

Rapid Determination of Iron in Water by Modified Thiocyanate Method

D.C. Goswami and H. Kalita

Defence Research Laboratory, Tezpur-784 001

ABSTRACT

A rapid spectrophotometric method for determination of iron in water by oxidising ferrous iron with ceric ammonium sulphate at room temperature followed by formation of ferric thiocyanate colour complex with potassium thiocyanate has been described. The method is simple and rapid as compared to other standard methods used in water analysis and iron content of water upto 5 ppm can be determined by this method with a maximum error of 2.8 per cent.

1. INTRODUCTION

There is no lack of colorimetric reagents for determination of iron, some reagents react with ferric ion and others with ferrous ion. Common reagents used for determination of iron in water are 1, 10-phenanthroline¹, 4, 7-biphenyl-1, 10-phenanthroline², ferrocyanide³, thioglycollic acid^{3,4}, and thiocyanate^{3,5}. With these chromogenic agents several steps are required for determination of iron and the methods are not rapid. This paper describes a rapid spectrophotometric method for determination of iron in water by oxidising the ferrous ion with ceric ion at room temperature followed by ferric thiocyanate colour complexation with potassium thiocyanate.

2. EXPERIMENTAL

Ceric ammonium sulphate in sulphuric acid has been used as the oxidising agent. 0.5 ml of 0.25 per cent ceric ammonium sulphate solution used is sufficient to oxidise 50 μg iron present in 5 ml test solution. With this concentration of ceric ammonium sulphate, a faint yellow colour always remains in test solution indicating the complete

oxidation of ferrous iron. The concentration of acid and thiocyanate used are 0.8.N and 0.3 M respectively in the final stage of ferric thiocyanate colour formation. The absorbance of the coloured solutions are measured in a spectrophotometer (Spekol, Carl-Zeiss, Jena) with a cell of 1 cm path length.

The test on effect of time on ferric thiocyanate colour was carried out with 1.0 ppm standard ferrous iron solution at 25°C by measuring the absorbance of the ferric thiocyanate colour at different interval of time. Similarly, the test on the effect of temperature was carried out with 1.0 ppm standard ferrous iron solution by measuring the absorbance at different temperatures ranging from 10°–40°C. Aqueous solutions of different salts in various concentrations were prepared and incorporated in the test with standard iron solutions to see their effects on development of colour complex. Anions tested were sulphate, phosphate, chloride, fluoride (as sodium salt), oxalate (as ammonium salt) and the cations tested were manganese, copper, zinc (as sulphate), cobalt, calcium (as chlorides). Finally, the precision and accuracy of the method was checked by determining the absorbance of standard iron solutions, and comparing the results of iron content of clear water samples with conventional thiocyanate method respectively.

2. Reagents

- (i) 0.25 per cent ceric ammonium sulphate in 8.8 N sulphuric acid.
- (ii) 40 per cent potassium thiocyanate solution.
- (iii) (a) Stock standard ferrous iron solution – 100 μg iron per ml.
(b) Working standard ferrous iron solution – 0.3 to 10 μg iron per ml

2.2 Procedure

To five ml of clear water sample in a test tube 0.5 ml of ceric ammonium sulphate solution is added and mixed thoroughly by shaking. Finally, 0.5 ml of potassium thiocyanate solution is added and again mixed properly. Exactly 5 minutes after addition of thiocyanate solution, the absorbance of ferric thiocyanate complex is measured at 480 nm in a spectrophotometer (Spekol, Carl-Zeiss, Jena).

A series of freshly prepared working standard ferrous iron solutions (upto 10 ppm iron) were treated similarly and the absorbances measured at 480 nm. From the calibration curve, plotted with concentrations of different standard iron solutions against absorbances, the iron content of the unknown sample is evaluated.

3. RESULTS AND DISCUSSION

It has been observed in the present study that ferric thiocyanate system obeys Beer's Law upto 10 ppm iron which is in conformity with the findings of Woods and Mellon⁶ where hydrochloric acid solution of *pH* 1.5–1.65 has been used. The colour intensity of ferric thiocyanate complex decreases with time (Fig. 1), this may be due to reduction of ferric ion by thiocyanate or its decomposition products. Using

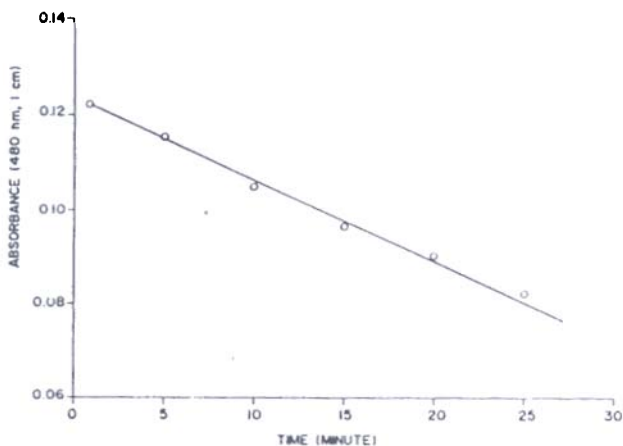


Figure 1. Effect of time on ferric thiocyanate colour complex

1.0 ppm standard ferrous iron solution, a decrease of about 4 per cent colour intensity after 5 minutes and 40 per cent after 30 minutes were observed. Sandell⁷ observed a decrease of about 10 per cent colour intensity after 10 minutes for a solution containing 4 ppm of iron in 0.5 N hydrochloric acid and 0.3 M thiocyanate solution.

Ovenston and Parker⁸ found that the colour intensity of ferric thiocyanate solutions decreased by about 1 per cent for every degree centigrade rise of temperature. In the present method using 1 ppm standard iron solution it has been observed that the colour intensity decreased by about 33.5 per cent when the temperature was raised from 10 to 40°C (Fig. 2). However, the decrease in colour intensity was comparatively smaller at lower temperature than at higher temperature. From 10° to 25°C, the decrease in colour intensity was about 10 per cent and from 25° to 40°C, the decrease was about 26 per cent.

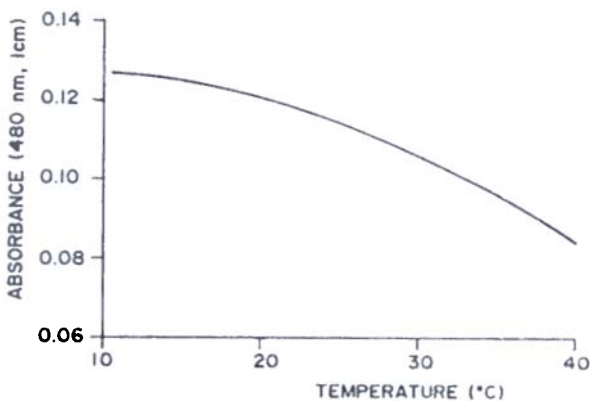


Figure 2. Effect of temperature on ferric thiocyanate colour complex

The results on the effect of diverse ions on ferric thiocyanate complex are given in Table 1. Of the different ions studied for interference chloride, sulphate, phosphate, manganese, zinc and calcium did not exert any significant effect on the ferric

Table 1 Effect of diverse ions on iron-thiocyanate complex

Ion tested (X)	Amount of Fe: X	*Absorbance (at 480 nm, 1 cm cell)
A. Control		
Standard iron solution 1.0 ppm	1:0	0.095
B. Anions		
Chloride	500	0.095
Sulphate	500	0.095
Phosphate	500	0.095
Fluoride	20	0.095
Oxalate	10	0.095
C. Cations		
Mn ⁺⁺	1:500	0.095
Zn ⁺⁺	1:500	0.095
Ca ⁺⁺	1:500	0.095
Co ⁺⁺	1:20	0.095
Cu ⁺⁺		0.045

*Absorbance measured at room temperature (36°C)

thiocyanate complex when their concentration were 500 ppm. Similarly, with fluoride and cobalt there were no interference when their concentrations did not exceed 20 ppm. Oxalate interfered when it exceeded 10 ppm in the test solution. Copper should be absent in the sample since it decreases the colour intensity by more than 47 per cent even at 1 ppm level.

The precision of the method was checked by measuring the absorbance of three standard ferrous iron solutions containing 1, 3 and 5 ppm iron and the results are given in Table 2. It was observed that the coefficient of variation varies from 0.524 to 1.453 per cent, which shows that the precision of the method is satisfactory. The results on the iron content of six clear water samples determined (in six replicates) by the present method and by the conventional thiocyanate method (oxidising ferrous iron with fuming nitric acid) along with their mean \pm SD are given in Table 3. The

Table 2. Precision of the method

Amount of iron present (ppm)	*Mean absorbance	Standard deviation	Coefficient of variation (%)
	0.115	0.001	0.870
3	0.344	0.005	1.453
5	0.572	0.003	0.524

*Mean of 10 determinations measured at 25°C

Table 3. Comparison of ceric ion oxidation method with nitric acid oxidation method

Sl. No.	*Iron (ppm)		Error of method II (%)
	Nitric acid oxidation (method I)	Ceric ion oxidation (method II)	
1.	1.102 ± 0.055	1.071 ± 0.011	2.8
2.	1.553 ± 0.029	1.547 ± 0.023	0.4
3.	1.824 ± 0.027	1.807 ± 0.027	0.9
4.	3.097 ± 0.084	3.035 ± 0.027	2.0
5.	4.377 ± 0.070	4.316 ± 0.047	1.4
6.	5.027 ± 0.029	4.965 ± 0.043	1.2

*Values are means ±SD of 6 determinations.

results show that the iron content of water upto 5 ppm can be determined by this method with a maximum error of 2.8 per cent. The difference in results between the two methods are due to non-boiling of water sample in ceric ion oxidation method.

In the conventional thiocyanate method the oxidation of ferrous iron is carried out with nitric acid at 80°C, and before complex formation with thiocyanate the sample is to be cooled to room temperature. Thioglycollic acid method requires several steps of evaporation, fusion, filtration, etc., before colour development. In the bathophenanthroline method there is scope for losses during solvent extraction steps. In the 1, 10-phenanthroline method there is scope for losses during transferring to volumetric flask and the method requires several steps including accurate adjustment of pH. The present method is free from all these problems and this simple procedure has the advantage that it is rapid and a large number of samples can be handled at a time without loss of precision. However, the method is not applicable for extremely turbid sample or sample containing clay materials. In spite of its limitations as mentioned above, the present method will be useful in the routine determination of iron in clear water samples.

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