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THERMOMETRIC DETERMINATION OF Cu^{II} BASED ON ITS CATALYTIC EFFECT ON THE OXIDATION OF HYDROXYLAMINE BY DISSOLVED OXYGEN

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ABSTRACT

A thermometric kinetic catalytic method has been developed for the determination of submicrogram amounts of Cu^{II} based on its catalytic effect on the oxidation of hydroxylamine by dissolved atmospheric oxygen. The rates of the reactions involved were obtained from the temperature–time curves and were found to be proportional to the Cu^{II} concentration over the range 50–500 ppb. The method was only subject to one serious interference, namely that of Fe^{III}, the effect of which can be lessened by using citrate.

The proposed thermometric catalytic method was applied to the determination of Cu^{II} in waters.

INTRODUCTION

The catalytic action of Cu^{II} on the oxidation of hydroxylamine by dissolved oxygen in alkaline media was studied in depth by Hughes and Nicklin [1], who put forward the following reaction mechanism

$$NH_2O^- + O_2 \rightleftharpoons H_2O_2 + NO^- \quad (1)$$

$$NO^- + O_2 \rightleftharpoons ONOO^- \quad (2)$$

They assumed the formation of peroxynitrite ions via nitrosyl ions, which yield nitrites in the following copper-catalysed reaction

$$ONOO^- + NH_2O^- \overset{Cu^{II}}{\rightleftharpoons} NO_2^- + NO^- + H_2O \quad (3)$$

Jardim and Rohwedder [2] studied this reaction and applied it to the catalytic determination of copper in natural samples with spectrophotometric monitoring of nitrite production via the formation of an azo dye between nitrite, sulphanilic acid and *N*-(1-naphthyl)ethylenediamine. The resulting

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determinative method was highly sensitive, though rather time-consuming and subject to strong interference from Co^{II} and Fe^{III}. According to the proponents of the method, the catalytic effect of Cu^{II} on the oxidation of hydroxylamine by dissolved oxygen involves the formation of superoxide ions; this was inferred from the results obtained by carrying out the reaction on previously deaerated samples or others containing the enzyme superoxide dismutase; in fact, nitrite production under such conditions was virtually negligible. This led these authors to attribute the responsibility for the oxidation of hydroxylamine to nitrite to the superoxide ions.

The literature antecedents presented above and the results obtained by our group in developing new thermometric kinetic catalytic methods [3–8] prompted us to undertake a comprehensive thermometric study of the above-mentioned catalysed reaction in order to develop a thermometric kinetic catalytic method for the determination of copper. We chose thermometric measurements because, unlike spectrophotometric or fluorimetric measurements, they do not require samples to be optically transparent or colourless, or that the analyte to be determined yield any absorption or fluorescence bands; in addition, they are subject to fewer interferences arising from the formation of coloured or fluorescent species and require much simpler instrumentation.

EXPERIMENTAL

Apparatus

The thermometric system used was described in detail in an earlier paper [8]. It consists of an adiabatic cell, a 100 kΩ thermistor (25 °C), a Wheatstone bridge, a helical stirrer powered by a synchronous motor, a stabilised power supply unit and an x–t recorder.

Reagents

The reagents used were a 2 M hydroxylamine solution prepared from the corresponding hydrochloride and neutralised with NaOH, a buffer of pH 9, prepared from 0.1 M sodium tetraborate by adjusting the pH with HCl, and a standard 1000 ppm Cu^{II} solution made from copper metal (Merck).

All reagents used were P.A. grade and solutions were made in distilled water.

Procedure

A volume of x ml of sample or Cu^{II} standard was placed in the thermometric cell, together with 10 ml of the buffer at pH 9 and $(40 - x)$ ml of distilled water. Once thermal equilibrium had been attained, 1 ml of 2 M hydroxylamine was injected and the corresponding thermometric curve was recorded.

RESULTS AND DISCUSSION

Preliminary assays showed the advisability of injecting the hydroxylamine rather than the Cu^{II} (samples) or buffer solutions for obvious operational and thermometric reasons. Under these conditions, no thermometric signal was obtained and the baseline was completely flat in the absence of Cu^{II}.

Figure 1 reflects the influence of the pH on the Cu^{II}-catalysed reaction. The results presented in Fig. 1 were obtained by adjusting the pH of the solutions with 0.1 M tetraborate or NaOH in the presence of 0.1 M tetraborate. As can be seen, the pH has a marked effect on the kinetics of the process, the maximum rate of which corresponded to pH 10.5, above or below which rates were considerably lower. The variation of the reaction rate with the pH in the region of maximum buffering was very slight; this and the greater reproducibility thus achieved led us to select a pH of 9, adjusted with 0.1 M tetraborate buffer, for the measurements. As can be seen, this choice resulted in slightly decreased sensitivity, which can be increased by varying the working conditions as required.

In their spectrophotometric study of this reaction [2], Jardim and Rohwedder found a similar behaviour up to pH 11, above which they performed no measurements. However, they stated that the absorbances obtained (nitrite production) when the pH of the solutions was adjusted with NaOH in the absence of tetraborate were much lower than in its presence. Our thermometric measurements behaved rather similarly (Fig. 1),

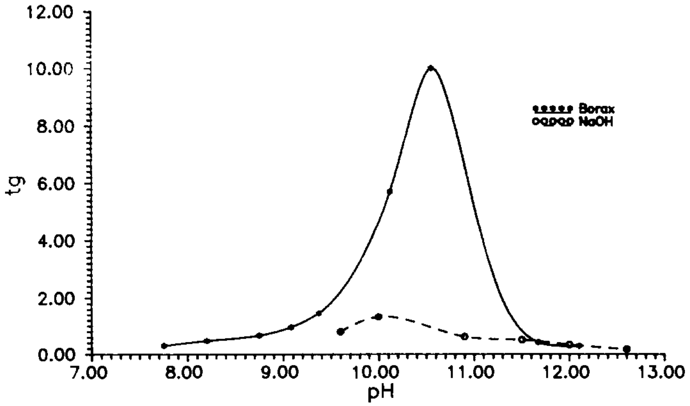

Fig. 1. Influence of the pH on the rate of the catalytic reaction: $[Cu^{II}] = 200$ ppb, $[NH_2OH] = 4 \times 10^{-2}$ M.

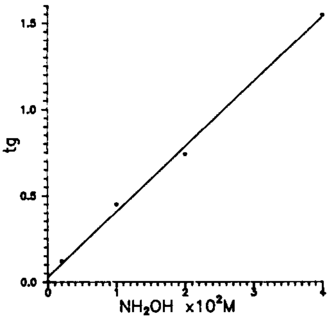

Fig. 2. Influence of the hydroxylamine concentration on the rate of the catalytic reaction: $[Cu^{II}] = 200$ ppb, pH = 9.0.

the differences in the reaction rates obtained in each instance being even more significant than those encountered by Jardim and Rohwedder, particularly above pH 10. On the other hand, the use of $NH_4Cl : NH_3$ buffers to adjust the pH of the solutions resulted in significantly decreased reaction rates and in the appearance of an induction period.

The above facts point to the occurrence of an activating effect, probably exerted by a complex formed between Cu^{II} and tetraborate ion.

Figure 2 shows the results obtained in studying the influence of the hydroxylamine concentration on the reaction kinetics. As can be seen, the reaction rate varied linearly with the aforesaid concentration up to 4×10^{-2} M, which was chosen as the working concentration—higher concentrations posed thermometric problems arising from the appearance of heats of dilution and were thus avoided.

Figure 3 shows the applicability range of the method, namely between 50 and 500 ppb Cu^{II} for a chart sensitivity of 10 mV. The reproducibility of the proposed method (rsd = 6%) was determined on eight samples containing 200 ppb Cu^{II}.

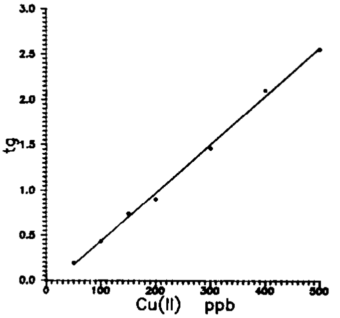

Fig. 3. Calibration graph: $S = 10$ mV, pH = 9.0, $[NH_2OH] = 4 \times 10^{-2}$ M.

TABLE 1

Tolerated amounts of interferents

Tolerated amount (ppm)	Ion
100 [a]	Cl^-, CO_3^{2-}, NO_3^-, SO_4^{2-}, PO_4^{3-}, K^I, Ca^{II}, Ba^{II}, Mn^{II}
20	Cd^{II}, Pb^{II}, Zn^{II}, Co^{II}
10	Al^{III}, Cr^{III}, Ni^{II}
1	Fe^{III}

[a] Maximum tested amount.

$[Cu^{II}] = 200$ ppb, pH = 9.0, $[NH_2OH] = 4 \times 10^{-2}$ M.

Study of interferences

In order to determine the potential interferences with the proposed method, we applied it to solutions containing 200 ppb Cu^{II} and 100 ppm of the following ions: chloride, carbonate, nitrate, sulphate, phosphate, K^I, Ca^{II}, Mg^{II}, Ba^{II}, Al^{III}, Fe^{III}, Co^{II}, Ni^{II}, Cr^{III}, Mn^{II}, Zn^{II} and Pb^{II}.

Table 1 lists the concentration of each species below which no interference was detected ($\pm 2\sigma$). As can be seen, only Fe^{III} poses a serious interference, probably through the occlusion of Cu^{II} in the ferric hydroxide precipitate formed. We tested various masking agents for iron such as fluoride, tartrate, EDTA and citrate to overcome its interference and found that only the addition of 2 ml of 0.01 M sodium citrate was effective in this respect—it increased the tolerated level of iron by a factor of 10. On the other hand, EDTA inhibited the catalytic action of Cu^{II}.

Applications

The proposed thermometric kinetic catalytic method was applied to the determination of copper in various types of water, namely, tap, well, purified and waste. The copper content of the first three was found to lie below the detection limit of the method (50 ppb); application of the standard-addition method revealed that the determination was not at all affected by any sample matrix effects. The copper concentrations of the three samples, determined by graphite-chamber AAS were 2, 20 and 6 ppb, respectively.

The results obtained by applying the proposed method to the waste water also showed that the sample matrix caused no interference; the Cu^{II} concentration of the sample was found to be 260 ppb—the graphite-chamber AAS method yielded 280 ppb Cu.

CONCLUSIONS

The thermometric kinetic catalytic method for the determination of Cu^{II} reported herein is faster, simpler and more tolerant of potential interferents than that proposed by Jardim and Rohwedder, also based on the same reaction, but using spectrophotometric rather than thermometric detection.

The proposed method yielded satisfactory results in the determination of copper in various types of water and allowed us to certify that their contents were within legally admitted ranges.

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