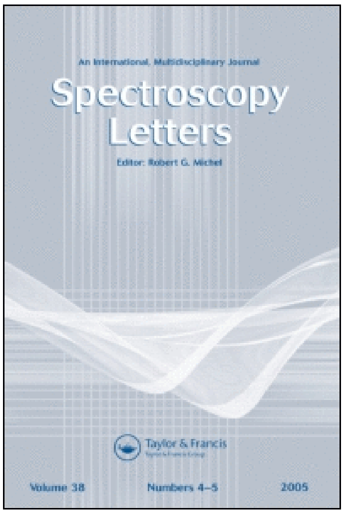

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

Kinetic Determination of Traces of Copper(II) by Its Catalytic Effect on the Oxidation of Sodium Pyrogallol-5-sulfonate by Hydrogen Peroxide

Snežana S. Mitić[a]; Gordana Ž. Miletić[a]; Mirjana V. Obradović[a]
[a] Department of Chemistry, Faculty of Sciences and Mathematics, University of Niš, Niš, Serbia

To cite this Article Mitić, Snežana S. , Miletić, Gordana Ž. and Obradović, Mirjana V.(2004) 'Kinetic Determination of Traces of Copper(II) by Its Catalytic Effect on the Oxidation of Sodium Pyrogallol-5-sulfonate by Hydrogen Peroxide', Spectroscopy Letters, 37: 1, 43 — 58

To link to this Article: DOI: 10.1081/SL-120028422

URL: http://dx.doi.org/10.1081/SL-120028422

SPECTROSCOPY LETTERS
Vol. 37, No. 1, pp. 43–58, 2004

Kinetic Determination of Traces of Copper(II) by Its Catalytic Effect on the Oxidation of Sodium Pyrogallol-5-sulfonate by Hydrogen Peroxide

Snežana S. Mitić,*[*] Gordana Ž. Miletić, and Mirjana V. Obradović

Department of Chemistry, Faculty of Sciences and Mathematics,
University of Niš, Niš, Serbia

ABSTRACT

A catalytic kinetic spectrophotometric method is developed for the determination of trace amounts of Cu(II). It is based on the catalytic effect of Cu(II) on the oxidation of sodium pyrogallol-5-sulfonate (PS) by hydrogen peroxide in acidic madium. The reaction was monitored spectrophotometrically by measuring the increase in absorbance of the oxidation product at 436.8 nm. The optimum operating conditions regarding concentration of reagents, pH, and temperature were established. The working curve is linear in the concentration range from 10 to 300 ng cm^{-3} and the detection limit is

---

[*] Correspondence: Snežana S. Mitić, Department of Chemistry, Faculty of Sciences and Mathematics, University of Niš, Visegradska 33, P.O. Box 224, 18 000 Niš, Serbia; E-mail: petra1974@yahoo.com.

DOI: 10.1081/SL-120028422
0038-7010 (Print); 1532-2289 (Online)

www.dekker.com

1.8 ng cm^{-3}. The interference effect of several species was also investigated and it was found that the most common cations and anions do not interfere with the determination. The developed procedure was successfully applied to the determination of Cu(II) in water and milk.

Key Words: Copper determination; Kinetic-spectrophotometric method; Sodium pyrogallol-5-sulfonate oxidation.

INTRODUCTION

Many analytical methods have been developed for the determination of copper, but the majority of them suffers poor selectivity. Among these methods are spectrophotometry, ion chromatography, and atomic absorption spectroscopy. Anodic stripping voltametry[1,2] and high performance liquid chromatography[3,4] have also been used for the determination of copper with high sensitivity and selectivity, but suffer from more or less time consuming procedures and/or expensive and complicated instrumentation.[1–4]

A few catalytic kinetic methods for Cu(II) determination at trace levels have been published using various types of indicator reactions.[5–7] Some of these methods are based on the oxidation of various reagents with H_2O_2. Most of these kinetic methods have a narrow dynamic range of determination and are applicable only to microgram amounts.[8] Prasad and Halafihi have developed a catalytic kinetic method for nanogram levels of Cu(II) based on its catalytic effect on the oxidation of cysteine by hexacyanoferrate (III) in acidic medium.[9] In some cases the sensitivities have been improved by addition of suitable ligands such as 2,2′-bipyridine and pyridine.[5,6] Besides, to improve sensitivity, the reactions are carried out at elevated temperatures.[6] In order to overcome these problems a successful attempt was made at developing and validating a rapid, sensitive, and selective kinetic method for the determination of Cu(II). In the present paper, a catalytic kinetic method for trace determination of Cu(II), based on its catalysis of the oxidation of sodium pyrogallol-5-Sulfonate (PS) by hydrogen peroxide, without using any activator is reported.

EXPERIMENTAL

Reagents and Apparatus

Preparation of a Sulfonated Product

A 3.7833 g sample of pyrogallol was dissolved in 100 cm^3 of 96% H_2SO_4. A solid product of sulfonate pyrogallol was formed after 48 hr at 25°C. The product was separated by filtration and dissolved in saturated NaCl solution to obtain the sodium-salt. After drying in a desiccator with $CaCl_2$, recrystallization from ethanol was performed in order to eliminate NaCl. Sodium pyrogallol-5-sulfonate is a white crystalline substance, soluble in water (14 g/100 g water at 20°C) and low concentrations of mineral acids.[10]

A $8.8 \times 10^{-3}\,\mathrm{mol\,dm^{-3}}$ solution of the reagent in water was used.

Hydrogen peroxide solution was prepared by appropriate dilution of the Merck pro analyze reagent and was standardized against potassium permanganate solution.

The perchloric acid solution ($0.12\,\mathrm{mol\,dm^{-3}}$) was prepared from the 70% reagent. A working solution of perchloric acid ($0.012\,\mathrm{mol\,dm^{-3}}$) was prepared by diluting the stock perchloric acid solution with deionized water.

The copper (II) solution ($1.0\,\mathrm{mg\,cm^{-3}}$) was prepared by dilution of a copper sulfate solution that had been standardized iodimetrically. A standard copper solution ($100\,\mathrm{ng\,cm^{-3}}$) was prepared by diluting the stock copper solution with deionized water.

All the stock solutions were stored in polyethylene containers. Working solutions of copper, hydrogen peroxide, and PS were prepared immediately before use.

A Perkin–Elmer Lambda 15 spectrophotometer, connected to a thermo-circulating bath was used for the measurements. The pH was measured by using a Radiometer PHM 29b pH meter and a combined glass–calomel electrode, GK 2311 C. The solutions were thermostatted at 25°C ± 0.1°C before the beginning of the reaction.

Procedures

Determination of Copper

Into a $10\,\mathrm{cm^3}$ standard flask with a glass stopper, a suitable aliquot of copper(II) solution was transferred. Then $1\,\mathrm{cm^3}$ of perchloric acid solution and $2\,\mathrm{cm^3}$ of PS solution were added and the solution was diluted to $9\,\mathrm{cm^3}$ with water. The solution was kept at 25°C ± 0.1°C in the thermostated bath. After the temperature of the solution had reached 25°C (about 10 min), $1\,\mathrm{cm^3}$ of hydrogen peroxide solution ($1.6\,\mathrm{mol\,dm^{-3}}$) was added to initiate the reaction. The spectrophotometer cell was rinsed well and filled with the solution. The absorbance at 436.8 nm was measured every 30 sec over a period of 3–8 min after the addition of hydrogen peroxide. The method of tangents was used and the slope of the linear section of the absorbance–time curve, $dA/dt = \tan\alpha$, was used as a measure of the reaction rate.

RESULTS AND DISCUSSION

Catalytic Action of Copper(II)

The absorption spectra of sodium PS in perchloric acid solution (Fig. 1, curve 1), PS–perchloric acid–hydrogen peroxide (curve 2) and PS–perchloric acid–hydrogen peroxide–copper(II) (curve 3) were recorded immediately after mixing. No characteristic absorption maxima are seen in the visible part of the spectrum of the PS–perchloric acid solution mixture. However, oxidation of PS by hydrogen peroxide in the presence of perchloric acid is characterized by a slight maximum at 436.8 nm that significantly increases in the presence of copper(II). Therefore, it can be concluded that copper(II) acts as a catalyst in the PS hydrogen peroxide oxidation reaction.

The dependence of the reaction rate on the H_2O_2 or PS contraction (see Figs. 3 and 4 below) indicates that the reaction proceeds through an intermediate complex of the catalyst–reductant–oxidant type[11,12] and finally, the activated complex decomposes into the products and the catalyst.

$$[\mathrm{PS - Cu(II) - H_2O_2}] \rightarrow \mathrm{Product + Cu(I)} \qquad (1)$$

$$\mathrm{2Cu(I) + H_2O_2 \rightarrow 2Cu(II) + 2OH^-} \qquad (2)$$

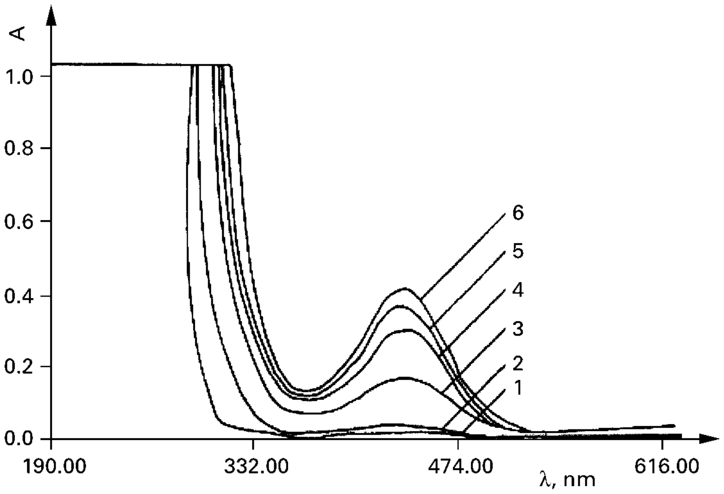

Figure 1. Absorption spectra of: (1) PS in $HClO_4$; (2) PS–$HClO_4$–H_2O_2; (3) PS–$HClO_4$–H_2O_2–Cu(II) mixture, immediately after the reagent were mixed; (4) PS–$HClO_4$–H_2O_2–Cu(II) mixture 4 min after mixing; (5) PS–$HClO_4$–H_2O_2–Cu(II) mixture 6 min after mixing, and (6) PS–$HClO_4$–H_2O_2–Cu(II) mixture 8 min after mixing.

It can be assumed that the second reaction proceeds much more quickly that the first.

The reduced copper(I) is oxidized to copper(II) by hydrogen peroxide, and then the copper(II) is allowed to react with PS again. Probably for this reason, a large excess of hydrogen peroxide with respect to the reagent is needed. The oxidation product was not identified. However, PS could be oxidized by a one-electron mechanism to produce a resonance-stabilized product, and a quinonoid species seems probable.

Effects of Reaction Variables

The influences of perchloric acid, temperature, and PS and hydrogen peroxide concentrations were studied for both the catalytic and noncatalytic reactions in order to establish optimum conditions for the determination of copper(II). Keeping all other experimental parameters constant, the perchloric acid dependence of the system was studied in the range of 1.2×10^{-3}–$6.0 \times 10^{-3}\,\mathrm{mol\,dm^{-3}}$ (Fig. 2). It can be seen that the greatest difference between the reaction rates occurs at $1.2 \times 10^{-3}\,\mathrm{mol\,dm^{-3}}$ and maximally decreases the catalytic reaction rate. The rate of catalytic reaction does not change, until the

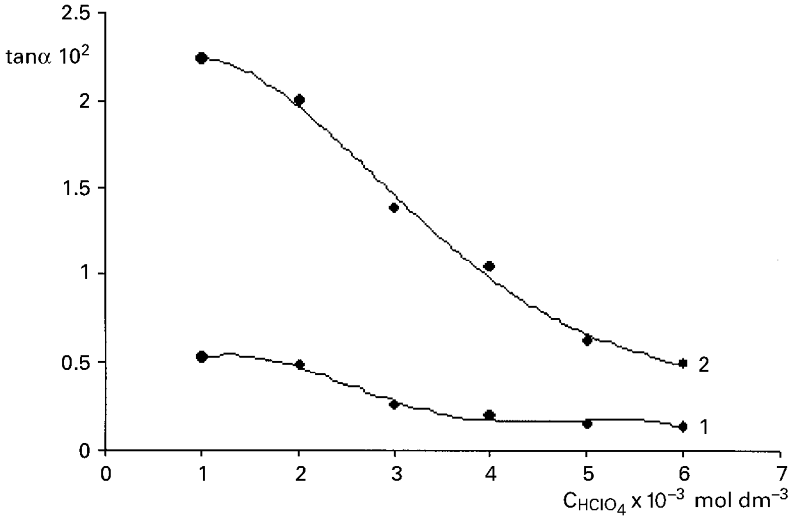

Figure 2. Dependence of the reaction rate on $HClO_4$ concentration. Initial concentrations: PS $= 8.8 \times 10^{-4}\,\mathrm{mol\,dm^{-3}}$; $H_2O_2 = 0.16\,\mathrm{mol\,dm^{-3}}$; Cu(II) $= 0.3\,\mu\mathrm{g\,cm^{-3}}$; $t = 22°C \pm 0.1°C$. (1) Catalytic reaction and (2) non-catalytic reaction.

rate of noncatalytic reaction increases for concentrations less than 1.2×10^{-3} mol dm^{-3}. For further work, a perchloric acid concentration of 1.2×10^{-3} mol dm^{-3} was selected.

The dependence of the reaction rate on H_2O_2 concentration is shown in Fig. 3. The figure shows that the difference between the rates of the catalytic and noncatalytic reactions increases with increasing hydrogen peroxide concentration. Both reactions are first order with respect to the H_2O_2 concentration. For further work, an H_2O_2 concentration of 0.16 mol dm^{-3} was selected.

The dependence of the reaction rates on the concentration of PS is shown in Fig. 4. It can be seen that the noncatalytic reaction is first order with respect to the PS concentration, whereas the catalytic reaction is first order with respect to PS concentration up to 8.8×10^{-4} mol dm^{-3} and zero order for higher concentrations. For further work, a PS concentration of 8.8×10^{-4} mol dm^{-3} was selected.

The influence of temperature on the reaction rate was studied in the range 22°C–34°C (Fig. 5). The reaction rate increased as the temperature increased between 22°C and 34°C. The rate of the reactions increased by about a factor of two as the temperature was increased from 22°C to 34°C. However,

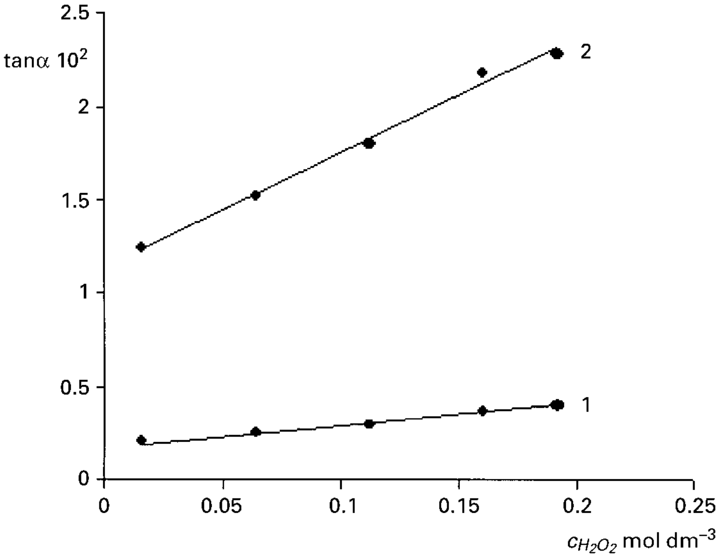

Figure 3. Dependence of the reaction rate on H_2O_2 concentration. Initial concentrations: PS = 8.8×10^{-4} mol dm^{-3}; $HClO_4 = 1.2 \times 10^{-3}$ mol dm^{-3}; Cu(II) = 0.3 μg cm^{-3}; $t = 22°C \pm 0.1°C$. (1) Catalytic reaction and (2) non-catalytic reaction.

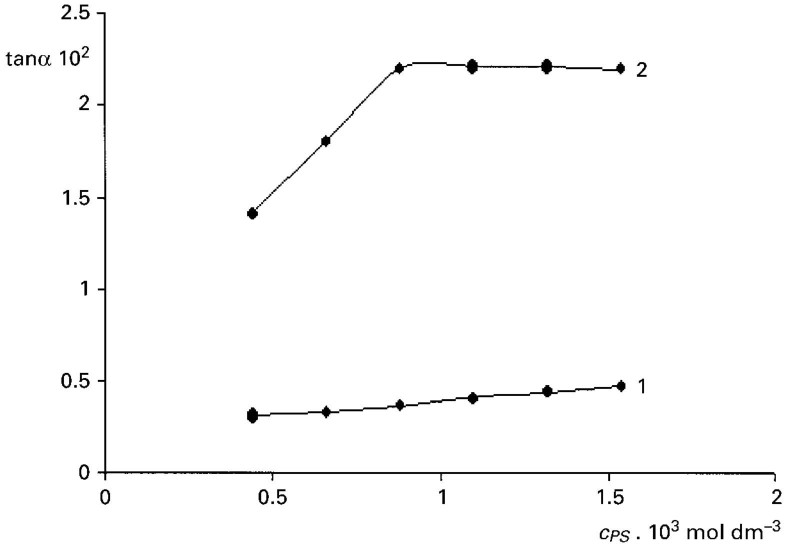

Figure 4. Dependence of the reaction rate on PS concentraction. Initial concentractions: $H_2O_2 = 0.16\,\mathrm{mol\,dm^{-3}}$; $HClO_4 = 1.2 \times 10^{-3}\,\mathrm{mol\,dm^{-3}}$; Cu(II) = $0.3\,\mu\mathrm{g\,cm^{-3}}$; $t = 22°C \pm 0.1°C$. (1) Catalytic reaction and (2) non-catalytic reaction.

although higher sensitivity could be obtained at the higher reaction temperature, it was troublesome to control the temperature precisely at the elevated temperature; hence, a reaction temperature of 25°C was chosen.

Calibration Graph

The tangent method was used to calculate the rate of the catalyzed reaction, which was plotted as a function of the copper concentration. The fixed time and the fixed absorbance (variable time) methods[13] were also used. For the fixed time method, measurements were made after 5 min. For the fixed absorbance method the inverse of the time necessary to obtain an absorbance of 0.3 was plotted against the copper concentration. In all cases, the calibration graph is linear in the concentration range indicated in Table 1. The accuracy and precision of the three methods applied for a Cu(II) concentration of $100.0\,\mathrm{ng\,cm^{-3}}$, is included in Table 1. It can be concluded that the fixed absorbance methods have a positive systematic error ($t'_{\mathrm{exp}} > t$), whereas the tangent method is more precise. Although the fixed time method is accurate and

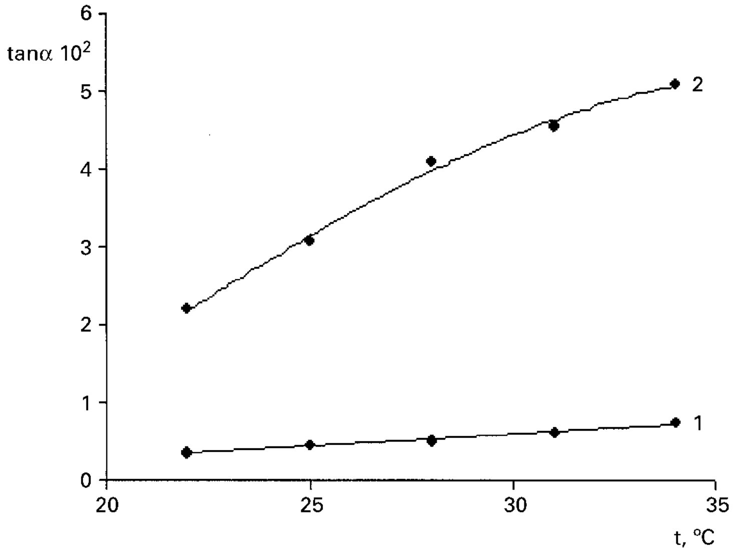

Figure 5. Dependence of the reaction rate on temperature. Initial concentrations: PS = $8.8 \times 10^{-4}\,\mathrm{mol\,dm^{-3}}$; $H_2O_2 = 0.16\,\mathrm{mol\,dm^{-3}}$; $HClO_4 = 1.2 \times 10^{-3}\,\mathrm{mol\,dm^{-3}}$; Cu(II) = $0.3\,\mu\mathrm{g\,cm^{-3}}$. (1) Catalytic reaction and (2) non-catalytic reaction.

precise, the permissible concentration range is slightly narrower than the tangent method. Therefore, the tangent method was recommended.

Three calibration lines were linear and suitable for the determination of the copper(II) concentration in the interval mentioned. A line measured at 31°C was steeper and more suitable for use than lines measured at 25°C or 28°C.

Table 1. Linear concentration range, accuracy, and precision of the kinetic method for the determination of copper (II).

Method	Concentration range of Cu(II) ($\mathrm{ng\,cm^{-3}}$)	RSD[a] (%)	t'_{exp}[b]
Tangent	10–300	1.9	0.90
Fixed time	50–300	3.5	1.72
Fixed absorbance	50–300	3.8	3.23

[a] Mean of five measurements.
[b] $t = 2.77$.

On the basis of our kinetic investigation, we formulated a kinetic equation for the oxidation of PS by hydrogen peroxide with copper as catalyst:

$$\frac{dx}{dt} = k_1 \cdot c_{\mathrm{HClO_4}}^{-0.5} \cdot c_{\mathrm{H_2O_2}} \cdot c_{\mathrm{PS}} \cdot c_{\mathrm{Cu(II)}}, \quad \text{for } c_{\mathrm{PS}} \leq 8.8 \cdot 10^{-4}\,\mathrm{mol\,dm^{-3}} \tag{3}$$

$$\frac{dx}{dt} = k_1' \cdot c_{\mathrm{HClO_4}}^{-0.5} \cdot c_{\mathrm{H_2O_2}} \cdot c_{\mathrm{Cu(II)}}, \quad \text{for } c_{\mathrm{PS}} \geq 8.8 \cdot 10^{-4}\,\mathrm{mol\,dm^{-3}} \tag{4}$$

where x is the product of oxidation of PS.

The kinetic equation for the noncatalytic reaction under the same conditions may be written as follows:

$$\frac{dx}{dt} = k_0 \cdot c_{\mathrm{HClO_4}}^{-0.7} \cdot c_{\mathrm{H_2O_2}} \cdot c_{\mathrm{PS}} \tag{5}$$

where k_1, k_1', and k_0 are the relative rate constants for the catalytic and noncatalytic reactions. On the basis of these equations, the relative rate constants for the catalytic and noncatalytic reactions were calculated.

A linear relationship between the logarithm of the relative rate constant and the reciprocal of the absolute temperature was found for the catalytic as well as the noncatalytic reaction. The activation energies were found to be 31.73 kJ mol^{-1} for the catalytic reaction and 45.12 kJ mol^{-1} for the noncatalytic reaction.

The minimum concentration of Cu(II) which could be determined by this method may be calculated by the method given by Perez-Bendito and Silva.[13] The limit detection is 1.8 ng cm^{-3}.

The precision and accuracy of the method are also investigated. The relative error ranges from 0.5% to 6.8% for the copper(II) concentration of 300.0–10.0 ng cm^{-3}.

Interference Studies

The influence of several foreign ions was investigated by 2S (S, standard deviation) criteria[12,13] on the determination for a constant copper concentration of 200 ng cm^{-3}. Anions and cations usually found in real samples are presented in Table 2. Many of the cations and anions do not interfere at a ratio of foreign ion to Cu(II) of 1000 : 1 and 100 : 1, respectively. When a disturbing effect is detected at a lower reactions, it can be distinguished as either positive (increase in the signal) or negative (decrease in the signal). The most important is Fe(III) because it acts as a catalyst of the oxidation reaction.[11] The interference of Fe(III) could be successfully eliminated by masking with fluoride (2.0 μg) and Fe(III) up to 1.0 μg cm^{-3}

Table 2. Effect of foreign ions on the determination of 200 ng cm^{-3} of copper(II) by the recommended method.

Tolerated ratio of foreign ion to Cu(II)	Positive interference	Negative interference
10	Co(II), MoO_4^{2-}	S^{2-}, Pb(II), Al(III), Mn(II), As(III), Se(IV)
0.8	I^-	
0.5	Fe(III), Cr(VI)	

Note: Ratio of foreign ion to Cu(II) tolerated = 1000, foreign ion tested Ca(II), Mg(II), Ba(II) and = 100, foreign ion tested Zn(II), Hg(II), Cd(II), Ni(II), AsO_4^{2-}, WO_4^{2-}, F^-, Br^-, SO_4^{2-}, PO_4^{3-}, $C_2O_4^{2-}$, citrate, tartrate, respectively.

did not interfere, as shown in Table 3. Nevertheless, interferences due to Cr(VI) and I^- are noticeable at the same concentration level as the Cu(II) ion.

APPLICATIONS

In order to check the validity of the proposed method it was applied to the determination of Cu(II) in drinking water and milk.

Treatment of Water Samples

The method was directly applied for the determination of copper in drinking water without any separation or preconcentration. A 3 cm^3 sample of the water was used for the recommended procedure.

Table 3. Effect of Fe(III) on the determination of 50 ng cm^{-3} of Cu(II).

Ion	Conc. added (μg cm^{-3})	Relative error[a] (%)
Fe(III)	0.025	15.2
	0.25[b]	0.8
	1.00[b]	2.8

[a] Mean of five measurements.

[b] 1 cm^3 of fluoride (working solution, 20 μg cm^{-3}) was added in the procedure described in Experimental.

Treatment of Milk Sample

In 10 cm^3 of milk, 2–3 drops of CH_3COOH were added. Using a water bath the sample was boiled dry and the residue was burned at a temperature of 400–450°C for 12 hr. After that, 1 cm^3 of concentrated HNO_3 was added and the sample was boiled dry again. The residue was kept for about 2–3 hr at the same temperature as before. After that the residue was dissolved in 2 drops of concentrated HNO_3 and diluted up to 25 cm^3 with deionized water. The concentration of this acid, after dilution with deionized water as indicated in the procedure, did not modify the working pH. After these treatments 3 cm^3 was used for the recommended procedure.

The technique described above was applied to the determination of traces of copper in drinking water and milk sample.

The results obtained by an interpolation of a calibration graph, and by the standard additions method are given in Table 4. The results obtained by the proposed method were compared with those obtained by the atomic absorption spectrometry. The values for drinking water and milk samples are in good agreement with those obtained by AAS method (Table 4). From these results, the proposed kinetic method seems to be applicable to the determination of copper in water and milk.

Table 4. Kinetic determination of copper(II) in water and milk.

	Cu(II) found (ng cm^{-3})		
	Kinetic method		
Sample	A[a]	B[b]	Atomic absorption method[c]
Drinking water[d]	26.3 ± 0.8	28.5 ± 1.2	25.0
Milk[e]	48.5 ± 0.8	47.5 ± 1.3	40.0
Milk[f]	52.0 ± 0.7	51.5 ± 1.1	51.0
Milk[g]	47.0 ± 1.0	46.8 ± 1.0	47.0

[a] Standard addition.
[b] Direct calibration.
[c] At 324.8 nm.
[d] Selected at Niš.
[e] Selected at Babusnica.
[f] Selected at Svrljig.
[g] Selected at Aleksinac.

Table 5. A comparasion of the proposed method with other kinetic methods.

Indicator reactions	Dynamic range or detection limit (ng cm^{-3})	Comments, conditions	Type of samples	Reference number
3-Methyl-2-benzothiazolinone-hydrazone + *N*-ethyl-*N*-(2-hydroxy-3-sulfopropyl)-3,5-dimethoxyanaline + H_2O_2	0.002–0.1	Temperature 30°C, activator used, photometric, time 15 min	Certified reference material, tap water, and human hair	[14]
N-Phenyl-*p*-phenylenediamine + *m*-phenylenediamine + H_2O_2	0.1–2.0 (0.05)	Temperature 55°C, micelles and activator used, FIA-photomet	River, lake, seashore water	[15]
3-Methyl-2-benzothiozolinone-hydrazone + *N*-ethyl-*N*-(2-hydroxy-3-sulfopropyl)-3,5-dimethoxyaniline + H_2O_2	0.005–0.75	Temperature 55°C, surfactant and activator used, FIA-photomet	Certified reference material, pepperbush	[16]
Hydroquinone + H_2O_2	0.2–1.5^a	Activator used, photometric	Blood serum	[8]
Arsenazo III + H_2O_2	0–1.2^b (2.5×10^{-11})^c	Photometric	Drinking water	[17]

o-Aminophenol + H_2O_2	0.5–20[d] (2.2×10^{-7})[c]	Extraction, catalytic, kinetic, photometric	Rice, maize, wheat, fluor, soyabean, mung bean	[18]
Gallocyanine + O_2	0.05–0.5[a]	Photometric	Soil, tap and simulated water	[19]
Pot. peroxysulfate + light green SF	0.005–0.1[b] (6.4)	Photometric	Natural water ore samples	[20]
Hexacyanoferrate(III) + cysteine	0–6.3 (0.15)	Photometric temperature 25°C	Synthetic samples, sea, river water	[9]
PS + H_2O_2	10–300 (1.8)	Photometric temperature 25°C	Drinking water, milk	Present paper

[a] $\mu g\ cm^{-3}$.
[b] $\mu g\ cm^{-3}/25\ cm^3$.
[c] $g\ dm^{-3}$.
[d] $\mu g\ dm^{-3}$.

COMPARISON AND CONCLUSION

A comparison of the proposed procedure with other procedures is given in Table 5. Few procedures[14–16] have good sensitivity, but analysis time and temperature in each case is higher than in the present proposed procedure. Unfortunately, these procedures involve the use of rare chemicals. Besides the procedures stated in Refs.[14–16] use additional chemicals as activators and surfactants, while procedures in Refs.[8,17–20] have detection limits in micrograms. In addition Ref.[20] utilises a time-consuming extractive procedure. In this respect, the method based on the hexacyanoferrate(III)-cystein system[9] can be successfully used for the quantitative determination of trace amounts of copper(II) in real samples at normal temperatures with a minimum analysis time and without using any activators or surfactants. Also, the proposed method is quite sensitive, precise, rapid, and selective and can be used to determine Cu(II) at concentrations as low as 1.8 ng cm^{-3}.

ACKNOWLEDGMENT

This research was supported by grant number 1211 from the Ministry of Sciences and Technology Serbia. The authors are grateful for the financial support provided by this Ministry.

REFERENCES

1. Zeng, A.; Liu, E.; Tan, S.N.; Zhang, J.; Gao, J. Stripping voltametric analysis of heavy metals at nitrogen doped diamond-like carbon film electrodes. Electroanalysis **2002**, *14*, 1294.
2. Cesar, A.G.; Joanna, L.H.; Jon, C.B.; Richard, G.C. Anodic stripping voltammetry of copper at insonated glassy carbon-based electrodes: application to the determination of copper in beer. Analyst **1999**, *124*, 1053.
3. Pilar, B.; Elena, P.; Diego, F.; Requel, D.; Abela, B.; Jose, M.F.; Jose, A.C. Copper fractionation by SEC-HPLC and ETAAS: study of breast milk and infant formulae when used in lactation of full-term newborn infants. Analyst **2001**, *126*, 571.
4. Katerina, P.; Christian, P.; Ilse, S.; Gregor, R.; Josef, F.K.H. Determination of Cu, Fe, Mn and Zn in blood fractions by SEC-HPLC-ICP-AES coupling. Analyst **1999**, *124*, 657.

5. Mottola, H.A.; Perez-Bendito, D. Kinetic determination and some kinetic aspects of analytical chemistry. Anal. Chem. **1996**, *68*, 257R and references cited therein.
6. Crouch, S.R.; Cullen, T.F.; Scheeline, A.; Kirkor, E.S. Kinetic determinations and some kinetic aspects of analytical chemistry. Anal. Chem. **1998**, *70*, 53R and refs cited therein.
7. Crouch, S.R.; Scheeline, A.; Kirkor, E.S. Kinetic determinations and some kinetic aspects of analytical chemistry. Anal. Chem. **2000**, *72*, 53R and references cited therein.
8. Petrova, Y.Y.; Beklemishev, M.K.; Bazhanova, A.N.; Druzhimin, A.A.; Dolmanova, I.F. Determination of copper by its catalytic effect on the oxidation of hydroquinone by hydrogen peroxide on supports. J. Anal. Chem. (Moscow) **2000**, *55*, 284.
9. Prasad, S.; Halafihi, T. Development and validation of catalytic kinetic spectrophotometric method for determination of copper (II). Microchim. Acta **2003**, *142*, 237.
10. Veselinović, D.S.; Obradović, M.V.; Mitić, S.S.; Đorđević, S.V.; Zarkzawska, J.S. Sulphonation of 1,2,3-trihydroxybenzene in concentrated sulphuric acid. J. Appl. Spectrosc. **1995**, *65*, 71.
11. Mitić, S.S.; Miletić, G.Ž; Obradović, M.V. Catalytic determination of nanogram amounts from iron (III) using its catlytic effect on the oxidation of sodium pyrogallol -5-sulphonate by hydrogen peroxide. Talanta **1995**, *42*, 1273.
12. Mitić, S.S.; Miletić, G.Ž; Kostić, D.A. Kinetic determination of traces of iodide by its catalytic effect on oxidation of sodium pyrogallol-5-sulphonate by hydrogen peroxide. Anal. Sci. **2003**, *19*, 913.
13. Perez-Bendito, D.; Silva, S. *Kinetic Methods in Analytical Chemistry*; Ellis Horwood: Chichester, 1998; 261.
14. Ohno, S.; Teshima, N.; Watanaba, T.; Itabashi, S.; Kawashima, T. Determination of ultratrace amounts of copper (II) by its catalytic effect on the oxidative coupling reaction of 3-methyl-2-benzothiazolinone hydrazone with *N*-ethyl-*N*-(2-hydroxy-3-sulfopropyl)-3,5-dimethoxaaniline. Analyst **1996**, *121*, 1515.
15. Nakano, S.; Nakaso, K.; Noguehik, K.; Kawashima, T. Catalytic flow-injection determination of copper at nanogram levels by using color formation of *N*-phenyl-*p*-phenylenediamine with *m*-phenylenediamine in the presence of pyridine and ammonia as activators. Talanta **1997**, *44*, 763.
16. Kawashima, T.; Itabashi, H.; Teshima, N.; Kurihara, M.; Makuno, S. Flow-injection determination of copper (II) based on its catalytic effect on the oxidative coupling of 3-methyl-2-benzothiazolinone hydrazone with

N-ethyl-*N*-(2-hydroxy-3-sulfopropyl)-3,5-dimethoxyaniline in Micellor medium. Anal. Sci. **1999**, *15*, 835.
17. Huang, D.; Zhong, Y. Guangdong Gonguge Daxue Xuebao **1998**, *15*, 65; Chem. Abstr. **1999**, *131*, 63071t.
18. Jiang, G.; Wong, X. Dongbei Shid Xmebao, Ziran Kexvaban **1999**, *3*, 123; Chem. Abstr. **2000**, *132*, 8511g.
19. He, R.; Wang, J.; Xing, H. Rare Met (Beijing) **1999**, *18*, 294; Chem. Abstr. **2000**, *139*, 189053c.
20. Zhu, C.Q.; Wang, L.; Li, Y.X. Fenxi Shiyanshi **1999**, *18*, 13; Chem. Abstr. **2000**, *132*, 102122c.

Received June 27, 2003
Accepted November 1, 2003

Marcel Dekker, Inc.
270 Madison Avenue, New York, New York 10016

Downloaded At: 03:03 30 January 2011

Request Permission or Order Reprints Instantly!

Interested in copying and sharing this article? In most cases, U.S. Copyright Law requires that you get permission from the article's rightsholder before using copyrighted content.

All information and materials found in this article, including but not limited to text, trademarks, patents, logos, graphics and images (the "Materials"), are the copyrighted works and other forms of intellectual property of Marcel Dekker, Inc., or its licensors. All rights not expressly granted are reserved.

Get permission to lawfully reproduce and distribute the Materials or order reprints quickly and painlessly. Simply click on the "Request Permission/ Order Reprints" link below and follow the instructions. Visit the U.S. Copyright Office for information on Fair Use limitations of U.S. copyright law. Please refer to The Association of American Publishers' (AAP) website for guidelines on Fair Use in the Classroom.

The Materials are for your personal use only and cannot be reformatted, reposted, resold or distributed by electronic means or otherwise without permission from Marcel Dekker, Inc. Marcel Dekker, Inc. grants you the limited right to display the Materials only on your personal computer or personal wireless device, and to copy and download single copies of such Materials provided that any copyright, trademark or other notice appearing on such Materials is also retained by, displayed, copied or downloaded as part of the Materials and is not removed or obscured, and provided you do not edit, modify, alter or enhance the Materials. Please refer to our Website User Agreement for more details.

Request Permission/Order Reprints

Reprints of this article can also be ordered at
http://www.dekker.com/servlet/product/DOI/101081SL120028422