Journal of the University of Chemical Technology and Metallurgy, 41, 2, 2006, 205-210

SPECTROPHOTOMETRIC DETERMINATION OF IRON (III) BASED ON ITS CATALYTIC EFFECT ON THE OXIDATION OF DIPHENYLAMINE WITH HYDROGEN PEROXIDE IN THE PRESENCE OF CETYLPYRIDINIUM CHLORIDE

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Received 04 January 2006
Accepted 20 April 2006

ABSTRACT

A new catalytic kinetic method for the determination of trace iron(III) over the concentration range 1 –100 ng ml^{-1} is described. The detection limit was 0.52 ng ml^{-1}. The sensitivity of the determination was increased in the presence of cetylpyridinium chloride (CPC).

The reaction rate was monitored spectrophotometrically by measuring the absorbance of the reaction product at 580 nm. The variables that affected the reaction rate were investigated and the reaction conditions were established.

Keywords: iron, catalytic reaction, spectrophotometry, diphenylamine, cetylpyridinium chloride.

INTRODUCTION

Iron is the fourth most abundant element in the earth's crust occurring in a variety of rock and soil minerals in oxidation states 2 and 3, but it is only a trace element in biologic systems. Evidence has been presented that at low levels iron is an essential element in the diet, whereas at higher concentrations it is toxic [1].

A number of sensitive analytical methods are available for the determination of iron. At present some of the most commonly used methods include spectrophotometry [2-4], chemiluminiscence [5], fluorescence analysis [6], polarographic and voltamperometric analysis [7,8], flow-injection analysis [5, 9, 10], atomic emission and atomic absorption spectrometry [11, 12] and others [13, 14].

Catalytic kinetic methods are an attractive alternative for the determination of trace elements. Such methods have the general advantage of combining high sensitivity with relatively simple procedures and apparatus [15].

A number of kinetic methods for the determination of iron at trace levels based on its catalytic action on the oxidation of various organic compounds has been reported in several reviews [16-18] and experimental papers [19-23]. The oxidants most frequently used are hydrogen peroxide or BrO_3^-, IO_4^-, $S_2O_8^{2-}$ ions and the typical substrates are aromatic amines, phenols and their derivatives. Although most of these methods are very sensitive, some of them suffer from severe interference or poor reproducibility. The addition of a ligand, as an activator to the reaction system in metal-catalysed reactions, improves their sensitivity and/or selectivity [15]. Another way for improving the sensitivity is the use of a surfactant, which has the ability to form organized assemblies (micelles, micro-emulsions and vesicles) [24-26]. More sensitive and selective methods that can de-

termine the low concentrations of iron rapidly and conveniently are still needed.

In this work a new substrate for the determination of trace iron(III) is proposed and a novel catalytic kinetic method based on the catalytic effect of iron(III) on the reaction between diphenylamine (DPA) and hydrogen peroxide in micellar medium is described.

The proposed catalytic method allows for the kinetic specrophotometric determination of iron(III) over the concentration range 1 –100 ng ml^{-1} with a detection limit of 0.52 ng ml^{-1}. The sensitivity of the determination was increased in the presence of cetylpyridinium chloride (CPC).

EXPERIMENTAL

Reagents

All solutions were prepared from analytical grade chemicals and doubly distilled water. The laboratory glassware was kept in HCl (1:1) overnight, followed by rinsing with distilled and doubly distilled water. A stock Fe(III) solution ($\approx$0.1 M) was prepared by dissolving $\approx$7 g of $FeCl_3.6H_2O$ (Merck) in 250 ml of 2 M HCl (Merck). Its exact concentration was determined gravimetrically. Working solutions were daily prepared by appropriate dilution with 0.01 M HCl. Diphenylamine (DPA) (Merck) stock standard solutions ($1.0x10^{-2}$ M) were prepared by dissolving the reagent in concentrated formic acid (Merck). Aqueous solutions of cetylpyridinium chloride (CPC) ($3.6x10^{-3}$ M, Serva) and hydrogen peroxide (from 35 %, Merck) were prepared.

Apparatus

Kinetic measurements were made on a Specol 11 spectrophotometer fitted with 1-cm cells. The spectrophotometer cell compartments were thermostated by circulating water. Absorption spectra were recorded on a Specord-UV-Vis spectrophotometer using 1-cm quartz cells. The acidity of the reaction mixture was controlled with a "Consort R 400" pH-meter.

General procedure

In a test tube were placed: 6.25 ml of $6.0x10^{-5}$ M DPA solution, 0 - 0.50 ml of standard Fe(III) solution or distilled water, and 0.25 ml of $3.6x10^{-3}$ M CPC solution. The test tube was kept at 30°C in a thermostated water bath for 10 min. Then 0.50 ml of 9.0 M hydrogen peroxide were added, the mixture was homogenized by shaking and transferred into the 1 cm constant temperature cell of the spectrophotometer. The absorbances were red at 580 nm 15 min after adding of hydrogen peroxide.

RESULTS AND DISCUSSION

Diphenylamine is extensively used in analytical chemistry as a specific reagent for the detection of nitrate anions [27]. The literature review showed that in the oxidation of DPA two products are formed - the colorless diphenylbenzidine and the blue-violet diquinonediimine, which has an absorbance maximum at λ_{max} = 583 nm [28].

During our initial experiments, the oxidation of N,N-diphenylamine by hydrogen peroxide in acidic medium yielded a blue-violet product with an absorbance maximum at λ =580 nm. The reaction was slow, but it was sharply increased by the addition of trace amounts of Fe(III).

DPA is insoluble in water but soluble in most organic solvents. Initially, we dissolved it in methanol and studied the reaction at different pH values, obtained by adding of appropriate volumes of 0.2 M sodium hydroxide to 100 ml of the three-component mixture of 0.04 M boric, phosphoric and acetic acid. The catalytic effect of Fe(III) in all cases was not appreciable, especially at higher pH values (above 4). That is why, we dissolved DPA in an another solvent – concentrated formic acid (pK_a=3.8), which is miscible with water and most polar organic solvent. The reaction rate increased significantly. In order to clarify whether strong acidity accelerates the reaction studied, we added small volumes of strong acid (HCl) to the reaction system. As a result the observed reaction rate dramatically decreased. Therefore, in all further experiments concentrated formic acid was used as the solvent for DPA. The pH-effect on the reaction rate was not further investigated since high concentrations of formic acid ensured optimal acidity in the reaction mixture.

The effect of the surfactant on the uncatalyzed and Fe(III)-catalyzed reaction is shown in Fig.1. In the absence of the catalyst (curve a,b), the reaction proceeded very slowly and was not influenced by the presence of

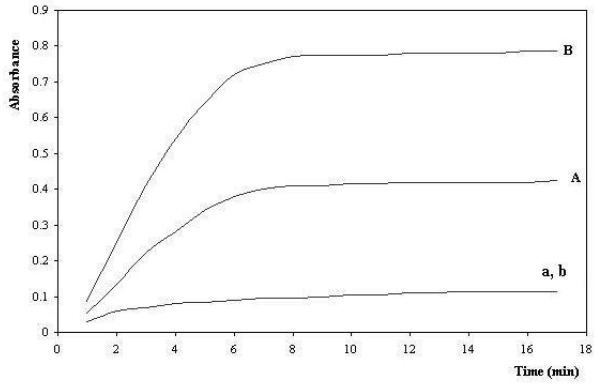

Fig. 1. Kinetic curves.
(a) uncatalysed and (b) CPC-catalysed; (A) Fe(III)-catalysed; (B) Fe(III)-CPC-catalysed reaction (30°C; 580 nm; 0.6 M H_2O_2; $2x10^{-7}$ M Fe(III); $1.2x10^{-4}$ M CPC; $5x10^{-5}$ M DPA in concentrated formic acid medium).

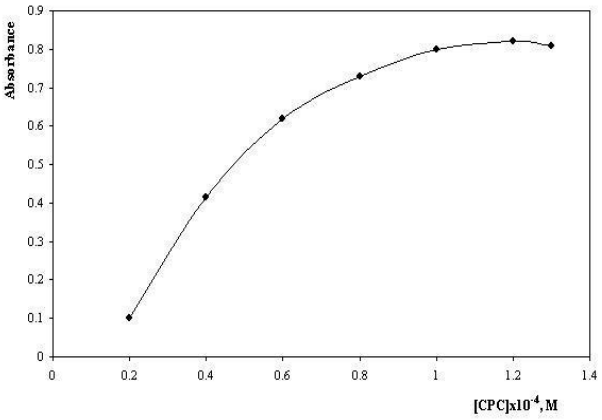

Fig. 2. Influence of CPC concentration.
(30°C; 580 nm; 0.6 M H_2O_2; $2x10^{-7}$ M Fe(III); $5x10^{-5}$ M DPA in concentrated formic acid medium).

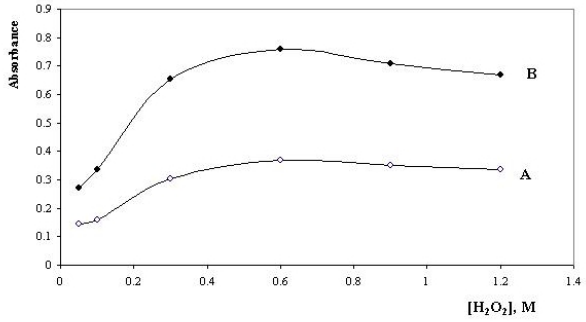

Fig. 3. Influence of hydrogen peroxide concentration.
(A) Fe(III)-catalysed; (B) Fe(III)-CPC-catalysed reaction (30°C; 580 nm; $2x10^{-7}$ M Fe(III); $1.2x10^{-4}$ M CPC; $5x10^{-5}$ M DPA in concentrated formic acid medium).

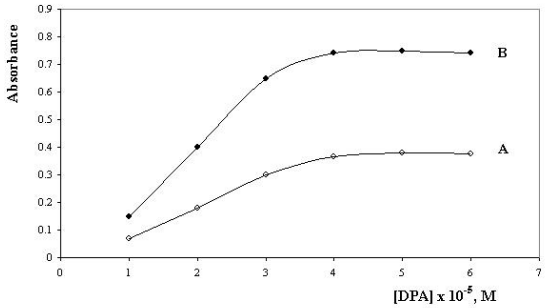

Fig. 4. Influence of DPA concentration.
(A) Fe(III)-catalysed; (B) Fe(III)-CPC-catalysed reaction (30°C; 580 nm; 0.6 M H_2O_2; $2x10^{-7}$ M Fe(III); $1.2x10^{-4}$ M CPC; in concentrated formic acid medium).

CPC. As can be seen, the surfactant had a strong positive effect only on the rate of the Fe(III)-catalyzed reaction (curve B). The saturation in the kinetic curves after 10 minutes allowed using the method of "the fixed time".

For finding the optimum experimental conditions, the influence of reaction variables, such as CPC, hydrogen peroxide and DPA concentrations, and temperature on the reaction rate, was studied in the absence and in the presence of a surfactant (Figs. 2-5).

The influence of the concentration of CPC on the Fe(III)-catalyzed reaction was investigated over the range 0 – 1.3 $x10^{-4}$ M (Fig. 2). A concentration of $1.2x10^{-4}$ M was finally selected.

Our experiments showed that in the presence of CPC the non-catalysed reaction remains unaffected by the changes in the acidity of the medium, temperature and reagent concentrations. That is why in the next figures only the dependencies of the reaction rate on the reaction conditions in the presence of Fe(III) are presented (Figs. 3-5). As can be seen from the results, the two profiles were similar for every parameter, whether the surfactant was present or not.

Fig. 3 reflects the influence of the hydrogen peroxide concentration on the Fe(III)-catalysed reaction in the absence (curve A) and in the presence (curve B) of a surfactant. The reaction rate increases with increas-

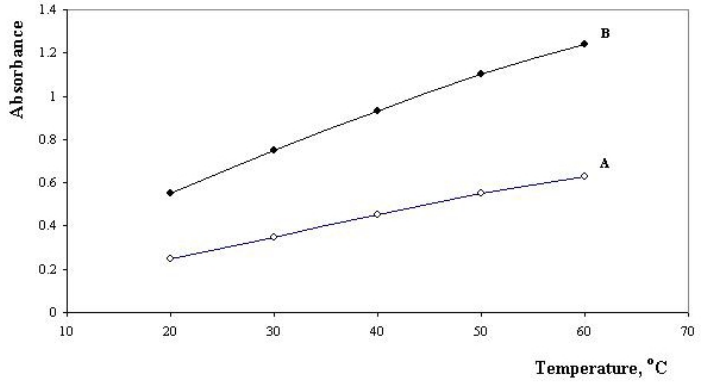

Fig. 5. Effect of temperature.
(A) Fe(III)-catalysed; (B) Fe(III)-CPC-catalysed reaction (580 nm; 0.6 M H_2O_2; $2x10^{-7}$ M Fe(III); $1.2x10^{-4}$ M CPC; $5x10^{-5}$ M DPA in concentrated formic acid medium).

ing hydrogen peroxide concentration up to 0.6 M H_2O_2. Higher concentrations do not increase the reaction rate, but instead a slight decrease is observed. Therefore, the concentration of 0.6 M of hydrogen peroxide was chosen as the optimal.

The effect of the diphenylamine concentration on the Fe(III) catalyzed reaction was also investigated, in order to obtain a constant and maximum sensitivity. The results reveal that the rate of the catalyzed reaction increases with increasing DPA concentration, attaining a maximum value, and then remains constant (Fig. 4).

The influence of the temperature was studied between 20 and 60 °C. As the reaction temperature increased, there was an increase of the reaction rate in both cases – in the absence and in the presence of a surfactant (Fig. 5). A temperature of 30 °C was adopted as optimal since it provides good reaction rate, best reproducibility and can be easily maintained.

The most suitable reaction conditions proved to be: λ 580 nm; temperature 30°C; $1.2x10^{-4}$ M CPC; 0.6 M H_2O_2 and $5.0x10^{-5}$ M DPA in a concentrated formic acid medium. Under these conditions a linear calibration graph in the range of 1 –100 ng ml^{-1} was obtained, using "the fixed time" method. This method was applied to the change in absorbance over an interval of 15 min from the initiation of the reaction because it provided better regression and sensitivity compared to the initial-rate method.

The equation of the calibration graph was: $A = 0.11+0.058\ C$, where C is the concentration of iron(III) expressed in ng ml^{-1}. The correlation coefficient of the graph was 0.9911. The relative standard

Table 1. Effect of diverse ions on the determination of iron(III) (23 ng ml^{-1}).

Foreign ion	Tolerated [ion] to [Fe(III)] mole ratio	
	Without surfactant	With surfactant
NH_4(I), Mn(II), F^-, Cl^-	1000	1000
Al(III), Mg(II), Sn(IV), Cd(II), Pb(II), Zn(II)	200	200
Ca(II), Ni(II), Cu(II), Co(II), Cr(III), Cr(VI), SO_4^{2-}	100	100
Ag(I), Mo(VI),	50	50
PO_4^{3-}	30	40
Fe(II)	5	4

deviation for ten replicate determinations of 23 ng ml^{-1} Fe(III) (n=10) was 3.9 %, and the detection limit calculated from LOD = KS_b/b (K =3, S_b is the standard deviation of the blank and b is the slope of the calibration graph) was 0.52 ng ml^{-1}.

Interference study

In order to determine whether the use of a surfactant resulted in increased selectivity for the determination of Fe(III), the effect of various ions on the proposed reaction in the presence and the absence of CPC was studied. The ions tested included those usually found in biological fluids because of the potential use of this method for determining Fe(III) in this type of matrix (Table 1).

The tolerance limit was defined as the concentration at which the species caused an error of less than $\pm$ 5 %. The interferences of various ions on the determination of 23 ng ml^{-1} Fe(III) are listed in Table 1. The results demonstrate that the catalytic reaction studied is quite selective and scarcely affected by the presence of the surfactant.

CONCLUSIONS

The kinetic spectrophotometric method developed for the determination of iron(III) in the presence of the surfactant CPC is simple and shows adequate selectivity, low limit of detection and good precision. The combination of micellar and chemical catalysis in the reaction studied resulted in increased sensitivity in the determination of the catalyst.

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