Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Supported Liquid Membranes Extraction of W(VI) Ions from HCL Solutions Containing Tartaric Acid

Muhammad Ashraf Chaudry[a]; M. Tayyib Malik[b]; M. Y. K. Nazir[b]
[a] PAKISTAN INSTITUTE OF NUCLEAR SCIENCE AND TECHNOLOGY, ISLAMABAD, PAKISTAN [b] CHEMISTRY DEPARTMENT, BAHADDIN ZAKIRA UNIVERSITY, MULTAN, PAKISTAN

To cite this Article Chaudry, Muhammad Ashraf , Malik, M. Tayyib and Nazir, M. Y. K.(1995) 'Supported Liquid Membranes Extraction of W(VI) Ions from HCL Solutions Containing Tartaric Acid', Separation Science and Technology, 30: 6, 1013 — 1023

To link to this Article: DOI: 10.1080/01496399508015413

URL: http://dx.doi.org/10.1080/01496399508015413

SEPARATION SCIENCE AND TECHNOLOGY, **30**(6), pp. 1013–1023, 1995

Supported Liquid Membranes Extraction of W(VI) Ions from HCl Solutions Containing Tartaric Acid

MUHAMMAD ASHRAF CHAUDRY*
PAKISTAN INSTITUTE OF NUCLEAR SCIENCE AND TECHNOLOGY
P.O. BOX 1356, ISLAMABAD, PAKISTAN

M. TAYYIB MALIK and M. Y. K. NAZIR
CHEMISTRY DEPARTMENT
BAHADDIN ZAKIRA UNIVERSITY
MULTAN, PAKISTAN

ABSTRACT

A transport study of W(VI) ions across tri-*n*-octylamine (TOA) xylene-based supported liquid membranes from aqueous solutions containing tartaric acid (TA) has been carried out. TA complexes with W(VI) ions to keep them in solution and enhance flux. The optimum conditions of transport found are 0.132 M TA and 0.001 M HCl in the feed, 3.7 M NaOH in the strip, and 0.66 M TOA in the membrane. Beyond these TA and TOA concentrations, there is a decrease in flux and permeability values which are 4.76×10^{-5} mol/m^2·s and 9.15×10^{-10} m^2/s, respectively. NaOH is a better stripping agent than NH_4OH for these metal ions. Increases in membrane phase viscosity and temperature reduce the values of these transport parameters.

INTRODUCTION

The solvent extraction study of W(VI) ions from aqueous solutions is important for the separation of these ions from other metal ions. Such studies have been performed using tri-*n*-butylphosphate (1) and trialkylamines (2, 3). HF has been used to prevent precipitation of tungstate ions in aqueous solution, and the W(VI) ions have been shown to be trans-

---

* To whom correspondence should be addressed.

ported from HCl aqueous solutions across tri-*n*-octylamine (TOA) xylene-based supported liquid membranes (SLM) (4). HF may corrode glass and other material containers. Hence, tartaric acid has been selected to prevent precipitation of tungstate ions in an aqueous feed solution. In the present work, extraction across a TOA-xylene-based SLM has been performed. Metal ions transport using SLM has not been performed previously by using tartaric acid in the feed. The parameters studied in this work are the effects of tartaric acid and HCl concentrations in the feed solution, stripping agents like NH_4OH and NaOH in the product solution, carrier (TOA) concentration in the membrane phase, and temperature on the transport of W(VI) ions across the above-described SLM.

EXPERIMENTAL

Liquid Membrane Cell (LMC)

The liquid membrane cell (with a half-cell volume of 106 cm^3) used in this study was the same as that described in Ref. 3. It provides an effective membrane area of 12.56 cm^2. The carrier-cum-diluent liquid was supported in Celgard 2400 polypropylene hydrophobic films of porosity 38%, pore size 0.02 μm, and thickness 25 μm by soaking the films in solutions of TOA in xylene of the required concentration for more than 24 hours.

Flux Measurement

The two compartments (half cells) of the LMC were filled with feed and stripping agent solutions, separated by the membranes described above, and stirred at more than 1500 rpm. Samples were taken from both the half cells after regular time intervals and analyzed for W(VI) concentration using the method derived in Ref. 5 and used previously in Ref. 4.

Chemicals

All the chemicals used were the same as those of Ref. 4 except for tartaric acid (TA) (Extra Pure, E. Merck) and HCl (AnalaR, BDH).

RESULTS AND DISCUSSION

The results obtained are given in Figs. 1–9 and explained in the following discussion.

It was shown in our previous work (4) that the $(WO_2F_4)^{2-}$ ion species may exist in the aqueous phase. In analogy to that, it is expected that H_2WO_4 may precipitate in the presence of HCl. In the presence of tartaric acid, the reaction may be

$$Na_2WO_4 + 2(HOCH_2COOH)_2 \rightarrow$$

$$Na_2WO_2[(HOCH_2COO^-)_2]_2 + 2H_2O \quad (1)$$

$$\downarrow$$

$$2Na^+ + WO_2[(HOCH_2COO^-)_2]_2 \quad (2)$$

$$\text{(I)}$$

where $(HOCH_2COO\ )_2$ represents the tartrate ion. The ionic species **I** may be written as $WO_2 . (Tartrate)^{2-}$ and tri-*n*-octylamine present in the membrane phase in contact with the acidic aqueous phase will react with W ions:

$$\underset{aq}{2H^+} + \underset{org}{2R_3N} + \underset{aq}{[WO_2(tartrate)_2]^{2-}} \rightarrow \underset{org}{(R_3NH)_2[WO_2(tartrate)_2]} \quad (3)$$

$$\text{(II)}$$

where "aq" and "org" indicate aqueous and organic phases. Species **II** will diffuse through the membrane liquid, react with the alkaline stripping solution on the other side of the membrane, and decompose:

$$(R_3NH)_2WO_2(tartrate)_2 + 2\,^-OH \rightarrow 2R_3N + 2H_2O + WO_2(tartrate)_2 \quad (4)$$

$$WO_2(tartrate)_2 + 4\,^-OH \rightarrow WO_4^{2-} + 2H_2O + 2(tartrate) \quad (5)$$

If the above transport mechanism is valid, then 1 mole of W ions is associated with 2 TOA molecules and 2 tartrate ions to form a neutral complex, **II**.

Based on Reaction (3), the equilibrium constant, K_w, for W can be expressed as

$$K_w = \frac{\underset{org}{[(R_3NH)_2(tartrate)_2]}G}{\underset{aq}{[H^+]^2}\underset{org}{[R_3N]^2}\underset{aq}{[WO_2(tartrate)^{2-}]}} \quad (6)$$

G is a factor based on the activity coefficients of all the species involved. Using ideas similar to those described in Ref. 4, the expression for the flux, J, may be written as

$$J = \frac{ATC_1^0\underset{aq}{[H^+]^2}\underset{org}{[R_3N]^2}}{\eta} \quad (7)$$

where T is the absolute temperature, η is the viscosity of the extracting medium, C_1^0 is the initial concentration of the metal ions under transport, and A is a constant.

In developing Eq. (7), the Wilke–Change relation for the diffusion coefficient, $D = kT/6\pi\eta\gamma$, has been used; k is Boltzmann's constant and r is the molecular radius of the diffusing species involved. In logarithmic form, Eq. (7) becomes

$$\log J = \log A + \log T - \log \eta + 2 \log[\mathrm{H}^+]_{\mathrm{aq}} + 2 \log[\mathrm{NR}_3]_{\mathrm{org}} + \log C_1^0 \tag{8}$$

and in general form

$$\log J = \log A + \log T - \log \eta + n \log[\mathrm{H}^+]_{\mathrm{aq}} + m \log[\mathrm{NR}_3]_{\mathrm{org}} + \log C_1^0 \tag{9}$$

where n and m are the number of moles of H^+ and tertiary amine involved in the complex formation reaction, respectively. Equation (9) will furnish the values of n at constant temperature, $[\mathrm{NR}_3]$, and C_1^0. Similarly, the value of m can be had from a plot of log $J\eta$ versus $\log[\mathrm{NR}_3]$ at constant T, $[\mathrm{H}^+]$, and C_1^0. C_1^0 may be kept constant for a short time if J is determined for a given time interval.

The ideas developed above are used to explain the results obtained for the various parameters studied, as explained below.

Effect of Tartrate Acid Concentration Variation

Figure 1 shows the effect of tartaric acid (TA) concentration on the flux and permeability of W(VI) ions across the membranes studied. A TA concentration increase enhances the flux up to 0.132 mol/dm^3, and then there is a decrease in J and P values, where P is the permeability of the W ions. P is determined from a plot of $-\ln C_{1t}^0/C_1^0$ versus t, the elapsed time. P is given by

$$-\ln \frac{C_{1t}^0}{C_1^0} = \frac{aPt}{Vl} \tag{10}$$

where a, V, and l represent the membrane effective area, the volume of the feed solution being used, and the membrane thickness, respectively. C_{1t}^0 and C_1^0 refer to feed solution concentrations at $t = t$ and $t = 0$, respectively. The slope of Eq. (10) furnished the value of P from a plot of $-\ln C_{1t}^0/C_1^0$ versus t.

The trend in J and P values is caused because initially TA helps dissolve the $\mathrm{H_2WO_4}$ species, i.e., it helps Reactions (1) and (2) to take place. Reaction (2) involves tartrate ions which are furnished from the ionization of tartaric acid.

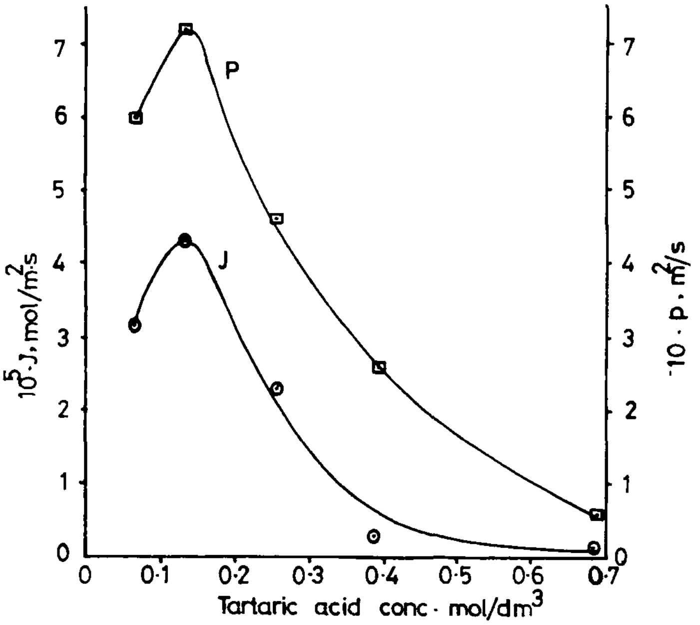

FIG. 1 Plot of flux (J) and permeability (p) of W(VI) ions against tartaric acid concentration.

With a limited TA concentration in the feed, TA is not fully ionized or its ionization is reversed, and therefore the rates of Reactions (2) and (3) also decrease, and so the J and P values are reduced. The plot of log J versus log[TA] is given in Fig. 2. It indicates that the line passing through the ascending points (log J, log[TA]) has a positive slope = 0.66, indicating that 0.66 mole of TA is associated with each mole atom of W ions, and so there may be other species, like $H_2WO_2Cl_2$, which may associate with the $(R_3NH)_2WO_2(tartrate)_2$ complex, where the mole ratio between W and the tartrate ions should be 2. The slope of the descending line, as shown in Fig. 2, is = −2.2, which indicates that the relation between log J and log[TA] should be of the following type:

$$\log J = -2.2 \log[\mathrm{TA}] + M \tag{11}$$

in the given TA concentration range. M is the intercept of the line, i.e., $J \propto 1/[\mathrm{TA}]$, or in other words, if log J is plotted against −log[TA], it should give the value of TA molecules associated with W ions from its slope. Therefore, here nearly 2 moles of TA are associated in the complex formed with W ions. This indicates that species like $WO_2(tartrate)^{2-}$ are more probable in a concentration range of 0.132 mol/dm^{-3} or above.
]

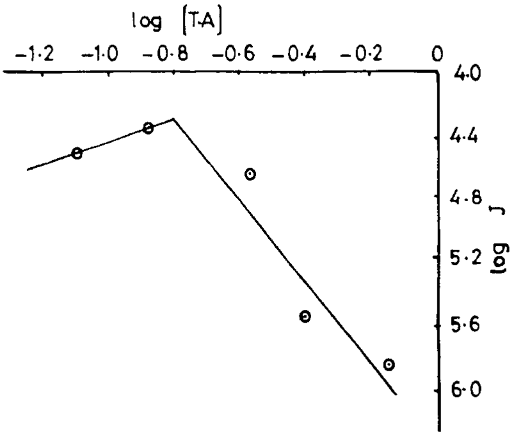

FIG. 2 Plot of log J versus log[TA].

Below that, a mixed species of tartaric acid and chloride ions may be present. From the present result it can be understood that below 0.132 molar TA, the percentage of species like W-chloride will be (2 − 0.66)/2 × 100 = 67%, and that of the $WO_2(tartrate)_2$ type species = 100 − 67 = 33%. The possibilities of the presence of $(R_3NH)_2WO_2(tartrate)Cl_2$ or $(R_3NH)_2WO_2(HO—CH_2COO^-, CH_2COOH)Cl_3$ types of complex species may not also be ruled out.

It is also possible that at TA concentrations less than 0.132 mol/dm^3, species like WO_2Cl_2 or $(WO_2Cl_3)^-$ are also present. Because the WO_2Cl_2 species is neutral, it may not be extracted to the required extent, thereby resulting in the lower flux of W ions.

Effect of HCl or Chloride Concentration Variation

Figure 3 presents the effect of HCl or chloride concentration variation on the transport of W ions across the SLM. Below 0.001 and above 1 M HCl concentrations, the W ions precipitate even in the presence of 0.132 M tartric acid. Below a 0.001 M HCl concentration there may also be incomplete dissolution of W ionic species. Hence, a 0.001 M concentration of HCl appears to be the optimum concentration.

The higher HCl concentration also increases the chloride ions in the solution, resulting in the precipitation of chloride species. Within the higher concentration range, if log J is plotted against log [HCl] (Fig. 4), the slope of the line is negative, indicating that $J \propto 1/[Cl^-]$. The value of the slope is 0.185, indicating that within the $[Cl^-]$ range studied the association of chloride ions with W ions may be 1:0.185. But this is in

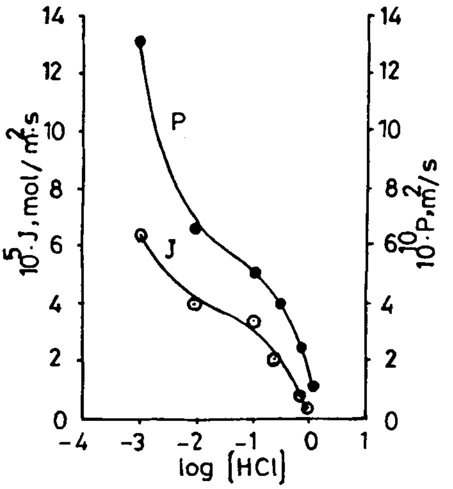

FIG. 3 Flux and permeability of W(VI) ions at different HCl concentrations in feed solution.

the presence of a 0.132 M tartaric acid concentration in the solution, the optimum concentration for tartrate species formation. Figure 3 shows a decrease in J and P values with an increase in chloride or HCl concentrations. This may be due to 1) an inverse effect of the increased number of protons to suppress tartaric acid ionization to form soluble and diffusible W species through the membrane, and 2) the formation of chloride species having less solubility or degree of association with W ions.

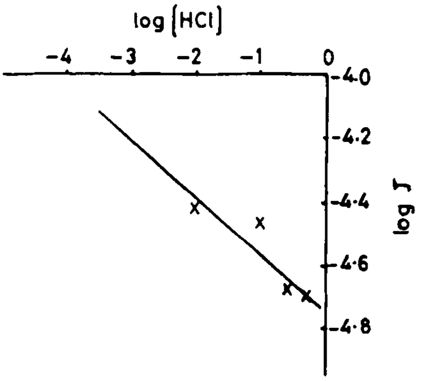

FIG. 4 Plot of log J versus log[HCl].

Effect of Tri-*n*-octylamine Concentration

An increase in TOA concentration in the membrane enhances the flux of W(VI) ions, as expected from Eq. (8). Figure 5 indicate the effect. It is quite clear from Fig. 5 that J and P values increase up to 0.65 mol/dm^3 TOA concentration and then decrease. J is indirectly affected by the organic membrane phase viscosity (η). The viscosity of membrane liquid phase increases with an increase in TOA concentration as observed experimentally. Hence, after a given limit the increase of J and P values is overcome by the effect of viscosity. A plot of log $J\eta$ versus log[TOA] is shown in Fig. 6. The slope of the line up to 0.66 M TOA membrane liquid is 1.93, indicating the association of 2 moles of TOA per mole of W ion. This is in agreement with the two tartrate ions association mentioned earlier. This further confirms the involvement of two protons (Eq. 3). Hence, 0.66 mol/dm^3 is the optimum concentration of TOA in the membrane for the transport of W ions.

Effect of Stripping Agents Concentration

This effect is indicated in Fig. 7. In the case of NaOH, the flux of W ions increases up to 3.75 mol/dm^3 concentration and then decreases. Reactions (4) and (5) are facilitated by the presence of hydroxyl ions in the strip solution. Beyond a 3.75 M NaOH concentration in the strip solu-

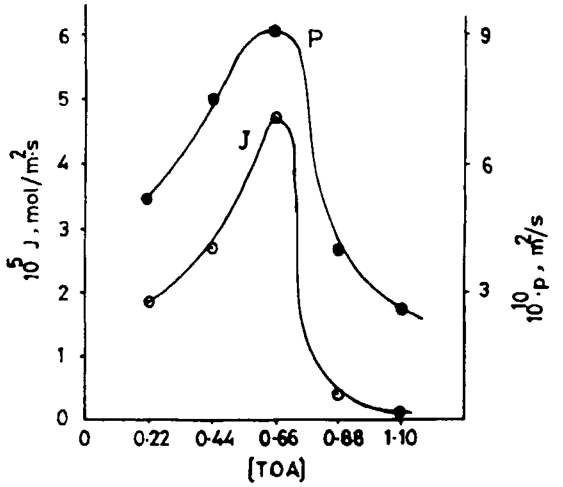

FIG. 5 Flux and permeability of W(VI) ions at different [TOA]-xylene concentrations in SLM.

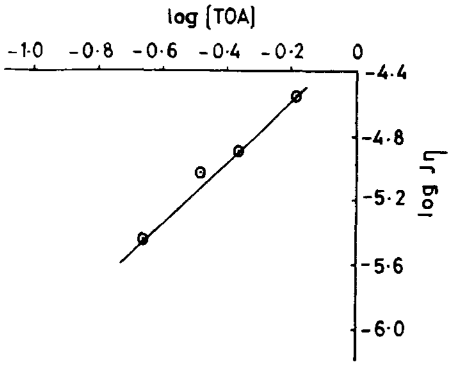

FIG. 6 Plot of log $J\eta$ versus log[TOA].

tion, the W ions may form species which are comparatively difficult to extract into the strip solution, i.e., the ratio between λ_1 and λ_2 is decreased, and as $J \propto (C_1^0\lambda_1 - C_2^0\lambda_2)$, so the $C_1^0\lambda_1 - C_2^0\lambda_2$ value decreases, and hence J decreases. This is in accordance with Fick's law of diffusion. λ_1 and λ_2 are the distribution coefficients for W ions on the feed and strip sides, respectively, with respect to the TOA organic membrane phase.

NH_4OH has a similar effect on J and P values, i.e., up to a 6.4 M NH_4OH concentration in the stripping phase, an increase in J and P has

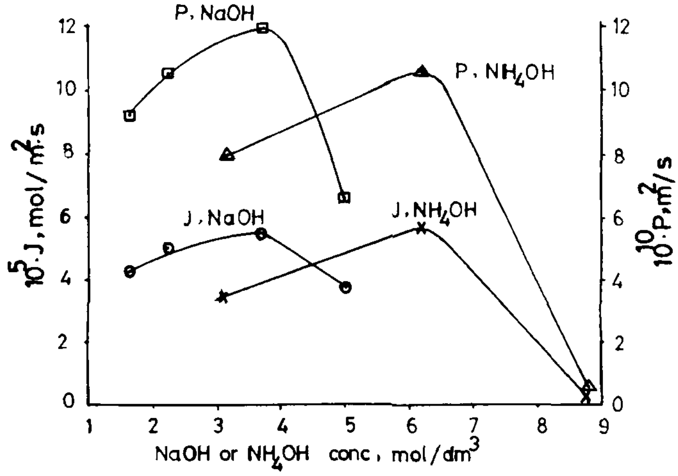

FIG. 7 Plot of flux (J) and permeability (p) of W(VI) ions versus stripping agent (NaOH or NH_4OH) concentration.

been observed, but then there is a decrease with a further increase in the concentration of NH_4OH in the stripping solution. This can be explained by arguments similar to those given above for the NaOH effect. The optimum concentration of NH_4OH in the stripping phase is 6.4 mol/dm^3. This may be due to the difference in strength of the two stripping agents (NaOH and NH_4OH).

Effect of Temperature

The temperature effect on the transport of W ions is shown in Fig. 8, from which it is quite clear that $J \propto 1/T$, i.e., transport decreases with an increase in temperature. According to Eqs. (8) and (9), temperature should have a positive effect on the transport of W ions. From this observation it is clear that Reaction (4) is exothermic. The heat released needs to be absorbed or removed to push the reaction in the forward direction. This is why the increase in the diffusion coefficient ($D = kT/6\pi\eta\gamma$) with an increase of T is overcome by the reduced extraction coefficient, which reduces the $\lambda_1 C_1^0$ value, and this contributes to the overall concentration gradiant within the membrane for the W-TOA-tartrate complex. T no doubt reduces the value of D, but this decrease may be marred by the ($\lambda_1 C_1^0 - \lambda_2 C_2^0$) factor decrease due to the decrease in $\lambda_1 C_1^0$ value.

CONCLUSIONS

The presence of tartaric acid can keep W(VI) ions in solution form and can complex with TOA molecules to form a $(R_3NH)_2WO_2(\text{tartrate})_2$-type

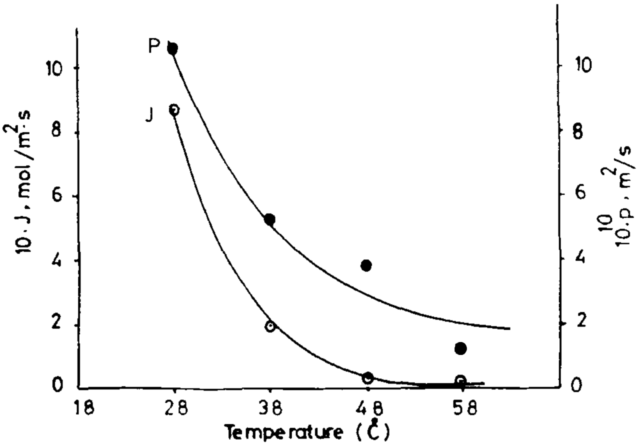

FIG. 8 Flux and permeability of W(VI) ions at different temperatures.

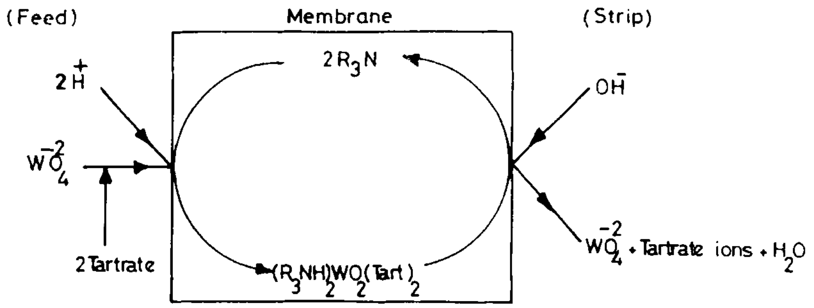

FIG. 9 Mechanism of W(VI) ions transport.

complex which diffuses through the membranes studied and is stripped in alkaline solution by chemical action. The optimum conditions of transport as found from this study are 6.4 mol/dm^3 TOA in the membrane, 0.132 mol/dm^3 TA, 0.001 mol/dm^3 HCl in the feed, and 3.75 mol/dm^3 NaOH or 6.4 mol/dm^3 NH_4OH as strippent.

The flux and permeability values found under the given conditions are 4.75×10^{-5} mol/m^2·s and 9.15×10^{-10} m^2/s, respectively.

The mechanism of transport is visualized in Fig. 9.

ACKNOWLEDGMENTS

The authors are thankful to Dr. I. H. Qureshi, Member Technical, and Dr. M. Zafarullah, C.S.O., for providing necessary facilities to complete this work.

REFERENCES

1. A. K. De and M. S. Rahman, *Talanta*, *11*, 11 (1964).
2. A. A. Palant, V. A. Rezichenco, and S. E. Nikiforva, *Zh. Neorg. Khim.*, *25*, 825 (1980).
3. T. Sato, T. Takayanagi, and K. Sato, in *Proceedings of the International Solvent Extraction Conference*, Moscow, USSR, 1988, p. 184.
4. M. Ashraf Chaudry, M. T. Malik, and M. Ahmad, *J. Radioanal. Nucl. Chem.*, *150*(2), 383 (1990).
5. F. D. Snell, *Photometric and Fluorometric Methods of Analysis*, Part 2, Wiley, New York, 1978, p. 1278.

Received by editor February 23, 1994
Revised August 22, 1994