supplied from Sigma-Aldrich, England.

### Methods and preparation

Tin (IV) antimonate was prepared as previously reported [14]. Briefly, adding 4 M antimony pentachloride solution to a 4 mol Sn (IV) chloride solution at Sn/Sb ratio 0.6 at 60 °C. Immediately the mixture was poured to 10 L of cool deionized water and left over night to settle down. The precipitate collected, by the aid of ultra centrifuge, was washed many times till no more chloride ion was detected in the filtration. The collected sample was dried at 60°C overnight and sieved to the desired particle sized. The samples were washed again with deionized water to remove the fine adherent particles and stored under dry atmosphere. Tin (IV) antimonate of 0.2–0.3 mm particle size were used as column bed. The column bed is made of Perspex; poly(methylmethacrylate) supplied by Perspex distribution Ltd. England; with 0.6 cm internal diameter. The column was filled with 3 g of tin (IV) antimonate to give bed length 4 cm. Both ends are blocked with glass wool.

The metal ions of  $1 \text{ g L}^{-1}$  concentration were prepared by dissolving the appropriate weight using deionized water. The pH's were adjusted with 0.1 M of hydrochloric acid or sodium hydroxide solution. The ionic strength of 0.6 was chosen to resemble the conditions of the low level radioactive waste [15].

The experimental arrangement was shown in Fig. 1. The arrangement contains two reservoir of  $200 \text{ cm}^3$  each. The reservoirs were connected from the bottom to the column as shown in Fig. 1. The potential difference was applied using DC power supply through two platinum electrodes of  $1 \text{ cm}^2$  surface area. The applied potential was varied in the



**Fig. 1** Schematic arrangement for the proposed ion separation: (1) DC Volt; (2,3) electrolyte reservoirs; (4) platinum electrodes; (5) column bed; (6) glass wool

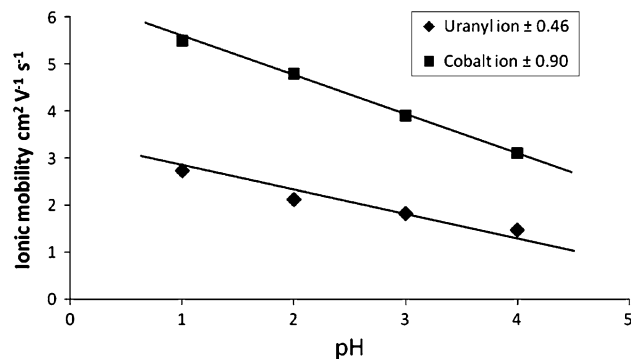
range between 40 and 80 DCV. Higher voltage was circumventing to avoid the gas bubble accumulated around the column matrix, which leads to short circuit. Water was circulated with a convenient flow rate, in the cooling jacket, to control the heat arising due to the applied volt. The anodic reservoir was filled with  $150 \text{ cm}^3$  solution of  $1 \text{ g L}^{-1}$  metal ion concentration at ionic strength of 0.6 and the designed pH. The cathodic reservoir was filled with blank solution identical to the anodic one except for the metal ion. After a specific interval period of time, the solution sample of  $0.1 \text{ cm}^3$  was withdrawn from the cathodic reservoir with the aid of automatic pipette. The samples were analyzed spectrophotometrically for the metal ion concentration. Thiocyanate spectrophotometric method was used to measure the metal ion concentration [16]. Double beam Jasco V530 spectrophotometer was employed to measure the absorbance.

Simulated sample, containing a mixture of  $1 \text{ g L}^{-1}$  of both cobalt and uranyl ions at 0.6 ionic strength and pH 1, was utilized to represent a real waste. For the purpose of statistical analysis all experiments were repeated 6 times and the results were averaged. Statistical calculations of linear regression, standard deviation, and confident limits were calculated.

## Results and discussion

### Effect of pH

The effect of pH values on the ionic mobility was studied. The results show that, as the pH increase the ionic mobility decrease linearly. The slope was found to be negative as shown in Fig. 2. The decrease in ion mobility with the increase of pH suggests the metal ion hydrolysis. The absence of multi platue and the linear relationship between ionic mobility and pH suggest that presence one type of hydroxo species under the experimental conditions



**Fig. 2** Variation of ionic mobility versus pH: uranyl ion (filled diamond), cobalt ion (filled square)

[17, 18]. The calculated ionic mobility of cobalt ion at pH 1 was found to be  $5.5 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ . However, uranium ionic mobility under the same conditions is given to be  $2.73 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ . This difference in ion mobility between cobalt and uranyl ions was due to the difference in ionic size. The ionic size of cobalt is less than uranyl ion at the same solution condition of pH [19]. Accordingly, uranyl ion was retained more than cobalt ion on the bed matrix. This difference in ion mobility was additionally magnified due to the electrostatic interaction between metal ions and tin (IV) antimonate bed matrix.

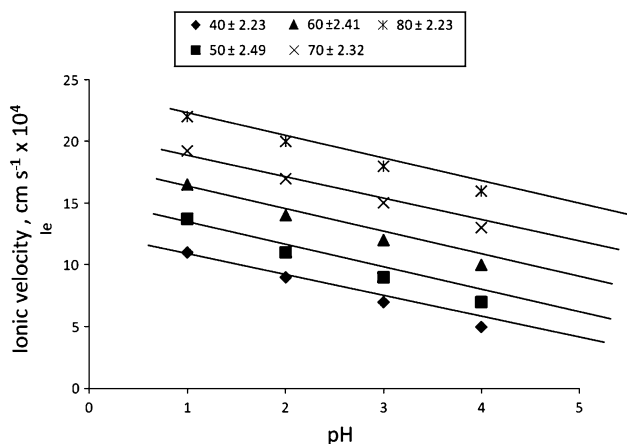
The calculated values of the ionic mobility were found to be less than those values estimated for ions separated via electrophoresis [20]. The low values of ionic mobility can be explained due to the electrostatic interaction between the ions and the bed matrix molecules as explained earlier.

### Effect of applied potential

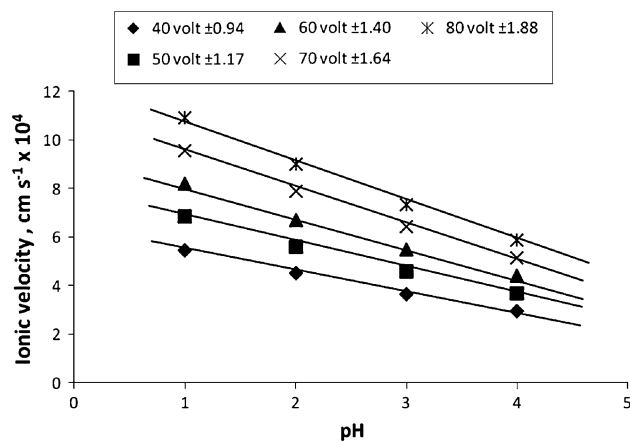
The effect of voltage was studied in the range varied between 40 and 80 V. Gas bubbles were formed at higher voltage around the tin (IV) antimonate particles and create an electric insulation gap preventing ion migration. Accordingly, higher voltage more than 80 V was avoided in any further experiments. The plots of pH versus ionic velocity for cobalt and uranyl ions at different volt were shown in Figs. 3 and 4. The plots were found to be linear under the given experimental condition for both ions.

### Theoretical plate height and retention factor

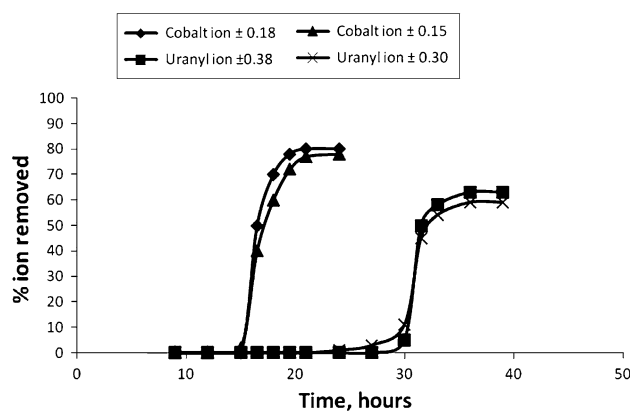
The number of theoretical plate (N) [21], were calculated at 40 V and pH 1 according to the following equation (1). The equation parameters are extracted from the breakthrough curve, as shown in Fig. 5.



**Fig. 3** Uranium ionic velocity versus pH at: 40 V (filled diamond), 50 V (filled square), 60 V (filled triangle), 70 V (times), and 80 V (asterisk)



**Fig. 4** Uranium ionic velocity versus pH at: 40 V (filled diamond), 50 V (filled square), 60 V (filled triangle), 70 V (times), and 80 V (asterisk)



**Fig. 5** Breakthrough curve for cobalt and uranyl ion extract on tin (IV) antimonate under 40 V and pH 1 in separate and mixture solution

$$N = \frac{V_{mb} \cdot \bar{V}}{(V_{mb} - \bar{V})^2} \quad (1)$$

where  $V_{mb}$  is the time to 50 % breakthrough,  $\bar{V}$  is the time to 0.157 % breakthrough.

The number of theoretical plates were calculated and given to be 354 and 210 for cobalt and uranium ions, respectively. Also the theoretical plate heights calculated corresponding to the 4 cm bed length were given to be  $1.1 \times 10^{-2}$  and  $1.9 \times 10^{-2}$  cm for cobalt and uranium ions, respectively. These values indicate the high column efficiency due to the applied electric field. The obtained number of theoretical plate was larger compared to N value (100) of uranyl ion separated on tin (IV) antimonate matrix without applied volt. [5]. This comparison shows the great effect of volt on the number of theoretical plates, supporting the proposed technique of applying potential to column bed matrix.

The column breakthrough capacities were calculated using Eq. (2) [22], and found to be 0.7 mmol g<sup>-1</sup> for cobalt ion and 0.4 mmol g<sup>-1</sup> for uranyl ion. Abdel Badei et al. [15] found that the saturation capacities of cobalt and uranyl ions separated on tin (IV) antimonate were 0.6 and 0.5 respectively, at pH 2 and 0.6 ionic strength.

$$Q_o = \frac{C_o}{W} V \tag{2}$$

where C<sub>o</sub> is the initial concentration in gram mole, V is the volume corresponding to the breakthrough time, W is the bed matrix material per gram.

The retention factor representing the strength of attraction of the ion to the column matrix is calculated according to Eq. (3);

$$R_f = \frac{C_o \times t_{0.5}}{W} \tag{3}$$

where R<sub>f</sub> is retention factor of breakthrough, C<sub>o</sub> is initial concentration in g L<sup>-1</sup>, W is weight of dry bed, t<sub>0.5</sub> is the time required to reduce C<sub>o</sub> to 0.5.

The calculated retention factors were given to be 1.83 and 3.5 for cobalt and uranyl ion, respectively. It is clear that the bed matrix retain uranyl ion more than cobalt ion. This difference in retention factor facilitates the ion separation under the experimental conditions of 40 volt and pH 1.

To obtain realistic results a simulated solution containing cobalt and uranyl ions mixture of 1 g L<sup>-1</sup> each was studied at 40 V, pH 1 and 0.6 ionic strength. Figure 5 shows that the breakthrough curves of the metal ions under investigation as single and mixture ions. It showed that the mixture solution maintained the same behavior as single ion solution. However, the difference between the percent of ion removal of single ion solution and the mixture solution was found to be in the range of 2.5 % for cobalt and 6 % for uranyl ion, respectively. This difference can be explained due to the counter ion effect and the electrostatic interaction between the metal ions and the positive exchange site in tin (V) antimonate cation exchanger. The graph also shows that the time required to 0.5 breakthrough was about 15 and 30 h for cobalt and uranyl ion respectively. The maximum percent ion removal was about 80 and 62 % for cobalt and uranyl ion, respectively. However, Kim et al. [13] studied the removal of uranium from contaminated soil and found that the removal percent was 98 % after 34 days from an original concentration of 4.01 × 10<sup>-3</sup> g g<sup>-1</sup> soil.

The diffusion coefficients were calculated for both ions using the following Nernst Eq. (4) [23];

$$D_i = \frac{u_i RT}{f |z_i|} \tag{4}$$

where D<sub>i</sub> is diffusion coefficient, f is Faraday's constant, u<sub>i</sub> is ionic mobility, z<sub>i</sub> is ionic charge, T is temperature, R is gas constant.

**Table 1** Analytical characteristics

Parameters	Cobalt ion	Uranyl ion
pH		
Linear regression	-0.986	-0.998
Two-side <i>t</i> test ( <i>n</i> - 2) <sup>a</sup>		
<i>t</i>	30.13	8.36
Column confident limit		
For break-through C/C <sub>o</sub> 0.5		
CL 99.9	16.5 ± 0.18	31.48 ± 0.38
CL 99	16.5 ± 0.15	31.48 ± 0.30

<sup>a</sup> Tabulated *i* value of 5 degree of freedom at *P* = 0.01

The calculated diffusion coefficients were found to be 7.06 × 10<sup>-6</sup> and 3.5 × 10<sup>-6</sup> cm<sup>2</sup> s<sup>-1</sup> for cobalt and uranyl ion, respectively. These values are 10<sup>4</sup> and 10<sup>3</sup> fold compared to the results of other workers as a result of applied potential. Abdel Badei et al. found that the diffusion coefficients were 6.13 × 10<sup>-10</sup> and 3.5 × 10<sup>-9</sup> cm<sup>2</sup> s<sup>-1</sup> for cobalt and uranyl ion, respectively, using tin (IV) antimonate ion exchanger [24]. These results indicate the feasibility and efficiency of the electric field application to the tin (IV) antimonate bed matrix in the separation process.

### Statistical analysis

Regression plots showed that there was a linear dependence of ionic velocity over the pH's range studied. Table 1 shows the significant correlation and confident limits of ionic mobility and column performance. The obtained values of two-side *t* test (*n* - 2) and *P* = 0.01 were given and found to be greater than the tabulated values concluding the existence of significant correlation [25].

The column confident limit was calculated for six column replicates. However, the values of the breakthrough time C/C<sub>o</sub> were used to calculate the CL<sub>99.9</sub> and CL<sub>99</sub>. The errors were calculated and found to be 1 and 1.2 % for cobalt and uranyl ion, respectively. Accordingly, the above statistical calculations indicate the reproducibility and validity of the proposed method.

### Conclusion

In this paper, the effects of applied potential and pH on the ionic velocity of cobalt and uranyl ions were examined. The calculated values of ionic mobility indicated the influence of both volt and pH on the ion velocity. The calculated diffusion coefficients support the idea of enhancing ion mobility over tin (IV) antimonate due to the potential application. The column performance investigation indicated the possibility

and efficiency of ion separation utilizing the proposed technique. Also, the bed matrix plays an important role in ion mobility. The results show the ability of employing applied potential to enhance the separation efficiency. Accordingly, the proposed applied potential to the chromatographic column is better than simple column chromatographic technique. The capacities were calculated and found to be  $0.7 \text{ mmol g}^{-1}$  for cobalt ion and  $0.4 \text{ mmol g}^{-1}$  for uranyl ion. More experiments are to be conducted to investigate the response of different metal ions to the proposed technique.

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