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Solvent Extraction Separation of Manganese (II) with Tributyl Phosphate

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NOTE

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Summary

A fast and selective method is proposed for solvent extraction of manganese with tributyl phosphate. It is possible to quantitatively extract manganese with 40% tributyl phosphate in xylene from solutions containing 1 *M* hydrochloric acid and 2.5 *M* aluminum chloride as the salting-out agent. The metal from the organic phase is stripped with water and is determined photometrically as its complex with formaldoxime. The probable composition of the extractable species at 1 *M* acidity is $[MnCl_2 \cdot 3TBP]$. It is possible to extract manganese in the presence of a twentyfold excess of common ions, but mercury, copper, iron, bismuth, and vanadium interfere. The standard deviation is ±1.05%.

Although several chelating agents are used for the solvent extraction of manganese, very few techniques in ion association systems are known. Pyridine (*1*) was used for its extraction but separation of phases was difficult. Pyridine thenoyltrifluoroacetone (*2*) mixture was then used for its extraction, but common elements showed interference. The tetraphenylarsonium chloride complex of manganese was extracted in chloroform from an alkaline medium (*3,4*). Among amines as extractants, dihexyl and didecylamine (*5*) proved satisfactory for permanganate ion, but the method was applicable at macro levels.

Tributyl phosphate (*6*) has been used to separate manganese and cobalt from nickel in neutral solutions; but the extraction is quantitative only at high salting-out agent concentrations. The existing methods are slow, are inapplicable at tracer concentration, and need optimum control of conditions. The method proposed in this paper is rapid, is simple, and can be adopted at tracer concentrations.

GENERAL PROCEDURE

To an aliquot of solution containing 49.5 μg Mn, add enough aluminum chloride, hydrochloric acid, and water to give concentrations of 2.5 *M* with respect to aluminum chloride and 1 *M* with respect to hydrochloric acid in a volume of 25 ml. Shake the solution for 7 min with 10 ml 40% (v/v) TBP in xylene. Separate the layers and strip manganese from the organic phase with two 10-ml portions of distilled water. Manganese from the aqueous phase is determined photo-

TABLE 1

Distribution Ratio as the Function of Acidity

Mn(II) = 49.5 μg, 2.5 *M* $AlCl_3$

TBP conc. *M*	HCl, *M* (initial)	Extraction % *E*	Distribution ratio, *D*
20% (0.73)	0.10	41.7	1.77
	0.25	50.0	2.50
	0.50	58.3	3.50
	0.75	60.4	3.82
	1.00	62.5	4.12
30% (1.09)	0.10	50.0	2.50
	0.25	54.2	3.25
	0.50	66.7	5.50
	0.75	75.0	7.50
	1.00	79.2	9.50
40% (1.46)	0.10	66.7	5.00
	0.25	83.8	12.58
	0.50	91.7	27.51
	0.75	100.0	∞
	1.00	100.0	∞
75% (2.74 *M*)	0.10	75.0	7.50
	0.25	91.7	27.51
	0.50	100.0	∞
	0.75	100.0	∞
	1.00	100.0	∞
100% (3.66 *M*)	0.10	75.0	7.500
	0.25	91.7	27.51
	0.50	100.0	∞
	0.75	100.0	∞
	1.00	100.0	∞

metrically with a blue filter as it forms a reddish-brown complex with formaldoxime (*7*).

RESULTS AND DISCUSSION

Effect of Varying Acid and TBP Concentration

The concentration of hydrochloric acid was varied from 0.10 to 1 *M* and the concentration of TBP from 20 to 100% (0.73 to 3.66 *M*) by dilution with xylene, in the presence of 2.5 *M* aluminum chloride as the salting-out agent. The results in Table 1 show that for quantitative extraction 40% TBP in xylene is essential. The optimum concentration is 1 *M* hydrochloric acid with 2.5 *M* aluminum chloride as the salting-out agent. The plot of log *D* versus log (TBP) at 1 *M* hydrochloric acid shows a slope of 2.7 (Fig. 1), which indicates that the probable composition of the extractable species is $MnCl_2 \cdot 3$ TBP. The optimum reagent concentration is 40% TBP in xylene.

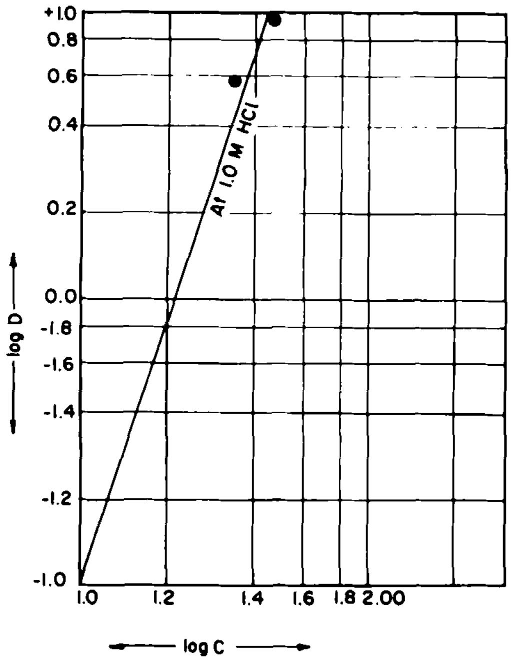

FIG. 1. Extraction as the function of TBP concentration.

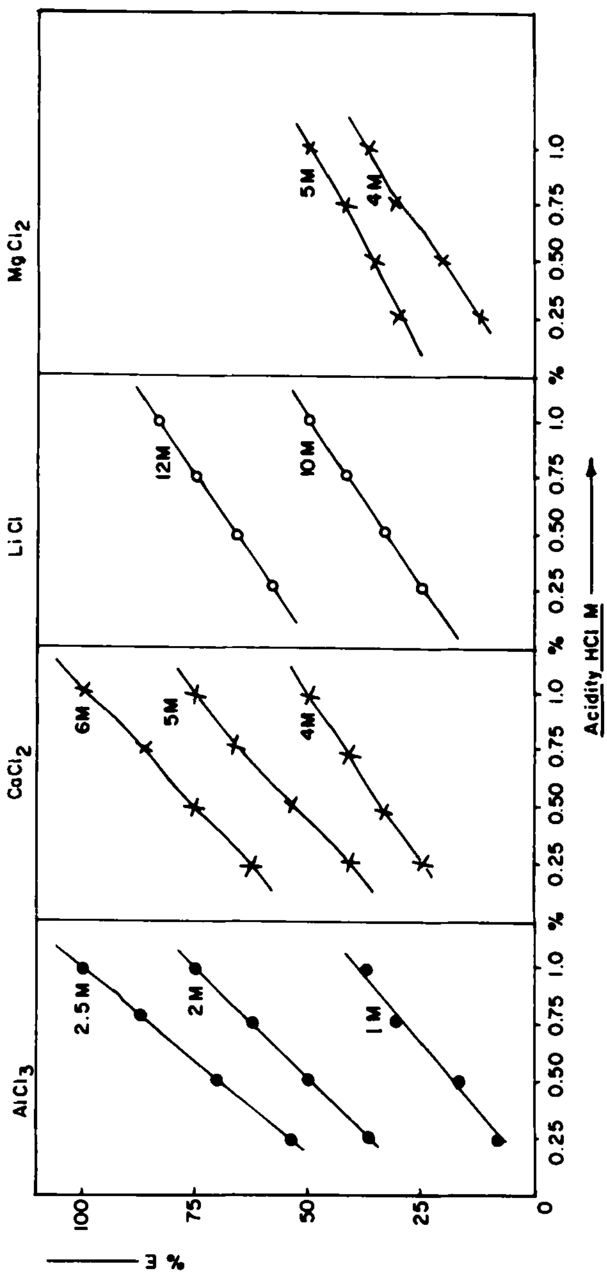

FIG. 2. Effect of salting-out agent.

TABLE 2

Effect of Diverse Ions

Mn(II) = 49.5 μg, 1 *M* HCl + 2.5 *M* $AlCl_3$; 40% TBP xylene

Foreign ion	Added as	Tolerance limit, μg
Pb^{2+}	$Pb(NO_3)_2$	500
Hg^{2+}	$HgCl_2$	none
Pd^{2+}	$PdCl_2 \cdot 2H_2O$	500
Au^{3+}	$HAuCl_4 \cdot xH_2O$	100
Ru^{3+}	$RuCl_3 \cdot 3H_2O$	500
Cu^{2+}	$CuSO_4 \cdot 5H_2O$	none
Cd^{2+}	$3CdSO_4 \cdot 8H_2O$	500
Sb^{3+}	$Sb_2(SO_4)_3$	500
Bi^{3+}	$Bi(NO_3)_3 \cdot 5H_2O$	none
Sn^{2+}	$SnCl_2 \cdot 2H_2O$	1000
Fe^{2+}	$FeSO_4 \cdot 7H_2O$	none
Fe^{3+}	$FeCl_3 \cdot 6H_2O$	none
Be^{2+}	$Be(NO_3)_2 \cdot 3H_2O$	1000
Zr^{4+}	$Zr(NO_3)_4$	500
Ce^{4+}	$Ce(SO_4)_2$	1000
Th^{4+}	$Th(NO_3)_4 \cdot 4H_2O$	500
U^{6+}	$UO_2(NO_3)_2 \cdot 6H_2O$	1000
Zn^{2+}	$ZnSO_4 7H_2O$	1000
Co^{2+}	$Co(NO_3)_2 \cdot 6H_2O$	1000
Ni^{2+}	$NiCl_2 \cdot 6H_2O$	1000
Ba^{2+}	$BaCl_2 \cdot 2H_2O$	1000
Sr^{2+}	$SrCl_2 \cdot 6H_2O$	1000
CrO_4^{2-}	K_2CrO_4	1000
$Mo_7O_{24}^{6-}$	$(NH_4)_6Mo_7O_{24}$	500
VO_3^{2-}	NH_4VO_3	none
SeO_3^{2-}	Na_2SeO_3	500
TeO_3^{2-}	Na_2TeO_3	500
WO_4^{2-}	Na_2WO_4	500
SCN^-	NH_4SCN	1000
$S_2O_3^{2-}$	$Na_2S_2O_3$	1000
F^-	NaF	500
Br^-	NaBr	500
PO_4^{3-}	Na_3PO_4	500
Cit^{3-}	Citric acid	none
$Tart^{2-}$	Tartaric acid	500
$Malon^{2-}$	Malonic acid	500
$Acorb^{2-}$	Ascorbic acid	500
$C_2O_4^{2-}$	Oxalic acid	none
$EDTA^{4-}$	EDTA (disodium salt)	500

Effect of Salting-Out Agent

The effect of varying concentrations of the salting-out agent on the extraction of manganese with 40% TBP-xylene from 0.25 to 1.0 *M* hydrochloric acid was studied. The results in Fig. 2 show that it is possible to quantitatively extract manganese at 1 *M* hydrochloric acid concentration in the presence of 2.5 *M* aluminum chloride, or 6 *M* calcium chloride. Lithium and magnesium chlorides do not exert any effect on the process of extraction.

Period of Equilibration

The period of shaking was varied from 2 to 15 min. It was observed that the extent of extraction increased from 75% after 1 min to 100% after 7 min and then remained constant up to 15 min. The optimum period of equilibration was thus at least 7 min.

Effect of Diversions

The various ions usually associated with manganese in minerals, etc., were tested for interference (Table 2). The tolerance limit was set at the amount required to cause ±2% error in manganese recovery. The results show that manganese can be extracted in the presence of twentyfold amounts of some ions, while ions such as lead, palladium, ruthenium, cadmium, antimony, zirconium, thorium, and some anions are tolerated in tenfold ratios. But mercury, copper, bismuth, iron, vanadate, citrate, and oxalate interfere. However, their interference can be eliminated by using a suitable masking agent.

The method is rapid, simple, and selective and permits separation and determination of manganese at tracer levels. The average recovery of manganese was 99.6 ± 0.4%. The standard deviation was +1.05% in ten determinations of 49.8 μg of manganese.

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