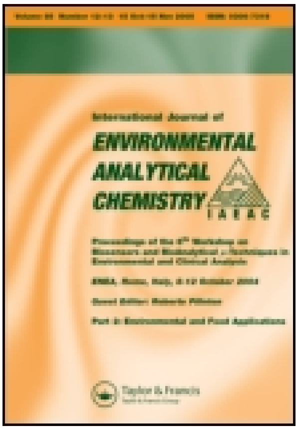

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Determination of trace amounts of Cu(II) in drinking and wastewater samples by a novel catalytic kinetic spectrophotometric method

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Determination of trace amounts of Cu(II) in drinking and wastewater samples by a novel catalytic kinetic spectrophotometric method

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The current method is based on the catalytic effect of Cu(II) on the oxidation of xylidyl blue (XB) by hydrogen peroxide (H_2O_2) in pH 10.5 borate buffer medium. The reaction was monitored spectrophotometrically by measuring the decrease in absorbance of XB at 570 nm. The optimum operating conditions regarding concentration of reagents, pH and temperature were studied and optimized in detail. A fixed time method was used for processing kinetic data. The working curve is linear in the concentration range of 2.5 to 75 μg L^{-1} of Cu(II). The maximum percentage error and relative standard deviation (RSD) for the determination of Cu(II) in the range of 2.5 to 75 μg L^{-1} have been calculated to be 3.6% and 0.5%, respectively. The detection limit and quantification limit were calculated statistically as 0.85 and 2.58 μg L^{-1}, respectively. The effect of possible interfering species was also investigated in real samples. The developed procedure was successfully applied to the determination of Cu(II) in different water samples such as tap water, drinking water and wastewater. Evaluation of the accuracy of the proposed kinetic method by using a certified environmental water sample (SRM 1640) was verified with the application of an alternative analytical technique such as ICP-AES (inductively coupled plasma atomic emission spectroscopy) and the obtained data were compared with those obtained by the presented kinetic method. It was found that the results of copper determination are statistically in agreement with its certified value and are comparable with those obtained by means of ICP-AES.

Keywords: catalytic effect; Cu(II); kinetic spectrophotometry; xylidyl blue

1. Introduction

Copper is an essential nutrient for which World Health Organization (WHO) recommends a daily intake of 30 μg per kg body weight [1]. Copper in drinking water can be an important source of dietary copper for humans [2]. A major source of copper in drinking water is corrosion of copper pipes, which can impart a taste to the water [3–5]. Copper in water may at times exceed health-based standards, resulting in increased potential for flavour changes and health concerns [3–6]. Drinking water standards have been established to prevent adverse health effects resulting from ingestion of too much copper. WHO recommends a limit of 2 mg L^{-1} Cu(II) to prevent adverse health effects from copper exposure [1]. WHO guidelines also state that a long-term intake of copper between 1.5 and 3 mg L^{-1} has no adverse health effects but greater levels than 5 mg L^{-1} in

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water can impart an undesirable bitter taste. The US Environmental Protection Agency (USEPA) developed a health-based action level of 1.3 mg L^{-1} Cu in drinking water [7] and an aesthetic-based standard of 1 mg L^{-1} Cu. Copper above this aesthetic standard level can stain plumbing fixtures and laundry as well as contribute to metallic- or bitter-tasting water [8]. USEPA databases from 2003 [9] identified 471 drinking water systems in violation of the copper health-based action level of 1.3 mg L^{-1} Cu. Recent problems with pinhole leaks (or nonuniform corrosion) in copper pipes have raised awareness and concerns about an increase in copper levels in drinking water [10].

The catalytic spectrophotometric method for trace determination in analytical chemistry offers distinct advantages and is a quite attractive method for achieving trace determination [12–16]. The analytical potential of catalytic kinetic methods, especially for environmental and industrial trace analysis, has progressed recently [12–19]. Several spectrophotometric methods are mainly based on the formation of complexes with Cu(II), which can meet the requirement of sensitivity for the determination of copper in various samples, has been reported but they do not possess sufficient selectivity [14,20,21]. Very recently a survey of various methods developed for Cu(II) determination has been presented by Prasad and Halafihi [12]. The catalytic effect of copper on many homogeneous redox reactions has also been frequently applied to the determination of Cu(II) at low detection limits [11–15,17–19]. Many of the kinetic methods based in different indicator reactions for determination of copper have been recently published with different and advanced analytical features [22,24–30]. Some of them have low sensitivity [25,29,30] or poor selectivity, which gives difficulties in their application in complex samples [35,41–45]. However, most of the indicator reactions used for catalytic determination of Cu(II) have been optimized with the view of their analytical applications rather than obtaining a complete understanding of the mechanistic features of the indicator reactions, which is a pre-requirement for exploitation of any reaction for its analytical application by kinetic method [28].

Hydrogen peroxide (H_2O_2) is a powerful oxidant that has been used to degrade harmful contaminants in wastewater, drinking water and soil. It can be used either directly in conjunction with a catalyst such as Fe(II), Cu(II), V(IV), UV light, or both. The basic concept of these systems is the decomposition of hydrogen peroxide with the formation of free radical intermediates, especially the hydroxyl radical. This radical is capable for reacting with a variety of organic compounds leading to either partial or complete degradation. It is well-known that copper also undergoes Fenton-type reaction and can lead to the oxidation of different compounds [29]. The copper-based systems have been used for degradation of synthetic dyes [30,31]. Some transition metal complexes together with hydrogen peroxide catalyze oxidation of organic compounds and some of them are active at alkaline pH. It was found in another study [32] that Cu(II)/pyridine/H_2O_2 system for the decolourization of structurally different synthetic dyes is effective at pH 3–9. In fact, hydrogen peroxide is a relatively weak oxidizing agent with a redox potential of 1.76 volt. Although hydrogen peroxide is a weak oxidant, it does have both electrophilic and nucleophilic properties. The electrophilic character arises from the fact that the O–O bond is easily polarized by either ultra violet (UV) irradiation at 254 nm or several one-electron reducing metal ions such as Fe(II), Cu(I), V(IV) and/or V(III). In alkaline solution, hydrogen peroxide dissociates to give perhydroxyl anion at especially $pH \geq pK_a$: 11.6. The perhydroxyl anion, HO_2^- is a powerful nucleophile and will attack substrates such as electron-deficient olefins (α,β-unsaturated ketones), aldehydes and phenolic azobenzene derivatives. Hydrogen peroxide is catalytically activated in the presence of several one-electron reducing metal ions such as Fe(III)/Fe(II), Cu(II)/Cu(I), V(V)/V(IV), V(IV)/V(III) redox couples. Also, hydrogen peroxide can be considered a mild reducing agent and used in some oxidations, notably phenol hydroxylation at $pH < 2–3$ owing to giving a powerful electrophile such as $H_3O_2^+$ [33]. In this context, hydrogen peroxide was chosen as an oxidant owing to its nucleophilic properties in presence of Cu(II) ions participating into catalytic cycle at pH 10.5 borate buffer media.

The purpose of the present work is to determine selectively traces of copper based on its catalytic effect on the oxidation of xylidyl blue (Magonsulfonate; 4-Hydroxy-3-[2-hydroxy-3-(2,4-dimethylphenylaminocarbonil)-1-azo-benzene sulfonic acid sodium salt]) with H_2O_2 in pH 10.5 borate buffer media. The proposed method is based on the measurements of change at (λ_{max}: 570 nm) wavelength of maximum absorption of xylidyl blue in alkaline media by applying fixed time method. The proposed kinetic method permits the quantitative determination of Cu(II) in the range of 2.5 to 75 $\mu g\,L^{-1}$.

2. Experimental

2.1 *Reagents and solutions*

A hydrogen peroxide solution (100 mL 1% (w/w) H_2O_2) was prepared from the 30% (w/w) H_2O_2 reagent by pipetting approximately 3.35 mL and diluting with deionized water. It is corresponding to a molar concentration of 0.332 M. A stock solution of the indicator dye solution (1×10^{-3} M) was prepared by dissolving it in deionized water. The working xylidyl blue solutions were obtained by dilution at suitable ratios with water. The borate buffer solution was prepared by mixing $Na_2B_4O_7$ (borax) (0.05 M) with NaOH (sodium hydroxide) solution (0.1 M) and using pH meter. The solution of $CuCl_2$ (copper (II) chloride) (1000 $mg\,L^{-1}$) was prepared by dissolving solid $CuCl_2$ salt at suitable amounts in water and diluting to 1 L. All stock solutions were stored in polyethylene containers. The working solutions of $CuCl_2$ and H_2O_2 were prepared immediately before use. Triply distilled water was used throughout. All labware used for handling solutions were cleaned with detergent solution, soaked in 1 : 1 (v/v) HCl, followed by vigorous shaking, rinsed thoroughly with deionized, distilled water.

2.2 *Instrumentation*

A Shimadzu Model UV-Visible 160 spectrophotometer equipped with a 1 cm quartz cell was used for absorbance measurements. The sequential spectrometer with an excitation in the ICP plasma (Spectro-Analytical Instruments, Germany) was used with the following parameters: frequency 27.12 MHz; power 1.1 kW; nebulizer-concentric Meinhard; analytical line for Cu 324.754 nm providing the highest sensitivity. A Grant LTG-6G model thermostatic water bath was usedfor temperature control. A stopwatch was used for recording the reaction time. A pH meter was used to determine pH values of solutions. The temperature was maintained constant in the reaction cell by circulating water at appropriate temperature around the cell compartment of the spectrophotometer throughout the experiment. All solutions were thermostatted to a working temperature of 30°C before the initiation of the indicator reaction.

2.3 *General procedure*

The pH of all working solutions around is set to a final value of 10.5. All working solutions were kept in the thermostatic water bath at 30 ± 0.1°C about 30 min. A suitable volume of standard reagent solutions borate buffer, xylidyl blue and Cu(II) were taken a reaction flask of 10 mL in that order. Indicator reaction was initiated with addition of H_2O_2 in certain volume. The solution was completed to 10 mL with deionized water, stirred and immediately transferred to the spectrophotometric quartz cell for the absorbance measurement. The rate of catalysed reaction, ΔA_S was spectrophotometrically monitored by using fixed-time method from the decreases in absorbance of indicator dye at fixed wavelength of 570 nm. The absorbance change within the first 3 min after the initiation of catalytic reaction was measured against deionized water. The rate of uncatalyzed reaction, ΔA_0 using the blank solution was followed the same way.

2.4 *Analysis of real water samples*

Tap water, drinking water and contaminated swimming pool water samples were collected in polyethylene containers cleaned with nitric acid, and then filtered through whatman no. 41 filter paper. Filtered samples were stored at 4°C until analysed. Tap water and drinking water samples were directly analyzed without any pre-treatment. The contaminated swimming pool water samples (with a pH of 7.5, total Cl_2 of $3.2\,mg\,L^{-1}$, free Cl_2 of $1.8\,mg\,L^{-1}$, total dissolved solids of $1275\,mg\,L^{-1}$, Ca-hardness of $230\,mg\,L^{-1}$, and cyanuric acid of $45\,mg\,L^{-1}$ as a stabilizer) were subjected to a pre-treatment before the kinetic analysis as follows: 250 mL of each contaminated pool water sample was transferred to a beaker of 300 mL. Solution was evaporated to a volume of 200 mL, then 3 g $Al_2(SO_4)_3$ (aluminium sulfate).$18H_2O$ was added to keep warm. The system was mixed until the solid completely dissolved. Then until Al^{3+} and Fe^{3+} ions were completely precipitated, drop by drop an aqueous NH_3 (ammonia) solution was added to it. Then to precipitate completely Ca^{2+} ions 3 g $(NH_4)_2CO_3$ (ammonium carbonate) was added. In order to accelerate precipitation with coagulation and drive away excess NH_3 the system was also heated for an additional time of 3 min. After cooling to room temperature, precipitate and solution was transferred to a reaction flask of 250 mL, diluted up to the line with pure water, thoroughly shaken and then filtered with filtration. The solution was transferred to a small beaker and 0.1 M NaOH solution was added to remove the excess $(NH_4)_2CO_3$. After evaporation by drying on the plain heater tray at 150°C, 3–4 drops of 0.05 M H_2SO_4 solutions, was added to re-dissolve the solid. Then the solution was transferred to colorimetric tubes. Solutions were analyzed according to the experimental procedure after adjusting of working pH to 10.5. Also, in order to test the accuracy of the kinetic method with recovery tests, the standard addition method was used.

3. Results and discussion

Xylidyl blue was selected as an indicator dye containing a reducing group, –OH, that can participate in pH-dependent electron transfer reactions in the range of 8.0 to 10.5. Ithas a aromatic ring carrying –OH, SO_3Na, –N=N- groups and an amidic group, which can catalytically be hydrolyzed in acidic and basic media, and has the potential of being a chelating agent. The reagent not only has a strong complex ability and forms various water soluble complexes with metal ions, but also the –N=N- group itself can produce coloru.

When the ligand is oxidized or reduced, the –N=N- group is destroyed, which results in the colour of solution becoming shallow, or even colourless. It is found in this study that at pH 10.5, trace levels of Cu(II) catalyzes the decolourizing reaction of xylidyl blue oxidized by H_2O_2 and based on this principle a novel method for the determination of trace copper was developed. The developed method is characterized by high sensitivity, operation simplicity, and low analytical cost. In this study xylidyl blue was used as chromogenic agent with reducing character, H_2O_2 as the oxidant, Cu(II) as the catalyst with oxidizing character. Based on the principle of catalytic reaction [34] and the above studies a possible mechanism for the Cu(II) catalyzed reaction is postulated as follows:

$$Cu^{2+} + 2OH^{-}Cu(OH)_2, \quad \text{and } Cu(OH)_2 \leftrightharpoons Cu^{2+} + 2OH^{-}, pK_{sp} = 18.79 \tag{1}$$

$$Cu(OH)_2 + D \rightarrow D = Cu(OH)_2 \tag{2}$$

$$D = Cu(OH)_2 \rightarrow \text{Oxidized-D radical or its dim erization products} + Cu^{+} + 2OH^{-} \tag{3}$$

$$\text{Dimerization products} + H_2O_2 \text{ or } HO2^{-}\text{further degradation products} \tag{4}$$

$$Cu^{+} + H_2O_2 \rightarrow Cu(H_2O_2) \quad \text{(Slow)} \tag{5}$$

$$2Cu(H_2O_2) \rightarrow Cu(OH)_2 + 2OH^{-}\text{(Fast)} \tag{6}$$

where D is the chromogenic reducing and metal binding agent taking place in catalytic cycle.

The reactions leading to xylidyl blue decolorization for the catalytic and non-catalytic reaction with perhydroxyl anion include uncomplexed dye, complexed dye and catalysed reaction. At higher pH values than a minimum pH of 7.84, which is required for precipitation of Cu(II) ions as $Cu(OH)_2$, it forms a stable complex in square planar geometry with anionic ligand in form of $D{=}Cu(OH)_2$ selectively coordinated through its azo-nitrogen and phenolic oxygen sites at pH 10.5. Because the solution medium is buffered into a higher pH value than 7.84, it is possible that Cu(II) ions, which is also present as $Cu(OH)_2$ complex in equilibrium rapidly react with the ionized indicator dye molecule to form a stable ternary complex product.

The first step in the proposed mechanism is the formation of a 1 : 1 Cu(II)-xylidyl blue complex at pH 10.5 borate buffer. It was reported earlier [35] that Cu^{2+} forms a 1 : 1 complex of high stability constant, (logK : 21) with calmagite being a ligand similar to structure of xylidyl blue except for amidic group. The Cu(II)-xylidyl blue complex is then slowly oxidized into a radical product, which is converted to two tautomeric forms by means of dimerization, and Cu(I). The more reactive species, the carbenium ion of these tautomeric forms is subject to a further degradation with the nucleophilic attack of hydroxyl radicals or perhydroxyl anion to it rapidly to yield the corresponding naphthoquinone and diazene species. Cu(I) is oxidized to Cu(II) in form of colloidal $Cu(OH)_2$ as a catalytic active species by H_2O_2 and thus the catalytic cycle continues, Equation (6). The mechanism of uncatalyzed reaction without catalyst involves two consecutive one-electron transfer steps, the initial formation of the dye radical followed by disproportionation [36,37].

It was observed that hydroxyl radicals react with calmagite being an arlyazonaphthol dye like xylidyl blue over a wide range of pH. The mechanism is based on the nucleophilic

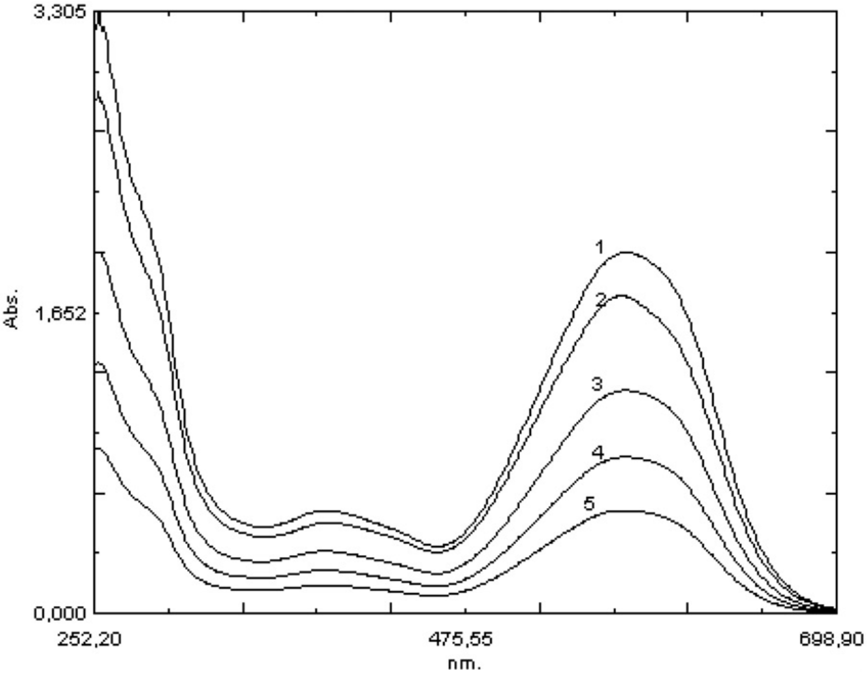

Figure 1. Absorption spectra. 1-pH 10.5 borate buffer+xylidyl blue (against water), 2-pH 10.5 borate buffer+xylidyl blue+H_2O_2 (against water), 3-pH 10.5 borate buffer+xylidyl blue+10 µg L^{-1} Cu(II)+H_2O_2 (against water), 4-pH 10.5 borate buffer+xylidyl blue+30 µg L^{-1} Cu(II)+H_2O_2 (against water), 5- pH 10.5 borate buffer+xylidyl blue+50 µg L^{-1} Cu(II)+H_2O_2 (against water). Conditions: 1.5 mL pH 10.5 borate buffer, 1.3 mL 1.0×10^{-3}M xylidyl blue and 0.7 mL 1.0% (w/w) H_2O_2 for the fixed-time method of 3 min and 30°C in final volume of 10.0 mL.

attack of hydroxyl radicals into the naphthol ring, indicating it produces a reaction intermediate with much broader absorption spectra in the range of 420 to 550 nm. While it is expected that addition to the aryl ring would produce hydroxy cyclohexadienyl radicals with weak absorption spectra in the range of 300 to 320 nm. Additionally, it is explained that the addition reaction into the naphthol ring is favoured at higher efficiencies owing to be its lower energy system and insensitive the radical product to oxygen. It was expressed that the reaction intermediate has a short lifetime (<200 µs) as it is efficiently bleached by bimolecular dimerization, i.e. reaction stoichiometry is one hydroxyl radical or one electron transfer per dye. It can be concluded that both catalytic- and noncatalytic-reaction is preceded according to a similar mechanism (Figure 1). This is based on nucleophilic addition of hydroxyl radicals into the naphthol ring in presence of excess H_2O_2 or HO_2^- ions at pH 10.5. A sharp absorption peak at 570 nm and a weak absorption peak around 400 nm are explained by the mechanism. Also, it is confirmed by the rapidly decreasing of the peak intensities with increase in copper concentration. A wavelength shift of 20 nm may be attributable to amidic group in structure of metal binding or reducing ligand. Also, when acrylonitrile was added to the reaction mixture with catalyst as a separate experiment, polymerization was observed after one day, indicating the presence of at least one of the free radicals such as hydroxyl, perhydroxyl and peroxy. This is other evidence that the indicator reaction with catalyst progress with a series of one-electron transfer mechanism based on the nucleophilic attack of radical species to ligand or metal-ligand complex. In a rate determining-slow step a peroxo-complex is formed as an intermediate, which then reacts in a very fast reaction to give the final product. In fact, the copper concentration in equilibrium (in the range of 2.5–75 $\mu g\,L^{-1}$) is higher than a minimum concentration of 0.103 $ng\,L^{-1}$, which is required for precipitation of Cu(II) ions as colloidal $Cu(OH)_2$ in presence of excess H_2O_2 at pH 10.5. Therefore, the regeneration of copper as catalytic species will be the fastest reaction among the other mechanistic reactions. The negative ΔS^{act} values have supported the idea of a highly structured transition state, which is formed as a result of the presence of the highly reactive and easily oxidizable cuprous species.

3.1 *Effect of reaction variables*

For the optimization of indicator reaction, the impact of reaction variables such as H_2O_2, xylidyl blue, pH, buffer and buffer composition, ionic strength and temperature of environment on reaction rate or analytical sensitivity was investigated in detail. Also the time to measure changes in absorbance was optimized for a time of approximately 10 min passing after the initiation of the catalytic reaction. For this purpose the calibration graphs of change in absorbance or analytical sensitivity, $\Delta(\Delta A)$: ΔA_S–ΔA_0 as a measure of the difference between the uncatalyzed and catalysed reaction rates at a fixed time (ΔA_t) versus concentration of Cu(II) in the linear calibration range were plotted at a fixed time ($t: 1, 3, 5, 7$ and 9 min) in a sufficient wide concentration range. It was found that the values of error, RSD and detection limits with the best correlation coefficient were be lowest for fixed time of first 3 min for 2.5–75 $\mu g\,L^{-1}$ Cu(II). Therefore, a fixed time of 3 min was chosen for the analysis of inorganic Cu(II) in water samples.

3.1.1 *The order of addition of reagents*

The order of addition of reagents was investigated for different reaction mixtures after dosing for each reaction mixture in terms of concentrations of reagents and catalyst was kept constant for catalytic reaction system in order to obtain the best sensitivity and the widest dynamic linear calibration range. Results have shown that the order of addition of reagents has had an apparent impact on the measurement. Owing to giving its maximum sensitivity, the optimum reagent addition order was taken into account as follows:

$$\text{pH 10.5 borate buffer} \rightarrow \text{xylidyl blue} \rightarrow \text{Cu(II)} \rightarrow H_2O_2$$

3.1.2 *Effect of pH*

All other experimental parameters kept constant and the dependence of the indicator system on pH by using the different buffers changing between 8.0–12.0 was examined under the experimental conditions. Results have shown that indicator reaction has the highest sensitivity in the presence of the pH 10.5 borate buffer at 570 nm (Figure 2). The effect of the volume of the buffer solution was also examined. From the experimental results, it was found that ΔA increased by increasing the buffer concentration in the beginning and then gradually reduced. When the volume of buffer was 1.5 mL, ΔA showed

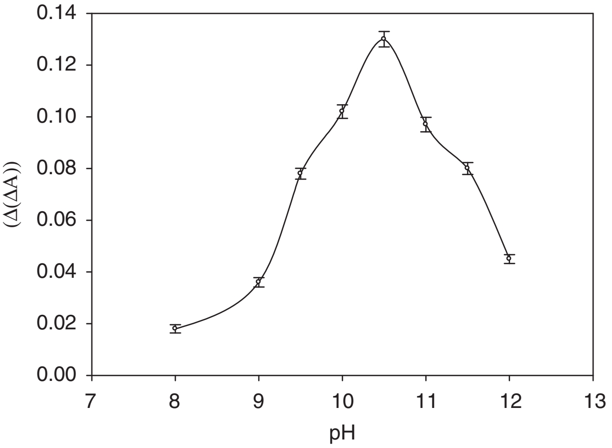

Figure 2. Dependence of analytical sensitivity on pH for catalytic indicator system. Optimal initial conditions: 1.3 mL 1.0×10^{-3} M xylidyl blue, 25 µg L^{-1} of Cu(II) and 0.7 mL 1.0% (w/w) H_2O_2 for a fixed-time of 3 min at 570 nm and 30°C.

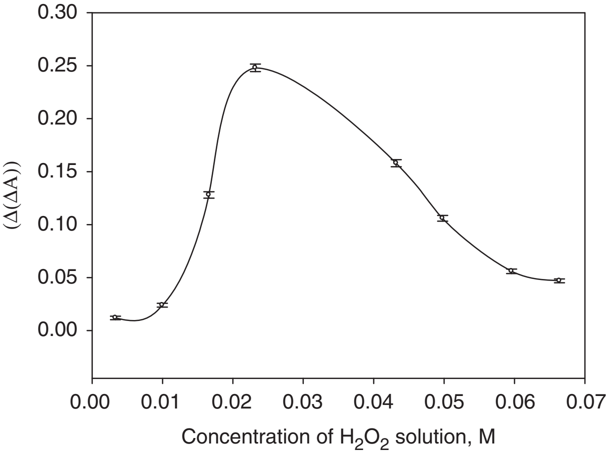

Figure 3. Dependence of analytical sensitivity on concentration of H_2O_2 solution for catalytic indicator system. Optimal initial conditions: 1.5 mL pH 10.5 borate buffer, 1.3 mL 1.0×10^{-3} M xylidyl blue and 25 µg L^{-1} of Cu(II) for a fixed-time of 3 min at 570 nm and 30°C.

a maximum and constant value. Therefore, 1.5 mL borate buffer (pH 10.5) was used as optimal value in the next experimental step.

3.1.3 *Effect of H_2O_2 concentration*

Effect of H_2O_2 concentration to analytical sensitivity was examined in the range of 3.32×10^{-3}–6.64×10^{-2} M under the experimental conditions. Results showed that ΔA increased with the increase in the concentration of H_2O_2 in the beginning and then quickly reduced. When the concentration of H_2O_2 was 2.32×10^{-2} M, ΔA gave a maximum value. Therefore, a H_2O_2 concentration of 2.32×10^{-2} M was used as the optimal value in this study (Figure 3).

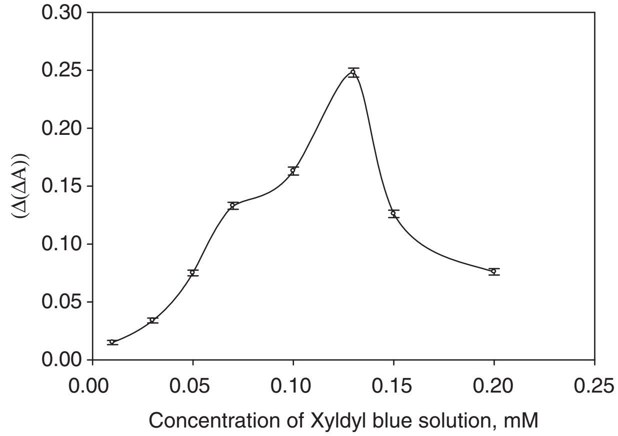

Figure 4. Dependence of analytical sensitivity on concentration of xylidyl blue solution for catalytic indicator system. Optimal initial conditions: 1.5 mL pH 10.5 borate buffer, 0.7 mL 1.0% (w/w) H_2O_2 and 25 μg L^{-1} of Cu(II) for a fixed-time of 3 min at 570 nm and 30°C.

3.1.4 *Effect of xylidyl blue concentration*

The effect of xylidyl blue concentration on the analytical sensitivity was investigated in the range of 0.01 to 0.2 mM under the experimental conditions. The results showed that high sensitivity could be obtained when concentration of xylidyl blue was low ($[XB] < 1.3 \times 10^{-4}$ M), but the linear detection range of Cu(II) as a catalyst was narrow. When the concentration of xylidyl blue was higher than 1.3×10^{-4} M, a great analytical signal error was easily caused and the repeatability was bad. This limiting effect in the detection range can be arising from either the increase in blank reaction rate or the aggregation of dye molecules at high concentrations. In order to guarantee high sensitivity and proper linear detection range, the indicator dye concentration of 1.3×10^{-4} M was taken into consideration as optimal value in this study (Figure 4).

3.1.5 *Effect of temperature on sensitivity*

Under the selected optimum conditions, the effect of reaction temperature on sensitivity (ΔA) was examined between 20−50°C. Results showed that the reaction rate increases with temperature rising to 30°C. The analytical sensitivity decreased proportionally until 55°C after 30°C. The cause of this state is the fact that the speed of uncatalyzed reaction is progressing faster than the speed of catalyzed reaction. Therefore, the reaction temperature of 30°C was taken into consideration as an optimal value (Figure 5). For evaluation of apparent activation parameters, the uncatalyzed and catalysed reactions were studied in the range of 18 to 30°C under experimental conditions. The Arrhenius plots of $-\ln \Delta A_C/\Delta t$ and $-\ln \Delta A_0/\Delta t$ versus $1/T$ was found to be linear with correlation coefficients of 0.9876 and 0.9888, respectively. By using the Arrhenius equation, the activation energies (E_a) for catalyzed and uncatalyzed indicator system were calculated and found to be 50.73 and 98.58 kJ mol^{-1}, respectively. Similarly, the Eyring plots of $-\ln \Delta A_C/T$ or $-\ln \Delta A_0/T$ versus $1/T$ were linear with correlation coefficients of 0.9863 and 0.9878 for a fixed-time of 3 min. The value of ΔH^{act} and ΔS^{act} for the catalyzed reaction

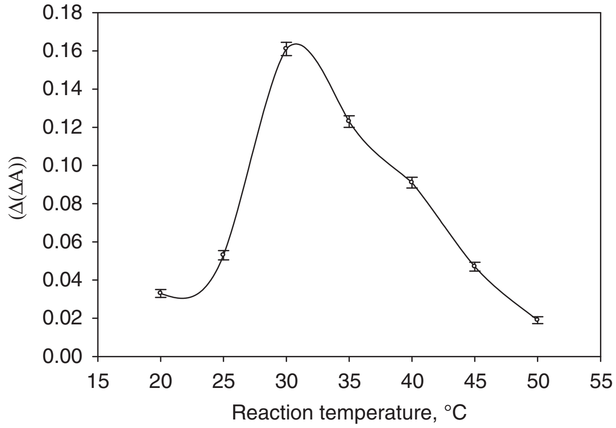

Figure 5. Dependence of analytical sensitivity on reaction temperature for catalytic indicator system. Optimal initial conditions: 1.5 mL pH 10.5 borate buffer, 1.3 mL 1.0×10^{-3} M xylidyl blue, 0.7 mL 1.0% (w/w) H_2O_2 and 25 μg L^{-1} of Cu(II) for a fixed-time of 3 min at 570 nm.

were evaluated from the slope ($-\Delta H^{act}/R$) and intercept [$\ln(k_b/h)+\Delta S^{act}/R$] of Eyring plots, and found to be 48.26 kJ mol^{-1} and −100,46 J K^{-1}mol^{-1}, respectively while the value of ΔH^{act} and ΔS^{act} for the uncatalyzed reaction were 96.41 kJ mol^{-1} and −299.31 J K^{-1}mol^{-1}, respectively. The values of Gibbs free energy (ΔG^{act}) of activation of the reaction products with and without copper as an catalyst at 298 K were 78.197 and 185,60 kJ mol^{-1}, respectively. As a result, it is clear that both catalyzed and uncatalyzed reactions are endothermic. Owing to its low activation energy (E_a) and free Gibbs enthalpy (ΔG^{act}), it may also be concluded that the catalyzed reaction is thermodynamically more favourable than the uncatalyzed reaction. Also, the negative entropy values demonstrates that the indicator reaction with and without catalyst is entropy controlled.

3.1.6 *Effect of reaction media*

Under optimal conditions selected, the effect of inert salts of media (ionic intensity) to the sensitivity (Δ(ΔA)) was examined in the concentration range of 0.005 to 0.25 M $NaNO_3$. Results showed that the sensitivity has changed very little with increasing concentration until 0.15 M, after this concentration exhibited a negative change with increasing inclination. This case predicated that the catalysed indicator reaction would give right response for catalyst in real life samples with low matrix. It can be expressed that inert salt effect should be checked at matrix systems with the high salt content such as sea water.

3.2 *Calibration curve*

Different Cu(II) standard calibration solutions were sampled to measure absorbance changes, ΔA(that is, ΔA_S or ΔA_0) of catalytic and noncatalytic system according to the optimal experimental conditions. The results showed that ΔA versus concentration of Cu^{2+} ion in the range of 2.5–75 μg L^{-1} obeyed a good linear relation. The regression equation was $\Delta(\Delta A) = 7.21 \times 10^{-3}$[Cu(II), μg L^{-1}] + 0.0501 with a reasonable correlation coefficient of 0.9795. The detection and quantification limits of the developed kinetic

Table 1. Tolerance levels of interfering species in the kinetic determination of 50 $\mu g\,L^{-1}$ Cu(II) under optimal reaction conditions as 1.5 mL pH 10.5 borate buffer, 1.3 mL 1.0×10^{-3} M xylidyl blue and 0.7 mL 1.0% (w/w) H_2O_2 for a fixed-time of 3 min at 570 nm.

Added interfering ion or ions	Tolerance ratio
K^+, Na^+ and NH_4^+	2500
HCO_3^-, NO_3^-, CH_3COO^-, HPO_4^{2-} and SO_4^{2-}	500
Ca^{2+}, Mg^{2+}, Pb^{2+}, VO_3^-, Ag^+, Hg^{2+}, $C_2O_4^{2-}$, Cl^- and F^-	250
Al^{3+}, Cd^{2+}, Mn^{2+}, Zn^{2+}, SCN^- and Br^-	100
Co^{3+}, Cr^{3+} and CrO_4^{2-}	30
Ni^{2+}, MoO_4^{2-} and Fe^{3+}*	20(35)
$Cr_2O_7^{2-}$, **	20(45)
$Cr_2O_7^{2-}$	10
Fe^{3+}	1

*In the presence of 2 mL 0.25 M NH_4F solution as masking agent in parenthesis.
**In the presence of 1–2 mL 0.05 M SO_3^{2-}solution in parenthesis.

method were 0.85 and 2.58 $\mu g\,L^{-1}$, respectively. Additionally, the maximum percentage of error and relative standard deviation was calculated to be 3.6 and 0.5 for seven replicate measurements in the concentration range of 2.5–75 $\mu g\,L^{-1}$, respectively.

3.3 *Interference study*

In order to determine the selectivity of the kinetic method, the effect of anionic and cationic interfering species to the catalytic reaction rate was studied at constant copper concentration of 50 $\mu g\,L^{-1}$ (Table 1). Results showed that when determining 50 $\mu g\,L^{-1}$ of copper by the kinetic method in final volume of 10 mL under the optimal reaction conditions and the relative error is below ±5%, the following concurrent ions had no interference on kinetic measurements. The allowable amounts of $Cr_2O_7^{2-}$ (dichromate) and Fe^{3+} ions as interfering species were lower than the other studied interferents. The usage of masking agents such as NH_4F and Na_2SO_3 for these ions interfering in the present method as well as using NH_3 and $(NH_4)_2CO_3$ solutions for suppressing the effect of foreign ions and improving the selectivity can be advised. However, the tolerance ratio for Fe^{3+} ion could be raised for 20 times when 2 mL of 0.25 M NH_4F solution is also added when necessary in addition to removal of the interference of Fe^{3+} ions as the insoluble compounds of iron hydroxide with aqueous NH_3 solution. After reduction of Cr^{6+} ions (especially a more aggressive ion, $Cr_2O_7^{2-}$) with 1–2 mL 0.05 M SO_3^{2-} solution in approximately pH 5.0, the effect of this interfering ion could be suppressed with the tolerance levels changing in the range of 20 to 45. Also, the interfering effect of Cr(VI) could be eliminated by reducing it to Cr(III) with ascorbic acid. Additionally, the interfering effect of Br^- and SCN^- ions also could be controlled by precipitating as insoluble silver salts and removing from reaction media via filtration.

3.4 *Analytical applications*

In order to establish the analytical accuracy and validity of the developed kinetic method in different water samples with complex matrix, the copper contents were determined

Table 2. Determination of trace amounts of copper present in tap water and wastewater samples under optimal reaction rate conditions by using the developed kinetic spectrophotometric method.

Water samples	Added Cu(II), μg L^{-1}	[a]Found Cu(II), μg L^{-1}	Recovery %
Tap water			
S_1	0	12 ± 1	–
S_2	25	38 ± 2	104
S_3	50	63 ± 3	102
[b]The contaminated swimming pool water (1)			
S_1	0	18 ± 1	–
S_2	15	34 ± 2	107
S_3	30	49 ± 3	103
[b]The contaminated swimming pool water (2)			
S_1	0	20 ± 1	–
S_2	15	36 ± 2	107
S_3	30	51 ± 3	103
Drinking water samples			
DW[1]	–	24 ± 2	–
	15	40 ± 2	107
	30	54 ± 2	100
DW[2]	–	20 ± 2	–
	15	36 ± 2	107
	30	51 ± 2	103
DW[3]	–	19 ± 3	–
	15	34 ± 2	100
	30	50 ± 2	103

[a] Confidence limits, which is known as the confidence interval at confidence level of %95 for five replicate analysis (a factor of 2.78 for probability level of 0.05 or confidence interval), $\mu = \bar{x} \pm ts/\sqrt{n}$ where t is a factor for probability level of 0.05 and four degrees of freedom (2.78), $\bar{x}$ an experimentally determined mean and s its standard deviation of five replicate measurements ($n:5$).

[b] Samples were collected and analyzed from the semi-Olympic contaminated-swimming pool water in City centre between one week

[1] Specific features of Erikli brand-drinking water: 7 mg $L^{-1}Cl^{-}$, 4 mg L^{-1} Ca^{2+}, 1.2 mg L^{-1} Mg^{2+}, 10.1 mg L^{-1} SO_4^{2-}, 0.5 mg L^{-1} F^{-}, pH : 7.3, hardness: 1.5. Free chlorine (Cl_2) and free ammonia (NH_3) is not available. Sample of 2 ml was taken for analysis of drinking water.

[2] Specific features of Fatsa brand-drinking water: 15 mg $L^{-1}Cl^{-}$, Ca^{2+} 14 mg L^{-1}, 1.4 mg L^{-1} Mg^{2+}, SO_4^{2-} 12 mg L^{-1}, pH : 6.2, hardness: 4.1. Nitrite and ammonia is not available. Sample of 2 ml was taken for analysis of drinking water.

[3] Specific features of Damla brand-drinking water: 15 mg $L^{-1}Cl^{-}$, 5.2 mg L^{-1} Ca^{2+}, 2 mg L^{-1} Mg^{2+}, 4 mg L^{-1} SO_4^{2-}, pH : 7, hardness: 1.5. Nitrite and ammonia is not available. Sample of 1 mL was taken for analysis of drinking water.

by using the standard addition method into tap water and wastewater samples. The results, which were found by adding standard copper solutions into different water samples (tap water, natural drinking water and wastewater) for determining copper, are also given in Table 2. Although the recoveries of standard copper solutions added to water samples are partly high for five replicate analyses at confidence level of 95%, these values can be regarded within quantitative limits. It can be suggested that the proposed kinetic method for determining the trace amounts of copper in real samples is useful and applicable to different samples.

In order to evaluate the analytical validation of the newly developed kinetic method, the method was also applied to the determination of copper in certified standard water

Table 3. Determination of Cu(II) ($\mu g\,L^{-1}$) in certified standard environmental water sample by using the present kinetic method and standard ICP-AES method.

SRM 1640[b]	Added, $\mu g\,L^{-1}$ Cu(II)	The proposed kinetic method		ICP-AES method[a]		Student *t*-test**	F-test***
		Found ± SD*, $\mu g\,L^{-1}$	Recovery%	Found ± SD*, $\mu g\,L^{-1}$	Recovery%		
After diluting five times	0	16.7 ± 0.5	98.0	16.8 ± 0.3	98.6	0.83	2.30
	5	21.8 ± 0.4	102.0	21.7 ± 0.3	98.0	0.62	2.27
	10	26.6 ± 0.3	99.0	26.7 ± 0.2	99.0	1.24	2.24
	30	46.9 ± 0.3	101.0	47.1 ± 0.2	101.0	1.24	2.23

[a] ICP-AES values for the copper content of certified environmental water sample.

[b] Standard reference material, SRM 1640 (Trace element in Natural Water) issued by National Institute of Standard and Technology (NIST). The certified value of copper is 85.2 ± 1.2 $\mu g\,L^{-1}$.

*Average value plus standard deviation of five replicate measurements.

**Statistical *t*-valueforeightdegrees of freedom (N_1+N_2-2) at 95% confidincelevel (2.31).

***Statistical F-value for eight degrees of freedom (N_1+N_2-2) at 95% confidence level (6.39).

Table 4. Comparison of the proposed kinetic method with the existing Cu(II)-catalyzed kinetic methods mentioned in literature.

Indicator reaction	Dynamic range (μg L^{-1})	Detection limit (μg L^{-1})	Conditions (temperature, λ_{max}, method)	Type of samples	Kinetic parameters and remarks	References
Hexacyanoferrate (III)+cysteine (RSH)	0–6.35	0.15	420 nm, 25°C and/or in absence of reproducible thermostatic bath, short analysis time of one minute, fixed time method	Synthetic and real samples		[12]
2,4-Dinitrophenylhydrazne-1,2-naphthoquinone-4-sulfonic acid +H_2O_2	2–200, 0.5–25	0.6, 0.2	570 nm, 40°C (25°C^a) fixed-time method, 10 min	Synthetic samples and river water		[19]
Pyrogallol-5-sulfonate+H_2O_2	10–300	1.8	436.8 nm	Water, milk		[23]
3-Methyl-2-benzothiazolinone hydrazone+H_2O_2	0–50	0.27	390 nm, 35°C fixed-time method, 40 min	River water and ground water		[25]
Oxidative coupling reaction of 3-hydroxyacetanilide with 3-methyl-2-benzothiazolinone hydrazone	8–160		530 nm, fixed time method, 20 s	Water and soil samples		[37]
Oxidative coupling reaction of 3-methyl-2-benzothiazolinone hydrazone with N-ethyl-N-(2-hydroxy-3-sulfo-propyl)-3,5-dimethoxyaniline	0.002–0.1		525 nm	Tap water and biological material		[38]
Ponceau S +sodium sulfide	2–400, 2–250	0.4 (fixed-time), 0.6 (slope method)	560 nm, 25°C fixed time method, 3 min	Cow's liver tissue, tap water and wastewater		[39]
Mercaptosuccinic acid+$K_2Cr_2O_7$	30–640, 640–1500	22	345 nm, room temperature	River water		[40]
Thioglycolic (TGA)/thiolactic acid (TLA)+$K_2Cr_2O_7$	8–1900 (TGA), 150–1920 (TLA)	65 for TGA, 80 for TLA	345 nm, 20°C	River and wastewater		[41]
Alkaline hexacyanoferrate (III)+citric acid	6.35–25400	4	420 nm, 60°C fixed time method, 3 min	Synthetic samples, tap water, river water and seawater	A positive salt effectandnegativeentropyvalue of -34.6 cal deg^{-1} mol^{-1})	[42]
Hexacyanoferrate (III)+cysteine (RSH)	0–6.35	0.15	420 nm, 25°C short analysis time of one minute in absence of reproducible thermostatic bath, fixed time method	Synthetic and real samples		[43]
Malachite green+H_2O_2	0–22	1.92	615 nm, 70°C fixed-time method, 20 min	Water sample and foodstuffs	k: 7.70×10^{-4} s^{-1} E_a: 112.3 kJ mol^{-1}	[44]

(continued)

Table 4. Continued.

Indicator reaction	Dynamic range ($\mu g\,L^{-1}$)	Detection limit ($\mu g\,L^{-1}$)	Conditions (temperature, λ_{max}, method)	Type of samples	Kinetic parameters and remarks	References
Methylene blue+L-ascorbic acid	100–1000	10	665 nm, 32°C fixed-time method, 2 min	Pharmaceutical products and electric copper wire		[45]
Rhodamine B+H_2O_2	0.8–5.6	–	555 nm, 100°C fixed-time method, 17 min	Serum		[46]
Neutral red+H_2O_2	0–116	0.52	454 nm, 60°C fixed-time method, 10 min	Human hair, nail		[47]
Ammonium molybdate+ascorbic acid	0–0.96	0.0154	660 nm, 43°C fixed-time method, 5 min	Human hair	k: $7.90\text{x}10^{-4}\,s^{-1}$ E_a: 107.3 $kJ\,mol^{-1}$	[48]
Xylidyl blue+H_2O_2	2.5–75	0.85	570 nm, 30°C fixed-time method, 3 min	Tap water, wastewater and drinking water	E_a: 50.70 $kJ\,mol^{-1}$ and ΔS^{act}: $-100{,}46\,J\,K^{-1}mol^{-1}$forthe Cu(II) catalyzed-reaction	The present method

sample(SRM 1640). For comparison of the results found by using the present method, the standard reference water sample was also analyzed by means ICP-AES method. It was found that the results obtained by the present method were in agreement with those of the ICP-AES method. To confirm both the accuracy and precision of the kinetic method with the recovery experiments, the known amounts of Cu(II) were added to the certified sample solution after diluting five times. The results are summarized in Table 3. The recovery of spiked copper (II) was found to be quantitative and the reproducibility was satisfactory. It was observed that the results of the SRM 1640 were in good agreement with the certified value of $85.2 \pm 1.2\,\mu g\,L^{-1}$ after multiplying the obtained value with the dilution factor.

4. Conclusion

In order to determine the Cu(II) at trace levels, the sensitivity and selectivity of this newly developed kinetic method is good, except for interference of Fe^{3+} and partly dichromate ions. The method, which is developed for determining the copper present in environmental water samples such as tap water, wastewater and of various natural drinking water samples, has a great analytical potential. The application of the method was verified with the results of the analysis of tap water, wastewater and three different drinking water samples. The data obtained to determine copper have shown that the performance of the method is very good in real water samples. Owing to the high selectivity of the method, for removal of anionic and cationic interfering ions except for Fe(III), no separation and preconcentration of samples is required. Validation of the kinetic method was made by determination of Cu(II) in a certified environmental water sample by using ICP-AES, and the results obtained using both methods have statistically shown a good agreement in view of accuracy and precision. The current method is simple and fast, and can be used to determine copper at low levels. The proposed method has the advantages of low cost, a linear range of 30 fold, reproducibility, accuracy and, most importantly, low DLs, comparable with the DLs obtained by the existing catalytic kinetic techniques for the determination of trace quantities of Cu(II) present in water samples [38–49] in Table 4. Also, it has a lower reaction temperature and time than the other kinetic methods.

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