

AMMONIUM OXALATE AS A MASKING AGENT FOR THE COMPLEXOMETRIC DETERMINATION OF MANGANESE(II)

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Abstract

A simple, rapid and accurate complexometric method for the determination of manganese in the presence of other metal ions is described, based on the selective masking ability of ammonium oxalate towards Mn(II). Manganese(II) along with other associated metal ions present in a given sample solution is first complexed with an excess of EDTA and the surplus EDTA is titrated with zinc sulphate solution at pH 5-6 (Hexamine buffer) using xylenol orange as indicator. A known excess of 5% aqueous solution of ammonium oxalate is then added to displace EDTA from Mn(II)-EDTA complex and swirled well. The released EDTA is again titrated with zinc sulphate solution as before. The method works well in the range 2.19-21.96 mg of manganese(II) with the relative error $\pm 0.46\%$ and standard deviation ≤ 0.03 mg. The effect of the presence of various diverse ions on the accuracy of the results has been studied. The method has been satisfactorily applied for the determination of manganese in alloys.

Keywords. Manganese determination, complexometry, masking reagent, ammonium oxalate

1. INTRODUCTION

Manganese is a mineral element that is both nutritionally essential and potentially toxic. It is an essential element in photosynthesis. For animals manganese is an essential component of over thirty-six enzymes that are used for the carbohydrate, protein and fat metabolism. Manganese is one of several trace elements that are necessary for bone health [1]. Although manganese is essential to man in low concentrations, at high concentrations it becomes quite poisonous [2, 3]. Chronic manganese poisoning has been found in miners who are either in manganese mines or in ore crushing mills. Manganese forms numerous alloys, many of which are extremely important in the manufacture of steel [4, 5]. 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.

The manganese in the solution can be rapidly determined by the oxidation of metal to permanganate followed by determination of the permanganate either spectrophotometrically or by the titration with a suitable reductant [6]. 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 bismuthate and pyrophosphate [7] methods are now generally used for the estimation of manganese in high grade manganese ores, ferromanganese and manganese metal. Persulphate-arsenite method [8] is used to determine manganese in steels and cast iron. The spectrophotometric determination of Mn(II) using 2-Hydroxy-4-methoxy acetophenone oxime (HMAO) [9] involves multistep synthesis. Stepwise complexometric determination of manganese was reported in presence of lanthanum and strontium using mixed metallochromic indicator [10]. During stepwise complexometric determination of calcium, magnesium and manganese, potassium cyanide [11] is used as masking agent for manganese. The reagents reported as releasing agent for complexometric determination of manganese

include Citric acid [12], Thioglycolic acid [13], 1, 10-phenanthroline [14] and tartaric acid [15].

Due to the various limitations of the earlier methods, there is a need of suitable simple reagent for the determination of manganese. The present study reports ammonium oxalate as a masking agent for the complexometric determination of manganese(II). The investigated method is free from the interference of many ions and does not require any heating or extraction step.

2. EXPERIMENTAL

2.1. Materials

All the chemicals used were of analytical reagent grade. A stock solution of Mn(II) was prepared by dissolving a known amount of manganese(II) sulphate (Merck) in distilled water. The solution was standardized by the pyrophosphate method [16]. Zinc sulphate solution (0.02 M) was prepared by dissolving a known amount of zinc sulphate (Merck) in distilled water and standardized by quinaldinate method [17]. EDTA solution (0.02M) was prepared by dissolving the required amount of disodium salt of EDTA (Merck) in distilled water. A freshly prepared solution (5 %) of ammonium oxalate (Merck) in distilled water was used as the masking reagent. Xylenol orange indicator was made by mixing it with grounded potassium nitrate crystals (1:100).

2.2. Standard Procedure

To a solution containing 2.19-21.96 mg of manganese(II) and varying amounts of diverse metal ions taken in a 250 mL conical flask, an excess of 0.02M EDTA was added. The solution was diluted to 60-70 mL with distilled water. The pH of the solution was adjusted to 5-6 using hexamine buffer. The surplus EDTA was titrated with 0.02 M zinc sulphate solution using xylenol orange indicator to a sharp color change from yellow to red. To this, a 5 % solution of ammonium oxalate was added in required amounts and swirled well. The released EDTA was again titrated with the same 0.02 M zinc sulphate solution as before. The second titre volume corresponds to the manganese content in the aliquot.

3. RESULTS AND DISCUSSION

3.1. Masking property of ammonium oxalate

Ammonium oxalate is a potential bidentate ligand containing oxygen of oxalate group as donor

atoms. It has been reported that ammonium oxalate forms a strong neutral complex MnC_2O_4 [18] with Mn(II) by coordinating through oxygen atoms of oxalate group. The stability constant of the Mn(II)-EDTA complex is reported to be 13.87 [19] and the stability constant of the Mn(II)-Oxalate is reported to be 19.42.¹⁹ The quantitative release of EDTA from Mn(II)-EDTA complex by ammonium oxalate at room temperature again confirms that Mn(II)-Oxalate complex is more stable than Mn-EDTA complex under the experimental conditions employed.

3.2. Effect of ammonium oxalate concentration

In order to find out the exact amount of ammonium oxalate required for the quantitative release of EDTA from Mn-EDTA complex and the influence of excess reagent on the accuracy of the result, titrations were carried out with solutions containing 4.39 mg of Mn(II) and varying amounts of 5 % ammonium oxalate solution added. From the plot (Fig. 1) of the volume of reagent added versus the recovery of Mn, it is clear that about 9 ± 0.3 mL solution of 5 % ammonium oxalate is required for each 4.39 mg of Mn. Addition of excess of the reagent over the required amount has no adverse effects on the experimental results.

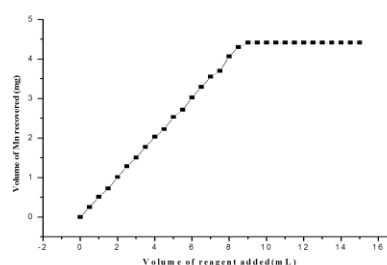


Fig. 1: Effect of 5 % ammonium oxalate on the release of 4.39 mg of Mn(II)

3.3. Reliability of the proposed method

To evaluate the precision and accuracy of the proposed method, determination of manganese at different concentration levels were carried out under optimized experimental conditions. Reproducible and accurate results (table 1) are obtained in the range 2.19-21.96 mg of manganese with the relative error ± 0.46 % and the standard deviation ($n = 5$) not exceeding 0.03 mg.

3.4. Effect of diverse ions

The recommended procedure was followed to study the possible interference due to various diverse

metal ions with solutions containing 4.39 mg of Mn. The results obtained are presented in table 2. The presence of the following ions did not interfere with in the concentration range studied: 15 mg of Cu(II), Co(II), Zn(II), Cd(II), Ni(II), Hg(II); 10 mg of Cr(III), Al(III), Fe(III), Bi(III), Ag(I); 8 mg of Rh(III), Ru(III), Zr(IV), Ti(IV), V(IV); 50 mg of tartarate, bromide, chloride, nitrate and sulphate. However, metal ions like Pd(II), Tl(III) and Sn(IV) show interference giving positive error, which is perhaps due to simultaneous release of EDTA from their respective M-EDTA complexes along with

Mn(II)-EDTA complex. Th(IV) results in dark red color upon adding hexamine under experimental conditions and interferes the determination of manganese. The interference of Pd(II) (up to 08 mg) and Tl(III) (up to 02 mg) can be obviated by the addition of 10% glycine (1.3 mL) and 1 % ascorbic acid (1 mL) respectively prior to EDTA complexation as secondary masking agents. Similarly, the interference due to Sn(IV) (up to 50 mg) and Th(IV) (up to 02 mg) can also be avoided by the addition of 10 % NaF (5-9 mL) as secondary masking agent.

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

Mn(II) Calculated (mg)	Mn(II) Found* (mg)	Standard Deviation (mg)	Student's 't' Value**	Relative Error (%)
2.19	2.18	0.01	2.23	-0.46
3.29	3.30	0.01	2.24	+0.30
4.39	4.41	0.02	2.23	+0.45
6.59	6.60	0.02	1.11	+0.15
10.98	10.99	0.03	0.75	+0.09
16.47	16.45	0.02	2.24	-0.12
21.96	21.95	0.01	2.24	-0.05

*Average of five determinations. **Student's t-test values for 5% level of Significance = 2.776.

Table 2: Determination of Manganese(II) (4.39 mg) in the presence of diverse ions.

Diverse ions	Quantity added (mg)	Manganese Found* (mg)	Relative Error (%)
Cu(II)	15	4.37	-0.46
Co(II)	15	4.40	+0.23
Zn(II)	15	4.38	-0.23
Cd(II)	15	4.41	+0.46
Ni(II)	15	4.37	-0.46
Hg(III)	15	4.41	+0.46
Tl(III)**	02	4.38	-0.23
Cr(IV)	10	4.41	+0.46
Al(III)	10	4.40	+0.23
Fe(III)	10	4.38	-0.23
Pd(II)**	08	4.41	+0.46
Bi(III)	10	4.37	-0.46
Rh(III)	08	4.41	+0.46
Ru(III)	08	4.38	-0.23
Zr(IV)	08	4.41	+0.46
Ti(IV)	08	4.40	+0.23
Th(IV)**	02	4.41	+0.46
V(IV)	08	4.38	-0.23
Sn(IV)**	50	4.41	+0.46
Ag(I)	10	4.37	-0.46
Tartarate	50	4.41	+0.46
Bromide	50	4.40	+0.23
Chloride	50	4.41	+0.46
Nitrate	50	4.39	0.00
Sulphate	50	4.37	-0.46

*Average of five determinations. **Masked using secondary masking agents.

4. ANALYTICAL APPLICATIONS OF THE METHOD

In order to demonstrate the analytical usefulness of the proposed method, it was applied to the determination of manganese in alloy samples.

Determination of manganese in alloy composition: Samples of manganese based steel

alloys (certified samples) were dissolved in concentrated HNO₃ and the oxides of nitrogen expelled with the use of concentrated H₂SO₄ 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 and the results are given in table 3.

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

Alloy Composition	Composition weight (%)	Mn(II) Found* (%)	Relative Error (%)
Manganin Cu + Mn+ Ni	84.00 + 12.00 + 04.00	11.99	-0.08
Ferromanganese Fe + Mn	20.00 + 80.00	79.88	-0.15
Silicomanganese Mn + Si	70.00 + 20.00	70.06	+0.09

*Average of three determinations.

5. CONCLUSION

The proposed method for the complexometric determination of Mn(II) offers advantages of simplicity, rapidity and reasonable selectivity over the other methods. The masking reagent, ammonium oxalate forms a soluble complex with manganese under experimental conditions, releases the EDTA instantaneously at room temperature and tolerates the presence of a number of metal ions without the need for the time consuming steps like heating or solvent extraction. Because no solvent extraction is required, the use of organic solvents, which are generally toxic pollutants, is avoided. In conclusion, the simplicity of the analytical procedure and the use of inexpensive facility make the technique very attractive for a wide spectrum of application.

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