

Extraction Chromatography of Co(II), Zr(IV) and Eu(III) Using Long Chain Fatty Acid and Different Eluting Agents

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Summary. Chromatographic studies have been performed on Co(II), Zr(IV) and Eu(III). Chromosorb, as an inert solid support, impregnated by 0.01 M 2-heptyl -2-methyl nonanoic acid (HA) in benzene as an extractant, has been prepared to produce the stationary phase. 0.1 M of HCl, HBr, KI, HNO₃, and H₂SO₄ solutions as well as de-ionized water were used as individual eluting agents. The distribution coefficients (K_d), the breakthrough capacities and the separation factors (α) have been obtained for the studied elements. Column performance as a function of flow rate, column capacity, column internal diameter and bed length were studied at room temperature, $23 \pm 2^\circ\text{C}$ by measuring the number of theoretical plates (H) obtained for Co, Zr and Eu elutions. Van Deemter equation was applied on Co, Eu and Zr elutions using 0.1M HNO₃, and the data revealed that the rate of sorption-desorption is in the order $\text{Co} < \text{Zr} < \text{Eu}$. Optimum separation of the elements has been obtained by using de-ionized water. Higher column performance was obtained with slower flow rate, higher HA loading, smaller internal diameter and longer column bed length at $23 \pm 2^\circ\text{C}$.

Introduction

The isotope ⁶⁰Co is one of the most important radiological isotopes because of its high gamma energies. Its separation from other radioelements is important in the processing and reprocessing of atomic fuel as well as in the treatment of radioactive wastes ^(1, 2). ⁹⁵Zr is one of the most important contaminant isotopes. The separation of this isotope from other elements and isotopes particularly fission products is important in processing and reprocessing of nuclear fuel ⁽³⁾. Europium has a very high cross-section for the capture of thermal neutrons ($\sigma = 4300$ barn). This property finds applications in

neutron detection and in atomic power stations. The use of γ - rays of ^{154}Eu has been recommended for the radiography of metal articles ⁽⁴⁻⁶⁾.

Chromatographic studies on the uptake of Co and U from nitrate solution on Al-13-phosphato-antimonic acid has been carried out ⁽⁷⁾. Extraction chromatography with macro-reticular polymer beads impregnated with mono thio-dibenzoyl-methane solution has been applied for the separation of Co(II) from Ni(II) and Fe(III) ⁽⁸⁾. Zr(IV) and other metal ions have been removed from simulated high level liquid waste by extraction chromatography utilizing the macroporous silica-based polymeric materials ⁽⁹⁾. Combined cation exchange and extraction chromatography techniques has been used for the concomitant separation of Zr, Hf, Th and the lanthanides from geological materials ⁽¹⁰⁾. Zr and other metals were determined in spent pressurized water reactor fuels by ion exchange and extraction chromatographic separations using ICP atomic emission spectrometric analysis ⁽¹¹⁾.

Chromatographic extraction, using HDEHP in kerosene loaded on XAD-4, was applied successfully for recovery of $^{152+154}\text{Eu}$ from a nitrate solution of medium level waste solutions containing other radionulides ⁽¹²⁾. Sorption of Am^{3+} and Eu^{3+} onto an extraction chromatographic resin material prepared by impregnating purified bis-(2,4,4-trimethylpentyl) -dithiophosphinic acid, commercially available as cyanex-301 into chromosorb was investigated ⁽¹³⁾. In the present work the extraction chromatography of Co(II), Eu(III) and Zr(IV) as di-, tri- and tetra-valent metal ions, have been studied using chromosorb impregnated by 0.01 M HA as the stationary phase and different eluents namely 0.1M solutions of HCl, HBr, KI, HNO_3 , H_2SO_4 as well as de-ionised water. The elution characteristics including the column conditions, the elution curves, the breakthrough curves have been investigated. The distribution coefficients, the breakthrough capacities and the separation factors were determined. Column performance as a function of flow rate, HA loading on the column (column capacity), column internal diameter and column bed length was studied at room temperature, 23 ± 2 °C. Van Deemter equation was applied on Co, Zr and Eu elutions by 0.1 M HNO_3 at room temperature. The slopes and

the intercepts of the straight lines were determined and discussed. The optimum separation conditions of these elements were deduced on the basis of the obtained results.

Experimental

Chemicals:

2-Heptyl-2-methyl nonanoic acid (HA), M.W 270.4, density ~ 0.9 g/mL, is A. R. product of Aldrich Chemie, Germany, used without further purification and diluted with benzene from Merck. Chromosorb, a product of Merck, was used as a solid support 0.18 - 0.25 mm (60-80 mesh size). 0.1M of HCl, HBr, KI, HNO₃, and H₂SO₄ were accurately prepared for elution processes. De-ionized water, was used either for elution or preparing the eluents. All chemicals were of analytical grade quality.

Radioactive tracers:

The radioactive isotopes ⁶⁰Co, ⁹⁵Zr and ¹⁵²⁺¹⁵⁴Eu were produced by neutron irradiation of high purity cobalt metal, analytical grade reagent ZrOCl₂.8H₂O and europium oxide, respectively in the Egyptian Research Reactor ET-RR-1 at Inshas for 48 hours. After cooling period the irradiated cobalt was dissolved in concentrated HCl to obtain a stock solution of ⁶⁰Co while the irradiated zirconium and europium were dissolved individually in two separate portions of 6 M HCl to obtain both ⁹⁵Zr and ¹⁵²⁺¹⁵⁴Eu active solutions. ⁹⁵Zr was purified from ⁹⁵Nb by extraction into solution of 0.5 M TTA in xylene⁽¹⁴⁾. In all the work the purity of the produced nuclides as well as their gamma-rays were assayed radiometrically and simultaneously using the multichannel analyser of HPGe detector, Canberra, USA, connected to Genei 2000 programme and 8096 channel. ¹³⁴Cs was obtained from Amersham, U. K.

Column conditions and capacity:

Clean and dry pyrex glass columns were used in this work. The cross-sectional area of the columns were measured as described before ⁽¹⁵⁾. The employed column fitted with tap at its lower end and a small glass wool plug, was 30 cm length and 1.01 cm internal diameter (i.d.), i.e. cross-sectional area (Φ) is 0.801 cm². The stationary phase material was prepared by impregnating 10 g of dry chromosorb beads with 25 mL of 0.01 M 2-heptyl-2-methyl-nonanoic acid (HA) in benzene and this mixture was left to dry in a drying oven at 40 °C for 12 hours. After cooling at room temperature, 23±2 °C, 4.05 g (W_b) of this dry solid phase were gently packed by tamping in the column filled with de-ionized water. Once this happened the tap was opened and continuous flow of liquid through the column began to pack the bed with keeping the water level always covering the solid beads. The beads became wetted and start to settle in the column. After complete settling, the tap was closed and water was maintained above the solid level by at least 1 cm in all circumstances.

The column bed length, L_b , was 8.5 cm and column bed size, V_b , 6.81cm³. The bed density, d_b , was 0.595 g/ cm³. The column capacity (HA loading) according to the used stationary phase was 6.761 mg of HA/ g of dry chromosorb (0.025 mmol of H⁺/ g dry chromosorb) and this capacity was equivalent to 0.67 w/ w % of HA in the prepared stationary phase. (w_s and v_s) weight and volume of of HA in the column were 0.027 g and 0.03 mL, respectively. The flow rate of the employed column was adjusted at 1 ml cm⁻² min⁻¹, at 23±2 °C.

Void volume measurements (v_o or v_m):

The void volume (v_o) of the used column or the volume of the mobile phase in the column (v_m) was measured, in mL, by determining the breakthrough of ¹³⁴Cs eluted with 1 M HNO₃, i.e. $K_d < 10^{-2}$ ^(15, 16). v_m was found to be 2.73 mL giving void fraction ($f = 0.4$).

Column procedure and measurements:

Tracer level mixture, 150 μ l, of the radioactive isotopes ^{60}Co , $^{152+154}\text{Eu}$ and ^{95}Zr dissolved in the appropriate aqueous mobile phase, was loaded on the top of the column. This small volume was taken to avoid sample overload and the peak asymmetry. Then the elements were eluted by the proper eluting agent with the adjusted flow rate in fractions of 1 ml and counting their gamma-rays as described above. The elution was continued till background readings. The elution curves as well as the breakthrough curves were drawn as relations between $(C/ C_o \times 100)$ versus eluate volume in ml, where:

C = radioactive counts/ min in each ml fraction of certain nuclide.

C_o = the original radioactivity loaded on the column of this nuclide.

The free column volumes to peak maximum k' (capacity factor) is determined from the equation ^(16, 17):

$$k' = \frac{V_{\max} - v_m}{v_m} \quad (1)$$

The distribution coefficient K_d was calculated from k' from the following equation (15- 17):

$$K_d = k' \frac{v_m}{v_s} = \frac{V_{\max} - v_m}{v_s} \quad (2)$$

where V_{\max} is the eluate volume to peak maximum (retention volume).

The breakthrough (dynamic) capacity of the element is obtained from the following equation (18):

$$\text{Breakthrough (dynamic) capacity} = \frac{V_{50\%} \times C_o}{W_b} \quad (3)$$

$V_{50\%}$ = eluate volume at 50 % breakthrough, mL.

W_b (bed weight) = 4.05 g,

C_o = initial molar concentration of the element.

The height equivalent to theoretical plate (HETP) or (H), was calculated, from the position and width of the Co, Eu or Zr peaks by the equation given by Glueckauf^(16, 19):

$$N = \frac{8V_{\max}^2}{W^2} = \frac{L_b}{\text{HETP}} = \frac{V_{\max}^2}{\sigma^2} \quad (4)$$

N = number of plates,

L_b = bed length, cm.

W = width of the elution peak at 1/e i.e. (0.37) times the maximum solute concentration, ml.

HETP or H = The height equivalent to theoretical plate, cm.

σ = standard deviation of the elution curve.

Results and Discussion

The main advantage of extraction chromatography versus liquid-liquid extraction lies in the simplicity of the device used to perform the separations⁽⁶⁾. Figures (1-6) show the elution curves of Co(II), Eu(III) and Zr(IV) representing di-, tri- and tetra-valent ions respectively, using different eluting agents. These eluting agents represent variety of ligands containing halide, nitrate, sulphate, and aquo- ligands. Table 1 gives V_{\max} , k' , K_d and separation factors (α) for all the elution peaks of the three studied elements. It is observed from Figure 6 that, no elution was observed at all for Eu(III) by de-ionized water.

It is well known generally that the optimum separation factor between two elements taking the values between $0.8 > \alpha > 1.2$ ⁽²⁰⁾. Accordingly, it is shown from Table 1 that the three elements are best separated using pure de-ionized water as an eluting agent.

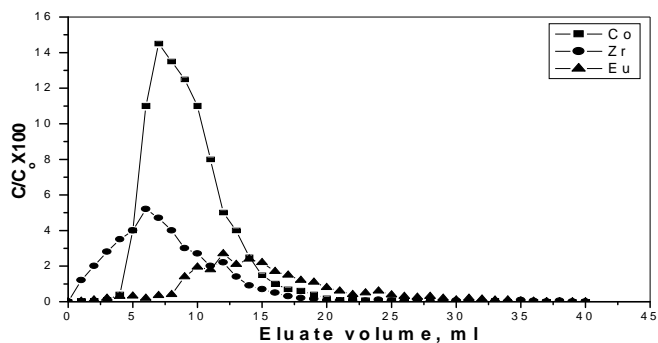


Fig. 1 Elution curves of Co(II) Zr(IV) and Eu(III) from a chromatographic column of HA-chromosorb, using 0.1M HCl at 23 ± 2 °C, HA is 0.672 w/w %, $L_b=8.5$ cm, i.d.=1.01 cm, $V_b=6.81$ cm³, $W_b=4.05$ g, $f=0.4$, $v_m=2.72$ ml, flow rate = 1 ml min⁻¹ cm⁻².

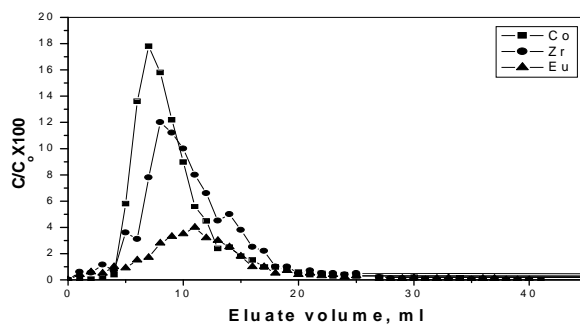


Fig. 2 Elution curves of Co(II) Zr(IV) and Eu(III) from a chromatographic column of HA-chromosorb, using 0.1M HBr at 23 ± 2 °C, HA is 0.672 w/w %, $L_b=8.5$ cm, i.d.=1.01 cm, $V_b=6.81$ cm³, $W_b=4.05$ g, $f=0.4$, $v_m=2.72$ ml, flow rate = 1 ml min⁻¹ cm⁻².

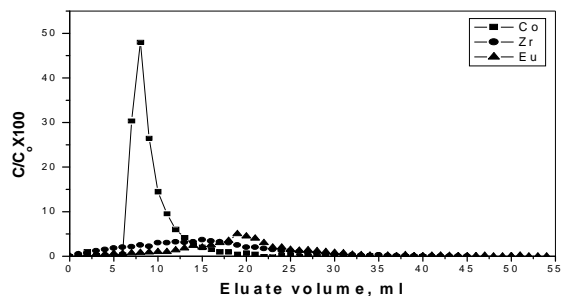


Fig. 3 Elution curves of Co(II) Zr(IV) and Eu(III) from a chromatographic column of HA-chromosorb, using 0.1M KI at 23 ± 2 °C, HA is 0.672 w/w %, $L_b=8.5$ cm, i.d.=1.01 cm, $V_b=6.81$ cm³, $W_b=4.05$ g, $f=0.4$, $v_m=2.72$ ml, flow rate = 1 ml min⁻¹ cm⁻².

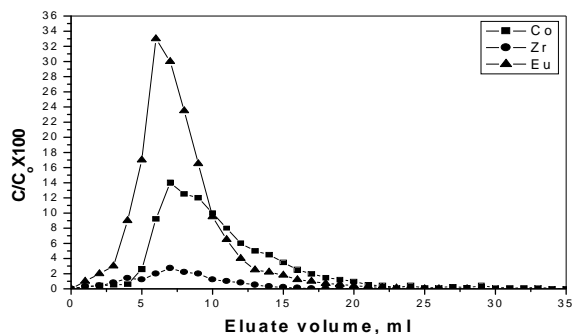


Fig. 4 Elution curves of Co(II) Zr(IV) and Eu(III) from a chromatographic column of HA-chromosorb, using 0.1M HNO₃ at 23±2 °C, HA is 0.672 w/w %, L_b=8.5 cm, i.d.=1.01 cm, V_b=6.81 cm³, W_b=4.05 g, f=0.4, v_m= 2.72 ml, flow rate = 1 ml min⁻¹ cm⁻².

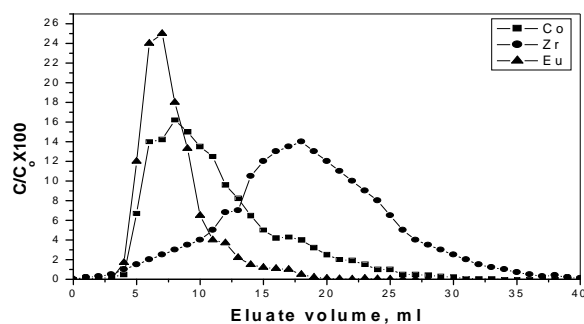


Fig. 5 Elution curves of Co(II) Zr(IV) and Eu(III) from a chromatographic column of HA-chromosorb, using 0.1M H₂SO₄ at 23±2 °C, HA is 0.672 w/w %, L_b=8.5 cm, i.d.=1.01 cm, V_b=6.81 cm³, W_b=4.05 g, f=0.4, v_m= 2.72 ml, flow rate = 1 ml min⁻¹ cm⁻².

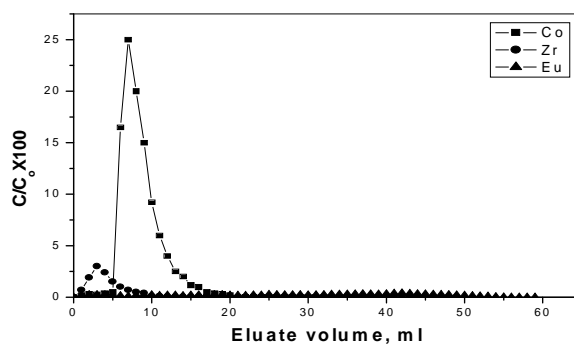


Fig. 6 Elution curves of Co(II) Zr(IV) and Eu(III) from a chromatographic column of HA-chromosorb, using de-ionized water at 23±2 °C, HA is 0.672 w/w %, L_b=8.5 cm, i.d.=1.01 cm, V_b=6.81 cm³, W_b=4.05 g, f=0.4, v_m= 2.72 ml, flow rate = 1 ml min⁻¹ cm⁻².

It is found that Zr(IV) is more eluted from the stationary phase by de-ionized water and Eu(III) not eluted at all (its K_d is very high) i. e. Eu is more bound to the stationary phase, while Co(II) is moderately adsorbed on the stationary phase. This may be attributed to the more extractability of Eu(III) toward the extractant (HA) than Zr(IV) and Co(II); therefore Zr(IV) can be separated in the water effluent from Co(II) under these experimental conditions while Eu(III) is retained on the stationary phase. Also it is found from Table 1 that weak separation is more obtained from 0.1M HNO₃, where the three elements have comparable K_d and separation factor values.

It is also observed from Table 1 that, with respect to halide ions, the three studied elements are best sorbed from KI solution than from HCl and HBr solutions where K_d values are higher and this behavior agrees with the sequence of formation of more stronger complex species between the studied metals and the halide ligands during elution processes according to the order: $Cl^- > Br^- > I^-$ (little deviation is observed with Eu which may be within the experimental error).

In a previous work it has been published that HA as a long chain carboxylic acid reacts with various metal cations via the following equilibrium^(6, 21)



Figure (7) shows the breakthrough curves for Co(II), Zr(IV) and Eu(II) using 0.1M HCl as an eluting agent. The volumes at 50 % breakthrough of the elements were determined from the three curves as 5.4 mL, 9 mL and 21 mL for Co, Zr and Eu, respectively and the dynamic (breakthrough) capacities of the solid sorbent toward the three elements were obtained from equation (3) and found to be 0.007, 0.016 and 0.046 mmol/ g for Co(II), Zr(IV) and Eu(III), respectively.

Table 1: k' , K_d , V_{max} and separation factors (α) of Co(II), Zr(IV) and Eu(III)

Eluent	K_d Co(II)	K_d Zr(IV)	K_d Eu(III)	$\alpha_{Co/Zr}$	$\alpha_{Zr/Eu}$	$\alpha_{Eu/Co}$
0.1M HCl	$k' = 1.56$ $K_d = 142$ $V_{max} = 7$	$k' = 1.2$ $K_d = 109$ $V_{max} = 6$	$k' = 3.4$ $K_d = 309$ $V_{max} = 12$	1.30	0.350	2.18
0.1M HBr	$k' = 1.56$ $K_d = 142$ $V_{max} = 7$	$k' = 1.93$ $K_d = 176$ $V_{max} = 8$	$k' = 3.03$ $K_d = 276$ $V_{max} = 11$	0.807	0.640	1.94
0.1M KI	$k' = 1.93$ $K_d = 176$ $V_{max} = 8$	$k' = 4.5$ $K_d = 410$ $V_{max} = 15$	$k' = 6.3$ $K_d = 533$ $V_{max} = 20$	0.429	0.769	3.03
0.1M HNO ₃	$k' = 1.56$ $K_d = 142$ $V_{max} = 7$	$k' = 1.56$ $K_d = 142$ $V_{max} = 7$	$k' = 1.2$ $K_d = 109$ $V_{max} = 6$	1.00	1.30	0.768
0.1M H ₂ SO ₄	$k' = 1.93$ $K_d = 176$ $V_{max} = 8$	$k' = 6$ $K_d = 546$ $V_{max} = 19$	$k' = 1.56$ $K_d = 142$ $V_{max} = 7$	0.322	3.85	0.807
De-ionized water	$k' = 1.56$ $K_d = 142$ $V_{max} = 7$	$k' = 0.1$ $K_d = 9.1$ $V_{max} = 3$	high (no elution)	15.8	very small 0.01 >	very high 100 <

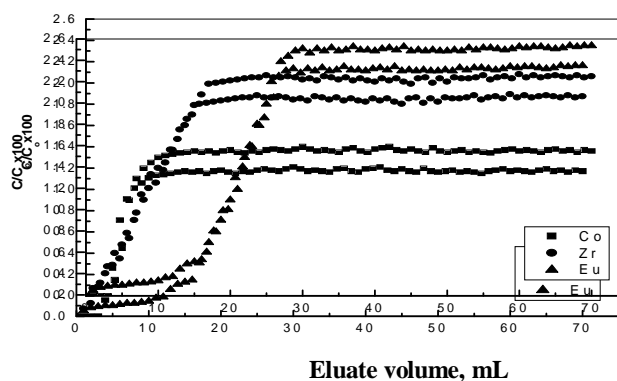


Fig. 7 Breakthrough curves of Co(II), Zr(IV) and Eu(III) using 0.1M HCl at $23 \pm 2^\circ\text{C}$; HA is 0.672 w/w %, $L_b = 8.5$ cm, i.d.=1.01 cm, $V_b = 6.81$ cm³, $W_b = 4.05$ g, $f = 0.4$, $v_m = 2.72$ mL, flow rate = 1 mL min⁻¹ cm⁻².

The column performance study:

A good method for measuring column performance is the calculation of the height equivalent to a theoretical plate (HETP or H) and studying the effect of flow rate on HETP at certain temperature as well as studying the effects of column capacity, column internal diameter and column bed length on the HETP and on the peak spreading⁽¹⁵⁾.

The plate theory assumed that the solute is at all times in equilibrium with both the mobile and stationary phases and the column is considered to be divided into a number of plates^(22, 23).

Table 2 shows width of each elution peak at 1/e of the peak maximum (W), the number of theoretical plates (N), HETP or H and standard deviation of each elution curve (σ), for the elution of Co, Zr and Eu from the column of HA-chromosorb by the employed eluents at 23 ± 2 °C. HETP for each peak was calculated from equation (4).

The values in Table 2 exhibit the features leading to some weakness in the column performance under the experimented conditions. These features are the obtained high values of W, H and σ for the elution curves and smaller number of theoretical plates (N). This observed reduction in the column performance may be attributed to the bigger internal diameter of the used column (1.01cm) with respect to the used bed length, the small amount of HA loaded in the column (0.67 w/w %), and to some packing defects. These observations will be discussed by the following studies.

The relation between the plate height (H) and the flow rate (v) at a given temperature is expressed by the Van Deemter equation^(15, 17):

$$H = A + \frac{B}{v} + C v \quad (6)$$

Where: A= particle size and eddy diffusion parameter, C= mass transfer parameter, and B = longitudinal diffusion parameter, v= flow rate

Figure (8) gives a graphical representation of this relationship at 23±2 °C using 0.1 M H₂SO₄. It is shown that H increases linearly with flow rate (within the experimental error) and three straight lines were obtained corresponding to Co, Zr and Eu. Since the data in Figure (8) shows a linear relationship between flow rate and plate height, the longitudinal diffusion parameter B/v is unimportant at the flow rates studied and drops out of the Van Deemter equation. The slopes of the straight lines give the (C) parameter. Extrapolation of the lines to zero flow rate gives the (A) parameter. Table (3) gives the values of (A) and (C) parameters with their errors and the S. D. of each line. Theoretically the (A) parameter should equal the particle size. It is found that (A) values for Zr and Eu lines (0.35±0.12 mm and 0.45±0.14 mm, respectively) are closer to the particles size range of chromosorb (0.18 - 0.25mm), than (A) value obtained for Co, (0.85 ± 0.0507 mm), which is obviously higher than this range. This deviation in practice may be due to irregular packing and irregular flow (channeling) in the column which in turn causes increased band spreading and larger values of (H), which reflects less column efficiency (15).

The slopes of the obtained straight lines, giving parameter (C), increases in the order:

$$C_{Co} > C_{Zr} > C_{Eu}$$

i.e. (C) parameter increases with decreasing atomic number (z) of the studied elements this means that mass transfer becomes less significant for higher z of the studied elements (and A parameter becomes more significant) in contributing to the plate height (15).

The difference in plate heights (H) between the studied elements, observed in Table 2, may be attributed to mass transfer effects between the stationary and mobile phases (16). As the (C) parameter increases, the rate of sorption-desorption decreases, i.e. rate of equilibrium attainment takes the order (15, 17): Co < Zr < Eu

Table 2: Number of plates, plate heights and peak widths for elution peaks of Co(II), Zr(IV) and Eu(III) by different eluting agents

Eluting Agent	Parameter	Co(II)	Zr(IV)	Eu(III)
0.1M HCl	N, p	10	3	12
	H, mm	8.5	28	7.08
	W, ml	6.25	9.38	10
	σ	2.21	3.46	3.46
0.1M HBr	N	12	8	10
	H	7.1	10.6	8.5
	W	5.63	8.13	10
	σ	2.02	2.83	3.48
0.1M KI	N	63	6	37
	H	1.35	14.2	2.3
	W	2.86	17.9	9.3
	σ	1.01	6.1	3.29
0.1M HNO ₃	N	8	8	12
	H	10.6	10.6	7.01
	W	7	7	5
	σ	2.47	2.48	1.73
0.1H ₂ SO ₄	N	6	15	16
	H	14.2	5.7	5.3
	W	9.44	13.9	5
	σ	3.27	4.9	1.75
De-ion. H ₂ O	N	19	5	No elution (high K _d)
	H	4.47	15.7	
	W	4.55	3.64	
	σ	1.61	1.3	

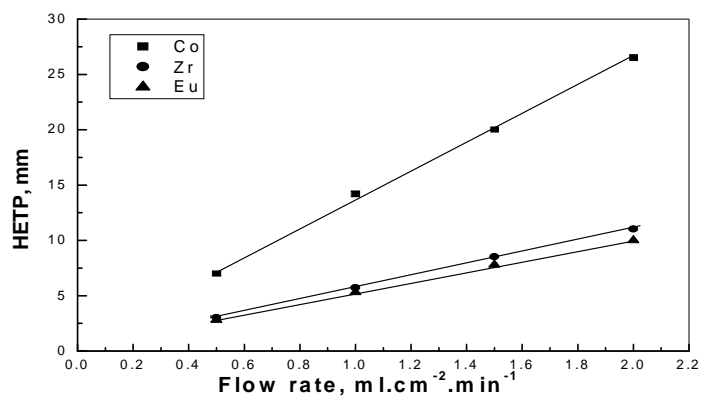


Fig. (8): Effect of flow rate on H, of Co, Zr, and Eu elutions by 0.1 M H₂SO₄ from extraction chromatographic column of HA- chromosorb (0.672 w/w %), bed size $V_b = 6.81\text{cm}^3$, $f=0.4$, $v_m=2.73\text{ ml}$, $23 \pm 2^\circ\text{C}$.

Accordingly, from the obtained (C) values, it may be concluded that flow phenomena may be the major cause of band spreading for Zr and Eu elutions, whereas for Co, slow rate of extraction from the stationary phase to the mobile phase may be the major cause of this spreading at the studied temperature⁽¹⁵⁻¹⁷⁾.

It is also observed from Figure (8) that smaller values of HETP are obtained at slower flow rates which is a better condition for column performance.

Table 4 shows the effect of HA loading in the stationary phase (column capacity), on void volume (v_m), void fraction (f), HETP (H) and K_d under the experimented conditions. It is found from this table that as HA w/w % increases in the stationary phase, f , v_m , H and K_d decrease. This observation refers to improvement of column performance with increasing HA loading in the experimented range. The data in Table 4 may be explained by the multi-level pore structure of chromosorb offered by Ottenstein, where (HA) is probably distributed through out the multi-level pore structure. According to Ottenstein, the liquid phase on a support surface selectively fills the smallest available pores first. Equilibration between the mobile and stationary phases would be slower in the secondary and tertiary pores (because of the longer and more inaccessible diffusion path) than in the primary pores and on the outside surface. The decrease in void volume with an increase in column capacity is a result of the gradual filling of the vacant pores with liquid HA⁽¹⁵⁻¹⁷⁾.

The effect of increasing column internal diameter (i.d.) on HETP is described in Table 5. It is found that increasing i.d. in the experimented range, increases H which is an indication to deficiency in column performance. One could expect an increase in plate heights with increasing internal diameter⁽¹⁶⁾.

Table 3: (A) and (C) parameters obtained by plotting Van Deemter equation for elution of Co, Zr and Eu by 0.1M H₂SO₄ from HA- chromosorb column at 23±2 °C.

Element	A (intercept)	C (slope)	R	S.D.
Co	0.850± 0.507	12.9± 0.370	0.99917	0.41413
Zr	0.35± 0.116	5.36± 0.085	0.99975	0.09487
Eu	0.45± 0.142	4.82± 0.104	0.99954	0.11619

R = Correlation coefficients of the obtained straight lines.

S. D. = Standard deviation of each line.

Table 6 describes the effect of changing the column bed length (L_b) on HETP under the experimented conditions. It is found that HETP decreases with increasing L_b which indicates an improvement of column performance with increasing bed length.

These phenomena can be explained in terms of the plate theory which states that larger number of plates and smaller their heights increases column performance because if the plates are more and smaller in length will causing more efficient solute exchange between the two phases in the column⁽²²⁾.

From the obtained data it is recommended that the best column performance, at the experimented temperature and conditions, has been achieved with columns of smaller internal diameter, longer bed length (L_b), of higher HA loading (higher column capacity) in the stationary phase, and minimum sample loading with keeping regular and slow flow rate.

The observed peak asymmetry in some of the obtained elution curves, as shown from Figures (1-6), is mainly attributed according to the plate theory, to the sample overload and to the variance in moving through the column between the higher and lower concentrations of the respective solute⁽²²⁾. Also, poorer or inefficient packing results in channeling in the stationary phase results in some tailing in elution peaks. Knox and Saleem⁽²³⁾ and Snyder⁽²⁴⁾ have explained this effect by changes in bed structure due to poorer packing of the small

particles of the solid particles (16). The change in packing structure with smaller particles is probably due to particle bridging which creates relatively large inter-particle channels and leads to a lower density and more disordered configuration. The net result of bridging would be to cause more velocity inequalities in the mobile phase stream, which would in turn cause increased band spreading and large values of (H) (25).

Table 4: Effect of HA loading (column capacity) on the plate heights of Co(II) elution by 0.1 M HCl.

wt of HA / g of dry support	w/w %	w_s ,g	v_s , mL	f	v_m ,mL	H, mm \pm 3.53%	v_m/v_s	V_{max} , mL	K_d
3.03 mg	0.300	0.012	0.013	0.47	3.2	10.1	246	6	215
5.05 mg	0.5	0.02	0.022	0.43	2.93	9.5	133	6.5	162
6.76 mg	0.671	0.027	0.03	0.4	2.72	8.8	91	7	144
8.07 mg	0.8	0.032	0.036	0.37	2.52	8.2	70	7.4	136
10.1 mg	1	0.04	0.044	0.30	2.04	7.5	51	7.5	136

Table 5: Effect of column internal diameter, i. d., on the plate heights of Co(II) elution by 0.1 M HCl, $L_b = 8.5$ cm.

i.d., cm	Φ , cm ²	L_b , cm	V_b , cm ³	W_b , g	d_b , g/ cm ³	H , mm $\pm 2.35\%$	K_d
0.5	0.198	8.5	1.68	1	0.595	7.8	144
0.7	0.387	8.5	3.29	1.96	0.596	8.3	141
1.01	0.801	8.5	6.81	4.05	0.595	8.7	143
1.2	1.13	8.5	9.61	5.72	0.595	9.2	141

Table 6: Effect of column bed length on the plate heights of Co(II) elution by 0.1 M HCl.

L_b , cm	A , cm ²	i.d. cm	V_b , cm ³	W_b , g	d_b , g/ cm ³	H , mm $\pm 4.7\%$	K_d
5	0.801	1.01	4.00	2.4	0.6	9.6	140
8.5	0.801	1.01	6.81	4.05	0.596	8.9	144
10	0.801	1.01	8.01	4.77	0.596	8.1	145
15	0.801	1.01	12.01	7.15	0.596	7.6	143

Conclusion

1. 2-heptyl-2-methyl nonanoic acid (HA) in benzene has been used for studying the extraction chromatography of Co(II), Zr(II) and Eu(III) using chromosorb as solid support at 23 +2oC.
2. The three elements are best separated using pure de-ionized water or 0.1M H₂SO₄ eluents.
3. It is found that weak separation is more obtained from 0.1M HNO₃ where the three elements have comparable K_d and separation factor values.
4. The obtained elution sequence by halide solutions took the order : Cl⁻ > Br⁻ > I⁻
5. The dynamic (breakthrough) capacities were determined to be 0.007, 0.016 and 0.046 mmol/g for Co(II), Zr(IV) and Eu(III), respectively on elution by 0.1M HCl.
6. By applying Van Deemter equation, it is found that on increasing the (C) parameter, the rate of equilibrium attainment takes the order: Co < Zr < Eu.

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