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Extraction separation studies of divalent manganese using N-n-octylaniline as a liquid anion exchanger

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ABSTRACT

A trace concentration of manganese (II) was quantitatively extracted at pH 10.5 in 0.01M sodium malonate with 0.022M N-n-octylaniline. It was eluted with 0.2N nitric acid and determined by spectrophotometrically. The various parameters influencing extraction viz. pH, sodium malonate concentration, N-n-octylaniline concentration, various eluents, elution time and effects of interfering ions were studied to determine the optimum conditions for separation of manganese. The method was extended for an analysis of manganese (II) in synthetic mixtures corresponding to alloys.

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KEYWORDS

Extraction chromatography;
Separation;
Manganese (II);
Alloy.

INTRODUCTION

Abundance of manganese in earth crust is only 1000 ppm. It is a micronutrient actively absorbed by plants and has an effect on fertility of soil^[1]. It is used in chemical and metallurgical industry. It is a component of enzyme^[2]. N-n-octylaniline is already used for extraction separation studies of palladium(II)^[3], platinum(IV)^[4], ruthenium(III)^[5], iridium(III)^[6] and rhodium(III)^[7] in our laboratory. Manganese(II) has been quantitatively extracted with acetyl derivative of calycox^[8]. The method suffers from interferences from silver and nickel. It also requires 2.0 M sulphuric acid for stripping. Manganese(II) was extracted with micro cyclic Schiff's base contains thiophenophenol^[9] in nitrobenzene with tetra phenyl borate as counter anion. Method suffers from strong interference from copper. Micro cyclic Schiff's bases^[10] extract manganese(II) at pH 7-11 and was determined by spectrophotometrically Cryptand

222^[11] in chloroform was extract manganese(II) with erythrosine as the counter anion. Method requires 5.0 M hydrochloric acid for stripping.

Very few methods are available for separation of manganese. Considering applications and demand of manganese it is a challenge to analytical chemists to develop separation method for a metal. In present communication manganese(II) was quantitatively extracted from 0.01M sodium malonate at pH 10.5 with 0.022M N-n-octylaniline and eluted with 0.2M nitric acid.

EXPERIMENTAL

Apparatus

A spectrophotometer [Elico model SL-159] with 10 mm path length quartz cells and pH meter [Control Hydrodynamic] used for absorbance and pH measurements.

TABLE 1 : Extraction behavior of manganese (II) as a function sodium malonate Mn(II) 100µg; N-n-octylaniline 0.022 M : pH 10.5; Eluent 50 mL 0.2 N nitric acid

Na malonate 'M'	% Recovery	Distribution coefficient, Kd
0.001	55.3	1.24
0.003	62.9	1.70
0.005	91.9	11.35
0.007	95.6	21.73
0.009	99.9	999.00
0.010	100.0	∞
0.012	100.0	∞
0.015	100.0	∞
0.020	100.0	∞
0.050	89.9	8.90
0.070	78.6	3.67
0.090	62.9	1.70
0.120	40.3	0.68
0.150	15.5	0.18
0.170	1.8	0.02

TABLE 2 : Extraction behavior of manganese (II) as a function of pH Mn(II) 100µg; N-n-octylaniline 0.022 M; Eluent 50mL 0.2 M nitric acid

pH	% Recovery	Distribution ratio, Kd
6.0	0.5	0.01
6.5	15.9	0.19
7.0	60.1	1.51
8.0	93.7	14.87
9.0	97.9	46.62
10.0	100.0	∞
11.0	100.0	∞
12.0	100.0	∞
13.0	94.4	16.86

Reagents

A stock solution of manganese(II) was prepared by dissolving 0.384 gm of manganese sulfate monohydrate ($MnSO_4 \cdot H_2O$) (Loba chem. Laboratories and fine Chem.) in distilled water and diluted to 250mL. The solution was standardized by complexometrically^[12]. A working solution of manganese(II), 100µg/mL was made from diluting stock solution with distilled water. N-n-octylaniline was prepared using method reported by Gardlund^[13]. The stock solution of N-n-octylaniline was prepared in chloroform. Other standard solutions of different metal ions were prepared by dissolving respective salt with distilled water and dilute hydrochloric

TABLE 3 : Extraction behavior of manganese (II) as a function of N-n-octylaniline Mn (II) 100µg; pH-10.5; Eluent 50mL 0.2 M nitric acid

N-n-octylaniline	Na-malonate	% Recovery	Distribution ratio, Kd
	0.004	24.5	0.32
	0.006	41.2	0.70
0.004 M (0.1%)	0.008	62.4	1.66
	0.010	79.5	3.88
	0.012	82.4	4.68
	0.014	87.2	6.81
	0.004	61.9	1.62
	0.006	70.2	2.36
0.013 M (0.3%)	0.008	75.3	3.05
	0.010	100.0	∞
	0.012	100.0	∞
	0.014	100.0	∞
	0.004	74.1	2.86
	0.006	84.4	5.41
0.022 M (0.5%)	0.008	99.3	141.86
	0.010	100.0	∞
	0.012	100.0	∞
	0.014	100.0	∞
	0.004	86.2	6.25
	0.006	91.5	10.76
0.030 M (0.7%)	0.008	99.9	999.00
	0.010	100.0	∞
	0.012	100.0	∞
	0.014	100.0	∞
	0.004	89.4	8.43
	0.006	97.6	40.67
0.043 M (1.0%)	0.008	100.0	∞
	0.010	100.0	∞
	0.012	100.0	∞
	0.014	100.0	∞

acid. All other chemicals used were of AR. Grade.

Preparation of anion exchange material

Silica gel (60-120 mesh) obtained from BDH India, dried at 120°C for 2-3 h. and stored in desiccators. It was packed in a U tube through which a stream of nitrogen was bubbled through a small Durand bottle containing 20.0mL dimethyldichlorosilane (DMCS) from (Acros Organics. New Jersey. USA). DMCS vapor was continued for 4 h. The silica gel was washed with anhydrous methanol, then dried. A portion of 5.0g silanated

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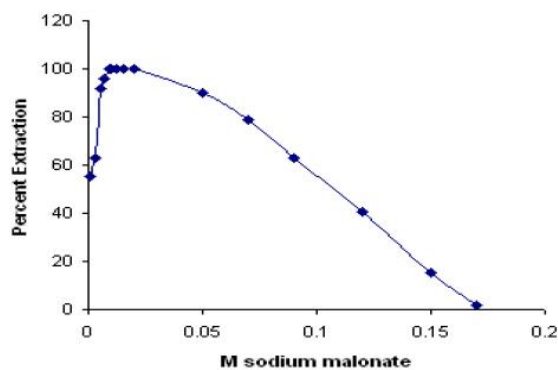


Figure 1 : Effect of sodium malonate concentration on percentage extraction

TABLE 4 : Effect of stripping agents Mn(II) 100 μ g; *N-n*-octylaniline 0.022M; Sodium malonate 0.01M; pH-10.5

Nitric acid M	% Recovery	Distribution ratio, Kd
0.03	15.0	0.18
0.05	24.9	0.33
0.10	81.5	4.41
0.15	99.2	124.00
0.20	100.0	∞
0.25	100.0	∞

Perchloric acid M	% Recovery	Distribution ratio, Kd
0.03	12.2	0.14
0.05	27.0	0.37
0.07	85.7	5.99
0.01	100.0	∞
0.15	100.0	∞
0.20	100.0	∞

silica gel was soaked with 0.022 mol/L *N-n*-octylaniline which was previously equilibrated with sodium malonate (0.01 mol/L) at pH 10.5 for 10 min, then solvent was evaporated to get nearly dried gel. The slurry of *N-n*-octylaniline coated silica gel in distilled water was prepared by centrifuging at 2000 r/min. The coated silica gel was packed into a chromatographic column to give a 6.0cm bed, the bed was covered with glass wool plug.

General procedure

An aliquot solution containing 100 μ g of manganese (II) was made up to 25.0mL by adjusting the concentration of with sodium malonate 0.01M mol/L and pH 10.5. It was passed through the column containing 0.022 mol/L *N-n*-octylaniline coated with silica gel at a flow rate of 1.0mL/min. After extraction, manganese (II) was stripped with 50ml 0.2N nitric acid and determined spectrophotometrically^[14].

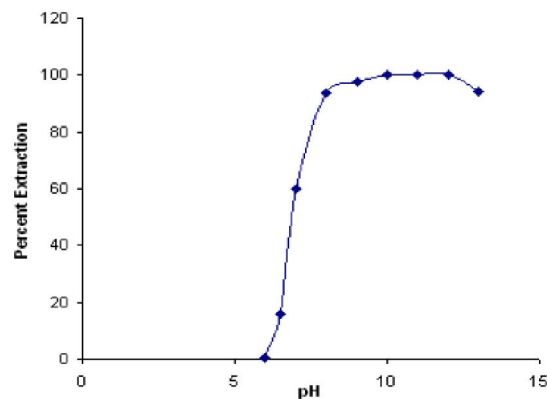


Figure 2 : Effect of pH

RESULTS AND DISCUSSION

Effect of acid concentration and pH on extraction

The extraction of manganese(II) was studied from 0.001 to 0.170 mol/L sodium malonate in a pH range 6.0-13.0. Metal ion was extracted quantitatively from 0.009-0.020 mol/L sodium malonate media at pH 10.0-12.0 (TABLE 1,2; Figure 1,2) with 0.022 mol/L *N-n*-octylaniline.

Effect of flow rate

The effect of flow rate on percentage extraction of manganese(II) was studied from 0.5ml/min to 3.0ml/min. It was observed that the increase in flow rate was inversely proportional to percentage extraction. Optimum flow rate was observed from 0.5mL/min to 1.0mL/min.

Effect of *N-n*-octylaniline concentration

The concentration of *N-n*-octylaniline was varied from 0.004 to 0.043 mol/L while the concentration of sodium malonate varied from 0.004 to 0.014 mol/L at pH 10.5 for manganese(II).

It was observed that for quantitative extraction of manganese(II) 0.013 to 0.043 mol/L *N-n*-octylaniline was sufficient in sodium malonate media at pH 10.5. The percentage extraction of manganese(II) increases with increase in concentration of *N-n*-octylaniline increases.

Effect of stripping agent

Optimum elution of the manganese(II) was observed at a concentration of nitric acid 0.20 to 0.25 M and perchloric acid from 0.03 to 0.2 M TABLE 4. In

TABLE 5 : Effect of foreign ions Mn(II) 100µg; N-n-octylaniline 0.022 M; Eluent 50mL 0.2 N nitric acid; Sodium malonate 0.01 M: pH 10.5

Foreign ion	Added as	Tolerance limit µg	Foreign ion	Added as	Tolerance limit µg
Cu(II)	CuSO ₄ .5H ₂ O	500	Ni(II)	NiCl ₂ .6H ₂ O	300
V(V)	V ₂ O ₅	300	Al(III)	AlCl ₃	300
U(VI)	UO ₂ (NO ₃) ₂ .6H ₂ O	300	Ir(III)	IrCl ₃ .xH ₂ O	150
Ga(III)	GaCl ₃	100	Fe(II)	FeSO ₄ .7H ₂ O	100
Tl(III)	TlNO ₃	200	Ti(IV)	TiO ₂	150
Zn(II)	ZnSO ₄ .7H ₂ O	300	Pb(II)	Pb(NO ₃) ₂	300
Sn(II)	SnCl ₂ .2H ₂ O	300	Au(III)	HAuClO ₄ .H ₂ O	100
Cd(II)	3CdSO ₄ .8H ₂ O	300	Os(VIII)	OSO ₄	300
Bi(III)	Bi(NO ₃) ₂ .5H ₂ O	100	Rh(III)	RhCl ₃ .xH ₂ O	200
H ₂ O ₂	H ₂ O ₂	0.5 mL	Ru(III)	RuCl ₃ .xH ₂ O	100
Co(II)	CoCl ₂ .6H ₂ O	300	Ag(I)	AgNO ₃	200
Pd(II)	PdCl ₂ .xH ₂ O	100	Tartrate	C ₆ H ₆ O ₆	500
Oxalate	(COOH) ₂ .2H ₂ O	500	Thiourea	S N ₂ H ₄ C	500
Citrate	C ₆ H ₈ O ₇ .H ₂ O	100	Tartarate	(CHOH.COOH) ₂	200
Succinate	(CH ₂ COONa) ₂ .6H ₂ O	300	Mo(VI)	(NH ₄) ₆ Mo ₇ O ₂₄ .2H ₂ O	300
Ascorbate	C ₆ H ₈ O ₆	500	EDTA	EDTA (Disodium salt)	150

TABLE 6 : Analysis of different grades of austenitic manganese steels N-n-octylaniline 0.022 M; Eluent 50 mL 0.2 N nitric acid; Sodium malonate 0.01 M: pH 10.5

Grade	Composition	Manganese (II)		% Recovery
		Amount Taken µg	Amount found µg	
A	Carbon(%C) 1.05-1.35		99.8	99.8
	Manganese (%Mn) min 11.0	100	99.6	
	Silicon (%Si) max 1.00		99.9	
	Phosphorous (%P) max 0.07			
B-1	Carbon(%C) 0.90-1.05		99.6	99.6
	Manganese (%Mn) 11.5-14.5	100	99.4	
	Silicon (%Si) max 1.00		99.7	
	Phosphorous (%P) max 0.07			
B-2	Carbon(%C) 1.05-1.20		99.7	99.7
	Manganese (%Mn) 11.5-14.5	100	99.8	
	Silicon (%Si) max 1.00		99.5	
	Phosphorous (%P) max 0.07			

actual process 0.2 M nitric acid was used for elution of manganese(II). Sulphuric acid elutes maximum 76.6% while hydrochloric acid, hydrobromic acid, ammonia and water has not given any illusion of metal.

Effect of foreign ions

Various foreign ions were added to fixed amount of manganese(II) (100µg) to study the effect of interference according to the recommended procedure. The

TABLE 6 : Analysis of different grades of austenitic manganese steels N-n-octylaniline 0.022 M; Eluent 50 mL 0.2 N nitric acid; Sodium malonate 0.01 M: pH 10.5

Grade	Composition	Manganese (II)		% Recovery
		Amount Taken µg	Amount found µg	
B-3	Carbon(%C) 1.12-1.28		99.8	99.7
	Manganese (%Mn) 11.5-14.5	100	99.6	
	Silicon (%Si) max 1.00		99.8	
	Phosphorous (%P)max 0.07			
B-4	Carbon(%C) 1.20-1.35		99.7	99.7
	Manganese (%Mn) 11.5-14.5	100	99.5	
	Silicon (%Si) max 1.00		99.8	
	Phosphorous (%P) max 0.07			
E-1	Carbon(%C) 0.70-1.30		99.6	99.7
	Manganese (%Mn) 11.5-14.5		99.7	
	Molybdenum (%Mo) 0.90-1.20	100	99.7	
	Silicon (%Si) max 1.00			
E-2	Phosphorous (%P) max 0.07			99.7
	Carbon(%C) 1.05-1.45		99.8	
	Manganese (%Mn) 11.5-14.5		99.7	
	Molybdenum (%Mo) 1.80-2.10	100	99.6	
E-2	Silicon (%Si) max 1.00			99.7
	Phosphorous (%P) max 0.07			

tolerance limit was set at the amount required to cause ± 1.5% error in the recovery of manganese(II) (TABLE 5). It was observed that the method was free from in-

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terference from a large number of cations and anions. The only cations showing interference in the method are mercury (II), chromium (VI), tungsten(VI), salysalate and iopdate.

Applications

Analysis of synthetic mixtures corresponding to alloy

The proposed method was successfully applied for the analysis of synthetic mixtures corresponding to different grades of aesthetic manganese steel samples containing manganese(II). The results of analysis matches with certified values (TABLE 6).

CONCLUSION

The method is simple, reliable and reproducible. The reliability of the method is verified by analyzing synthetic mixture corresponding to alloys. The method is free from large number of cations and anions.

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