

Extraction and separation studies of manganese(II) with Cyanex 301

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Liquid-liquid extraction of manganese(II) has been carried out in the presence of ammonium sulphate with Cyanex 301 in toluene. Mn(II) is quantitatively extracted in the pH range 7.0-9.5 in presence of 1.0 M ammonium sulphate with 5×10^{-3} M Cyanex 301 in toluene. Mn(II) from the organic phase is stripped with 1.0 M H_2SO_4 . Various parameters like reagent concentration, time, effect of diluents and tolerance limit of diverse ions have also been studied. Mn(II) has been successfully separated from commonly associated metals like Cu(II), Ni(II) and Fe(III). The method has been employed for determination of Mn(II) in real samples.

Manganese(II) has been extracted with 0.15 M thionyltrifluoroacetone in the pH range of 6.7-8.0 from acetone-benzene mixture¹. Among organophosphorous reagents HDEHP², TBP³ and TOPO⁴ are known to extract Mn(II) while Cyanex 272⁵ and Cyanex 302⁶ extract Mn(II) from sulphate media. With tri-*n*-butyl sulphide in CCl_4 the extraction of Mn(II) was negligible even after shaking for 30 min⁷. Extraction behaviour of some 3d-transition metals using Cyanex 925⁸ and Cyanex 301^{9,10} as extractants were investigated. However it was observed that these methods suffer from limitations like critical pH⁵, high reagent concentration^{6,9,10}, poor extraction³ and interferences¹.

Experimental

A GBC 911A UV-visible spectrophotometer with 10 mm Corex quartz cuvettes and Systronics MK VI combined digital pH-meter were used.

Cyanex 301 (Cytec Canada Inc.) was used directly without further purification. Stock solution of Mn(II) was prepared by dissolving $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (3.602 g) in 1L of distilled water containing 5 ml of conc HCl. The solution of Mn(II) was standardised complexometrically with Eriochrome Black T as indicator¹¹. Working standard solutions of Mn(II)

were prepared by appropriate dilution of the stock solution.

General procedure

An aliquot containing 100 μg of Mn(II) and 1.0 M ammonium sulphate was taken. The pH of the resulting solution was adjusted to 8.0 using dil. hydrochloric acid and ammonia solution. The total volume of the aqueous phase was made up to 10 ml to which an equal volume of 5×10^{-3} M Cyanex 301 in toluene was added. The two phases were allowed to settle and separate after a shaking period of 6 min. The Mn(II) loaded organic phase was stripped with 1.0 M H_2SO_4 and then Mn(II) in the aqueous phase was determined spectrophotometrically by potassium periodate method¹².

Results and discussion

The optimum conditions required for the extraction of Mn(II) were found by varying the pH (2.0-10.25) (Fig. 1) and Cyanex 301 concentration (1×10^{-4} - 1×10^{-2} M) dissolved in toluene. The extraction was found to be quantitative in the pH range 7.0-9.5 while

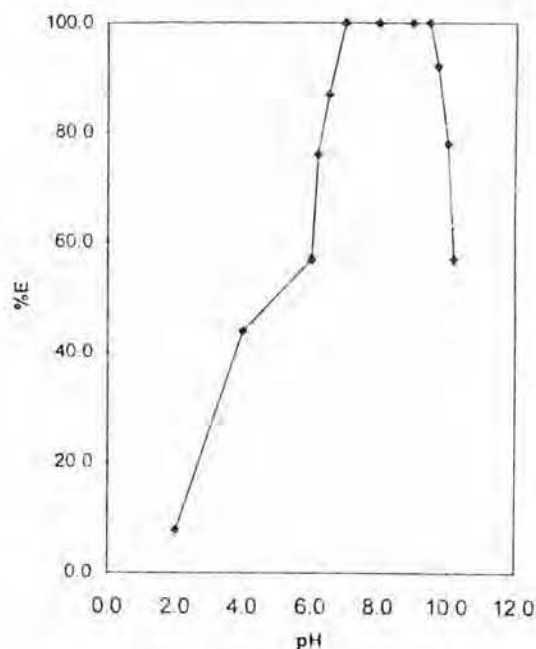


Fig. 1—%E versus pH for extraction of Mn(II) with 5×10^{-3} M Cyanex 301 in toluene in presence of 1.0 M ammonium sulphate

the minimum concentration of Cyanex 301 required for quantitative extraction was $5 \times 10^{-3} M$. By using the slope analysis method the metal to reagent stoichiometry, Mn(II) : Cyanex 301, was found to be 1:2.

The recovery of Mn(II) from the organic phase was carried out using different acids such as HCl, HClO₄, HNO₃ and H₂SO₄. Quantitative stripping was observed with 1.0 M HCl, HNO₃ and H₂SO₄ and 2.0 M HClO₄ respectively. However, 1.0 M H₂SO₄ was used as a stripping agent for further experimental studies. The minimum shaking time required for complete extraction of Mn(II) was found to be 6.0 min. with no adverse effect on the percentage extraction of Mn(II) for longer shaking periods. Various salting-out agents such as sulphates of K⁺, Na⁺, Mg²⁺ and Al³⁺ were tried for extraction of Mn(II) amongst which 1.0 M ammonium sulphate was found to be the most suitable salting-out agent as it provided a high anion concentration in the aqueous phase. The effect of several ions on extraction of Mn(II) was studied with Cyanex 301 in toluene and the tolerance limit was set at the amount causing an error of $\pm 2\%$ on weight basis. It was found that alkali and alkaline-earth metals were tolerated in the ratio of 1:50 and 1:20 while anions like chloride, bromide, iodide, sulphate, sulphite, nitrate, nitrite, thiocyanate, tartarate and peroxide were tolerated in the ratio of 1:40. Similarly tolerance limit for Be(II), V(V) and In(III) was found to be 1:5, while for Cu(II), Cd(II), Co(II) and Ni(II), it was 1:4, 1:3, 1:2 and 1:1 respectively.

Separation of manganese(II) from multicomponent mixtures

A mixture of Cu(II) and Mn(II) was separated by first extracting Cu(II) in 0.5 M HCl with $8 \times 10^{-3} M$ Cyanex 301 in chloroform while Mn(II) which remained in the aqueous phase was extracted at pH 8.0 in the presence of 1.0 M ammonium sulphate with $5 \times 10^{-3} M$ Cyanex 301 in toluene. Copper(II) was measured directly in the organic phase at 440 nm while Mn(II) was stripped from the organic phase with 1.0 M H₂SO₄ and then determined spectrophotometrically.

Ni(II) and Mn(II) were separated by first extracting Ni(II) at pH 8.0 with $5 \times 10^{-3} M$ Cyanex 301 in chloroform while Mn(II) remained in the aqueous phase. Mn(II) was then extracted at pH 8.0 in presence of 1.0 M ammonium sulphate with $5 \times 10^{-3} M$

Table 1—Separation of Mn(II) from multicomponent mixtures

Metal ions	Conc., μg	Aqueous phase	Stripping agent	Recovery, %
Cu(II)	25	0.5 M HCl	—	100.00
Mn(II) [†]	100	pH=8.0	1.0 M H ₂ SO ₄	99.75
Ni(II)	20	pH=8.0	—	100.00
Mn(II) [†]	100		1.0 M H ₂ SO ₄	99.75
Fe(III)	50	pH=2.0	2.0 M HCl	99.80
Mn(II) [†]	100	pH=8.0	1.0 M H ₂ SO ₄	99.75
Cu(II)	25	0.5 M HCl	—	100.00
Fe(III)	50	pH=2.0	2.0 M HCl	99.80
Ni(II)	20	pH=8.0	—	100.00
Mn(II) [†]	100		1.0 M H ₂ SO ₄	99.75

[†]Extraction of Mn(II) was carried out in presence of 1.0 M ammonium sulphate

Table 2—Analysis of manganese(II) in real samples

Alloys	Mn(II), %		Recovery, %
	Cert.	Found [†]	
Pyrolusite	63.2	62.9	99.52
EN 36A steel	0.300	0.297	99.00
Monel metal	2.0	1.98	99.00

[†]Average of three determinations

Cyanex 301 in toluene. Nickel(II) was measured directly in the organic phase at 340 nm while Mn(II) was stripped from the organic phase with 1.0 M H₂SO₄ and determined spectrophotometrically.

In a mixture containing Fe(III) and Mn(II) the metal ions were easily separated from each other by extracting Fe(III) at pH 2.0 with $5 \times 10^{-3} M$ Cyanex 301 in chloroform followed by extraction of Mn(II) in the presence of 1.0 M ammonium sulphate at pH 8.0 with $5 \times 10^{-3} M$ Cyanex 301 in toluene. Fe(III) and Mn(II) were measured spectrophotometrically after stripping the organic phase with 2.0 M HCl and 1.0 M H₂SO₄ respectively.

In mixture containing Cu(II), Ni(II), Fe(III) and Mn(II), each component could be resolved by first extracting Cu(II) in 0.5 M HCl with $8 \times 10^{-3} M$ Cyanex 301 in chloroform then extracting Fe(III) at pH 2.0 with $5 \times 10^{-3} M$ Cyanex 301 in chloroform followed by extraction of Ni(II) at pH 8.0 with $5 \times 10^{-3} M$ Cyanex 301 in chloroform. Copper(II) and nickel(II) were determined directly in the organic phase at 440 nm and 340 nm respectively. However Fe(III) and Mn(II) were stripped from the organic phase with 2.0 M HCl and 1.0 M H₂SO₄ respectively (Table 1).

Application to real samples

The proposed method was extended for the determination of Mn(II) in real samples like pyrolusite, EN 36A steel and Monel metal. The values obtained are in good agreement with the certified values (Table 2).

The proposed method of separation is simple, rapid and selective over the earlier existing methods. It requires lower reagent concentration, lower stripping agent concentration, can tolerate large amount of diverse ions and requires less than 15 min. for the estimation.

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