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Elution Characteristics of Zn(II) and Sn(II) Using Extraction Chromatographic Technique

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Summary. Extraction chromatographic behavior of radioelements Zn(II) and Sn(II) has been studied using chromosorb impregnated by 0.01 M 2-heptyI-2-methylnonanoic acid (HA) in benzene. This represents the stationary phase packed in the chromatographic column. Different aqueous media were employed as the mobile phase for eluting the sorbet elements. Column specifications as well as the elution conditions have been described. Both elution and breakthrough curves have been performed. The dynamic capacity and the distribution coefficient values have been determined. Extraction characteristics and separation feasibility of the investigated elements have been discussed in the light of the obtained results.

Introduction

2-HeptyI-2-methylnonanoic acid, abbreviated as (HA), is a long chain fatty acid and it is expected that little work might be done using it till now. There is a similarity between HA and versatic acids in which all of them are monocarboxylic acids with long alkyl chains. Versatic acids had been used for extraction and separation of many metals especially transition ones. Thermodynamic studies on the extraction of Am(H[), Eu(m), Zn(H) and Cs by HA in benzene had been carried out(ll2). HA had been used in the extraction chromatography of Am(m), Eu(IH), Zn(TI) and Cs(I) using chromosorb as a solid support and the eluting agent was nitrate solution of 0.1 M ionic strength (H^+/ Na^+ $NO3^+$). Group separation of the four elements was achieved into two pairs: Am-Eu and Zn-Cs.(3J Versatic-10 which is 2-ethyl-2-methyl heptanoic acid extract metal ions by cation exchange mechanism. Medium active waste solutions generated in the reprocessing of spent nuclear fuel always contain actinides and fission products and the removal of these

elements is an important aim. In this respect, solvent extraction process using 20% versatic acid in dodecane had been used.(4J A selective method had been developed for separation of Zr from a variety of elements applying reversed phase extraction chromatography. High molecular weight carboxylic acid, versatic-10 was used as a stationary phase on a column of silica gel. Similar work had been carried out on Th using acetate buffer of pH-4 as the mobile phase, where Th had been separated from many metal ions by exploiting the differences in pH and by selective elution , and on In from acetic acid and sodium acetate solution, where the optimum conditions for extraction were studied based on the critical study of the relevant factors as effects of pH, flow rate and elution A rapid and sensitive method was developed to determine Zn and Sn with other trace elements in ground waters in Bangaladeshe, using high resolution inductively coupled plasma-mass spectrometer.

The separation and analysis of zinc at trace level is very important in biological and medical investigations, since it represents the active agent of many phannaceuticals. The isotope ^{65}Zn is one of the most important contaminant isotopes, as it has high gamma energies, so its separation from other radioelements is of great importance Zinc and tin have been widely used in the developing processes for producing amorphous transparent conductive oxide films Tin is used in the production of indium ^{111}In can be produced from UISn via the reaction ^{112}Sn (n, 2n, E.C)^{111} In is one of the most important radionuclides for nuclear medical applications, and for labeling proteins and peptides.

In the present work, extraction chromatography of Zn(TI) and Sn(n) have been studied using chromosorb impregnated by 0.01M 2-heptyl-2-methylnonanoic acid (HA) in benzene as the stationary phase and different aqueous media as the mobile phase. In this respect the elution characteristics including the column conditions, the elution curves and the breakthrough curves have been performed aiming at investigating the optimum conditions for inter-separating these important elements.

Experimental

Chemicals

2-Heptyl-2-methylnonanoic acid (HA) is A. R. product of Aldrich Chemie, W. 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 h size. 0.1M of HC1, HBr, KI, HN03l H2SO4 and NaOH were accurately prepared r lution processes. Bidistilled water was used either for elution or preparing the elunts. All chemicals were of analytical grade quality.

Radioactive tracers

^{65}Zn and ^{113}Sn were produced by irradiating 0.lg of the respective ^{64}Zn and ^{112}gn targets by (n,y) reactions in the Egyptian atomic reactor E-RR-1 at Inshas. The irradiated samples were dissolved in 6 M HC1 and aqua regia to obtain initial concentrations (Co) 0.031 M and 0.017 M for Zn(H) and Sn(H) respectively. Cooling time of about 24 hour is sufficient to ensure the decay of 1)3mln produced with U3Sn. The purity of the produced nuclides were assayed radio metrically using the multichannel analyzer at the photopeak activities 1115.4 and 511 keV for ^{65}Zn and 255.2 keV for ^{113}Sn. In all the work the gamma-rays of the two nuclides were assayed radio metrically using the single channel analyzer Nucleus-500 Sealer and 2010 Amplifier, USA, connected to Nal/Tl detector.

Column conditions

The used column was 30 cm length, 1.1 cm internal diameter. The weight of the stationary phase was 4.07 g and its bed height was 8.5 cm. The flow rate was 1.2 ml/min.

Procedure

10 g of dry chromosorb beads was impregnated by 20 ml of 0.01M of HA in benzene and dryed in the drying oven at 40°C for 10 hours to produce the stationary phase. 4.07 g of this dry solid was well packed in the used column and the flow rate was regulated as mentioned. The eluting solvents used were 0.1 M of HC1, HBr, KI, HNO_3 H_2SO_4, NaOH and distilled water. 0.05 ml of both radioactive nuclides were loaded individually on the top of the closed column,

then eluted by the respective eluent and the eluates were collected in fractions of 1ml for gamma-ray counting. The elution was continued till background readings. The elution curves as well as the breakthrough curves were drawn.

Results and Discussion

Figures (1-7) show the elution curves of Zn(II) and Sn(II) together, different eluting agents each of 0.1 M, namely: HG1, HBr, KI, HNO3, H2S04) Nap; and distilled water, respectively as individual eluting agents. It is observed from flu figures that V_{max}, which is the eluate volume at maximum elution or the position of elution peaks of both elements are 9, 6.2, 6,7, ,7,15 and 8 ml for elution of Zn(II) j 5, 7, 9, 5, 8, 8 and 20 for elution of Sn(H) by 0.1 M of HC1, HBr, KI, HNO3, NaOH and distilled water, respectively. The distribution coefficients, IQ determined as described elsewhere. 9) These values were tabulated in Table 1. well known that the optimum separation factor between two elements taking the value between $0.8 > a > 1.2$.

Accordingly, it is shown from the data in Table 1 that the two elements are best separated using 0.01M2-heptyl-2-methylnonanoic acid. benzene which impregnate chromosorb and using water as the mobile phase, where Zn(II) is eluted first from the stationary phase according to its Kj value (1.93), while Sn(II) is highly adsorbed on HA in the stationary phase with relatively high Kj value; 6.33, this may be due to more reactivity of Zn(II) than Sn(IT) toward H2O ligand therefore • Zn(H) can be separated in the water effluent from Sn(H) under these experimented conditions by a comparatively high separation factor; a, of Sn/Zn =3.2i Furthermore, Sn(II) can be separated in the aqueous effluent from Zn(II) by relatively high separation factors using 0.1M HC1 and 0.1M NaOH as eluents where a reaches! 2.76 and 2.33, respectively. Again this may be due to higher adsorption of Zn toward HA in the chloride and hydroxide media more than Sn(n) which exhibits easier elution under such conditions.

Figure 8 show the breakthrough curves for Zn(H) and Sn(II) using 0.1M HC1 an eluent from the stationary phase of 0.01 HA in benzene impregnating chromosorb. The volume of 50% breakthrough of both elements is determined from these two figures as 10 ml and 20 ml for Zn and Sn, respectively and used to obtain the dynamic capacity of the solid sorbent toward the two elements.

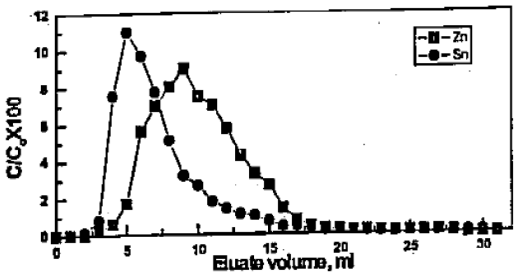

Fig.(1): Elution curves of Zn(II) and Sn(II) using 0.1M HCl at 30±1°C

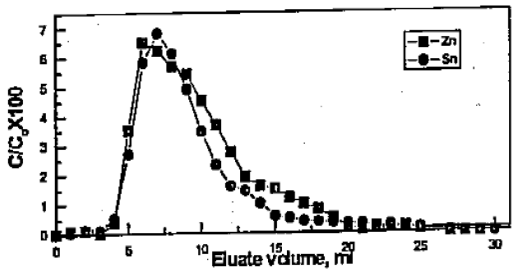

Fig.(2): Elution curves of Zn(II) and Sn(II) using 0.1M HBr at 29±1°C.

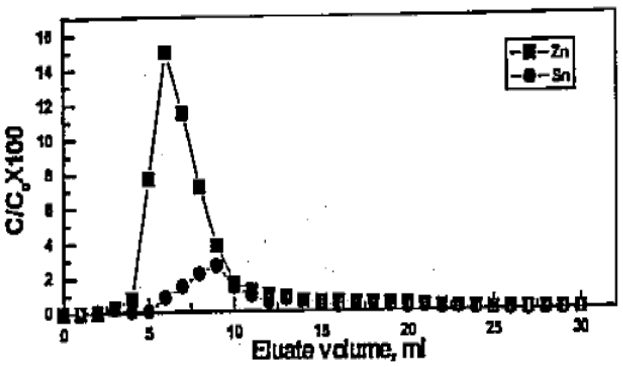

Fig.(3): Elution curves of Zn(II) and Sn(II) using 0.1M KI at 30±1°C.

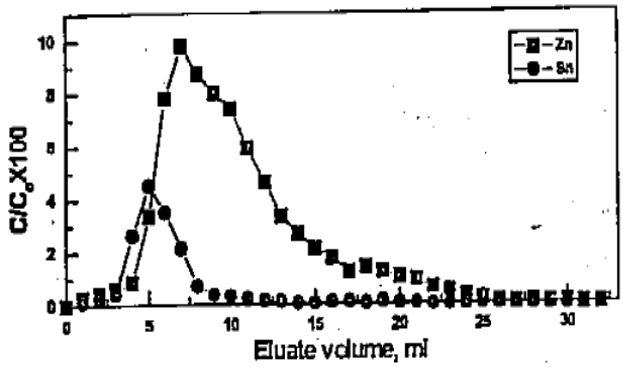

Fig.(4): Elution curves of Zn(II) and Sn(II) using 0.1M HNO_3 at 28±1°C.

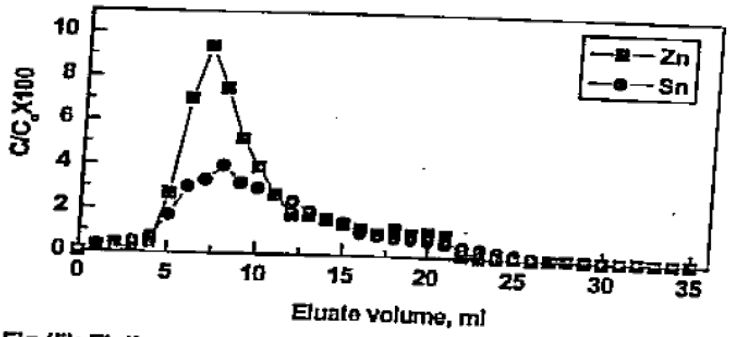

Fig.(5): Elution curves of Zn(II) and Sn(II) using 0.1M H_2SO_4 at 29±1°C.

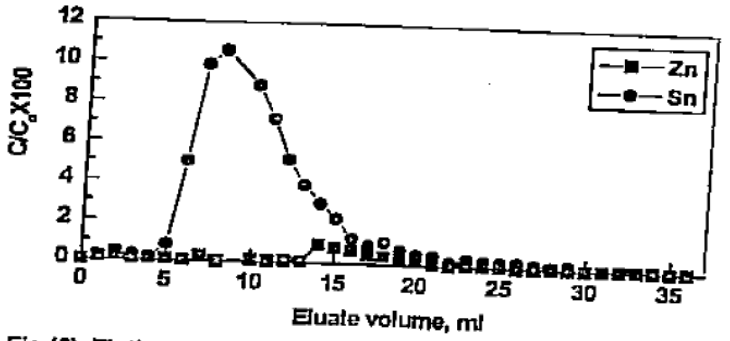

Fig.(6): Elution curves of Zn(II) and Sn(II) using 0.1M NaOH at 29±1°C.

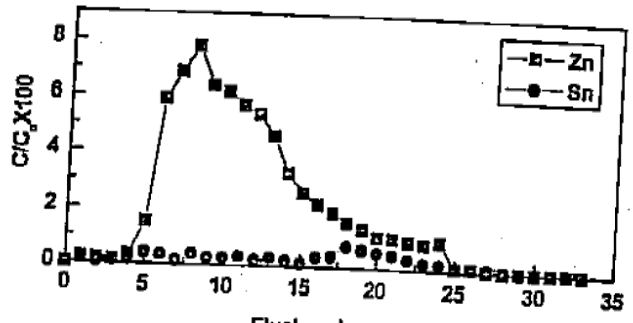

Fig.(7): Elution curves of Zn(II) and Sn(II) using distilled water at 30±1°C.

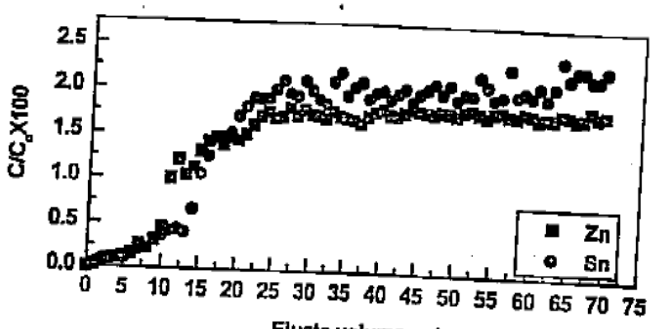

Fig.(8): Breakthrough curves of Zn(II) and Sn(II) from 0.1M HCl; C_o = 0.031M and 0.017M for Zn(II) and Sn(II) respectively, at 30±1°C.

these capacities were determined to be 0.076 mmol/g and 0.084 mmol/g for Zn(n) and Sn(n) respectively.

In a previous work it has been published that HA as a long chain carhoxylic, reacts with various metal cations via the following equilibrium

$(M^{n+})_{aq}\ (HA)_0$ ---- $(Man)_0 + nH^+$ (1)

Also, it is well established that salts of oxo-acids of Zn(II) such as nitrate in aqueous solutions are quite strong and easily hydrolysed, therefore Zn(OH)+ is the most acceptable species to be present in the aqueous phase. Accordingly, the mechanism of Zn(II) extraction can be formulated by the following stoichiometric equations

$\{Zn^{2+}\}_{aq}+2\ (HA)_0$ === $\{ZnA_2\}0 + 2H^+_{aq}$ (2)

$(Zn^{2+})_{aq} + (HA)_0 + H_2O$=== $\{ZnOHA\}_0 + 2H^+$ aq+ (3)

Table 1. IQ values of Zn(II) and Sn(H) and the separation factors (a).

Eluent	K_d Zn(II)	K_d Sn(II)	Separation factor (α); Zn/Sn	Separation factor (α); Sn/Zn
0.1M HCl	2.3	0.83	2.76	0.362
0.1M HBr	1.27	1.56	0.77	1.303
0.1M KI	1.2	2.3	0.522	1.92
0.1M HNO_3	1.56	0.83	1.88	0.532
0.1M H_2SO_4	1.56	1.93	0.81	1.234
0.1M NaOH	4.5	1.93	2.33	0.43
Dist. water	1.93	6.33	0.31	3.28

Conclusion

2-Heptyl-2-methylnonanoic acid in benzene has been used for the extraction chromatography of Zn(H) and Sn(II) using chromosorb as solid support in the chromatographic column. 0.1M HCI, HBr, KI, HN03, H2SO4, NaOH and distilled water were used as eluting agents for both elements. Elution curves revealed differences in Kj values that permit high separation factors between the two elements. The optimum separation was obtained with the following sequence: H_2O>HCl>NaOH where the separation factors were 3.28, 0.362 and 0.43, respectively.

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