

## Spectrophotometric Determination of As(III) by Colour Reduction Method

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Spectrophotometric method for trace determination of As(III) has been developed on the basis of reduction of absorbance of  $\text{KMnO}_4$  solution by As(III). Up to  $6.0 \mu\text{g/mL}$  of As(III) can be determined with a standard deviation of  $0.082 \mu\text{g/mL}$ .

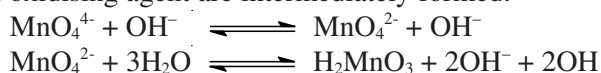
**Key Words:** Spectrophotometric studies, Colour reduction, Trace determination, Absorbance.

### INTRODUCTION

In the present paper, a simple and rapid spectrophotometric method for determination of As(III) based on the decrease in colour intensity of alkaline  $\text{KMnO}_4$  solution is presented. For analytical purposes, the reductions of permanganate, ( $\text{Mn}^{\text{VII}}$ ) to manganate ( $\text{Mn}^{\text{VI}}$ ) and subsequently to manganese dioxide, ( $\text{Mn}^{\text{IV}}$ ) are the stages through which reaction proceeds.

Holluta<sup>1</sup> in the course of his studies of the reaction between permanganate and formate observed that with increasing alkalinity, reduction of permanganate proceeds more and more towards manganate. Permanganate behaves similarly towards not too strong reducing agents.

Mechanism of the permanganate oxidation in alkaline solution has been thoroughly investigated<sup>2</sup> and it was assumed that hydroxide radical which are real oxidising agent are intermediately formed.



The effect of hydroxide ion concentration on the velocity of two reduction steps in alkaline solutions is well recognizable from the two chemical equations. As temperature increases rate of the above reaction is greatly enhanced.

Hence,  $\text{OH}^-$  concentration and temperature are two important parameters in the reduction of alkaline  $\text{KMnO}_4$  solution.

The correct choice of the alkalinity of the solution is not sufficient to ensure that only one of the two reduction steps is reached. A definite course of reaction, however, is ensured under suitable conditions when barium(II) salts are added.

**Role of Ba(II) ions:** Barium permanganate [ $\text{Ba}(\text{MnO}_4)_2$ ] is readily water soluble<sup>3</sup>. Solubility of barium manganate ( $\text{BaMnO}_4$ ) is  $2.46 \times 10^{-10}$  g/L at 25 °C. If barium nitrate or barium chloride is added to alkaline permanganate solution, the barium manganate formed during the reaction precipitates so rapidly that under optimum conditions it can not be further reduced<sup>3</sup>. The barium manganate forms deposits very well and settles down.

Alkaline permanganate *i.e.*, Mn(VII) is reduced quantitatively to manganese(VI) after addition of As(III) in the presence of  $\text{Ba}^{2+}$ . Thus, addition of As(III) decreases colour intensity of alkaline  $\text{KMnO}_4$  solution at 540 nm.

### EXPERIMENTAL

Absorbance measurements were made on a SPECTROCHEM spectrophotometer using optical glass cell with 10 mm path length. AR grade chemicals and deionized water after distillation were employed throughout the work.  $\text{KMnO}_4$  solution was standardized by volumetric method<sup>4</sup>. A working solution of  $1 \times 10^{-3}$  M  $\text{KMnO}_4$  was prepared by dilution. Standard As(III) solution was prepared from AR grade  $\text{As}_2\text{O}_3$ .

**Procedure for the determination of As(III):** 5 mL of  $1 \times 10^{-3}$  M  $\text{KMnO}_4$  solution were placed in 50 mL volumetric flask 5 mL of  $1 \times 10^{-3}$  M  $\text{Ba}(\text{NO}_3)_2$ , 10 mL of  $5 \times 10^{-3}$  M NaOH were added to it, followed by a suitable aliquot of As(III) solution or a sample containing up to 300  $\mu\text{g}$  of As(III). The volume was made up with deionized distilled water. The flask was kept in boiling water bath for 15 min. After cooling solution was centrifuged and absorbance was measured at 540 nm against distilled water as blank.

### RESULTS AND DISCUSSION

The present method is based on the decrease in absorbance at 540 nm ( $\lambda_{\text{max}}$ ) of permanganate solution on addition of As(III).

Reduction of colour intensity of permanganate solution by As(III) was studied in presence of different concentrations of NaOH in the range of 0.1N to 0.0001N and optimum base concentration range for reproducible decrease in absorbance of permanganate solution was found to be 0.005N to 0.0001N NaOH. All analytical work was carried out using 0.001N NaOH (Table-1).

The effect of the barium nitrate concentration on the decrease in the colour intensity of permanganate solution due to As(III) was studied. The optimum barium nitrate concentration range for reproducible decrease in the absorbance was found to be 0.0001 to 0.0003 M  $\text{Ba}(\text{NO}_3)_2$ . All analytical work was carried out using 0.0001 N NaOH (Table-2).

TABLE-1  
EFFECT OF NaOH CONCENTRATION  
Concentration of  $\text{KMnO}_4$  -  $1 \times 10^{-4}$  M,  $\text{Ba}(\text{NO}_3)_2$  -  $1 \times 10^{-4}$  M, As(III) - 3.0 ppm

Conc. of NaOH (N)	Optical Density	Conc. of NaOH (N)	Optical Density
0.1	0.083	0.0014	0.153
0.05	0.094	0.0012	0.154
0.01	0.116	0.0010	0.153
0.005	0.153	0.0008	0.154
0.002	0.155	0.0006	0.153
0.0018	0.154	0.0004	0.151
0.0016	0.153	0.0001	0.155

TABLE-2  
EFFECT OF  $\text{Ba}(\text{NO}_3)_2$  CONCENTRATION  
Concentration of  $\text{KMnO}_4$  =  $1 \times 10^{-4}$  M, NaOH =  $1 \times 10^{-3}$  N, As(III) = 3 ppm

Concentration of $\text{Ba}(\text{NO}_3)_2$ (M)	Optical density
0.0001	0.153
0.0002	0.153
0.0003	0.151
0.0004	0.139
0.0005	0.127

It was found that reduction of permanganate was complete after placing the volumetric flask in boiling water bath for 10 min. After cooling the solution, reduced colour intensity retains its absorbance at the same value for at least 3 h. All the analytical work was carried out by placing volumetric flask in boiling water bath for 15 min (Table-3).

TABLE-3  
EFFECT OF TIME IN BOILING WATER BATH  
Concentration of  $\text{KMnO}_4$  =  $1 \times 10^{-4}$  M,  $\text{Ba}(\text{NO}_3)_2$  =  $1 \times 10^{-4}$  M,  
NaOH =  $1 \times 10^{-3}$  N, As(III) = 3 ppm

Time (min)	Optical density	Time (min)	Optical density
05	0.157	20	0.153
10	0.153	25	0.150
15	0.153	30	0.145

#### Optimum range, sensitivity and accuracy

It has been found that the calibration curve obtained by plotting the decreasing absorbance values of  $1 \times 10^{-4}$  M  $\text{KMnO}_4$  solution against As(III) concentrations at 540 nm is linear up to 6.0  $\mu\text{g}$  of As(III) per mL (Table-4).

TABLE-4  
CALIBRATION CURVE  
Conc. of  $\text{KMnO}_4 = 1 \times 10^{-4}$  M,  $\text{Ba}(\text{NO}_3)_2 = 1 \times 10^{-4}$  M,  $\text{NaOH} = 1 \times 10^{-3}$  N

Concentration of As(III) (ppm)	Optical density	Concentration of As(III) (ppm)	Optical density
0	0.208	4	0.134
1	0.189	5	0.116
2	0.171	6	0.097
3	0.153	–	–

Precision and accuracy of the method were tested by analyzing eleven samples each containing 3  $\mu\text{g}/\text{mL}$  of As(III). The amount of As(III) for a decrease in the absorbance by 0.001 was found to be 0.005  $\mu\text{g}/\text{mL}$  (Table-5).

TABLE-5  
REPRODUCIBILITY OF THE METHOD  
Concentration of  $\text{KMnO}_4 = 1 \times 10^{-4}$  M,  $\text{Ba}(\text{NO}_3)_2 = 1 \times 10^{-4}$  M,  
 $\text{NaOH} = 1 \times 10^{-3}$  N, As(III) = 3 ppm

Absorbance	As(III) Found (ppm)	Error (%)
0.153	3.00	0.00
0.152	3.05	+ 1.66
0.151	3.10	+ 3.33
0.151	3.10	+ 3.33
0.154	2.9	- 3.33
0.152	3.05	+ 1.66
0.152	3.05	+ 1.66
0.152	3.05	+ 1.66
0.151	3.10	+ 3.33
0.155	2.85	- 5.00
0.153	3.00	0.00
Average		0.76

Mean absorbance at 540 nm was 0.152 with a standard deviation of 0.0011 and relative standard deviation of 0.74 %.

The average of eleven determinations carried out using 3 ppm of As(III) is  $3.000 \pm 0.023$  ppm. The relative standard deviation is 2.7 %.

#### Interference studies

Interference due to foreign ions in the determination of As(III) was studied for several cations and anions. It was found that Cu(II) and Mo(VI) do not interfere at low concentrations (up to 400 ppm) for 3 ppm As(III). Cations like Ni(II), Co(II), Cr(III), Cr(VI), Fe(II) interfere seriously.

Reducing species like  $\text{SO}_3^{2-}$ , Sn(II), oxalic acid, *etc.* also interfere. Chloride ions are tolerated up to a concentration of 500 ppm for 3 ppm of As(III).

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### REFERENCES

1. J.Z. Holluta, *Phys. Chem.*, **113**, 464 (1924).
2. M.C.R. Symons, *J. Chem. Soc.*, 3976 (1954).
3. H.I. Schlesinger and H.B. Siems, *J. Am. Chem. Soc.*, **46**, 1965 (1924).
4. A.I. Vogel's, Textbook of Quantitative Inorganic Analysis, Longmann Group Ltd, London, edn. 6, p. 352 (1978).

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