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

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To cite this Article Ray, Uday Sankar and Modak, Sagar Chandra(1981) 'Solvent Extraction of Thorium with Versatic 911', Separation Science and Technology, 16: 1, 87 — 96
To link to this Article: DOI: 10.1080/01496398108070228
URL: http://dx.doi.org/10.1080/01496398108070228

SEPARATION SCIENCE AND TECHNOLOGY, 16(1), pp. 87–96, 1981

Solvent Extraction of Thorium with Versatic 911

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Abstract

The distribution of Th(IV) between an aqueous solution and a high-molecular weight synthetic carboxylic acid, Versatic 911 (Shell Co. Ltd., London), diluted with benzene was studied. Thorium was quantitatively extracted at pH 4.0–4.9 from 0.1 *M* acetic acid solution. The study of the effects of pH, extractant concentration, metal concentration, diluent, and contact time on the extraction of thorium(IV) was performed. The metal/Versatic 911 ratio was determined in the extracted species and the experimente showed that the ratio is 1:4. The extraction dependence upon acetate ion concentration was also examined. Thorium(IV) was separated from magnesium, calcium, strontium, barium, manganese, cobalt, nickel, zinc, cadmium, lanthanum, praseodymium, neodymium, samarium, gadolinium, and mercury. The proposed methods are very simple, rapid, and fairly selective, and can be carried out both at micro and macro levels. Important quantitative separations of thorium from synthetic mixtures were also carried out.

INTRODUCTION

There are several reports in the literature on the extraction of metal ions by carboxylic acids (*1*). Gindin et al. (*2, 3*) investigated C_7–C_9 acids while Fletcher et al. (*4*) worked with commercially available naphthenic acids and versatic acids. Spitzer et al. (*5*) studied the selective extraction and separation of iron(III) from copper(II) and copper(II) from cobalt(II). The typical carboxylic acids, Versatic 9, SRS-100 (Shell Co. Ltd., London) were used in this laboratory (*6–9*) for the extraction of di-, tri-, and tetravalent metals. The compositions of the extracted species of several metals using Versatic 911 as extractant were investigated by several workers (*10–13*). The present study was undertaken to investigate the extraction behavior of thorium(IV) with Versatic 911 in benzene.

Versatic 911 is a mixture of saturated tertiary monocarboxylic acids of C_9, C_{10}, and C_{11} chain length, manufactured from C_9–C_{11} olefins (*14*). The average molecular weight of the water-white Versatic 911 is 175, and the specific gravity is 0.92.

The extraction of metals by carboxylic acid occurs by a cation-exchange mechanism in which an ionizable proton of carboxylic acid is exchanged for a cationic metal species. In its simplest form the mechanism can be expressed by

$$M^{4+} + \overline{4R{-}COOH} \rightleftharpoons \overline{M(RCOO)_4} + 4H^+ \qquad (1)$$

Barred species are in the organic phases.

While this equation is adequate for most practical purposes, it does not truly represent the extraction mechanism. Thus dimerization of the acid in an organic solvent or solvation of the extracted species by the carboxylic acid occurs in some cases. The carboxylic acid and the metal chelate formed have very little solubility in the aqueous solutions but are soluble in organic solvents.

It is evident from Eq. (1) that the extraction of metals by carboxylic acids is dependent on the pH of the aqueous phase. Use is made of this fact in the quantitative extraction and separation of metals by liquid–liquid extraction with Versatic 911.

EXPERIMENTAL

Apparatus

Separatory funnels (250 mL) were used for extraction experiments. The pH measurements were carried out with an Elico pH meter (Elico, Model LI-10, Hyderabad, India).

Reagents

Versatic 911 is a mixture of tertiary C_9–C_{11} monocarboxylic acids.

Versatic 10 is a mixture of C_{10} isomeric tertiary monocarboxylic acids.

Both Versatic 911 and Versatic 10 are manufactured by Shell Co. Ltd., London.

Thorium acetate solution (1.04 mg/mL). About 3.8 g of $Th(NO_3)_4 \cdot 6H_2O$ (E. Merck) was dissolved in double-deionized water. Acetate solution of thorium was obtained by precipitation of the metal hydroxide and subsequent dissolution in 0.2 *M* acetic acid, and the solution was standardized by the complexometric titration with EDTA (ethylene diamine tetraacetate) using xylenol orange indicator (*15*).

The chemicals and solvents used were all of analytical grade unless otherwise mentioned.

General Extraction Procedure

The procedure of the experiment was based on the solvent extraction technique. The ratio of the volumes of the aqueous phase and the organic phase was maintained at 2:1. The aqueous phase was made up from a portion of solution (10 mL) containing 10.4 mg of thorium in 0.2 *M* acetic acid. Sodium hydroxide solution was added for adjustment of pH. The total volume of the aqueous phase was made up to 20 mL, i.e., the ultimate concentration of thorium in the aqueous phase was 2.24×10^{-3} *M*. The solution was transferred into a separatory funnel and shaken with 10 m*L* of 16% Versatic 911 in benzene for 5 min. Contact time was varied from 0.5 to 10 min. The distribution ratio reached a constant value after 2 min of shaking, therefore a contact time of 5 min was used in all experiments. The two layers were allowed to settle for 10 min. The aqueous phase was then separated and the equilibrium pH was measured. To remove any trace of organic solvent entrained in the separated aqueous phase, the latter was washed with 5 mL benzene. The resulting benzene extract was mixed with the separated organic phase. The amount of thorium present in the aqueous phase was estimated by EDTA titration. Then 20 mL of 2 *N* nitric acid solution was added to the funnel, and the mixture was shaken for 5 min. The two phases were allowed to settle and separate. The aqueous layer was carefully withdrawn and again washed with 5 mL of benzene to remove any entrained solvent present in the separated aqueous phase (acid extract). The amount of thorium extracted in that phase was estimated. The procedure was followed except for the variations indicated.

RESULTS AND DISCUSSION

Effect of Variables on the Extraction pH

The extraction behavior of thorium(IV) with Versatic 911 at various pH's is illustrated in Fig. 1. The experiments were performed at constant acetate concentration (0.1 *M*). With constant extractant concentration (16%) and constant metal concentration (2.24×10^{-3} *M*), extraction of thorium increases with increased pH and becomes quantitative at pH 4–4.9. The optimum pH range for quantitative extraction is therefore 4–4.9. The distribution ratio (*D*) and the percentage extractions of thorium(IV) at different pH's are shown in Table 1. The distribution ratio was calculated from the extraction data using the relation

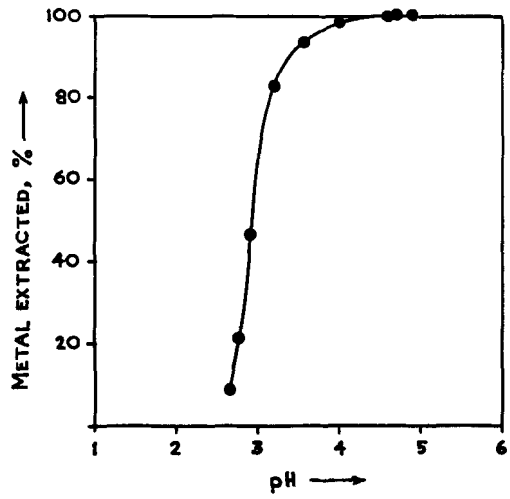

FIG. 1. Extraction of Th(IV) with Versatic 911 as a function of pH.

TABLE 1

Extraction of Thorium(IV) as a Function of pH

pH	Extraction of Th(IV) (%)	Distribution ratio (D_{Th})
2.75	21.5	0.5
2.90	46.8	1.7
3.2	82.8	9.6
3.55	93.6	29.5
4.00	98.00	98.0
4.60	99.50	398.0
4.70	100.00	∞
4.90	100.00	∞

$$D = \frac{V}{V'}\left(\frac{100}{100-x} - 1\right)$$

where V and V' are the respective volumes of the aqueous and the organic phases and x is the percentage of thorium extracted (*16*).

Versatic 911 Concentration

The effect of solvent concentration on extraction was studied by varying the concentration of Versatic 911 from 0.1 to 30% using benzene as diluent. The results are shown in Table 2. In the case of pure solvent (Versatic 911), the emulsion-forming tendency increases. To minimize

TABLE 2

Extraction of Thorium as a Function of Versatic 911 Concentration

Versatic 911 (%)	Extraction, E (%)	Distribution ratio (D_{Th})
0.10	27.50	0.70
0.25	89.80	17.60
0.50	95.9	47.40
1.00	97.9	96.0
4.00	99.1	220.0
10.00	99.7	867.0
16.00	100.0	∞
30.00	100.00	∞

TABLE 3

Effect of Diluent on Extraction of Thorium

Diluent	Dielectric constant	Metal extracted (%)	Distribution ratio (D)
Carbon tetrachloride	2.2	99.5	398.0
Benzene	2.3	100.0	∞
Xylene	2.4	99.9	2098.0
Toluene	2.4	99.5	398.0
Diisopropyl ether	3.9	99.8	998.0
Chloroform	4.8	99.0	198.0
Butanol	16.1	99.5	398.0

this tendency, all the experiments were carried out using 16% Versatic 911 in benzene.

Various Diluents

Thorium was extracted with 16% Versatic 911 solution in various diluents (Table 3). The ratio of organic to aqueous phase was maintained at 1:2. Quantitative extraction of thorium was achieved in all cases.

Metal Ion Concentration

Thorium was extracted quantitatively when the metal ion concentration was varied from 0.52 to 5.1 g/L under optimum conditions. The results are shown in Table 4.

Equilibration Times

The contact time was varied from 30 s to 10 min. The extraction was

TABLE 4

Effect of Thorium Concentration on Extraction

Concentration of Th in the aqueous phase (g/L)	Th extracted (%)	Distribution ratio (D)
0.52	100	∞
1.30	100	∞
2.60	99.95	3998
3.90	99.85	1331
5.10	99.85	1331

TABLE 5

Effect of Contact Time on Extraction and Stripping of Thorium

Extraction		Stripping	
Contact time	Th extracted (%)	Contact time	Th extracted (%)
30 s	98.0	30 s	98.7
1 min	99.8	1 min	98.7
2 min	100.0	2 min	99.0
5 min	100.0	5 min	100.0
10 min	100.0	10 min	100.0

quantitative within 2 min, and back-extraction was complete within 5 min. The results are shown in Table 5. Contact time and stripping time was kept 5 min in all experiments.

Acetate Ion Concentration

The extraction dependence of thorium(IV) upon the acetate concentration showed that the extraction decreases with an increase of acetate ion concentration. The experiments were carried out at constant pH, constant metal ion concentration (2.24×10^{-3} M), and constant extractant concentration (16%). In Fig. 2 it is shown that in these conditions log D is proportional to $-\log$ [acetate], the slope of logarithmic curve being -4.1. Therefore, four acetate ions are released in the extracting procedure.

The dependency of extraction of thorium(IV) on the extractant concentration is shown (Fig. 3) by plotting log D against log [Versatic 911]. The extraction experiments were carried out at constant metal concentration (2.24×10^{-3} M), constant acetate concentration (0.1 M), and constant pH. Plot of log D against log [Versatic 911] produces a straight line with slope 2.1. Shigematsu et al. (*10*) showed that Versatic 911 in

TABLE 6

Effect of Different Type of Liquid Cation Exchangers

Type of liquid cation exchangers	Diluent	Extraction (%)	Distribution ratio (D_{Th})
Versatic 911 (16%)	Benzene	100.0	∞
	Xylene	99.9	2098
	Toluene	99.5	398
	Chloroform	99.0	198
	Butanol	99.5	398
Versatic 10 (16%)	Benzene	100	∞
	Xylene	100	∞
	Toluene	100	∞
	Chloroform	100	∞
	Butanol	100	∞

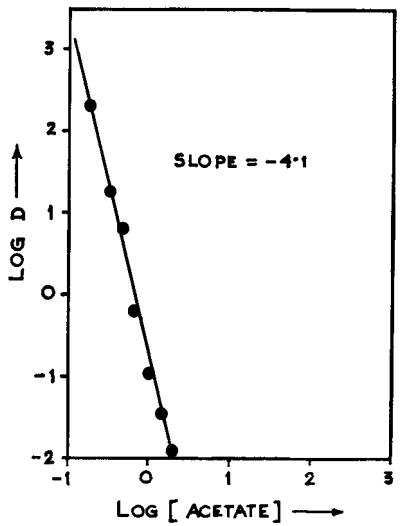

FIG. 2. Acetate ion dependency on the extraction of Th(IV) with Versatic 911.

benzene diluent exists as a dimer. Taking into account this evidence, the extraction mechanism of thorium(IV) is proposed to be

$$Th^{4+} + \overline{2R_2H_2} \rightleftharpoons \overline{ThR_4} + 4H^+$$

where the barred species are in the organic phase. R_2H_2 refers to the dimeric form of Versatic 911 in benzene solution. The thorium(IV)/ Versatic 911 ratio in the extracted species is therefore 1:4.

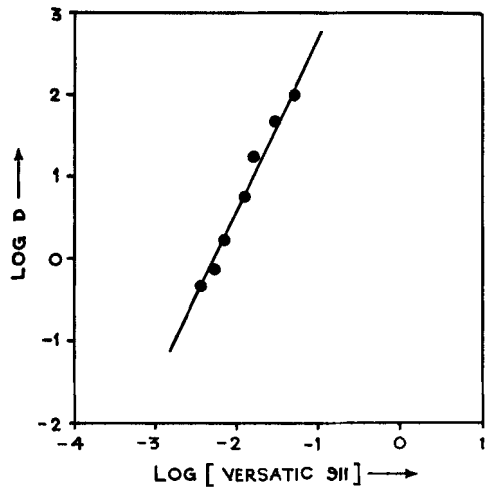

FIG. 3. Extraction dependency of Th(IV) on Versatic 911 concentration at pH 4.7.

TABLE 7

Effect of Diverse Ions on the Extraction of Thorium(IV) with Versatic 911 [Thorium(IV), 10.4 mg, pH 4.7]

Diverse ions	Amount added	Source	Thorium extracted (%)	Separation factor (D_{Th}/D_M)
Mg^{2+}	10 mg	$MgSO_4 \cdot 7H_2O$	99.8	4.98×10^4
Ca^{2+}	"	$CaCl_2 \cdot 6H_2O$	99.8	3.33×10^4
Sr^{2+}	"	$SrCl_2 \cdot 6H_2O$	99.5	6.63×10^4
Ba^{2+}	"	$BaCl_2 \cdot 2H_2O$	99.5	1.99×10^5
Mn^{2+}	"	$MnCl_2 \cdot 4H_2O$	99.0	2.47×10^4
Co^{2+} [a]	"	$CoSO_4 \cdot 4H_2O$	98.8	2.49×10^4
Ni^{2+} [a]	"	$NiSO_4 \cdot 7H_2O$	99.6	8.3×10^4
Zn^{2+} [a]	"	$ZnSO_4 \cdot 7H_2O$	99.4	1.44×10^4
Cd^{2+} [a]	"	$CdSO_4 \cdot 4H_2O$	99.8	1.66×10^5
La^{3+}	"	$La(NO_3)_3 \cdot 6H_2O$	99.0	5.41×10^3
Pr^{3+} [a]	"	$Pr(NO_3)_3 \cdot 6H_2O$	99.6	1.66×10^5
Nd^{3+} [a]	"	$Nd(NO_3)_3 \cdot 6H_2O$	99.2	1.13×10^4
Sm^{3+} [a]	"	$Sm(NO_3)_3 \cdot 6H_2O$	99.6	1.24×10^4
Gd^{3+} [a]	"	$Gd(NO_3)_3 \cdot 6H_2O$	99.4	6.25×10^3
Hg^{2+} [a]	"	$HgCl_2$	99.5	9.70×10^3

[a] In order to remove interferences due to coextraction, experiments were carried out at pH 4.3.

TABLE 8
Quantitative Separation of Thorium(IV) from Synthetic Mixtures Using Versatic 911 (pH 4.3)

Sample no.	Synthetic mixture	Thorium extracted (%)
1	Th(IV) + Co(II) + Ni(II)	99.9
2	Th(IV) + Ni(II) + La(III)	99.6
3	Th(IV) + Co(II) + Ni(II) + La(III)	99.6
4	Th(IV) + Mn(II) + Co(II) + Ni(II)	99.5
5	Th(IV) + Ca(II) + Sr(II) + Ba(II)	99.6

Extractive Separations

The extractive separation procedure is very simple and rapid, requiring in most cases only pH control. Thorium has been separated from manganese, cobalt, nickel, zinc, cadmium, mercury, calcium, magnesium, strontium, barium, lanthanum, praseodymium, neodymium, samarium, and gadolinium. The interfering ions are cerium, lead, and uranium. The effects of diverse ions and the separation factors (D_{Th}/D_M) are shown in Table 7.

Separation of Thorium from Synthetic Mixtures

Thorium(IV) was separated quantitatively from such synthetic mixtures as (1) cobalt, nickel, thorium; (2) nickel, lanthanum, thorium; (3) cobalt, nickel, lanthanum, thorium; (4) manganese, cobalt, nickel, thorium; and (5) calcium, strontium, barium, thorium. The synthetic mixtures were prepared by mixing 10 mg of each metal. The results are shown in the Table 8. In all cases, quantitative recovery of thorium(IV) was made possible under the recommended extraction conditions.

Acknowledgments

The authors thank Shell Co. Ltd., London, for the gift samples of Versatic 911 and Versatic 10. Financial support from U.G.C., India, is sincerely appreciated. The authors are also grateful to Prof. A. K. De, Department of Chemistry, Visva-Bharati (India), for his constant help in the research work.

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Received by editor May 20, 1980