Indirect complexometric determination of manganese(II) using tartaric acid as a masking agent

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Abstract : A complexometric method for the determination of manganese in the presence of other metal ions based on the selective masking ability of tartaric acid towards manganese is described. Manganese(II) present in a given sample solution is complexed with a known excess of EDTA and surplus EDTA is titrated against lead nitrate solution at pH 5-6 using xylenol orange as the indicator. A known excess of 10% solution of tartaric acid is then added. The mixture is then shaken well and the EDTA released from Mn-EDTA complex is titrated against the standard lead nitrate solution. Reproducible and accurate results are obtained for 1.10 to 33.0 mg of manganese(II) with relative error ≤ 0.51% and standard deviations ≤ 0.12 mg. The interference of various ions are studied. This method was applied to the determination of manganese(II) in its alloy composition.

Keywords : Complexometric, manganese(II) determination, masking, tartaric acid.

Introduction

Manganese forms numerous alloys, many of which are extremely important in the manufacture of steel[1,2]. Today the major use of manganese is as an alloying and cleansing agent for steels, iron and non ferrous metals. In non ferrous metals it improves their strength, ductility and hot-rolling properties. It is used as an alloying agent and cleanser in aluminium alloys, aluminium bronzes constantan, manganese bronze, monel, nickel-silver and nickel-chromium resistance alloys. Hardfield manganese steel which contains about 13% manganese and 1.25% carbon has remarkable properties. It is used for parts of excavators, rail crossings and other parts which are subjected to severe mechanical conditions of service. One of the most important non-metallurgical uses of manganese is in electrical batteries in which manganese dioxide acts as a depolarizer in the leclanche type of electrical cell.

Some of the simple methods reported for the rapid determination of manganese in solution are oxidation of metal to permanganate followed by determination of the permanganate either spectrophotometrically or by titration with a suitable reductant[3]. In the photometric method, oxidation to permanganate is conveniently achieved by treating the sample with an excess of potassium periodate in nitric acid medium. The titrimetric, bismuthate and pyrophosphate[4] methods are now most generally used for manganese in high grade manganese ores, ferromanganese and manganese metal. Manganese is determined gravimetrically as ammonium manganese phosphate, NH_4MnPO_4 and then ignited to pyrophosphate, $Mn_2P_2O_7$ [5]. Manganese is also determined in steels and cast iron by the persulphate-arsenite method[6]. Many of the known methods for determination of Mn^{II} by spectrophotometric methods by using 2-hydroxy-4-methoxy acetophenone oxime (HMAO)[7] involves multistep synthesis. Complexometric determination of manganese was reported in presence of lanthanum and strontium as stepwise determination using mixed metallochromic indicator[8], potassium cyanide[9] as masking agent in relation to stepwise determination of calcium and magnesium are found be applicable for specific situation. Citric acid[10], thioglycolic acid[11] and 1,10-phenanthroline[12] were reported as releasing agent for complexometric determination of manganese, however it

was found to be not suitable in presence of Hg^{II}, Tl^{III}, Fe^{III} and Co^{II}, Cu^{II}, Hg^{II}, Pd^{II}, Zn^{II}, Ni^{II}, Tl^{III} respectively in spite of their severe interference. In spite of all limitations of reported methods it is found that there is a need of more suitable simple reagents for the determination of manganese. In this regard the present work describes the suitability of simple and commonly available tartaric acid as a masking agent for the determination of manganese(II) under ordinary condition.

Experimental

All the reagents used were of analytical reagent grade or chemically pure grade. Manganese sulphate solution (0.55 mg/mL) was prepared by dissolving a known amount of manganese sulphate. The titrant lead nitrate solution (0.02 M) was prepared in distilled water and standardized by the quinaldate method[13]. EDTA solution (0.02 M) was prepared using its disodium salt of EDTA in distilled water. Solutions of various metal ions were prepared by dissolving calculated amounts of metal salts in distilled water. A 10% solution of tartaric acid was prepared in distilled water. Xylenol orange indicator was made by mixing it with grounded potassium nitrate crystals (1 : 100).

Procedure :

To an aliquot of solution containing 1.10–33.0 mg of manganese(II), 5 mL and proportionally increased volume of 0.02 M EDTA solution in excess was added and diluted to about 80 mL. About 0.03 g of xylenol orange indicator was added and pH of the solution was adjusted to 5.0 to 6.0 using hexamine (10 $\pm$ 2 g). The excess of EDTA was titrated with lead nitrate solution. To this solution 5 to 50 mL of 10% tartaric acid solution was added and mixed well by shaking. The liberated EDTA was then titrated with lead nitrate solution. This second titre value corresponds to the amount of manganese(II) present.

Results and discussion

The formation constant (log β) of Mn^{II}-EDTA complex is 21.9 yielding a log conditional stability constant[14] of 5.36 at pH 5.0. Mn^{II} forms stable water soluble complex with tartaric acid with the formula[15] $[Mn\{O_2CCH(O)CH(O)CO_2\}]^{2-}$. The sensitivity of this

method is established by the effects of various quantities of 10% tartaric acid solution used for the recovery of 4.8 mg of Mn^{II} present in the aliquot. It is found that 10 mL of 10% tartaric acid solution used for the recovery of 4.8 mg of manganese.

Accuracy and precision :

The determination of manganese(II) in manganese sulphate solution were performed at a different concentrations of manganese(II) using the above reagents. The results are given in Table 1.

Table 1. Determination of manganese(II) in manganous sulphate solution

Mn^{II} present (mg)	Mn^{II} found[a] (mg)	Standard deviation[a] (mg)	Student's 't' value[b]	Relative error (%)
1.10	1.08	0.02	2.23	–0.10
2.20	2.21	0.01	2.01	+0.45
3.30	3.36	0.05	2.23	+0.30
4.40	4.39	0.01	1.11	–0.11
5.50	5.50	0.00	0.79	0.00
6.60	6.61	0.01	2.79	+0.15
7.70	7.74	0.04	1.78	+0.51
8.80	8.82	0.01	1.78	+0.27
9.90	9.91	0.01	2.38	+0.22
11.0	11.02	0.02	2.23	+0.18
16.5	16.43	0.07	2.28	–0.42
22.0	21.91	0.09	2.16	–0.40
27.5	27.39	0.11	2.08	–0.40
33.0	32.88	0.12	2.32	–0.36

[a]Average of five determinations.
[b]Student's 't' value for 5% level of significance.

Effect of foreign ions :

The effect of different cations and anions in the quantitative determination of Mn^{II} was investigated at 9.60 mg of Mn^{II} in solution using 10% tartaric acid as masking agent. There is no interference by the ions listed in Table 2, except Th^{IV}, which is interfering in detection of sharp end point due to imparting red colour, it can be avoided by adding secondary masking agent sodium fluoride solution.

Applications :

Analysis of alloys of manganese(II) in alloys :

Samples of manganese based steel alloys (certified samples) were dissolved in concentrated HNO_3 and the

Table 2. Determination of 6.60 mg of manganese(II) in the presence of diverse ions

Diverse ion	Quantity added	Manganese found[a]	Relative error
	(mg)	(mg)	(%)
Zn^{II}	10	6.64	+0.60
Co^{II}	10	6.59	–0.15
Cd^{II}	10	6.54	–0.90
Ni^{II}	10	6.59	–0.15
Al^{III}	10	6.59	–0.15
Fe^{III}	5	6.59	–0.15
Hg^{II}	10	6.60	0.00
Tl^{III}	25	6.59	–0.15
Cu^{II}	5	6.60	0.00
Zr^{IV}	15	6.60	0.00
Ti^{IV}	35	6.59	–0.15
Sn^{II}	20	6.57	–0.45
Mo^{IV}	15	6.54	–0.90
Ba^{II}	10	6.57	–0.45
$Th^{IV b}$	12	6.58	–0.30
CH_3COO^-	50	6.59	–0.15
Br^-	50	6.59	–0.15
NO_3^-	50	6.64	–0.60
SO_4^{2-}	50	6.59	–0.15
Cl^-	35	6.60	0.0

[a]Average of three determinations.

[b]Using secondary masking agent sodium fluoride.

oxides of nitrogen expelled with the use of concentrated H_2SO_4 until evolution of brown fumes ceased. The residue was extracted with water and made up to 100 mL in a standard flask. Aliquots of 5–10 mL used for each titration by the recommended procedure. The results are given in Table 3.

Table 3. Determination of manganese(II) in solutions of alloy steels

Alloy	Composition	Mn^{II} found[a]	Relative error
	(mg)	(mg)	(%)
Fe + Mn (Ferro manganese)	20.00 + 80.00	79.89	–0.14
Mn + Si (Silico manganese)	70.00 + 20.00	70.07	+0.1

[a]Average of three determinations.

Conclusion

The proposed method for determination of manganese(II) is facile, rapid and has reasonable analytical range,

without the need of heating or cooling during the process. Reagent tartaric acid does not form precipitate under the experimental process, enhances sharpness of endpoints. The lack in effect of diverse ions on accuracy and precision makes the method more suitable for analysis of alloys. Reagent tartaric acid is water soluble, nontoxic and odour free makes convenient to use in laboratory for analyst on the context of green chemistry.

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