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A NEW KINETIC THERMOMETRIC METHOD FOR THE DETERMINATION OF IRON TRACES BASED ON THE CATALYTIC ACTION OF THE Fe^{III}-EDTA COMPLEX ON THE OXIDATION OF HYDROXYLAMINE

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ABSTRACT

A new kinetic thermometric method for the determination of iron traces, based on the catalytic action of the Fe^{III}–EDTA complex on hydroxylamine oxidation by dissolved oxygen, is proposed. The use of EDTA allows the selective and sensitive determination of trivalent iron at the $\mu g\ l^{-1}$ level, namely between 10 and 500 $\mu g\ l^{-1}$, with a relative standard deviation of 4.8% for 80 $\mu g\ l^{-1}$ of Fe ($n = 8$). The proposed method was applied to the determination of iron in water, beer and wine, where it provided similar results to those of the standard atomic absorption spectrometric procedure.

INTRODUCTION

The oxidation of hydroxylamine has been widely used for the determination of various metals through their catalytic action on the process [1].

On the other hand, both EDTA and its analytical applications have been the subject of much study, particularly in connection with its complex-forming ability [2,3]. The stability of EDTA complexes is known to increase—with a few exceptions—with decreasing atomic weight of the constituent metal within each group of the periodic table and with increasing valence [2]. Thus, the complex with Fe^{III} has the highest stability constant of all EDTA complexes, excluding that with V^{III}.

Iron is usually determined by spectrophotometry or atomic absorption spectrometry (AAS). The former method, widely used at the $mg\ l^{-1}$ level, is based on the colour of the complexes formed between Fe^{II} or Fe^{III} and various ligands such as α,α'-dipyridyl, *o*-phenanthroline, EDTA and NTA

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[4–10]. These methods have the shortcoming that the analyte must be optically transparent and, as a rule, that the determination limit of the analyte is of the order of a few mg l^{-1}. Atomic absorption determinations, apart from the costly equipment involved, call for solvent extraction steps, which makes procedures more laborious, or a graphite chamber if the $\mu g\ l^{-1}$ level is to be achieved.

Among the few kinetic methods devised for the determination of iron at the $\mu g\ l^{-1}$ level, spectrophotometric methods are worth special mention on account of their high sensitivity. Kreingol'd et al. [11] achieved a detection limit of 2×10^{-3} mg l^{-1} by exploiting the catalytic effect of iron on the reaction between hydrogen peroxide and acid chrome dark blue; Viñas et al. [12] determined iron over the range 1–30 ng ml^{-1} through its catalytic effect on the reaction between Methylene Green and periodate; Alexiev and Stoyanova [13] achieved a sensitivity to Fe^{III} of 2×10^{-8} M by oxidizing sulfanilic acid with sodium periodate using 1,10-phenanthroline as activator. All three groups, however, reported major selectivity problems posed by various metal ions interfering strongly with the photometric measurements.

In addition to the simplicity of the instrumentation required, thermometric methods have the advantages that determinations are performed directly and optical transparency of the analyte is not required [14–18].

In an earlier study [19] the catalytic action of Cu^{II} on the oxidation of hydroxylamine was studied, and it was found that, although Fe^{III} strongly inhibited the reaction, the effect was of catalytic nature in the presence of EDTA. This prompted study of the catalytic action of the Fe^{III}–EDTA complex (FeY^-) on the oxidation of hydroxylamine by dissolved oxygen, which takes place according to

$$2NH_2O^- + 2O_2 \overset{FeY^-}{\rightleftharpoons} NO_2^- + NO^- + H_2O_2 + H_2O$$

and was monitored thermometrically. The Fe concentration was obtained from the slope of the recorded curve.

The proposed method is as sensitive as the spectrophotometric methods used for the same purpose, and is more selective.

EXPERIMENTAL

Apparatus

The thermometric set-up used was described in detail elsewhere [18]. It consisted of an adiabatic cell, a 100 kΩ thermistor (25 °C), a Wheatstone bridge, a helical stirrer actuated by a synchronous motor, a stabilized power supply and an *x–t* recorder.

Reagents

The following reagents were used: 2 M hydroxylamine prepared from the hydrochloride and neutralized with NaOH; 0.01 M EDTA as the disodium salt; 0.1 M phosphate buffer made from hydrogen dipotassium salt and adjusted to pH 12.5 with NaOH; and Fe^{III} standard, 1000 mg l^{-1} prepared by dissolving the nitrate salt in 0.01 M HCl. All chemicals used were PA-grade reagents and distilled water was used throughout.

Procedure

In a thermometric cell were placed $(34 - x)$ ml of distilled water, x ml of the sample to be assayed to obtain a final Fe concentration between 10 and 500 ng ml^{-1}, 5 ml of the 0.01 M EDTA solution and 10 ml of buffer of pH 12.5. EDTA must be added before the buffer to avoid precipitation of iron. Once thermal equilibrium was attained, 1 ml of a 2 M hydroxylamine solution was injected into the cell and the thermometric curve was recorded.

RESULTS AND DISCUSSION

Instrumental parameters

The influence on the reaction rate of the variables involved was studied to determine the values that yielded the highest possible sensitivity and the broadest determination range.

Figure 1 shows the influence of pH on the Fe^{III}-catalysed reaction. The different pH values were obtained by using various 0.1 M potassium phosphate buffers (mono and dipotassium salts) adjusted with HCl or

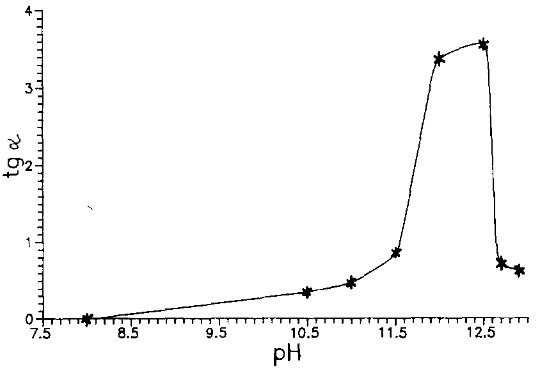

Fig. 1. Influence of pH on the reaction rate. $[Fe^{III}] = 400$ ng ml^{-1}; $[EDTA] = 0.001$ M; $[NH_2OH] = 0.04$ M.

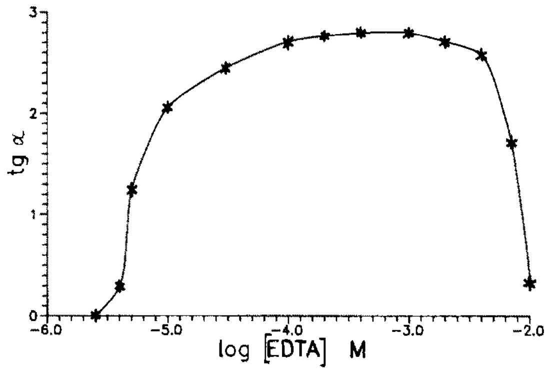

Fig. 2. Influence of EDTA concentration on the reaction rate. $[Fe^{III}] = 200$ ng ml^{-1}, $[NH_2OH] = 0.04$ M; pH 12.5.

NaOH as required. This buffer was preferred to others also assayed (borax, bicarbonate, ammonia/ammonium) as it provided better results.

As can be seen from Fig. 1, the slope of the thermometric curve increased abruptly above pH 11.5, and the buffer of pH 12.5 provided the highest sensitivity in the determination of Fe^{III}. More basic buffers resulted in a considerably slower reaction rate as a result of the precipitation of the iron.

Figure 2 shows the influence of the EDTA concentration on the reaction kinetics. As can be seen, the reaction started only at a ligand concentration of the order of Fe^{III} (200 ng ml^{-1} = 3.58×10^{-5} M). Above this, the slope of the thermometric curve increased sharply to a constant value at EDTA concentrations between 10^{-4} and 2×10^{-3} M, above which it started to decrease markedly. We thus chose 10^{-3} M as the optimal EDTA concentration.

Figure 3 reflects the influence of the hydroxylamine concentration. As can be seen, the slope of the working curve remained constant above 0.03 M, so we used a working concentration of 0.04 M.

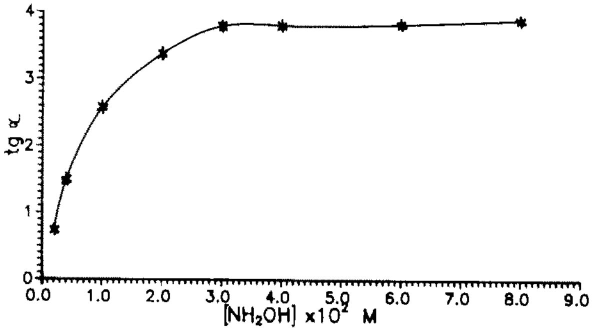

Fig. 3. Influence of hydroxylamine concentration on the reaction rate. $[Fe^{III}] = 400$ ng ml^{-1}; $[EDTA] = 0.001$ M; pH 12.5.

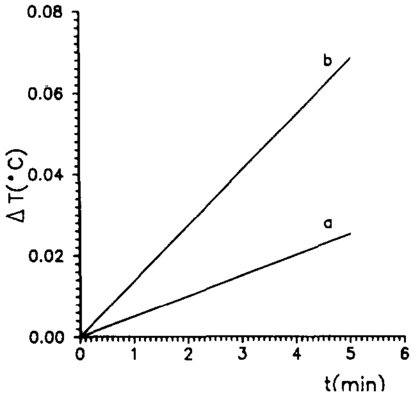

Fig. 4. Temperature–time curves for (a) the blank and (b) 80 ng ml^{-1} Fe^{III}.

Calibration graph

Under the optimal conditions described above a calibration graph was run, which revealed the proposed method to be applicable over the Fe^{III} concentration range 10–500 ng ml^{-1}, with a chart sensitivity of 10 mV. The equation of the curve obtained was

$$\tan \alpha = 0.1074 + 7.96 \times 10^{-3}[\mathrm{Fe^{III}}]$$

with a linear correlation coefficient $r = 0.9991$.

The different tangent values were obtained by subtracting the slope of the thermometric curves recorded at the different concentrations from that of the blank (Fig. 4). The relative standard deviation for 80 ng ml^{-1} of Fe^{III} was 4.8% ($n = 8$).

Effect of foreign ions

The effect of various potential interferents on the determination was studied by adding 100 mg l^{-1} of each to an Fe^{III} sample containing 200 ng ml^{-1} of the analyte.

Table 1 lists the maximum tolerated concentration of each of the species assayed. As can be seen, Cu^{II}, Co^{II} and Cr^{III} gave rise to the most disturbing

TABLE 1

Tolerated foreign ion concentrations

Ion	Concentration (mg l^{-1})
Cl$^-$, NO$_3^-$, SO$_4^{2-}$, CO$_3^{2-}$, PO$_4^{3-}$, Na^I, K^I, Ba^{II}, Cd^{II}, Pb^{II}	100 [a]
Zn^{II}, Ni^{II}, Al^{III}	50
Ca^{II}	20
Mn^{II}	10
Cu^{II}, Co^{II}, Cr^{III}	5

[a] Maximum concentration assayed.

[Fe^{III}] = 200 ng ml^{-1}; [EDTA] = 0.001 M; [NH$_2$OH] = 0.04 M; pH 12.5.

effects—the first two were positive and the third was negative. Their interference can be significantly lessened by adding 2 ml of 25% NH_3 to the samples as the ammine complexes formed mask the above interferents, the effect of which is felt above 50 mg l^{-1} for Cu^{II} and above 20 mg l^{-1} for Co^{II} and Cr^{III}. The interfering effect of Ca^{II} (e.g. in hard waters) can be halved by using twice the recommended EDTA concentration.

The tolerated levels for foreign ions thus amply surpass the usual concentrations of the different ions in waters and other beverages; otherwise, the effect of the ion in question can be readily lessened by one of the above-described procedures.

Applications

The proposed method was tested by determining the Fe^{III} concentration in different types of sample by the standard-addition method.

Table 2 lists the analyte volumes used, and the results obtained by the proposed method and the standard AAS procedure.

The thermometric determinations were carried out directly, after checking for the absence of matrix effects, with the exception of the beers which, like red wines, require pre-mineralization. Once mineralized, these samples must be neutralized with NaOH to avoid significant pH changes in the thermometric cell.

The Fe concentration in the mineral and waste-water samples was below the detection limit of the proposed method; however, as the determinations were affected by no sample matrix effect, the Fe contents specified by international legislation can be certified.

The determination of Fe in wines and beers was carried out by adding 2 ml of 25% NH_3 to overcome the potential interfering effect of other ions.

The Fe^{III} concentrations found by the proposed thermometric method were virtually coincident with those obtained by AAS as, under the working conditions, all iron present occurred in its trivalent state.

TABLE 2

Application of the proposed method to various types of samples

Sample	V_{sample} (ml)	$[Fe^{III}]_{therm}$ (mg l^{-1})	$[Fe^{III}]_{AAS}$ (mg l^{-1})
Mineral water	25	< 0.010	0.004 [a]
Waste-water	25	< 0.010	0.006 [a]
Tap-water	25	0.027	0.028 [a]
White wine (Navarra)	1	3.7	3.5
Rosé wine (Jumilla)	0.5	9.8	9.3
Beer (lager)	2.5	0.33	0.32

[a] By use of a graphite chamber.

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