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# A selective complexometric method of determination of manganese(II) using L-Cystine as masking agent

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## Abstract

*The determination of manganese(II) in the existence of various other different metal ions, a transparent speedy and accurate complexometric method is explained, depending on the selective masking ability of L-Cystine against Mn(II). Along with other associated metal ions, Mn(II) present in a given sample solution is first complexed with the surplus of EDTA and the leftover EDTA is then titrated against Zinc sulphate solution in the presence of Xylenol Orange as an indicator at pH5.0-6.0.A known excess of 1% L-Cystine solution is then supplemented to discharge the EDTA from Mn(II)-EDTA complex and mixed well. The displaced EDTA is again titrated with Zinc sulphate solution. The method goes well in the range 2.19-15.39mg of manganese(II) with the relative error ±0.5 and standard deviation ≤0.03mg The issue of the existence of various other metal ions on the exactitude of the results has been studied. And the method can be used for the determination of Manganese in alloys.*

**Keywords:** Manganese determination, EDTA titration, complexometry, masking, L-Cystine**.**

## Introduction

Manganese is a silvery grey metal and exists in three allotropic forms which are stable over various temperature ranges. It is brittle and hard, tough to fuse, but accessible to oxidize. Manganese metal and its ions show paramagnetic behavior.

Manganese is not so reactive towards non-metals at ordinary temperatures. However, when heated it reacts vigorously. About 80% of manganese produced is used in the manufacture of manganese steel. Manganese, when added to steel, performs two functions. If added in small amounts, it acts as a scavenger (cleansing agent) in removing oxygen and sulphur forming manganese oxide and manganese sulphide, which can be easily eliminated. This improves the strength of the final product. When added in large amounts up to 14%, it imparts special hardness and toughness to the steel.

Manganese(II) is an important constituent of an animal as well as plant enzymes. The Mn(II)enzymes produced in the liver, convert nitrogenous waste products into urea which is carried by the blood to the kidneys which excrete it into the urine. Manganese is an essential element for plant growth. It, along with fertilizers, enriches the soil[1].

The other methods used for the determination of manganese include gravimetry, atomic absorption spectrometry, and spectrophotometry[2]. Since EDTA forms stable complexes with most of the metal ions, it is not selective. Therefore determination of Manganese(II) is complicated by direct EDTA titration in the existence of other metal ions[3]. Hence the common proceeding is to bind manganese(II) in sync with the other metal ions by EDTA and then carefully break up the Mn(II)-EDTA complex with a suitable masking agent. The liberated EDTA is then titrated against standard metal ion solution. The releasing agents reported earlier for the complexometric determination of manganese include Citric acid[4], Thioglycolic acid[5], 1,10-phenanthroline[6]and ammonium oxalate[7].

Due to the limitations of the earlier methods, there is a requirement of suitable simple reagent for the determination of manganese. The present study includes L-cystine as a highly fussy masking agent for the determination of manganese (II) bya complexometric method. This method does not require heating and the method is free from the interference of many ions.

## Methodology

**Materials:** All analytical reagent grade chemicals were used. A stock solution of Mn(II) was prepared by dissolving a fixed amount of manganous sulphate solution inmillipore water. The solution was standardized by the pyrophosphate method[8]. The titrant, 0.02M Zinc sulphate solution preparation was done by dissolving a fixed quantity of Zinc sulphate crystals in millipore water.2.5% L-Cystine was prepared by dissolving L-cystine in a small quantity of 2M HCl solution.0.02MEDTA solution was prepared by solubilising the required amount of disodium salt of ethylene diammine tetra acetic acid (EDTA) in millipore water.

Xylenol orange indicator was made by mixing it with potassium nitrate crystals in the ratio 1:100.

**Standard procedure:** To a solution containing 2.19-15.39 mg of manganese(II) in the existence of other metal ions taken in a 250ml conical flask, an exuberance of 0.02MEDTA was added, then the concentration of the solution was decreased by adding 60-70ml of millipore water. Solid hexamine was added to fix the pH to 5.0-6.0. Then the remaining EDTA in the conical flask was titrated against 0.02M Zinc sulphate solution using Xylenol Orange as an indicator. The colour change was from yellow to orange. To the same solution 2.5% L-Cystine was added in the required quantity and shaken well. The EDTA which was liberated from Mn-EDTA complex on adding L-Cystine was titrated against Zinc sulphate solution (0.02M). The new titre value corresponds to the manganese content in the aliquot.

## Results and discussion

**Masking ability of L-Cystine:** L-Cystine contains nitrogen, sulphur and oxygen as donor sites and it's a polydentate ligand. It has been reported that L-Cystine forms a strong complex with Mn(II). The stability constant of the complex Mn-EDTA is found to be lesser than the stability constant of Mn-L-Cystinecomplex. The stability constant of Mn-EDTA complex is 13.87[9] which is less than the stability constant of Mn-L-Cystine complex[10]. The liberation of EDTA from Mn(II)-EDTA complex quantitatively by L-Cystine at lab temperature again confirms that Mn-EDTA complex is less stable than Mn-L Cystine complex under the experimental conditions employed.

**Effect of L-Cystine concentration:** To find the exact amount of L-Cystine required for the quantitative liberation of Mn(II) from Mn-EDTA complex, titrations were carried out by taking 4.89mg of Mn(II) and varying amounts of L-Cystine was added. From the plot (Figure-1) of the volume of reagent added versus volume of Mn(II) recovered, it is clear that to release 4.39mg of Mn(II) from Mn-EDTA complex 1.5ml of 2.5% L-Cystine was required. Inclusion of excess of the reagent over the requisite amount has no adverse effect on the experimental results.

**Reliability of the proposed method:** To evaluate the accuracy and precision of the recommended method, estimation of manganese at different concentration levels were carried out under optimized experimental conditions. Reproducible and accurate results are achieved in the range 2.19- 15.39mg of manganese with relative error 0.9% and the standard deviation not exceeding 0.03 (Table-1).

**Effect of various other ions:** The study of possible interference due to various metal ions in the determination of 4.39mg of Mn(II) was done using the recommended procedure. The results obtained are show in Table-2.

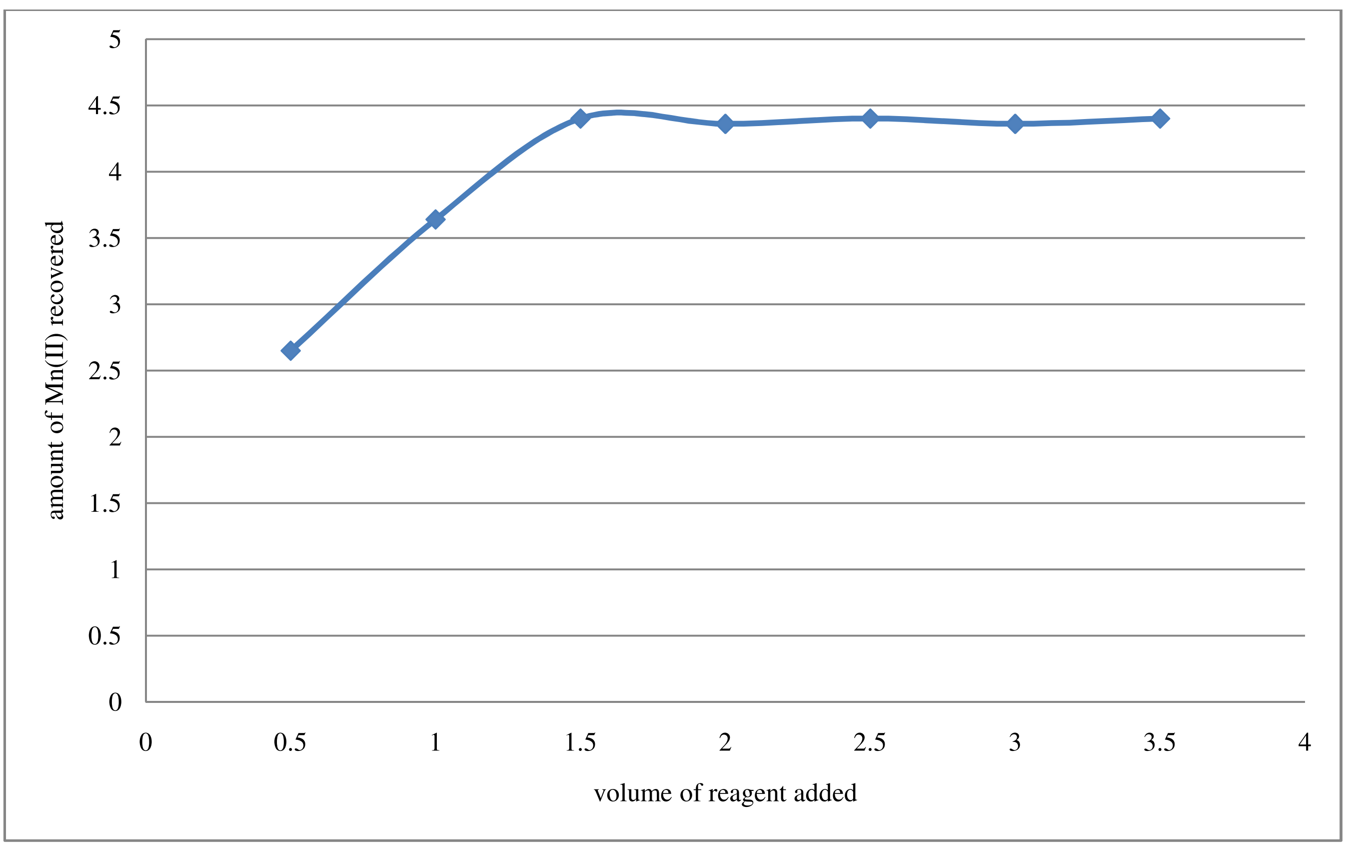


**Figure-1:** Effect of L-Cystine concentration.

**Table-1:** Estimation of manganese in manganous sulphate solution.

| Mn(II) Calculated (mg) | Mn(II) experimentally found* (mg) | Standard deviation (mg) | Relative error(%) | Student's t test |
|---|---|---|---|---|
| 2.19 | 2.184 | 0.005 | -0.274 | 2.448 |
| 3.29 | 3.308 | 0.008 | 0.547 | -4.811 |
| 4.39 | 4.390 | 0.027 | 0.000 | 0.000 |
| 5.49 | 5.485 | 0.008 | -0.091 | 1.491 |
| 6.59 | 6.590 | 0.027 | 0.000 | 0.000 |
| 7.69 | 7.687 | 0.008 | -0.039 | 0.802 |
| 8.79 | 8.790 | 0.013 | -0.005 | 0.067 |
| 9.89 | 9.880 | 0.009 | -0.101 | 2.500 |
| 10.99 | 11.000 | 0.007 | 0.091 | -3.162 |
| 12.09 | 12.086 | 0.009 | -0.033 | 1.000 |
| 13.19 | 13.190 | 0.007 | 0.000 | 0.000 |
| 14.29 | 14.296 | 0.024 | 0.042 | -0.557 |
| 15.39 | 15.384 | 0.015 | -0.039 | 0.885 |

*Average of 5 determinations.

**Table-2:** Determination of Manganese(II) (7.69mg)in the existence of varied ions.

| Varied ions | Quantity supplemented (milligram) | Manganese Found* (milligram) | Relative error (%) |
|---|---|---|---|
| Pb(II) | 200 | 7.68 | -0.13 |
| Sn(II) | 40 | 7,67 | -0.26 |
| Zr(v) | 30 | 7-.65 | -0.52 |
| Mo(VI) | 40 | 7.7 | 0.13 |
| Ni (II) | 40 | 7.69 | 0.00 |
| Al(III) | 30 | 7.71 | 0.26 |
| As(V) | 30 | 7.67 | -0.26 |
| Bi(III) | 40 | 7.65 | -0.52 |
| Ce(III) | 30 | 7.72 | 0.39 |
| Cd(II) | 40 | 7.74 | 0.65 |
| Co(II) | 40 | 7.69 | 0.00 |
| Cu(II) | 30 | 7.68 | -0.13 |
| Fe(III) | 30 | 7.65 | -0.52 |
| Hg(II)** | 10 | 7.68 | -0.13 |
| Pd(II)*** | 10 | 7.65 | -0.52 |
| Acetate | 160 | 7.70 | 0.13 |
| Chloride | 140 | 7.72 | 0.39 |
| Oxalate | 140 | 7.68 | -0.13 |
| Sulphate | 160 | 7.67 | -0.26 |
| Phosphate | 200 | 7.65 | -0.52 |

*Average of 5 determinations. **obstruction ofHg(II)can behindered by pre masking Hg(II)with5% acetyl acetone(10ml)[11], ***The obstruction of Pd(II) can be hindered by using DL-methionine(3ml(1%)) for each 10mg of Pd(II)[12].

**Table-3:** The determination of manganese(II) in alloy samples.

| 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.

## Conclusion

Any extraction, reconstruction of pH or heating is not required in this recommended method, it is simple rapid and reliable. L-Cystine does not form any precipitate with the metal ion, (which is to be determined) and the titrant. The recommended method is suitable for the determination of Manganese in its complexes and its alloys. The advantage of the proposed method when compared to other methods is that there is no interference of most of the metal ions and this method is highly selective in the determination of manganese in the existence of various metal ions.

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