Talanta 108 (2013) 1–6

Contents lists available at SciVerse ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Highly sensitive determination of trace copper in food by adsorptive stripping voltammetry in the presence of 1,10-phenanthroline

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ARTICLE INFO

Article history:
Received 27 November 2012
Received in revised form
13 February 2013
Accepted 13 February 2013
Available online 5 March 2013

Keywords:
Copper
Trace determination of copper
Adsorptive stripping voltammetry
1,10-phenanthroline
Food samples

ABSTRACT

A highly sensitive, rapid, simple and selective adsorptive stripping assay for the determination of trace copper(II) is proposed. The methodology is based on the adsorptive accumulation of copper(II)–1,10-phenanthroline complexes onto a glassy carbon electrode, followed by oxidation of the adsorbed species by voltammetric scanning using square-wave voltammetry. The influences of experimental variables on the sensitivity of the proposed method, such as the effects of pH, ligand concentration, accumulation time, accumulation potential and interferences, were investigated. Under optimal conditions, the proposed method showed linearity from 0.1 ng mL^{-1} to 50 ng mL^{-1}. The 3 S/N detection limits were 0.0185 ng mL^{-1}, and the relative standard deviations ($n=10$) were 0.09–4.71% for intra-day and 0.05–7.14% for inter-day analyses, respectively. The application of the proposed method to the direct analysis of food samples yielded results that agreed with those obtained from including inductively coupled plasma–optical emission spectrometry (ICP–OES) assays according to a paired t-test. The results are a step toward the development of an alternative and reliable analytical method for food research, which requires the direct determination of copper.

1. Introduction

The presence of trace metals, particularly heavy metals, in parental nutrition assumes a specific relevance because some of them are potentially dangerous or even toxic. Therefore, control of the finished product's metal content is recommended. Copper is an essential element that plays an important role in many body functions, such as hemoglobin synthesis, connective tissue development, normal function of the central nervous system, and oxidative phosphorylation [1]. However, excessive intake of copper would lead to accumulation of the metal in liver cells and hemolytic crisis, jaundice, and neurological disturbances [2]. Wilson's disease (hepatolenticular degeneration) is a well-known disease caused by excessive copper [3]. However, cases of copper deficiency in patients on unsupplemented hyperalimentation are well documented [4].

Water and food are the potential sources through which copper enters human bodies; thus, the determination of copper in water and food samples could afford some important information. In addition, a high copper content can promote rancidity and off-flavors in foods and beverages. Therefore, the quantitative analysis of copper at trace or even ultra-trace concentration levels in food is required.

Several analytical methods are available for the determination of copper at low concentrations, including inductively coupled plasma–optical emission spectrometry (ICP–OES) [5], electrothermal atomic absorption spectrometry (ETAAS) [6,7], X-ray fluorescence (XRF) [8], flame atomic absorption spectrometry (FAAS) [9,10], inductively coupled plasma–mass spectrometry (ICP–MS) [11,12], and capillary electrophoresis (CE) [13]. Even though ICP–OES and AAS are the most used techniques in the determination of traces of copper, the low copper concentration level in parental solutions is not compatible with the detection limits of these techniques. To attain accurate, reliable and sensitive results, preconcentration is required before the samples are analyzed directly using the analytical technique when the concentrations of the elements in the sample are excessively low. This requirement complicates the analytical method and leads to long analysis times and high costs. Spectrophotometry is one method that is effective for the determination of copper [14]. It involves less-expensive instrumentation compared to the previously mentioned techniques. However, the drawback of this technique is that it is highly sensitive only when appropriate chromogenic reagents are available.

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0039-9140/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.talanta.2013.02.031

To improve on these weak points, electrochemical analysis with various electrodes was investigated as a potential novel analysis system. Anodic stripping voltammetry (ASV) is an established method for trace metal–ion analysis in contaminated samples such as water and food because of the sensitive, selective, rapid and portable nature of these techniques [15]. In the context of copper determination, adsorptive stripping voltammetry at a hanging-mercury-drop electrode [16–26] has been reported to provide enhanced sensitivity and specificity for quantitative analysis. The detection limits observed during the previous work are typically low enough for the detection of copper in real samples; however, most of the investigators used a mercury electrode. Thus, because of the toxicity, stability, and volatility issues that arise from the use of mercury, a need exists for the development of alternative electrodes that possess the same attractive properties as mercury. For example, adsorptive stripping voltammetry of copper has been reported using carbon-paste electrodes [27–30] and glassy carbon electrodes [15,31]. However, the determination of trace or ultra-trace levels of metal ions in real samples is a challenging task.

Electroanalysis using 1,10-phenanthroline at a glassy carbon electrode via voltammetry has been shown to indirectly quantify copper [31]. However, an important problem remains with respect to realizing a direct analysis method, and the protocol has not yet been fully explored in the analysis of real samples. In this work, we aim to develop a straightforward, rapid, simple, sensitive, and specific methodology for the trace detection of copper in food samples. The present procedure is shown to be viable for the trace detection of copper ions in food samples and does not require any sample pre-concentration during the measurement step to enhance the sensitivity. We also show that no sample pre-treatment is required for the application of the complex, which provides a sensitive and selective protocol for the analysis of copper in real complex samples.

To the best of our knowledge, this is the first report on the use of a glassy carbon electrode for the analysis of copper ions in the presence of 1,10-phenanthroline in "real world" contaminated samples.

2. Experimental

2.1. Instrumentation

Square-wave voltammetry (SWV) experiments were performed using a model PGSTAT 101 Autolab Electrochemical System controlled with the NOVA software package (Kanaalweg 29-G 3526 KM Utrecht, The Netherlands). All experiments were performed using a conventional three-electrode system with a glassy carbon (GC) electrode with a diameter of 3.0 mm as the working electrode, a platinum wire as the auxiliary electrode, and a standard Ag/AgCl (3 M KCl) reference electrode.

2.2. Reagents and solutions

Sodium chloride (NaCl) was purchased from Merck. Copper(II) sulfate ($CuSO_4$) and hydrochloric acid were purchased from BDH. 1,10-Phenanthroline was purchased from Fluka (Buchs, Switzerland). All reagents were of analytical grade. The copper(II) stock solution (100 $\mu g\,mL^{-1}$) was prepared by dissolving the appropriate weight of $CuSO_4$ in 0.1 mol L^{-1} NaCl at pH 4.5 (1.0 mol L^{-1} HCl was used to adjust the pH). A 0.1 mol L^{-1} stock solution of 1,10-phenanthroline was prepared by dissolving an appropriate amount of 1,10-phenanthroline in 0.1 mol L^{-1} HCl. Water with a resistivity of 18 $M\Omega\,cm^{-1}$, which obtained from a Millipore Milli-Q purification system (Millipore, Benford, MA, USA), was used throughout the experiments.

2.3. Electrochemical procedure

The GC electrode was polished with 1.0 μm and 0.3 μm alumina. After the electrode was rinsed with double-distilled water, it was sonicated in water and in absolute ethanol for 1 min each. The standard/sample (10 mL) was pipetted into an electrochemical cell. Then, 10 μL of the 1,10-phenanthroline stock solution was added, which corresponded to a final concentration of 10^{-4} mol L^{-1}. The potential was set to −0.5 V, whereas the accumulation time was set to 120 s. The square-wave voltammetric parameters were a step potential of 20 mV, a pulse amplitude of 50 mV, and a frequency of 5 Hz. The voltammograms were recorded by applying a positive-going potential from −0.2 V to +0.4 V. The oxidation peak for copper(II)–1,10-phenanthroline complex occurred at +0.05 V, and its current was used for the measurement of the copper(II) concentration. All data were obtained at room temperature.

2.4. Calibration curve, limit of detection and precision

Calibration was performed under optimized conditions with standard solutions with concentrations that ranged from 0 ng mL^{-1} to 100 ng mL^{-1} with respect to copper(II). For each standard solution, three replicate measurements were performed. The calibration data were evaluated by linear regression analysis using the Excel software package. The limit of detection and limit of quantification were determined via the 3 S/N and 10 S/N methods, which reflect the concentrations of copper(II) that produced signals that exceeded three times and ten times the blank signal, respectively. The precision of the peak heights was estimated by performing 10 replicate measurements of standard solutions that contained 0.5, 5.0 and 30.0 ng mL^{-1} of copper(II).

2.5. Sample preparation

The juices samples, which included orange juice, vegetable juice, tea and honey, were purchased from a local supermarket. The juices were filtered using Whatman No. 1 filter paper. One milliliter of each solution was transferred to a volumetric flask and diluted to 10 mL with supporting electrolyte before analysis via the electrochemical procedure. The sample solutions obtained had concentrations within the range of the calibration graph. ICP–OES assays [32] were employed for purposes of comparison.

2.6. Data analysis

Standards and samples were analyzed, and the currents were integrated. Standard curves were obtained by plotting the net current as a function of the analyte concentration and fitting the data to a linear equation. To compare the two measurement systems, which are supposed to be equivalent, the results were tested using the paired t-test.

3. Results and discussion

3.1. Adsorptive characteristics of copper(II)–1,10-phenanthroline complexes

Preliminary experiments were performed to identify the general features that characterize the preconcentration of the metal ion–1,10-phenanthroline complexes on the electrode–solution interface. Fig. 1 displays the stripping square-wave voltammograms of

30 ng mL^{-1} copper(II) in the presence of 1,10-phenanthroline at pH 4.5 after 120 s of accumulation at −0.5 V. The stripping potentials were scanned positively between −0.2 V and +0.4 V (vs. Ag/AgCl). Curve 1a shows the anodic stripping voltammogram obtained when the supporting electrolyte contained only copper ions; no peak was obtained. Curve 1b illustrates the anodic stripping voltammogram of 1,10-phenanthroline in the absence of copper; this voltammogram shows a small anodic peak at +0.02 V, which may represent the oxidation of 1,10-phenanthroline. Curve 1c presents the anodic stripping voltammogram of copper(II) complexed with 1,10-phenanthroline. As evident in the figure, the complexes strongly adsorbed onto the glassy carbon electrode and produced a strong oxidative peak current at +0.05 V. All of the these results indicate that copper(II) and 1,10-phenanthroline could be produced as a complex and these complexes could be oxidized by oxidative scanning. These results indicate that the use of 1,10-phenanthroline as a ligand results in strong performance and remarkably high sensitivity for the detection of copper(II). Therefore, the electrochemical behavior of copper(II) can be investigated using this proposed procedure. Furthermore, a comparison of the voltammograms shows that the intensity of the copper oxidative peak not only depends on the duration of the pre-concentration step but also depends on the presence or absence of 1,10-phenanthroline, which reveals the adsorptive nature of the response. To find the optimum experimental conditions, the effect of chemical and instrumental factors on the intensity and shape of the oxidation peak current were studied; the results are reported in the following section.

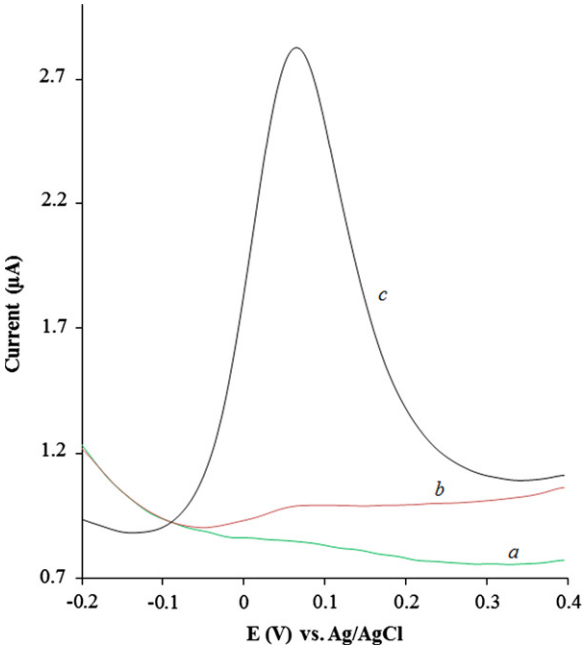

Fig. 1. Stripping square-wave voltammograms of 30 ng mL^{-1} copper(II) in 0.1 mol L^{-1} NaCl at pH 4.5 on (a) bare GC, (b) a blank of 1.0×10^{-4} 1 mol L^{-1} 1,10-phenanthroline without copper(II), (c) a sample with 1.0×10^{-4} 1 mol L^{-1} 1,10-phenanthroline. The deposition potential was −0.5 V, and the accumulation time was 120 s.

3.2. Optimization of parameters

With respect to electrochemical detection, the supporting electrolyte and pH had a significant effect on the ionization and redox reaction of the analyte. Therefore, the supporting electrolyte and pH were optimized for the electrochemical detection of copper(II) in the presence of 1,10-phenanthroline. The effects of several supporting electrolytes, such as KCl, HCl and NaCl, were tested by fixing all concentrations to 0.1 mol L^{-1}. The peak intensity and the peak shape were taken into consideration in the selection of the supporting electrolyte. Among these electrolytes, NaCl provided the best response in terms of both the peak intensity and the peak shape (data not shown). Hence, NaCl was selected as a suitable supporting electrolyte for all subsequent experiments. Next, the effect of pH on the pre-concentration

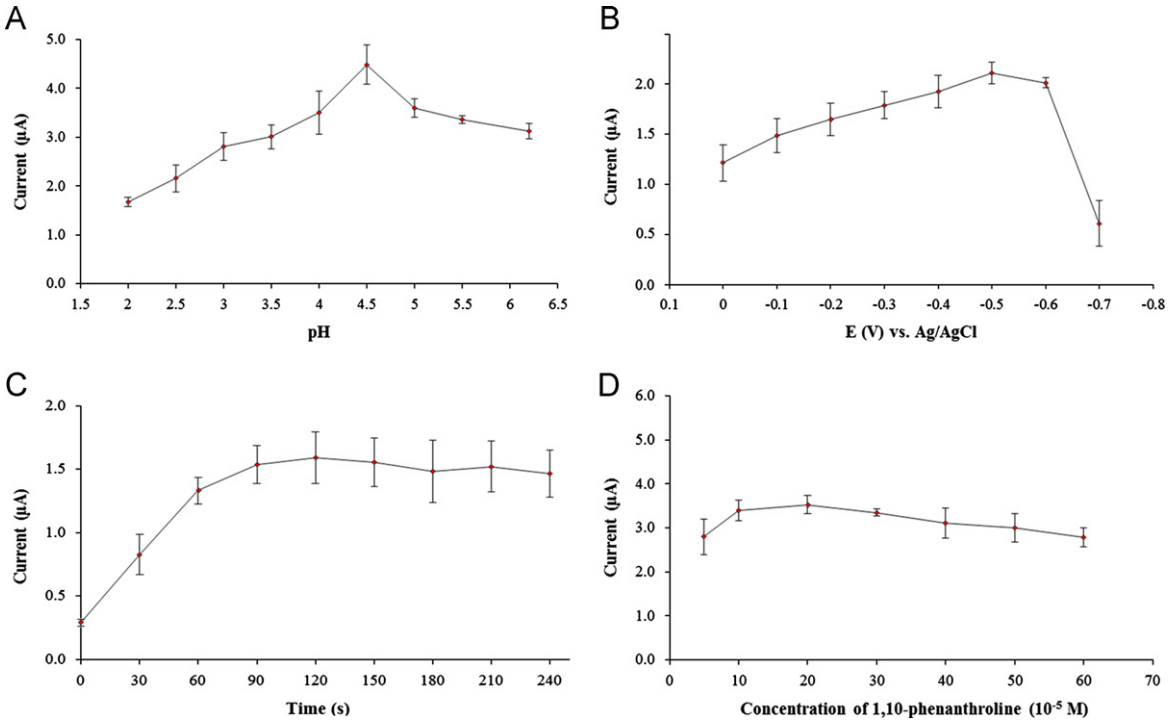

Fig. 2. Effect of optimized experimental conditions for the determinate copper(II) such as pH of supporting electrolyte (A), accumulated potential (B), accumulated time (C) and concentration of 1,10-phenanthroline (D). All other conditions were the same as those in Fig. 1.

stripping process was investigated. The pH values were examined in the range of 2.0–6.2 using a solution that contained 30 ng mL^{-1} of copper(II) and 10^{-4} mol L^{-1} of 1,10-phenanthroline, as shown in Fig. 2A. The maximum peak current was achieved at pH 4.5. A decrease in the current responses was observed when the pH values were greater than 4.5.

The effect of accumulated potential on the stripping-peak current for the copper(II) complex of 1,10-phenanthroline was examined individually over the potential range of 0.0 V to −0.7 V. As shown in Fig. 2B, the peak current increased linearly as the potential was increased from 0.0 to −0.5 V, most likely because of the increased accumulation of the complex on the electrode surface. The peak current decreased at potentials more negative than −0.5 V, possibly because of the un-uniform formation of complexes, which were easily diffused out before analysis. Therefore, a potential at −0.5 V was used in all subsequent experiments.

The effect of accumulation time on peak current was also studied. Fig. 2C indicates that, when the accumulation time was increased to 120 s, the peak current linearly increased. The peak current showed little increase when the accumulation time was greater than 120 s. As expected for the adsorption processes, the dependence of the peak current on the accumulation time was limited by the saturation on the electrode surface, which resulted in the current reaching a plateau at longer accumulation times. Thus, an accumulation time of 120 s was used throughout this work. This accumulation time not only offered good sensitivity but also provided a short analysis time.

Different concentrations of 1,10-phenanthroline in the range of 0.5×10^{-4}–6.0×10^{-4} mol L^{-1}, in the presence of 30 ng mL^{-1} copper(II) ion, and in the presence of 0.1 mol L^{-1} NaCl as a supporting electrolyte were studied. The results are shown in Fig. 2D. As evident in the figure, the peak height increased up to a 1,10-phenanthroline concentration of 1.0×10^{-4} mol L^{-1}. The peak intensity was almost constant in the ligand concentration range of 1.0×10^{-4}–3.0×10^{-4} mol L^{-1}. When the ligand concentration was greater than 3.0×10^{-4} mol L^{-1}, the peak intensity diminished as a result of full electrode surface coverage. This decrease in peak current at higher ligand concentrations is, in turn, is due to an inhibition of the adsorption of complexes by a competitive coverage by the free ligand [33]. As a result, a large electrode surface area is available for adsorption of the metal complexes in the case of increased ligand concentration. Therefore, a chelating agent concentration of 1.0×10^{-4} mol L^{-1} was selected as the optimum concentration for subsequent experiments.

3.3. Method validation

3.3.1. Analytical performance

Under the optimized conditions, a linear relationship between the oxidation peak current of the copper(II) complex and the concentration of copper(II) was obtained in the range of 0.1–50.0 ng mL^{-1} after an accumulation time of 120 s by fitting the equation $y=0.0529x+0.0587$, where x is the copper(II) concentration expressed in ng mL^{-1} (Fig. 3); this equation resulted in a square correlation coefficient (R^2) of 0.9990. The detection limit and quantification limit, which were calculated based on three times (3 S/N) and ten times (10 S/N) the signal of the blank, were 0.0185 ng mL^{-1} (2.91×10^{-10} mol L^{-1}) and 0.0619 ng mL^{-1} (or 9.73×10^{-10} mol L^{-1}), respectively. Compared to previously published works, particularly those that pertain to adsorptive stripping voltammetry [16–26], the proposed method provided the lowest detection limit, not including the results obtained from Ref. [25,29]. However, the benefits of this present work are that shorter accumulation times are required and that an environmental working electrode is used. The precision of the analytical process was calculated by determining the RSD for the repeated

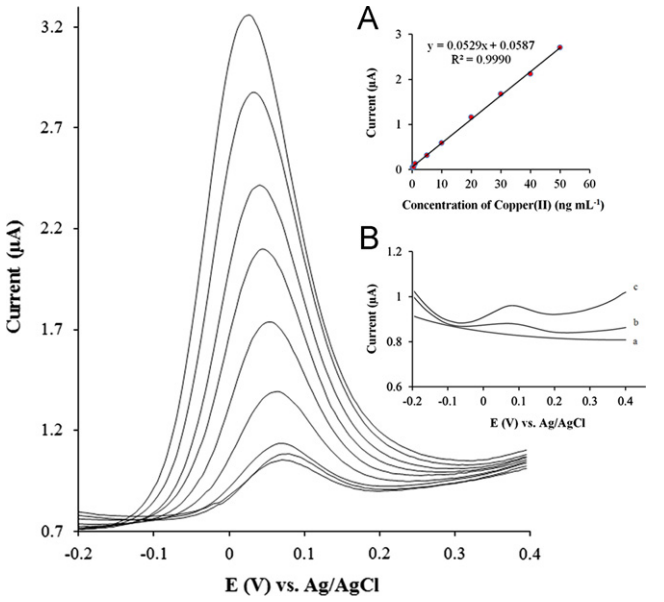

Fig. 3. Stripping square-wave voltammograms of the copper(II)+1.0×10^{-4} 1 mol L^{-1} 1,10-phenanthroline with different concentrations of copper(II): 0.1, 0.5, 1.0, 5.0, 10, 20, 30, 40 and 50 ng mL^{-1}. Calibration plots (insert A.) for increasing concentrations of copper(II). Stripping square wave voltammograms (insert B.) of background 0.1 M NaCl pH 4.5 (a), 0.1 M NaCl pH 4.5 mix with 1,10-phenantroline (b) and 0.0185 ng mL^{-1} copper(II). All other conditions were the same as those in Fig. 1.

measurement of a solution that contained the complete set of standard compounds. To evaluate the repeatability of the analytical process, three concentrations (0.5, 5.0 and 30.0 ng mL^{-1}) were studied. These spiked concentration levels were chosen to verify the results obtained from low, medium and high concentrations with respect to the probable concentration range of interest in samples of food supplements.

The intra- and inter-day precision and recovery obtained from the proposed method are summarized in Table 1. The intra-day RSDs and recoveries of copper(II) were found to vary over the ranges of 0.090–4.7% and 98.58–111.56%, respectively, whereas the inter-day RSDs and recoveries of copper(II) were found to vary over the ranges of 0.050–7.1% and 97.83–108.74%, respectively. This outstanding performance makes the developed method attractive for use as an analytical system for the analysis of copper(II) in real samples.

3.3.2. Interference study

The effects of various interfering species that accompany copper in food were studied using a copper(II) solution with a concentration of 30 ng mL^{-1}. These species, which were tolerated at a reasonably high concentration, show the high selectivity of the proposed method. The maximum tolerable concentrations of foreign species are shown in Table 2, where the tolerance limit was defined as the concentration of foreign species that produced a change in intensity of the peak current of ±5%. According to the results, no interference was caused by the cations and anions. These results confirmed that the proposed method provides good selectivity for the determination of copper(II) in real samples.

3.4. Application to real samples

The proposed method was used for the determination of copper(II) in food samples, i.e., orange juice, vegetable juice, tea and honey. There are four types of real samples (honey, tea, vegetable juice and orange juice). For each type of sample, we selected

Table 1
The intra- and inter-day precisions and recoveries of the method present ($n=3$).

Samples	Spiked level ($ng\,mL^{-1}$)	Intra-day		Inter-day	
		Mean of % recovery ($x \pm SD$)	RSD (%)	Mean of % recovery ($x \pm SD$)	RSD (%)
Orange juice					
Sample 1	0.5	102.47 ± 3.0	3.0	105.51 ± 3.9	3.7
	5.0	101.49 ± 2.2	2.1	97.83 ± 2.3	2.4
	30.0	99.87 ± 0.2	0.27	99.91 ± 0.28	0.28
Sample 2	0.50	105.19 ± 2.8	2.7	108.68 ± 3.9	3.6
	5.0	107.13 ± 3.7	3.5	102.09 ± 7.2	7.1
	30.0	99.70 ± 0.24	0.24	99.70 ± 0.26	0.3
Sample 3	0.50	104.81 ± 1.4	1.3	107.64 ± 4.2	3.9
	5.0	101.56 ± 3.7	3.6	104.08 ± 1.6	1.6
	30.0	99.99 ± 0.41	0.42	99.73 ± 0.17	0.17
Vegetable juice					
Sample 1	0.50	102.94 ± 2.3	2.2	98.73 ± 5.0	5.1
	5.0	103.27 ± 3.5	3.4	106.18 ± 5.9	5.6
	30.0	99.66 ± 0.37	0.37	99.55 ± 0.29	0.3
Sample 2	0.50	103.46 ± 4.9	4.7	101.38 ± 5.7	5.6
	5.0	102.74 ± 3.4	3.4	104.74 ± 5.0	4.8
	30.0	99.85 ± 0.2	1.2	99.81 ± 0.19	0.2
Sample 3	0.5	106.75 ± 4.1	3.8	99.16 ± 6.9	7.0
	5.0	100.20 ± 2.6	2.6	104.17 ± 2.2	2.1
	30.0	99.88 ± 0.28	0.28	99.76 ± 0.16	0.16
Tea					
Sample 1	0.50	103.01 ± 2.3	2.1	100.94 ± 4.7	4.6
	5.0	111.56 ± 1.9	1.7	107.88 ± 3.3	3.0
	30.0	99.59 ± 0.16	0.16	100.25 ± 1.1	1.1
Sample 2	0.50	98.58 ± 0.89	0.91	103.55 ± 6.0	5.8
	5.0	104.16 ± 0.22	0.21	106.56 ± 2.0	1.9
	30.0	99.83 ± 0.090	0.090	99.82 ± 0.050	0.050
Sample 3	0.50	101.54 ± 1.1	1.0	101.05 ± 1.6	1.6
	5.0	107.37 ± 4.1	3.8	99.82 ± 5.5	5.5
	30.0	99.71 ± 0.28	0.26	100.07 ± 0.23	0.23
Honey					
Sample 1	0.50	103.77 ± 1.1	1.1	103.48 ± 1.8	1.7
	5.0	107.65 ± 1.1	1.6	108.74 ± 1.5	1.4
	30.0	99.68 ± 0.17	0.17	99.66 ± 0.15	0.15
Sample 2	0.50	102.69 ± 2.5	2.5	104.89 ± 3.9	3.7
	5.0	109.15 ± 2.0	2.0	103.05 ± 5.0	4.9
	30.0	99.70 ± 0.12	0.12	100.58 ± 1.4	1.4
Sample 3	0.50	105.89 ± 4.8	4.5	106.86 ± 5.0	4.7
	5.0	104.93 ± 3.0	2.8	103.75 ± 4.0	3.9
	30.0	99.90 ± 0.13	0.15	99.89 ± 0.11	0.11

Table 2
Tolerance ratio of interfering ions in the determination of 30 $ng\,mL^{-1}$ of copper ($n=3$).

Ions	Tolerance ratio (W_{ion}/W_{cu})
CH_3COO^-, Glucose, K^+	1500
PO_4^{3-}, NO_3^-, NO_2^-, Ba^{2+}, Ascorbic acid	1000
Br^-, CO_3^{2-}, IO_3^-	500
HPO_4^{2-}, Ca^{2+}, HCO_3^-	300
Mg^{2+}, I^-, EDTA	200
Pb^{2+}, Cd^{2+}, SO_4^{2-}	100
Zn^{2+}, Mn^{2+}	50
Fe^{2+},Li^+, SCN^-, Co^{3+}, Hg^{2+}	30
Ag^+, CN^-	10

3 brands and divided into three samples as sample 1, sample 2 and sample 3, respectively. The obtained results were compared with those from an inductively coupled plasma–optical emission spectrometer. Table 3 lists the results obtained upon application of the proposed method and the conventional method. The results were compared with those provided by the ICP–OES method by the paired t-test. The calculated t was found to be 0.8689. The critical value of t (tabulated t) for $n-1$ degrees of freedom ($n=3$) is 3.18 ($P=0.05$), and the calculated value of t is less than this critical value. Therefore, the null hypothesis is not rejected: the methods do not give significantly different results with respect to copper(II) concentration. These results showed good agreement with the results obtained by the standard method, which means that the alternative proposed method can be accepted.

Table 3
Results obtained from the determination of copper in various real samples ($n=3$).

Samples	Proposed method ($ng\,mL^{-1}$) ($n=3$)	Standard method[a] ($ng\,mL^{-1}$) ($n=3$)
Orange juice		
Sample 1	21.02 ± 0.98	23.61 ± 1.86
Sample 2	11.32 ± 1.1	11.19 ± 5.21
Sample 3	93.61=2 ± 0.97	92.08 ± 7.3
Vegetable juice		
Sample 1	19.47 ± 1.5	18.30 ± 2.0
Sample 2	19.17 ± 2.0	22.10 ± 4.4
Sample 3	7.61 ± 1.2	6.72 ± 3.1
Tea		
Sample 1	3.50 ± 0.46	4,98 ± 1.1
Sample 2	6.61 ± 1.7	6.45 ± 4.8
Sample 3	3.64 ± 0.9	2.93 ± 3.4
Honey		
Sample 1	5.64 ± 0.94	10.18 ± 2.8
Sample 2	5.23 ± 0.69	3.72 ± 4.4
Sample 3	20.37 ± 1.6	16.25 ± 4.2

[a] Inductively Couple Plasma–Optical Emission Spectrometer (ICP–OES).

4. Conclusions

A highly sensitive, selective, rapid and low-cost electroanalytical method was developed for the determination of ultra-trace levels of copper ions in food samples. The method did not require any separation steps and was directly applied to the determination of ultra-trace levels of copper ions in food samples. The method exhibits an excellent linear dynamic range (0.1–50.0 $ng\,mL^{-1}$) and a low detection limit (0.0185 $ng\,mL^{-1}$) with an accumulation time of 120 s. The results showed that the method is sensitive and accurate for real samples, and the results for these samples were in good agreement with the values obtained using inductively couple plasma–optical emission spectroscopy. Overall, the present method is promising for the electroanalysis of trace copper(II) using an environmentally friendly procedure. Therefore, the proposed method is recommended as an alternative option for the analysis of various products contaminated with copper.

Acknowledgments

The authors gratefully acknowledge partially financial support from Srinakharinwirot University under the Government Budget 2555, National Research Council of Thailand (NRCT) under the project High Throughput Screening/Analysis: Tool for Drug Discovery, Diagnosis and Health Safety and Thai Government Stimulus Package 2 (TKK2555), under the Project for Establishment of Comprehensive Center for Innovative Food, Health Products and Agriculture (PERFECTA).

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