Pergamon

0039-9140(93)E0036-D

Talanta, Vol. 41, No. 4, pp. 617–623, 1994
Copyright © 1994 Elsevier Science Ltd
Printed in Great Britain. All rights reserved
0039-9140/94 $6.00 + 0.00

THE SORPTION BEHAVIOUR AND SEPARATION OF SOME METAL THIOCYANATE COMPLEXES ON POLYETHER-BASED POLYURETHANE FOAM

A. B. FARAG,[2] M. S. EL-SHAHAWI[1]* and S. FARRAG[1]
[1]Chemistry Department, Faculty of Science, UAE University, Al-Ain, P.O. Box 17551, United Arab Emirates
[2]Chemistry Department, Faculty of Science, Qatar University, Doha-2713, State of Qatar

(*Received* 15 *April* 1993. *Revised* 18 *November* 1993. *Accepted* 18 *November* 1993)

Summary—The preliminary screening tests on the preconcentration of lanthanum(III), aluminium(III), molybdenum(VI), gallium(III) and tungsten(VI) thiocyanate complexes in aqueous media by unloaded foam indicated a reasonable percentage of metal ions were retained on the foam. The influence of various parameters affecting the retention of these complex species from the aqueous media by the foam were critically studied and the possible mechanisms of the sorption of the compounds were suggested. However, owing to the complex chemical nature of the polyether–polyurethane foam, several mechanisms may be involved simultaneously. Attempts for the quantitative retention and recovery of the tested complexes by the foam columns were also made and satisfactory results were obtained. The height equivalent to theoretical plates (HETP) of the foam columns were calculated from the chromatograms and break through capacity curve and were found in the range 1.8–2.3 mm at flow rates up to 15 cm^3/min. The proposed foam column method has been successfully used for the separation of a series of complex mixtures of the tested metal thiocyanate complexes in aqueous media. The membrane properties of the foam sorbents offer unique advantages over conventional bulk type granular sorbents in rapid, versatile effective separations and preconcentrations of different complexes from fluid samples.

It is known that metal thiocyanate complexes are effectively extracted in the form of ion-association complexes into oxygen-containing organic solvents[1,2] and this has been widely used for the separation of metals.[3] However, the volatility and toxicity of organic solvents sometimes pose problems in the practical operation of the process, and multiple extraction must be used.[3] Concentration of the resulting volume of solvent down to a volume required for an appropriate concentration of the species to be measured often results in interference from material present in low concentration in the organic solvent.[4,5]

Systematic studies on the metal-selective separation by solid polymer membrane technologies under hydraulic pressure have been made.[6–10] The sorption of ion-association complexes is assumed to be important in the development of solid membranes which selectively rejects metal species or are permeated by them.[10] The sorption behaviour of the metal thiocyanate complexes by solid polymer membrane followed a Langmuir-type adsorption isotherm.[10]

Recently, after the pioneering work of Bowen,[11,12] Braun and Farag,[13–15] and Chow *et al.*,[16,17] the use of polyurethane foam (PUF) has been established and found wide application in different separation procedures from aqueous thiocyanate media.[16–20] The retention behaviour of Au, Fe, Ga, Hf, In, Mo, W, Tc, Nb, Pa, Sb (V), Sn (IV), Ta and Zn on polyether-based polyurethane foam in HCl–KSCN medium have been reported by Caletka *et al.*[21,22]

The application of polyurethane foams sorbents in trace elements led to the revealing of the potentialities of their special geometrical form: spherical membrane-shaped geometry and to the proposal of their general use in column operations as a substitute for the traditional granular supports in extraction chromatography.[23–26] The resilient property and quasi-spherical membrane geometry combined with the high retention capacity due to large surface area has made polyurethane foam the preferred

---

*Author for correspondence. Permanent Address: Chemistry Department, Faculty of Science at Damiatta, Damiatta, Egypt.

sorbent over conventional solvents and other extraction techniques for the separation of elements by selective sorption on the foam.[25,26]

This paper reports the effect of various parameters on the extraction and separation of some metal ions from aqueous thiocyanate media by unloaded foams and conclusions concerning the most probable sorption mechanism by the polyurethane foam have been drawn.

EXPERIMENTAL

Reagents and materials

All reagents and chemicals were of analytical reagent grade. Polyurethane foam, an open cell polyether type (bulk density 30 kg/m^3) was supplied by Greiner K.G. Schaum (Stoffwerk Kremsmunster, Austria). The foam cubes were cut, washed and finally dried as previously described.[14] Stock solutions (1 mg/cm^3) of lanthanum(III), aluminium(III), molybdenum(VI), gallium(III) and tungsten(VI) were prepared in distilled water. Stock solutions ($1M$) of lithium, ammonium, sodium, potassium and rubidium chlorides were also prepared in distilled water. A universal buffer solutions series of Britton-Robinson were used. The average standard deviation of the weight of the foam was 1.6%.

Apparatus

A Unicam Sp-90A series atomic absorption spectrometer with a conventional 10-cm slat burner head for an air-acetylene flame and an inductively coupled plasma (ICP) Jobin Yvon (JY 38) were used. Mechanical shaker type G10 Gyrotary (New Brunswick, Scientific Co.), and an Orion pH meter and glass columns of 12 cm height and internal diameter 1.5 cm were also employed.

General procedures

Batch experiments. To investigate the effect of shaking time on the uptake of the tested metal ions (La, Al, Mo, Ga and W) by the unloaded foam, the foam cubes (0.2 g) were equilibrated with 25 cm^3 of ammonium thiocyanate ($0.1M$) solution containing 5 mg of the tested metal ions in separate polyethylene bottles. These solutions were shaken for various time intervals and the foam cubes were then separated by decantation. The amount of the metal ion remaining in the aqueous solution was measured by atomic absorption spectrometry. The sorption behaviour of the complexes were evaluated from the degree of sorption (E) and the distribution ratio (D):

$$E = \frac{[M]_i - [M]_F}{[M]_i} \times 100 \qquad (1)$$

$$D = \frac{[M]_i - [M]_F}{[M]_F} \times \frac{V_s}{W} \qquad (2)$$

where $[M]_i$ and $[M]_F$ are the initial and final metal concentrations, respectively in the solution; V_s is the volume of solution (cm^3) and W is the weight of dry foam (g). Following these procedures, the effect of pH, acidity, thiocyanate concentration and ionic strength on the sorption behaviour of the tested metal ions were critically examined.

Column experiments. In the column experiments, 1 g of dry foam was packed into the column using the vacuum method of foam column packing.[14] Aqueous thiocyanate solution (0.1–0.5 dm^3) sample containing 1 mg of the tested metal ions (La, Al, Ga, Mo or W) were passed through the foam column at 1–5 cm^3/min flow rate at the optimum conditions of each metal ion. The columns were then washed with 100 cm^3 of ammonium thiocyanate solution. The tested metal ions were quantitatively extracted. Elution of the retained species from the foam column were quantitatively obtained by percolating selective eluating agents for each metal ion. The effluent and washing solutions were collected in a 100-cm^3 measuring flask and measured by ICP. Chromatographic separation of the mixtures Mo-La-Al; Al-W-Ga; W-La (or Al), La-Ga (or W) and Ga-Al (or La) were carried out employing the foam packed column procedures.

RESULTS AND DISCUSSION

Static experiments

Preliminary batch experiments have shown that the uptake of the investigated metal ions (La, Al, Ga, Mo and W) from aqueous thiocyanate solutions by the unloaded foam is rapid and equilibrium is reached in less than 1 hr followed by a plateau. A better extraction percentage (>90%) was obtained within a short period of time (~20 min) for tungsten(VI). Representative results are given in Fig. 1.* It was shown that the maximum extractibility of Ga and Al are reached at shorter times (4–6 min) than that for Mo and La.

---

*Each point in figures represent average of 5 measurements, $n = 5$ with relative standard deviations in the range 1.6–1.8%.

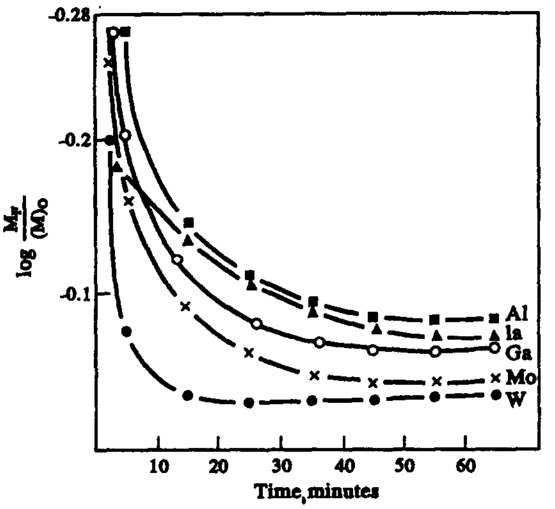


Fig. 1. Effect of shaking time on the sorption profiles of tungsten(VI), molybdenum(VI), gallium(III), lanthanum(III) and aluminium(III) by the foam from aqueous thiocyanate media.

The effect of pH and acidity (HCl or $HClO_4$) up to 6*M* on the extraction of the tested metal ions from aqueous thiocyanate media by the unloaded foam were carried out. The sorption profiles of the investigated species are summarized in Figs 2 and 3. The extraction percentage of W, La and Mo (Fig. 2) increased by increasing the hydrochloric acid concentration while for gallium and aluminium (Fig. 3) the extraction efficiency increased as the acidity decreased. The increased acidity could initiate the decomposition and polymerization of thiocyanate or isothiocyanic acid in aqueous solution.[25]

The effect of acidity on the distribution ratio of the tested species from the thiocyanate media by the unloaded PUF is given in Fig. 4. The *D* values of Mo, W and La increased sharply while for Al and Ga the extraction decreased with increasing initial acid concentration. The sorption behaviour of aluminium and gallium may be attributed to the competitive extraction of hydrochloric of perchloric acid and complex species of thiocyanate in aqueous solution.[17–19] Solvent extraction mechanism and other processes are possibly involved in the uptake of these metal complexes. The specific sites on the foam membrane presumably are capable of absorbing lanthanum(III), molybdenum(VI) and tungsten(VI), via an ion exchange mechanism.

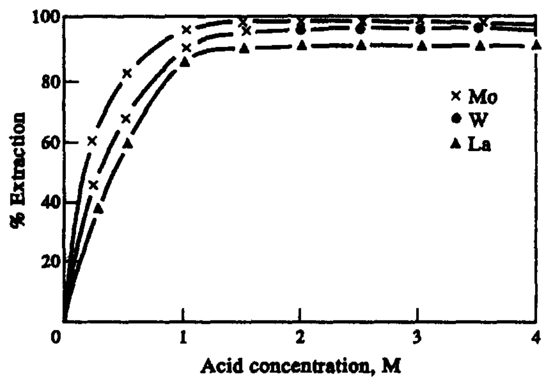


Fig. 2. Effect of acid concentration on the sorption profiles of molybdenum(VI), tungsten(VI) and lanthanum(III) by the foam.

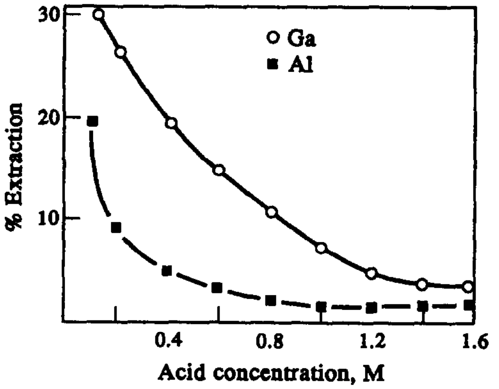


Fig. 3. Effect of acid concentration on the sorption profiles of gallium(III) and aluminium by the foam.

Figure 5 shows the effect of thiocyanate concentration on the sorption profiles of the tested metal complexes. The degree of sorption of metal thiocyanate complexes by the unloaded foams decreases in the order

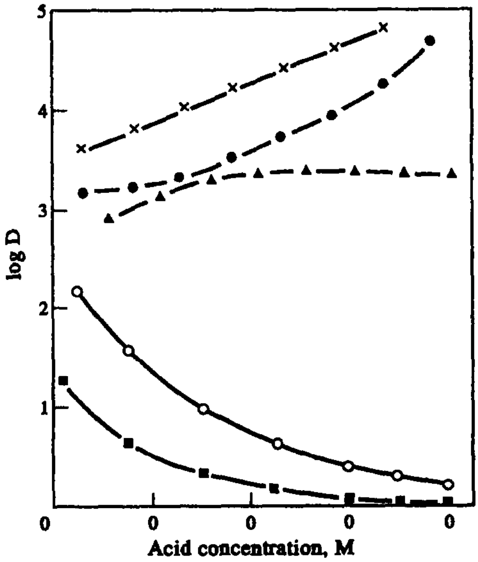


Fig. 4. Effect of acid concentration on the distribution coefficients of the tested metal ions between the aqueous thiocyanate media and polyurethane foams. La (▲); Al (■); Ga (○); W (●) and Mo (×).

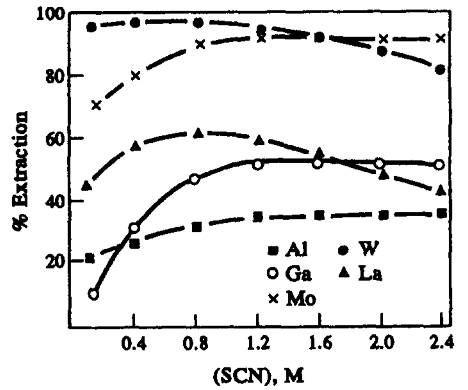
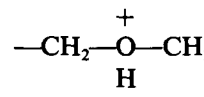


Fig. 5. Effect of thiocyanate concentration on the sorption of the tested metal ions by the unloaded foams.

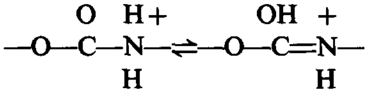
W > Mo > La > Ga > Al. It is reported that polyether-type polyurethane foam successfully sorbs these complexes[14,15] and the chemical structure of the PUF material has such a subtle effect on the sorptivity of metal complexes analogous to that in metal extraction by organic solvents of various structure and polarity.[10,14]

The sorption profiles of La, Ga and Al thiocyanate complexes by the unloaded foam increased sharply with increasing the thiocyanate concentration, possibly due to the formation of anionic octahedral complexes such as $(NH_4)_{3-n}M(SCN)_n$,[27] where M = La, Ga or Al. The sorption of these complex species could be due to the anion exchange properties of PUF which may act as a weak or strong anion exchanger. The existence of anion exchange sites arise from the tendency of both the nitrogen atoms of the urethane linkage and or the ether oxygen atoms to accept protons at higher acid concentration to give:



$$-\mathrm{CH_2}-\underset{\mathrm{H}}{\overset{+}{\mathrm{O}}}-\mathrm{CH_2}- \qquad (3)$$

or



$$-\mathrm{O}-\overset{\mathrm{O}}{\mathrm{C}}-\underset{\mathrm{H}}{\overset{\mathrm{H+}}{\mathrm{N}}}- \rightleftharpoons -\mathrm{O}-\overset{\mathrm{OH}}{\mathrm{C}}=\underset{\mathrm{H}}{\overset{+}{\mathrm{N}}}- \qquad (4)$$

and hence the polyether-type foam will have anion-exchange sites of various strengths.[14,15] Sorption of these three thiocyanate complexes could also be through a ligand addition mechanism since polyurethane foam contains large numbers of lone electron pairs on its nitrogen or oxygen atoms which are supposedly involved in the coordination of interaction with the anionic complex species.[16–18,26]

$$[M(\mathrm{SCN})_n]^{3-n} + mL \rightleftharpoons [M(\mathrm{SCN})_n L_m]^{3-n} \qquad (5)$$

where L represents the lone pair of electron and its associated atom in the polyurethane and $m + n = 6$ in all cases. Higher concentrations of ammonium thiocyanate and acid decreased the sorption profiles of molybdenum and tungsten (Fig. 5). This may be attributed to the increased influence of thiocyanic acid and 5-amino-1,2,4-dithiazole-3-thione formed during sorption of these complex species by PUF.[23–28] This behaviour also could be due to the competitive extraction of ammonium thiocyanate which may be expected to be somewhat extractable as the neutral octahedral $Mo(SCN)_6$ and $W(SCN)_6$ complex species.[27–29]

The sorption of a neutral thiocyanate metal complex could occur, depending on experimental conditions as reported elsewhere.[19,29] Tungsten(VI) at high acidity is present as WO^{4+} which reacts with SCN^- to form anionic species $[WO(SCN)_n]^{4-n}$. These are possibly sorbed on PUF through a cation chelation mechanism.[17,23] According to this mechanism complexation of cations, *e.g.*, K^+, NH_4^+ or H_3O^+, takes place in the PUF cavities through ion-dipole interaction and/or hydrogen bonding.[18] The anionic species formed, *i.e.*, $[WO(SCN)_n]^{4-n}$, are then extracted as counter ions to the captured cations in the PUF cavities.[25,26]

The effect of thiocyanate concentration on the distribution ratio of the tested metal ions Al, Ga, La, Mo and W by the unloaded foams are summarized in Fig. 6. The D values for La, Ga and Al increased with increasing thiocyanate concentration possibly due to the ability of these metal ions to form anionic octahedral complexes $[M(SCN)_6]^{3-}$ which are highly extractable by the unloaded foams. The D values of molybdenum(VI) and tungsten(VI) decreased with increasing thiocyanate concentration. For molybdenum(VI), D increases with C_{SCN^-} with a small maximum at $\sim 0.4M$ thiocyanate concentration and remains almost constant.

The effect of various concentrations of lithium, sodium, potassium and ammonium chlorides on the sorption profiles of the tested metal ions by the unloaded foam at the optimum conditions of concentration of thiocyanate and acidity of each tested ion were carried out. Representative results are given in Fig. 7. The sorption profiles of La(III), Al(III) and MO(VI) thiocyanate complexes increased with the increase of the cation size in the following order of cations: $NH_4^+ > K^+ > Na^+ > Li^+$ [Fig. 7(a)] while for tungsten(VI) and gallium(III) [Fig. 7(b)], the sorption percentage increased in the

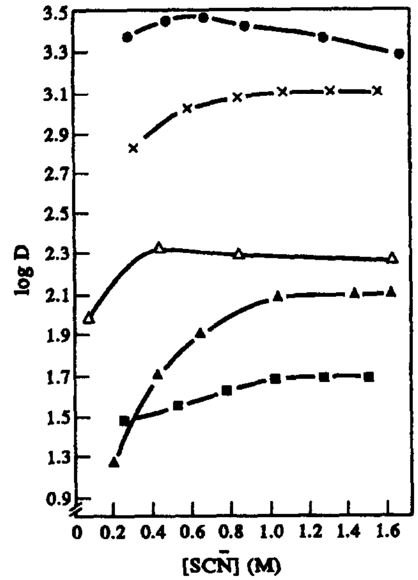


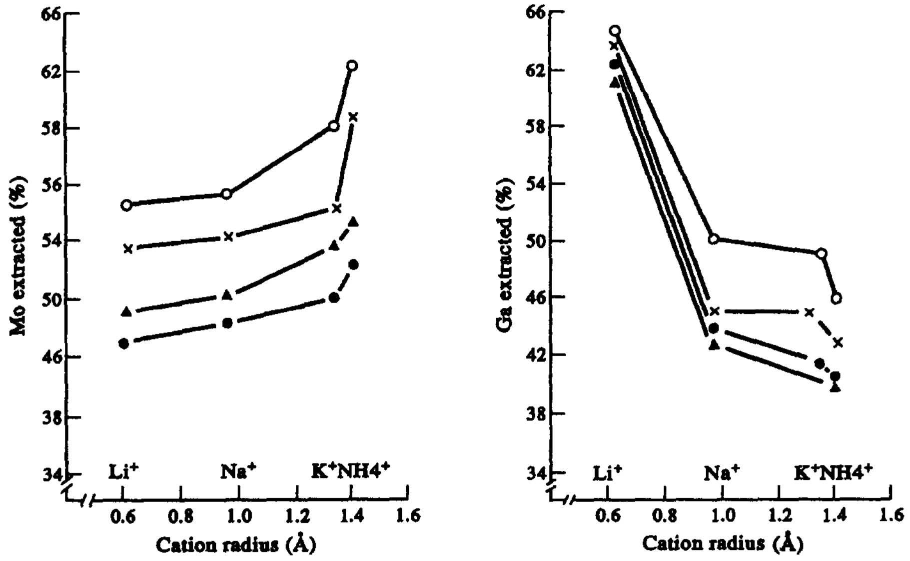
Fig. 6. Effect of thiocyanate concentrations on the distribution ratios of the tested metal ions between the aqueous thiocyanate media and polyurethane foams. W (○); La (×); Mo (△); Ga (△) and Al (■).

following order: $Li^+ > Na^+ > K^+ > NH_4^+$. Therefore, the ion-dipole interaction of NH_4^+ with oxygen sites of PUF are possibly highly predominating in the extraction of Al^{3+}, La^{3+} and Mo^{6+} ions. The ability of the anionic thiocyanate complexes of these metal ions to form ion-pairs increases with increasing cation size ($NH_4^+ > K^+ > Na^+ > Li^+$) and possesses a maximum in the presence of NH_4^+. These results are in agreement with the data recently reported by Palagyi and Braun *et al.*[24,25] Therefore "cation chelation mechanism" is the most probable mechanism for the sorption of these complex species. In accordance with this mechanism, the polyalkenoxy chains of the PUF sorbent form a helical structure.[23] The helical structure of the foam sorbent forms a clathrate with suitable simple cations and the anionic metal complex is then sorbed on these cationic sites.[24] Many cations, M^{p+} (*e.g.*, Na^+, K^+, Li^+, NH_4^+ or H_3O^+) are capable of being multiply complexed by the PUF at specific sites giving a solid phase (or matrix) species which can be required as equivalent to an ion exchange matrix or to a solvated cations in solid solutions as follows:

$$M^{p+} + \overline{\text{site}} \rightleftharpoons \overline{(\text{M. site})^{p+}} \qquad (6)$$

$$\overline{(\text{M. site})^{p+}} + \text{Me}\,X_n^{m-} \rightleftharpoons \overline{(\text{M. site})^{p+}\ldots\,\text{Me}\,X_n^{m-}} \qquad (7)$$

The chelated cation $(\text{M. site})^{p+}$ and the accompanying anions Me X_n^{m-} are possibly associated within the PUF matrix. If considerable sorption of another ion association complex containing M^{p+} and some moderately extracted anion, A^- occurs before or concurrently with the sorption of Me X_n^{m-}, then the latter may be more conveniently regarded as sorbed by an anion exchange process in which it is exchanged for



(a) (b)

Fig. 7. Effect of the size of various univalent cations on the sorption profiles of molybdenum (a) and gallium (b) thiocyanate complexes by polyurethane foam. Salt concentrations are 0.2*M* (○); 0.4*M* (×); 0.6*M* (▲); 0.8*M* (●).

A^- at the positive sites that result from chelation of M^{p+} by the polymer. A matrix similar to anion-exchanger results at which exchange of the anionic counter-ions can occur and the sorption mechanism of Me X_n^{m-} may then be:

$$M^{p+} + A^- + \overline{\text{site}} \rightleftharpoons \overline{(\text{M. site})^{p+}} + A^- \quad (8)$$

$$\overline{mA^-} + \text{Me}\,X_n^{m-} \rightleftharpoons mA^- + \overline{\text{Me}\,X_n^{m-}} \quad (9)$$

The sorption profiles of Ga(III) and W(VI) by the PUF from acid thiocyanate increases in the order: $Li^+ > Na^+, K^+$ [Fig. 7(b)]. Similar trends were obtained in the solvent extraction of uranium(VI) by ethers and polyether foams.[29] Solvent extraction is therefore the most probable mechanism for the sorption of the complex species of Ga and W by the unloaded foams as follows:[29]

$$nK^+ + \text{Me(SCN)}_m^{n-} \rightleftharpoons /(K^+)_n \;\; \text{Me(SCN)}_m^{n-}/\text{aq} \quad (10)$$

$$/(K)_n^+ \text{Me(SCN)}_m^{n-}/_{\text{aq}} \rightleftharpoons /(K^+)_n \;\; \text{Me(SCN)}_m^{n-}/\text{foam} \quad (11)$$

Mossbauer spectroscopy studies on the sorption of Fe(III) from acid thiocyanate media also supported the above mentioned approach. The sorbed species by PuF was $Fe(SCN)_3$, similar to diethyl ether extraction.[30] In the thiocyanate-containing system, the difference between aqueous and etheric solution is almost negligible and $Ga(SCN)_3$ species are probably present in both solvents with the PUF-sorbed species. A six-coordinated complex $Ga(SCN)_3.3D$ is probably formed with some of the donor groups (D) of the polyurethane foam in agreement with an earlier observation.[31]

Column experiments

In these experiments distilled water samples containing 1 mg of each metal ion at the optimum thiocyanate and acid concentrations of maximum sorption were percolated through separate PUF columns as described in the experimental procedure. Complete sorption and recovery of the metal ions were achieved from the foam column. Molybdenum(VI) and lanthanum(III) ions were eluted from the foam column with acetone while aluminium(III), gallium(III), and tungsten(VI) were recovered with HCl (1*M*), NH_4OH (2*M*) and HCl-acetone (1:1), respectively and determined by ICP.

The dependence of the sorption profile of molybdenum(VI) on the flow rate was investigated by percolating 1 mg of Mo(VI) through the foam column at various flow rates up to 15 cm^3/min. Complete retention was obtained up to 10 cm^3/min and it decreased significantly at a higher flow rate. The height equivalent to theoretical plates (HETP) were calculated from the elution curves and found to be in the range 1.8–2.3 ± 0.1 mm at 5–15 cm^3/min flow rate. The HETP were also obtained from the break through capacity curve and were found in the range 2.0–2.2 ± 0.15 mm (average of 5 determinations). The average standard deviations for the HETP was found in the range 1.6–1.8%.

Separation of the tested metal thiocyanate complexes from each other is possible from different volumes (0.1–1 dm^3) of the aqueous thiocyanate solution. A mixture containing 1 mg of molybdenum was separated from 1 mg of lanthanum (or aluminium) at the optimum conditions of pH and thiocyanate concentration for molybdenum sorption by PUF at 1–5 cm^3/min. Sorption of molybdenum took place while La or Al complexes were not retained on the foam columns and collected quantitatively in the effluent. Molybdenum(VI) was then recovered from the column by 100 cm^3 of acetone at 3–5 cm^3/min flow rate. Separation of the ternary mixture Al-W and Ga (or Mo) were also carried out. A mixture containing 1 mg of each of these ions in aqueous thiocyanate solution (0.1–0.5 dm^3) at pH 7.5 was percolated through the foam column at 1–2 ml/min. Sorption of aluminium only took place and eluted with HCl 200 cm^3 of (1*M*), while W and Ga (or Mo) were passed through the column without retention. Separation of 1 mg of W from La or Al (1 mg) in aqueous solution containing NH_4CNS (1*M*) and HCl (4*M*) was also carried out on the unloaded foam column. Sorption of W took place at 0.5–1 ml/min while Al or La was passed through the column without extraction.

Separation of 1 mg of La from Ga or W (1 mg) were also carried out from aqueous thiocyanate (1*M*) solution at pH ≃8. Lanthanum(III) was only retained on the foam column and eluted with 200 cm^3 acetone at 0.5 ml/min while gallium(III) or tungsten was passed through the column without sorption. Separation of 1 mg of Ga from Al (or La) mixture from aqueous NH_4CNS (1*M*) at pH 4 in the presence of LiCl was also obtained on the PUF column. Gallium was only retained and eluted with 100 ml of ammonia solution (2*M*) at 1–2 ml/min while the other metal ions were passed through the foam column without sorption.

REFERENCES

1. R. Bock, *Z. Anal. Chem.*, 1951, **133,** 110.
2. C. Rozychi, *Chem. Anal.*, 1969, **14,** 755.
3. T. Sekine and Y. Hasegawa, *Solvent Extraction Chemistry*, Dekker, New York, 1977.
4. T. Saito and K. Hagiwara, *Z. Anal. Chem.*, 1983, **315,** 201.
5. S. Voerman, *Bull. Environ. Cont. Toxic.*, 1969, **4,** 64.
6. Q. T. Ngugen, P. Aptel and J. Neel, *J. Member. Sci.*, 1980, **6,** 71.
7. T. Hayashita, M. Takagi and K. Ueno, *Sepn. Sci. Techn.*, 1983, **18,** 461.
8. *Idem, ibid.*, 1984, **19,** 315.
9. M. Igawa, A. Saito, N. Sasamura, M. Tanaka and M. Seno, *J. Membr. Sci.*, 1983, **14,** 59.
10. T. Hayashita and M. Takagi, *Talanta*, 1985, **32,** 399.
11. H. J. M. Bowen, *J. Chem. Soc. A.*, 1970, 1082.
12. H. J. M. Bowen, *British Patent 1*, 1973, **305,** 375.
13. T. Braun and A. B. Farag, *Anal. Chim. Acta*, 1972, **61,** 265.
14. T. Braun, J. D. Navratil and A. B. Farag, *Polyurethane Foam Sorbents in Separation Science*, CRC Press, Boca Raton, Florida, 1985.
15. T. Braun, *Z. Anal. Chem.*, 1989, **333,** 785, and references therein.
16. A. Chow and D. Buksak, *Can. J. Chem.*, 1975, **53,** 1373.
17. R. F. Hamon, A. S. Khan and A. Chow, *Talanta*, 1982, **29,** 313.
18. S. J. Al-Bazi and A. Chow, *ibid.*, 1982, **29,** 507.
19. *Idem, ibid.*, 1983, **30,** 487.
20. G. J. Moody and J. D. R. Thomas, *Chromatographic Separation and Extraction with Foamed Plastics and Rubbers*, Marcel Dekker, New York, 1982.
21. R. Caletka, R. Hausbeck and V. Krivan, *Talanta*, 1986, **33,** 315.
22. *Idem, Anal. Chim. Acta*, 1990, **229,** 127.
23. A. Roychaudhuri, S. K. Roy and A. K. Chakraburty, *Talanta*, 1992, **39,** 1377.
24. S. Palagyi and T. Braun, *J. Radioanal. Nucl. Chem.*, 1992, **163,** 69, and references therein.
25. S. Palagyi, T. Braun, Z. Homonnay and A. Vertes, *Analyst*, 1992, **117,** 1537, and references therein.
26. S. Palagyi and T. Braun, *Separation and Preconcentration of Trace Elements and Inorganic Species on Solid Polyurethane Foam Sorbents* in Z. B. Alfassi and C. M. Wai (eds.), *Preconcentration Techniques for Trace Elements*, CRC Press, Boca Raton, Florida, 1992.
27. S. J. Al-Bazi and A. Chow, *Anal. Chem.*, 1983, **55,** 1094.
28. *Idem, Talanta*, 1984, **31,** 189.
29. J. J. Oren, K. M. Gough and H. D. Gesser, *Can. J. Chem.*, 1979, **57,** 2032.
30. F. E. Beamish, *The Analytical Chemistry of the Noble Metals*, Pergamon Press, Oxford, 1972.
31. M. N. Abbas, A. Vertas and T. Braun, *Radiochem. Radioanal. Lett.*, 1982, **54,** 17.