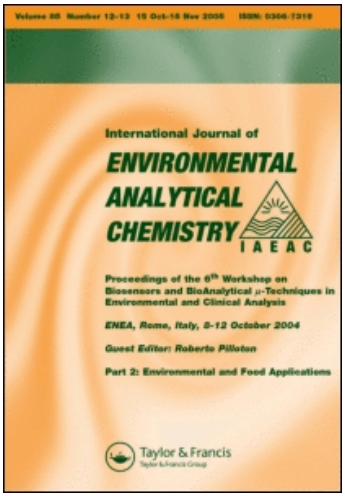

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2-(5-Bromo-2-Pyridylazo)-5-Dimethylaminophenol (5-Br-DMPAP) as a Reagent for Spectrophotometric Determination of Iron (III)

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2-(5-Bromo-2-Pyridylazo)-5-Dimethylaminophenol (5-Br-DMPAP) as a Reagent for Spectrophotometric Determination of Iron(III)

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A new colour reaction of iron(III) with 5-Br-DMPAP has been studied systematically. In dilute acetic acid solution (0.06–0.8 N), iron(III) can form a coloured complex with the above-mentioned reagent.

The complex exhibits maximum absorption at 600 nm, and the value of the apparent molar absorption coefficient is found to be 7.6×10^4. The composition of the complex is also established as Fe(III):5-Br-DMPAP = 1:2 by the methods of continuous variation and mole ratio, as well as slope ratio.

The Lambert–Beer law is obeyed in the range of 0 to 0.8 μg iron/ml.

Proposed new method is reasonably selective and sensitive for iron(III) and was satisfactorily applied to the determination of iron(III) in irrigation water.

KEY WORDS: Iron(III) determination, 5-Br-DMPAP, spectrophotometry, irrigation water.

INTRODUCTION

The classical thiocyanate is the reagent most often used for determining small amounts of iron. However, the results obtained by the method depend considerably on the exact adjustment of experimental conditions. Well-known 1.10-phenathroline and its derivatives are insensitive.

In recent years, many spectrophotometric methods have been recommended for the determination of microgram amounts of iron, and these methods based on colour reactions with some heterocyclic azo reagents have been investigated.[1–4]

Generally, they have the following advantages: (1) high sensitivity and selectivity; (2) simplicity and rapidity; (3) good reproducibility; and (4) very low absorbance of the reagent blank. In the work presented here the complex formation of 5-Br-DMPAP with iron(III) was studied spectrophotometrically as a basis for its use in the determination of microgram amounts of iron.

5-Br-DMPAP has two particular features of interest. First, its sensitivity is approximately three times higher than that of reagents (e.g. bathophenanthroline, ferrozine and 2,4,6-tri(2′-pyridyl)-s-triazine etc.) which have been widely used in water analysis.[5]

Secondly, the complex is formed with Fe(III) and this may be useful in speciation studies.

This method has been applied to the determination of iron in irrigation waters with good precision and accuracy.

EXPERIMENTAL

Apparatus

A Model 721 spectrophotometer (3rd Analytical Instruments Factory, Shanghai, China) was used in visible region of the spectrum.

Reagents

All solutions were prepared with analytical reagent-grade reagents using distilled water, unless stated otherwise.

Stock standard solution of iron(III): 100 μg/ml.

Dissolve 0.4317 g $Fe_2(SO_4)_3 \cdot (NH_4)_2 \cdot SO_4 \cdot 24H_2O$ in water containing 10 ml of 6 N acetic acid, and dilute to 500 ml with water.

Prepare a working solution by suitable dilution.

5-Br-DMPAP (Tianjin Chem. Indus. Mfg.), 0.02% (m/v) in 95% ethanol.

Recommended procedure

By pipette, place a volume of the working solution containing not more than 20 μg of iron into a 25-ml calibrated flask. Add 5 ml of 3 N acetic acid, 2 ml of 95% ethanol, and 2 ml of 0.02% 5-Br-DMPAP solution.

Dilute to the mark with water, and mix well. Allow to stand for 10 min. and measure the absorbance in a 1-cm cell at 600 nm against a reagent blank, carried through the above-described procedure.

RESULTS AND DISCUSSION

Absorption spectra

The absorption spectra of the reagent and its iron(III) complex have been measured over the range 370 to 700 nm (see Figure 1).

The absorption maximum of the reagent is at 450 nm. The curves for the complex show two absorption maxima at 550 and 600 nm, respectively. At the latter wavelength, the complex shows good sensitivity. Consequently, in further experiments, the absorbance was measured at 600 nm.

Effect of acidity on colour development

When the acetic acid concentration was varied from 0.03 to 1.2 N, the absorbance of the complex were maximal and constant for the acidity range 0.06–0.8 N. An acetic acid concentration of about 0.6 N (corresponding to 5 ml of 3 N acetic acid) was therefore selected as optimal.

Effect of amount of 5-Br-DMPAP

In 25 ml of final solution, 1.0 to 4.0 ml of 0.02% 5-Br-DMPAP solution gives maximum and constant absorbance with 10 μg of iron

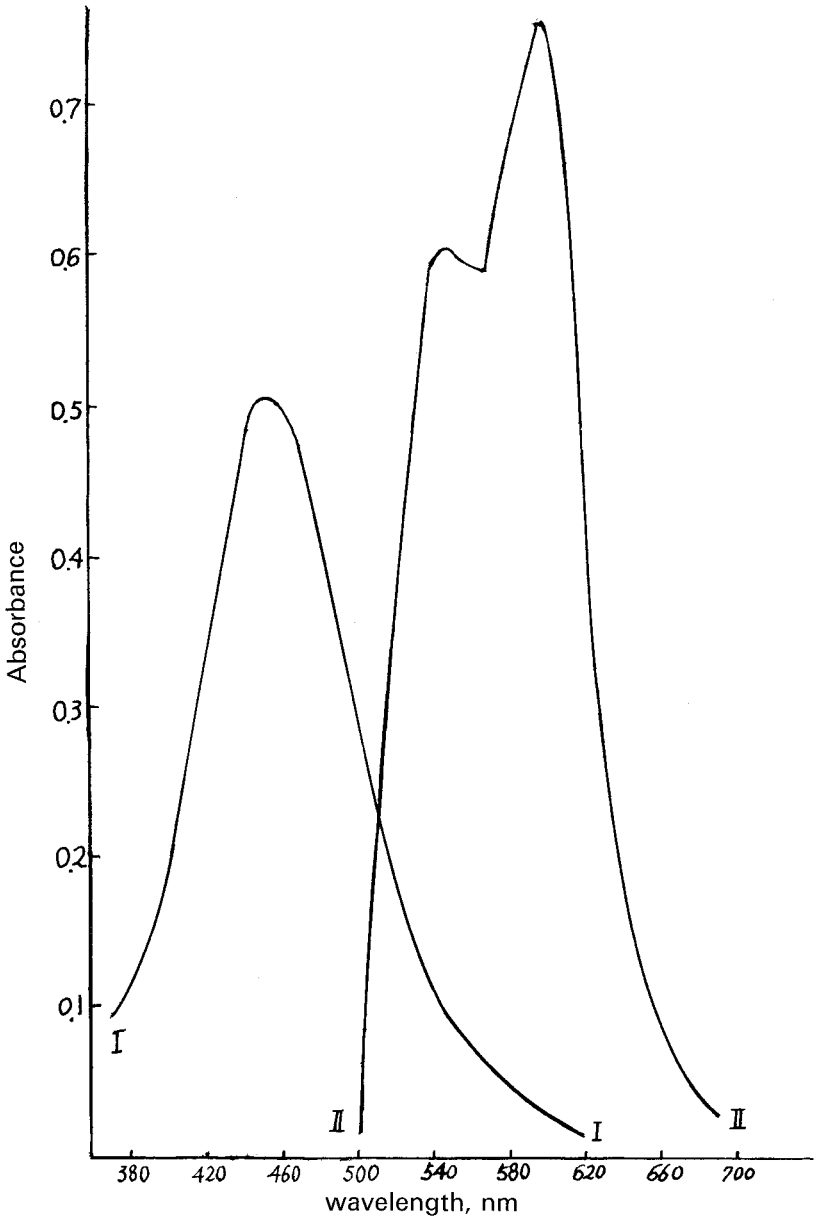

FIGURE 1 Absorption spectra of 5-Br-DMPAP and of its Fe(III) complex
Curve I. 5-Br-DMPAP (against water as reference), 1.0-cm cell.
Curve II. Fe(III)-5-Br-DMPAP complex (against reagent blank as reference), Fe(III) taken 20 μg, 1.0-cm cell.

(III), so use of 2.0 ml of the reagent solution is recommended for the determination (see Figure 2).

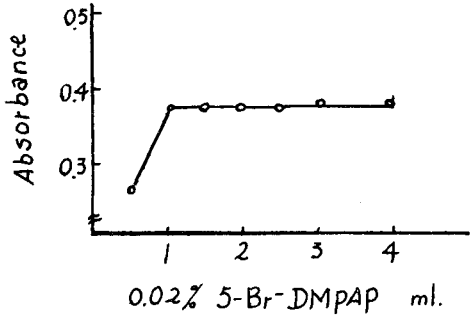

FIGURE 2 Effect of amount of reagent on absorbance of complex Iron(III) taken, 10 μg.

Effect of medium

Experimental results indicated that the 5-Br-DMPAP and its iron complex are sparingly soluble in water but dissolve readily in ethanol.

Besides, the addition of ethanol to the solution is recommended, because the stability of the complex formed is increased. It was found that the addition of 1 to 10 ml of 95% ethanol caused virtually no variation in the absorbance (see Figure 3).

Hence, in all experiments 2.0 ml of 95% ethanol were used.

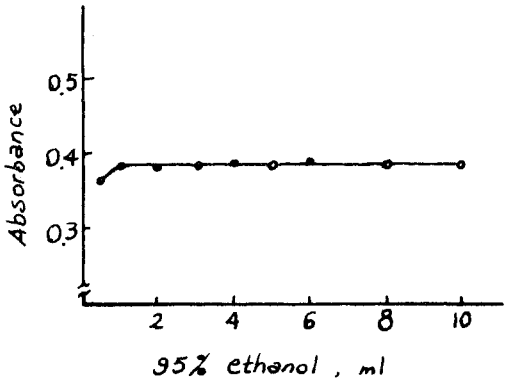

FIGURE 3 Effect of concentration of ethanol Iron(III) taken, 10 μg.

Characteristics of the complex

At room temperature, the complex is completely formed in 10 minutes, and the absorbance remains stable for 24 hours.

The composition of the complex was studied by Job's continuous variations method[6] and the slope ratio method.[7]

Using either method the metal to ligand ratio was found to be 1:2 for the binary (Fe-5-Br-DMPAP).

Under optimum conditions a linear relationship between absorbance and the amount of iron(III) was found in the range 0–20 μg per 25 ml. The correlation coefficient of the calibration graph is 0.9997. The colour reaction has a molar absorptivity of 7.6×10^4 litre.mol^{-1}.cm^{-1} at 600 nm, and the Sandell's sensitivity was estimated to be 0.74 ng Fe(III)/cm^2, corresponding to $\log I_0/I = 0.001$.

The detection limit has been determined to be $[= 2 \times \sqrt{2} \times t_{(0.05)} \times S_{wb} = 19.9\ \mu g/1$ for iron(III).

Effect of foreign ions

Various ions which are generally associated with iron in irrigation water were tested for interferences.

K^+, Na^+, NH_4^+, NO_3^- and Cl^- do not interfere, even when present in large excess. The following ions do not interfere (amount given in μg): Ca^{2+}, Mg^{2+} (each 2000), Ba^{2+}, Pb^{2+}, Mn^{2+} (each 1000), Si(IV) (500), Cd^{2+}, Zn^{2+}, Al^{3+}, Mo(VI), La^{3+}, As(V) (each 100), Ni^{2+}, Cr(VI), Sn(IV), Cu^{2+} (each 10), Co^{2+} (5) and Ti(IV) (2).

Because iron(III) may be masked by fluoride, therefore, F^- interferes.

Application to irrigation water samples

The method has been applied satisfactorily to the determination of iron in various waters, as follows: Place a volume of water sample (10–50 ml, according to the iron content) in a 100-ml beaker. Add 0.5 ml of HNO_3 and 5 drops of 30% H_2O_2 solution, and evaporate the dryness on a boiling-water bath. Then dissolve the residue in 5 ml of 3 N acetic acid, and transfer to a 25 ml volumetric flask.

The absorbance of the coloured solution was measured according to the procedure described above.

Several water samples were analysed, and the results are presented in Table I.

The recoveries of standard iron added to four water samples were in the range 98.6–100.6%.

TABLE I

Determination of iron in irrigated water

Sample water	Individual value of analysed result, p.p.m.				Average	Standard deviation	Coefficient of variation %
River	1.20	1.20	1.20	1.20	1.200	0	0
	1.20	1.20	1.20				
Pond	0.125	0.124	0.125	0.125	0.1247	0.00049	0.391
	0.124	0.125					
Well	0.191	0.187	0.191	0.191	0.1904	0.00151	0.794
	0.191	0.191	0.191				
Pipe water	0.0472	0.0464	0.0482	0.0472	0.04737	0.000637	1.345
	0.0482	0.0472	0.0472				

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