Estimation of manganese in samples by Tributyl Amine- A solvent extraction study

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Abstract-Solvent extraction of Mn (II) from hydrochloric and nitric acid solutions with Tributlamine (TBA) in xylene has been studied. The extractions efficiency from both the acid media was nearly quantitative. Role of different variables (extractant, metal ion, acidity, foreign ions etc) on the extraction process has been studied. Probable extracted species [Mn X_2.(TBA)], is also suggested. Estimation of manganese in food as well as pharmaceutical samples has been successfully attempted following the method of extraction.

Key words-Extraction , Mn (II), Tributyl amine (TBA),alloys, Pharmaceutical samples.

I. INTRODUCTION

Manganese among non-ferrous elements, plays an important role in dry battery technology, chemical industry etc. Hence, extraction of manganese from all possible sources needs attention. Solvent extraction of Mn (II) has been carried out by earlier workers using amines [1] and other extracting agents [2-7] from different mineral acid media. The present communication describes extraction of Mn (II) by Tributylamine (TBA) from hydrochloric and sulphuric acid solutions.

II MATERIALS& METHODS

A stock solution of 0.25 M TBA (Fluka AG) in chloroform was prepared and diluted to get the required concentration. 1.52 gm of manganese sulphate monohydrate was dissolved in 1lt double distilled water. Mn(II) stock solution was prepared & was standardized with standard EDTA solution complexometrically. All the required reagent solutions were prepared by using double distilled water and AnalaR grade chemicals.

2.1Mn(II) extraction -

Distribution studies of Mn(II) was done by shaking 10ml of specific concentration of manganese salt and mineral acid with 10ml portion of Tributylamine (TBA) in xylene (0.025M) pre-equilibrated with 0.1M mineral acid. The two phases were separated after 5 minutes. By using 10ml of 0.1M HNO_3 Mn(II) was stripped from the organic phase. With the help of AAS method, concentration of Mn(II) was determined in both the phases.

III.RESULTS AND DISCUSSION

3.1 Acid variation-

The distribution ratio (Kd) increases with increase in the concentration of the acid up to 4.0M acidity in hydrochloric acid solutions and from nitric acid media, it was found to increase up to 3.85M acidity followed by decrease in extraction thereafter. (HCl and HNO_3).

3.2 Composition of the extracted species-

Extraction isotherm method and distribution ratio method were adopted to determine the Composition of the extracted species. The limiting ratio of the metal to TBA was observed unity in the extraction isotherm method with both the acid systems. Straight lines were obtained in the log-log plots of Kd vs. TBA from these acid solutions. Solvation number of unity was obtained from the data on slope analysis curves from both the acid solutions.

Extraction of Mn(II) has been explained by the following salvation mechanism:

$Mn^{2+} + TBA + 2\ X^{--} \Leftrightarrow [Mn\ X_2.\ (TBA)]$, where X= Cl^- or NO_3^-

3.3 Effect of stripping agents-

After extraction, stripping of Mn (II) was done by 10ml agents of various concentrations (0.2- 1.0M) of acetic acid, sulphuric acid nitric acid and NaOH solutions. Among all these reagents, only 1.0M HNO_3 was found to be a good stripping agent. Mn(II) cannot be stripped out in a single extraction. It was done three times with equal volumes of 1.0M HNO_3. 99.5% of Mn(II) can be recovered from the organic phase.

3.4 Variation of diluent-

Effect of diluent on extraction using solvents with different dielectric constants showed that. quantitative extractions were obtained with xylene as diluent. Carbon tetra chloride, chloroform, cyclohexane, hexane and toluene, yielded more than 80% extraction efficiency. Poor extraction was found with nitrobenzene and n- heptane as diluents. So, in this study chloroform was used as a diluent.

3.5 Effect of diverse ions-

Extraction of manganese has been done both in presence and absence of various cations and anions (Table 2).When 27.5µg of was taken in the presence of 100 µg of anions they were tolerated in the ratio of 1:5. 145 µg of sodium, cesium metals with 27.5 µg of manganese (II) were tolerated in the ratio of 1:5 while others elements were tolerated in the ratio of 1:3 but transition metals were tolerated in similar ratio of 1:2.

It was noticed that cations like aluminum(III),chromium(VI) chromium(III),copper(II),magnesium(II),molybdenum(VI),nickel(II) & vanadium(V) and anions (bromide ,nitrate, sulphate, phosphate oxalate etc.) were not tolerated at all in any ratio to show interference in the extraction(Table -2).

Table 2: Estimation of manganese (II) from a binary mixture (Mn= 27.5 µg)

[TBA] = 2.5 x 10^{-2} M (From hydrochloric acid media)

Foreign ions	Amount tolerated (µg)	Ratio
Na^+, Cs^+, Sr^{2+}	145	1:5
Sb^{3+}, Sn^{4+}, Bi^{3+}, As^{3+} and Ti^+	215	1:4
Pd^{2+}, Co^{2+} and Pb^{2+}	180	1:3
Fe^{3+} and Cd^{2+}	110	1:2
K^+ and Zr^{4+}	75	1:1
Al^{3+}, Mg^{2+}, V^{5+}, Cr^{6+} Cr^{3+}, MoO_4^{2-} Ni^{2+} and Zn^{2+}	0	Interfere
Br^-, CH_3COO^-, SO_4^{2-}, PO_4^{3-}, NO_3^- $C_2O_4^{2-}$ and $S_2O_3^{2-}$	0	Interfere

3.6 Analysis of Mn(II) in alloy and pharmaceutical samples -

The current extraction method has been extended to estimate manganese content in alloys food and pharmaceutical samples. Exactly ten tablets were weighed and powdered finely with the help of mortar..About 1.0 gm of accurately weighed (powdered) sample equivalent to one tablet was transferred into a 100ml volumetric flask and 50ml of 0.01M H_2SO_4 was added followed by shaking for about 15 min. The mixture was diluted and filtered by using whatmann filter paper 40. The clear solution so obtained was used as stock solution. Different concentrations are prepared by diluting the stock solution.

1.0 gm of exactly weighed sample of alloy containing manganese was dissolved in 10 ml of aquaregia. It was evaporated to dryness and extracted with 10 ml of dilute oxalic acid solution. It was then made up to 100 ml. An aliquot (20 ml) of the filtered effluent sample was heated to 1/5th of the initial volume. It was then made up to

100 ml. 10ml of this solution and or the above solution was extracted with an equal volume of 2.5X 10^{-2} M TBA in xylene [12]. After separation of two phases, Mn (II) from the organic phase was stripped with 10 ml of 1.0M nitric acid and estimated the manganese content by AAS as per the procedure described above. The results are presented in Tables-3&4.

Table -3: Determination of Manganese in Alloys

Material	Carbon	Manganese	Silicon	Iron	Amt of Mn(II) taken (ppm)	Amt of Mn(II) found (ppm)*	% Recovery
Cast Iron	3.430	0.880	2.120	91.0 - 91.2	92.0	91.35	99.29
Carbon steel	0.007-1.3	0.3-1.0	0.005-0.5	98.1-99.5	94.5	93.52	98.96
Wrought iron	0.05-0.25	0.01-0.1	0.02-0.2	99.0-99.8	97.0	96.76	99.75

*Average of three determinations

Table-4: Estimation of Mn (II) in food and pharmaceutical samples

Sample	Mn (II) present (ppm)	Mn (II) found by extraction (ppm)	% recovery
Ragi	3.00	2.82	94.00
Green gram	4.05	3.86	95.30
Ferrous fumerate(300mg)	114.10	113.45	99.43
Ferrous dextrin(50mg)	100.22	99.96	99.74

IV. CONCLUSIONS

Extraction and estimation of manganese content in alloy, natural food and pharmaceutical samples by the current proposed method takes less than 20 min and it is very simple, rapid and selective method. The average recovery % of manganese was found to be 99.6% each determination requires a minimum amount of 20 minutes time.

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