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A SIMPLE AND EFFECTIVE SPECTROPHOTOMETRIC METHOD FOR THE DETERMINATION OF MANGANSESE (II) WITH RES-ACETOPHENONE GUANYLHYDRAZONE (RAG)

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ABSTRACT

In present work we report here a new simple effective spectrophotometric method for the determination of Manganese(II) with Res-acetophenone guanylhydrazone [RAG]. A standard procedure of the absorption spectra of the reagent and the complex is recommended. The absorbance measurements are carried out at 410 nm [Molar extinction co-efficient is 0.7604 x 10^4 lit. mole cm^{-1}] at pH 8.9. Beer's law is valid up to 10.0 ppm. Sandell's sensitivity of the method is 0.0616 µg/cm^2. The Job's variation and mole ratio method show that the composition of Mn(II) RAG complex is 1:2. The instability constant is 1.378x10^{-11}. The method is applied for the determination of manganese in mild steel, tea leaves and coffee powder.

KEY WORDS : RAG, Manganese(II) , Spectrophotomety, Sandell's sensitivity, Beer's law.

INTRODUCTION

A large number of methods for the spectroscopic determination of manganese have been reported [1-6], but very few are in practice. Res-acetophenone guanylhydrazone (RAG) has been used as sensitive reagent for Mn(II). It forms an intense yellow colored complex with

manganese at pH 8.9, which leads to the development of a simple and rapid spectrophotometric method for the determination of manganese at tracer level.

MATERIALS AND METHODS

A standard solution of Mn(II) (1 mg/ml i.e. 1.822 x 10^{-2} M) was prepared by dissolving 0.308 g of A.R. grade Mn(II)sulphate monohydrate in 100 ml distilled water containing a few drops of sulphuric acid. The solution was standardized with Volhard's method volumetrically. [7] A stock solution of 0.5 x 10^{-2} M reagent (RAG) was prepared by dissolving 0.104 g of it in 100ml ethyl alcohol. The buffer solutions were prepared by dissolving appropriate amounts of boric acid and sodium hydroxide.

Procedure

A suitable aliquot of the solution containing 50 µg of Mn (II) was taken in a 10ml volumetric flask. To this, was added 1.75 ml of reagent (RAG) solution of concentration (5.0 x 10^{-3} M) and diluted to 2/3 volume of the flask. Then pH of the solution was adjusted to 8.9 by adding buffer solution and diluted to volume with distilled water. The absorbance of the Mn(II)-RAG complex was measured at 410 nm against reagent blank. The concentration of Mn(II) in an unknown solution was determined from a calibration curve obtained under identical conditions.

RESULTS AND DISCUSSION

The absorption spectrum of Mn(II)-RAG complex recorded at pH 8.9 shows a peak at 410nm. At this wavelength, the molar extinction coefficient of the complex is 0.7604 x 10^4 lit. $mole^{-1}.cm^{-1}$ and of the reagent 0.0300 x10^4 lit. $mole^{-1}cm^{-1}$. About five-fold molar excess of the reagent concentration was sufficient for full color development of the complex. The Beer's law is valid up to 10.0 ppm of Mn (II). Sandell's sensitivity [8] of the method is 0.0616 $\mu g/cm^2$. The composition of the complex was determined by Job's continuous variation method [9] and mole ratio method[10] These methods indicate the formation of a single complex having the composition 1:2 [Mn(II) : RAG]. The degree of dissociation was obtained by mole ratio method and was found to be 0.1029. The apparent instability constant[11] was found to be 1.378 x 10^{-11}. To study the effect of diverse ions, Mn(II) was determined in presence of various cations and anions. It is evident that Mn(II), like ions such as Zn(II), Ba(II), Cu(II), Ni(II), Mg(II), Ag(I), Bi(III), Co(II), Cd(II), $EDTA^{-4}$ and citrate ions interfere seriously and can be tolerated in presence of appropriate masking agents.

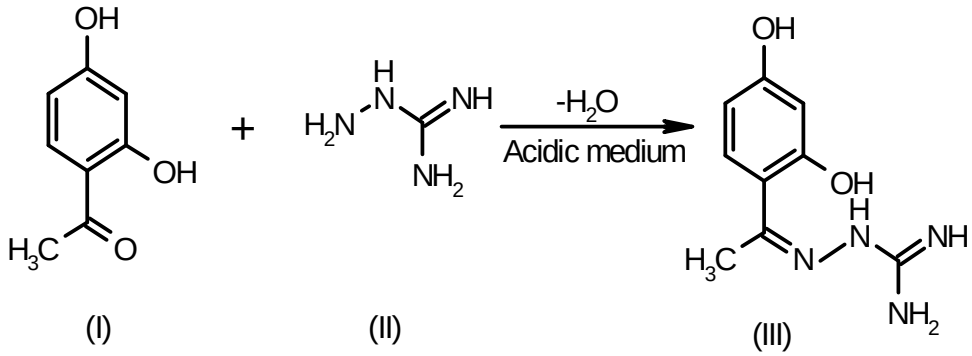
Experimental

The spectral measurements were done on ELICO(CL–27) visible digital spectrophotometer, equipped with 10.01 mm matched pair of glass cuvettes. The pH measurements were done on ELICO (L1-120) digital pH meter, using glass calomel combination electrode. For standardization of pH meter, potassium hydrogen phthalate (pH = 4.01) and borax (pH = 9.18) buffers were used.

SYNTHESIS OF RAG

For the synthesis of Res-acetophenone guanylhydrazone (RAG), aminoguanidine bicarbonate was used instead of amino guanidine dihydrochloride, which simplified and gave much better yield. A solution of amino guanidine bicarbonate, 1.0g in 50% nitric acid and Res-acetophenone, 2.054g in 10ml absolute ethanol were mixed together. The mixture was kept in ice cold water for half an hour. The pale yellow colored product was separated by filteration and crystallized from absolute ethanol (~2.0g) (percentage = 65.48 % ee) M.P. = $94^0 \pm 1^0$C. The molecular formula was confirmed on the basis of micro-elemental analysis as $C_9H_{12}N_4O_2$. Calculated percentage of elements was C = 51.92%, H = 5.76% N = 26.92% and O = 15.38%. Experimental percentage of elements was found to be C = 51.37%, H = 5.59% and N = 27.13%. The reagent RAG is soluble in ethyl alcohol, methyl alcohol and acetone but insoluble in benzene, chloroform and carbon tetrachloride.

Scheme



(I) (II) (III)

Res-acetophenone Aminoguanidine Res-acetophenone guanylhydrazone (RAG)

Applications

The method was applied in the determination of Mn(II) in the analysis of mild steel, tea leaves and coffee powder.

1) Analysis of Manganese (II) in mild steel

A known weight, 0.1 g of the sample of mild steel was dissolved in 10 ml of 1:1 HCl with mild heating. A few drops of Conc.HNO_3 were added carefully. The resulting solution was evaporated to dryness. The residue was dissolved in 5.0 ml of 0.5 N HCl and diluted to 250ml in volumetric flask with distilled water. A suitable aliquot (2.0ml) of this diluted solution was taken. The manganese was then determined as Mn(II)-RAG complex by recommended procedure and measured at 410nm against reagent blank. The results of the analysis are summarized in table.1

Table.1: Analytical data of Manganese (II) in Mild steel

Alloy	Manganese(II)*, %		Relative standard deviation
	Certified	Experimental	
Mild steel (1e, BAS)	0.60	0.593	0.084

*Average of five determinations

2) Analysis of Manganese (II) in Tea leaves and Coffee Powder

A weighed sample (1.0 g) was digested with 2.0ml of 3:1 v/v mixture of nitric acid and perchloric acids. It was heated gently to dryness. This procedure was repeated again with 2.0ml of acid mixture and was diluted with distilled water to 25ml in a volumetric flask. A suitable aliquot (0.5ml) of this diluted solution was taken. Manganese was then determined as Mn(II)-RAG complex as per recommended procedure. The recovery of Mn(II) was tested by adding a known amount of Mn(II) to the sample solutions. Applying the recommended procedure, Mn(II) was found to be recovered to ~ 100% in all cases. Table.2 shows the quantitative recoveries of manganese added to the sample.

Table.2: Analytical data of Manganese (II) in Tea leaves and Coffee Powder

Sample	Mn(II)Found* µg	Mn(II)added, µg	Total recovery of Mn(II)		Average Mn(II) content
			µg	%	
Tea leaves	3.25	3.0	6.19	~ 100	81.0
Coffee powder	1.73	1.5	3.20	~ 100	43.0

* Average of five determinations

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