ORIGINAL PAPER

A Novel Captopril Chemiluminescence System for Determination of Copper(II) in Human Hair and Cereal Flours

M. H. Sorouraddin · M. Iranifam · A. Imani-Nabiyyi

Abstract A novel chemiluminescence (CL) reaction, captopril–H_2O_2, for determination of Cu(II) at nanogram per milliliter level in batch-type system has been described. The method relies on the catalytic effect of Cu(II) on the oxidation of captopril with hydrogen peroxide in alkaline medium. The optimization step was performed using univariate methodology and the factors studied were: pH and concentrations of the utilized reagents. Under the optimum conditions, calibration plot was linear in the range of 0.1–2.0 ppm. Limit of detection was 30 ppb and relative standard deviation for five replicate determinations of 0.8 ppm Cu(II) was 1.89%. The proposed method was successfully applied to the determination of Cu(II) in human scalp hair and cereals, rice and wheat, flour with satisfactory selectivity and sensitivity. The results were validated by comparison with a standard method (FAAS). The possible mechanism of the new CL reaction has also been discussed.

Introduction

Chemiluminescence (CL) is generally defined as the emission of light (ultraviolet, visible, or infrared) during the process of a chemical reaction [1, 2]. The first application of CL as an analytical tool was developed in the early 1950s [3] and since then, most of the aspects relevant to this phenomenon, namely, theoretical concepts, instrumentation, and methodologies, have made dramatic progress [4]. Besides the approval expressed by some reviewers [4], a cursory search on the online scientific databases will reveal that the development of new or enhanced analytical methodologies relying upon the use of CL phenomenon is presently a very active field of scientific inquiry. CL offers some widely recognized advantages such as high sensitivity, wide linear range, minimal and inexpensive instrumentation, very reduced background noise (leading to better limits of detection), and broad range of analytical applications. Furthermore, it can easily be coupled with flow-stream systems as well as with various separation systems (in particular, chromatographic methods). It is therefore widely used as either a detection system or as a direct analytical tool [1, 2, 5, 6].

Copper is a vital mineral not only for mammals, but also for plants. It is required for critical enzyme systems [7]. While copper deficiency leads to serious medical conditions, at higher than normal levels, it turns out to be toxic [7–9]. That's why considerable care must be exercised as to both its over-consumption and its deficiency. Due to these considerations, the trace copper content in beverages and foodstuffs must be controlled [10, 11], as well as its status in the human body [9]. The validity of hair mineral analysis for copper status has been well established [12]. On the other hand, wheat-flour bread, and rice are the staple diet of many people in Iran and some other Asian countries. As a result, analysis of human hair, wheat, and rice with respect to their Cu(II) content can be of benefit for medical or health program purposes in such countries.

Kawashima et al. [13] have reviewed the CL methods for determination of Cu(II) in both batch-type and continuous flow analysis systems. Most recently, some miscellaneous articles describing the CL determination of Cu(II) have also been published [14, 15]. We have previously explored a new CL system, thiosemicarbazide (TSC)-H_2O_2-CTMAB [16], where the catalytic effect of Cu(II) on the proposed CL system was utilized for the determination of the copper content of human hair and wheat flour at trace levels. Despite the fact that CL methods of analysis, in general, suffer from lack of sufficient selectivity [17–20], the method had the

M. H. Sorouraddin (✉) · M. Iranifam · A. Imani-Nabiyyi
Department of Analytical Chemistry, Faculty of Chemistry,
University of Tabriz, Tabriz, Iran
e-mail: soruraddin@tabrizu.ac.ir

virtue of relatively good selectivity. Based on the proposed system, we have also reported some novel oscillating CL systems [21, 22].

Captopril, 1-[(2S)-3-mercapto-2-methylpropionyl]-L-proline, is an orally active inhibitor of the angiotensin-converting enzyme and is developed for the treatment of high blood pressure on its own or in combination with other drugs. This compound can also be used to treat congestive heart failure [23]. Captopril was subjected to some preliminary tests and we could elicit CL from this compound upon its oxidation with H_2O_2. Cu(II) catalyzes this novel CL reaction and hence, can be quantitatively analyzed on this basis.

The authors were not blind to the fact that captopril is more expensive than TSC. However, the new CL reagent possesses the good analytical features of TSC combined with the advantage of linear calibration plot over a wider concentration range of Cu(II) and some better selectivity.

Experimental

Apparatus

Intensity of the emitted light was measured by a Junior LB 9509 luminometer (BERTHOLD Technologies, Germany). CL intensity was recorded in relative arbitrary units (a.u.). The Model AA-6300 atomic absorption spectrophotometer (SHIMADZU Corp., Japan) was used for flame analyses. All pH measurements were made with a digital pH-meter (Metrohm 744). Experiments were carried out at ambient temperature ca. 21 °C and under mechanical stirring.

Reagents and solutions

All reagents were of analytical grade and were purchased from Merck (Darmstadt, Germany) unless otherwise stated. Doubly distilled water was used throughout. The stock standard solution of Cu(II) (1 mg ml^{-1}) was prepared from copper(II) sulfate. A 0.1 mol l^{-1} stock solution of captopril (Fluka) was prepared in water. Hydrogen peroxide solutions of desired concentrations (m/v %) were prepared by diluting suitable amounts of 30% H_2O_2 to 5 ml. The solutions were consumed freshly. pH values were adjusted using appropriate amounts of 2 mol l^{-1} sodium hydroxide solution. A 2.0% (m/v) stock solution of N-cetyl-N,N,N-trimethylammonium bromide (CTMAB) was prepared in water. Strong base anion exchanger packed in Teflon column (70 mm length×10 mm i.d.) was used for eliminating the anionic interferences.

General procedure

Reactions were carried out in a 12×47 mm test tube placed in the luminometer sample holder. A 2.0 ml portion of the solution containing 0.1–2 µg ml^{-1} Cu(II), 0.001 mol l^{-1} captopril and 0.4% (m/v) CTMAB at pH 12 (adjusted with NaOH) (reagent 1) was placed into a test tube. Then 1.0 ml of 4.0% (m/v) H_2O_2 solution (reagent 2) was injected into the test tube to initiate the chemiluminescence reaction. Afterwards, the lid of the luminometer was closed and the recorded CL signal was read on the monitor of a PC connected to the instrument.

Sample treatment

Wet ashing of human hair

Hair sample was brought into solution, following a combination of two previously described procedures [24, 25]. For cleanup of the sample, we adopted the procedure carried out by Pournaghi-Azar and Dastangoo [24], while that of Sreenivasa Rao et al. [25] was followed for the very digestion process, because although the latter researchers report a simpler and less time-consuming procedure, they don't point out any cleanup steps. The sample was rinsed with acetone, chloroform, and doubly distilled water, respectively and then dried at 60 °C [24]. About 1 g of the dried sample was accurately weighed and placed in a 50 ml beaker and 12 ml of 2:1 HNO_3–H_2O_2 acid mixture was added. The mixture was heated on a hot plate at 150 °C for 35 min. After cooling for about 1 h the digested sample was decanted into a 50 ml volumetric flask and brought to the volume (50 ml) with added washings of distilled water used for rinsing the beaker. The resultant solution was passed through the ion exchanger III (strong base anion exchanger) packed column with a flow rate of 4 ml/min. The amount of Cu(II) in the collected solution was determined according to the procedure described in "General procedure" section and taking advantage of the standard addition method.

Wet ashing of wheat flour

The procedure for wet ashing of wheat flour described by Nohut et al. [26] was adopted. Wheat flour was thermally desiccated at 90 °C for 24 h and a portion of 5.00 g was digested with nitric acid and perchloric acid, and heated gently on a hot plate to dryness. The ash was then dissolved in water; the mixture was filtered and afterwards, it was diluted to10 ml with distilled water. This solution was passed through the ion exchanger column with flow rate of 4 ml/min. The amount of Cu(II) in the collected solution was determined according to the procedure described in the "General procedure" section and using the standard addition method.

Wet ashing of rice flour

The same procedure as that used for wheat digestion [26] was used for digesting rice flour, except that the sample was first treated with concentrated nitric acid for 3 h and then the

Fig. 1 CL emission intensity vs. time profile after mixing reagent 1 with reagent 2. Reagent 1: 1 ppm Cu(II), 0.4% (*m/v*) CTMAB, 0.001 mol l^{-1} Captopril (pH 12); Reagent 2: 4% (*m/v*) H$_2$O$_2$
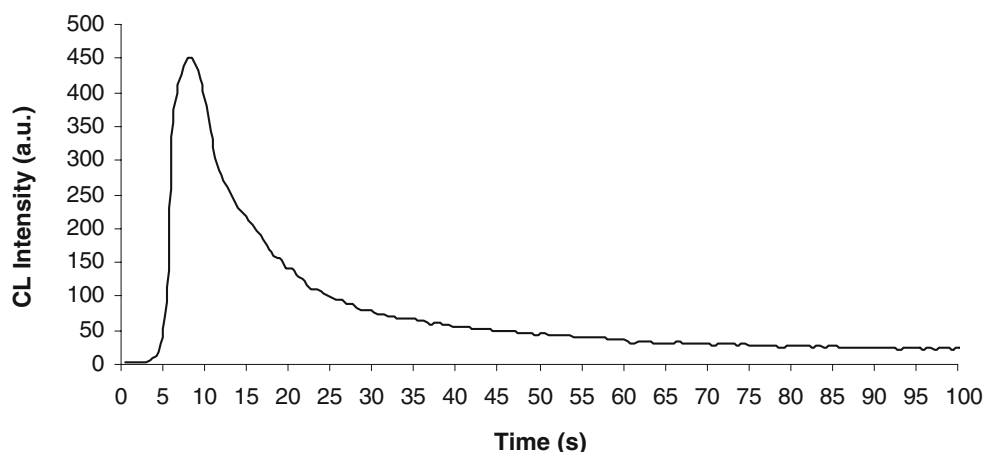
addition of acid mixture and heating followed. This prevents the mixture from frothing up and eliminates overflow of the digestion mixture.

Results and discussion

Preliminary investigations revealed that upon addition of H$_2$O$_2$ into the mixed solution of Cu(II)–captopril–surfactant in alkaline media, CL occurred and intensity of the emitted light was dependent on the Cu(II) concentration. The utilization of surfactants in CL reactions has offered many advantages [27, 28]. In this study, role of the surfactant for acquiring CL emission was of profound importance to a degree that in its absence, hardly any signal is detectable. The effect of anionic (sodium dodecyl sulfate, SDS), cationic (CTMAB), and non-ionic (Triton X 100) surfactants on the CL emission was studied. As revealed, in contrast to SDS and Triton, which caused no mentionable improvement in the situation, CTMAB reinforced the CL emission; thus this was chosen for upcoming experiments.

Kinetic aspect

Amongst the most important characteristics of CL reactions is their kinetic profile. Figure 1 depicts the CL intensity–time profile for the new reaction. Height of the profiles was taken as the analytical signal for the rest of the study. The profile illustrated in Fig. 1 was recorded for 1 μg ml^{-1} Cu (II), 0.4% (*m/v*) CTMAB, 0.001 mol l^{-1} captopril and 4.0% (*m/v*) H$_2$O$_2$ at pH 12. As it is clear from the figure, the maximum signal appears after a few couples of seconds elapsed after the instance of mixing the reagents, and the signal is decayed relatively slowly.

### Optimization of the CL conditions

A number of the variables affecting the CL reaction were optimized using the univariate methodology in order to

establish the conditions corresponding to the most intense light emission. Figure 2 depicts the effect of pH on the CL intensity. The figure suggests optimum pH value equals 12. This pH was attained taking advantage of sodium hydroxide solution. The effect of captopril concentration on the light intensity is depicted in Fig. 3. The CL signal was maximized at 0.001 mol l^{-1} and this value was chosen for subsequent experiments. Figure 4 illustrates the influence of hydrogen peroxide concentration on the CL intensity. The illustrated results led us to taking 4.0% (*m/v*) hydrogen peroxide as the optimum choice.

The effect of concentration of CTMAB on the reaction was also examined. The results are plotted in Fig. 5. According to the plot, 0.4% (*m/v*) was considered as the optimum concentration of the surfactant. The reinforced occurrence of CL in the presence of micelles is probably the outcome of the following possible causes: (1) Solubilization. The CL of lucigenin was enhanced by nonionic surfactant Triton X 100 micelles because the insoluble lucigenin and excited intermediate become more soluble in
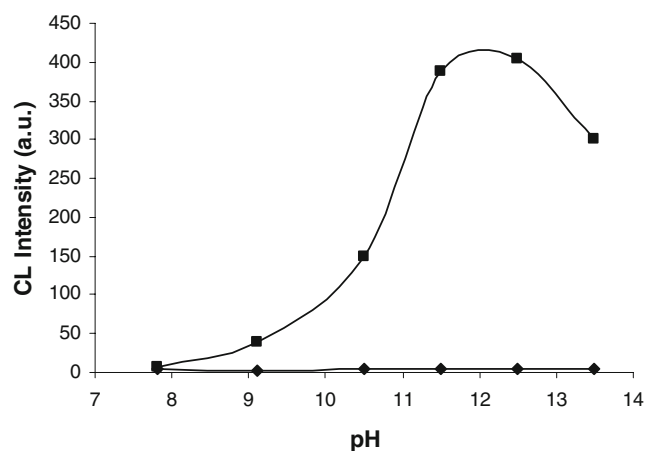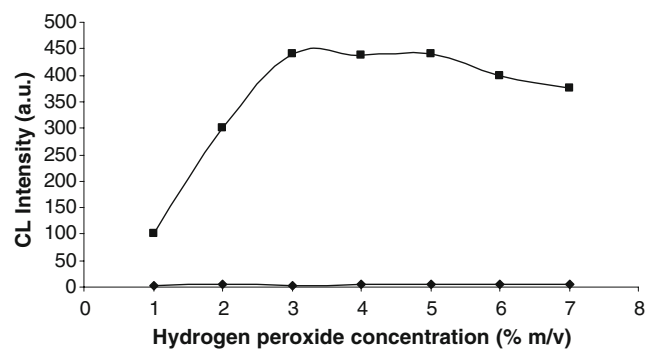

Fig. 2 The effect of pH (reagent 1) on CL emission intensity in the presence (■) or in the absence (♦) of Cu(II). Reagent 1: 1 ppm Cu(II), 0.5% (*m/v*) CTMAB, 0.001 mol l^{-1} Captopril; reagent 2: 5% (*m/v*) H$_2$O$_2$
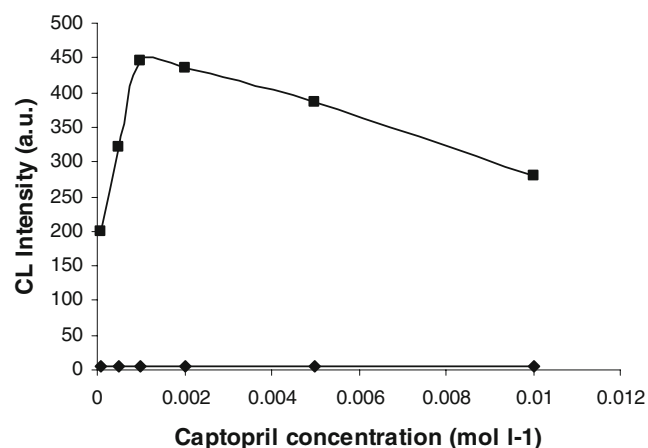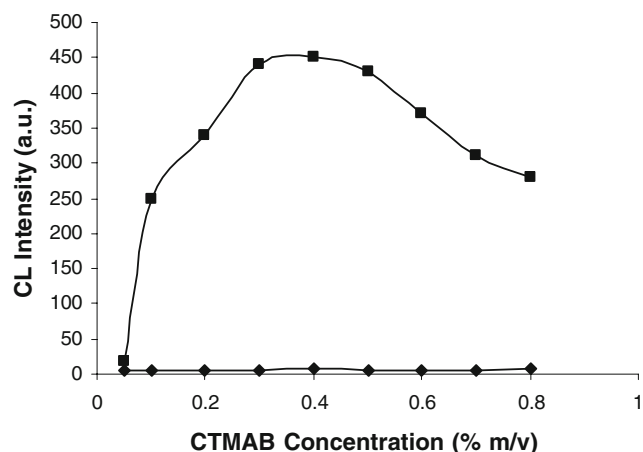
Fig. 3 The effect of Captopril concentration (reagent 1) on CL emission intensity in the presence (■) or in the absence (♦) of Cu(II). Reagent 1: pH 12, 1 ppm Cu(II), 0.5% (m/v) CTMAB, Captopril; reagent 2: 5% (m/v) H_2O_2

Fig. 5 The effect of CTMAB concentration (reagent 1) on CL emission intensity in the presence (■) or in the absence (♦) of 1 ppm Cu(II). Reagent 1: pH 12, 1 ppm Cu(II), 0.001 mol l^{-1} Captopril, CTMAB; reagent 2: 4% (m/v) H_2O_2

the micellar medium [27]. (2) Electrostatic effect. The electrostatic effect of the ionic surfactant helps to concentrate the counter ion reactant [29]. (3) Altering the microenvironment of the CL reaction. The cage structure of the micelle is helpful for stabilizing the excited state and prevents it from quenching [30, 31]. (4) Altering the pH of the microenvironment [28], as pH is an important parameter for most CL reactions. In the studied CL system, all the above possible explanations seem to be reasonable except the first one, since there is no insoluble CL reagent in the system. Based on the explanation (2) and our previous experiences [16, 32], the enhanced CL in the presence of cationic CTMAB micelles may be the consequence of more efficient reaction of captopril with $^\bullet O_2^-$ radicals in the Stern layer of the micelle. This may be the case because $^\bullet O_2^-$ is attracted to the positively charged CTMAB micellar surface, forming a dioxetane intermediate, which initiates the reaction with captopril.

Analytical parameters

Aimed at determining Cu(II), the calibration curve was constructed based on a series of eight standard solutions. Under the optimum conditions, the following linear equation was fitted to the calibration data in the concentration range 0.1–2 µg ml^{-1}

$$I = 5.11 + 442.04X, \quad r = 0.996$$

where, I stands for the CL intensity (in arbitrary units), X is the concentration of Cu(II) expressed in µg ml^{-1}, and r is correlation coefficient. The limit of detection (c_{LOD}, the analyte concentration giving a signal equal to the blank signal plus three standard deviation of the blank) was calculated on the basis of the calibration data and the equation of the regression line, in the way put forward by Miller and Miller [33]. It was obtained that $c_{LOD}=0.03$ µg ml^{-1}. Relative standard deviation (RSD) for determination of 0.8 µg ml^{-1} Cu(II) was 1.89% for five replicate measurements.

Fig. 4 The effect of H_2O_2 concentration (reagent 2) on CL emission intensity in the presence (■) or in the absence (♦) of 1 ppm Cu(II). Reagent 1: pH 12, 1 ppm Cu(II), 0.5% (m/v) CTMAB, 0.001 mol l^{-1} Captopril; reagent 2: H_2O_2

Table 1 Tolerable concentration ratios with respect to Cu(II) for some interfering species

Interferent	Tolerable concentration ratio
K^+, Na^+	1,000
Ba^{2+}, Mg^{2+}	500
NH_4^+, Ca^{2+}, Pb^{2+}, Sr^{3+}	250
Al^{3+}, Fe^{3+a}	100
Zn^{2+}	50
Fe^{3+}	25
Ni^{2+}, Mn^{2+}	10
Co^{2+}	1

[a] In the presence of 1,000 ppm F^-

Table 2 Results of the determination of Cu(II) in human hair, rice flour, and wheat flour, with the proposed method compared with that of a standard method

Sample	Amount found[a] (μg/g) via	
	Proposed method	FAAS
Human hair	25.2±0.3	25.0±0.1
Rice flour	1.30±0.03	1.32±0.02
Wheat flour	0.67±0.03	0.70±0.02

[a] Mean of three determinations

Interferences

To investigate the interference effect of various cations, solutions containing 0.7 μg ml^{-1} Cu(II) and interfering species in different interferent-to-analyte ratios were subjected to the proposed method (Table 1). A foreign ion was considered to be tolerable when it gave a determination error no more than 5%. The tabulated results show that the most serious interferent was Co(II), while Ni(II), and Mn(II) interfere to a lesser degree. Furthermore, high concentrations of some anions, especially NO_3^-, interfere with the CL reaction and cause precipitation. This problem can be overcome by passing sample solutions through an anion exchanger column.
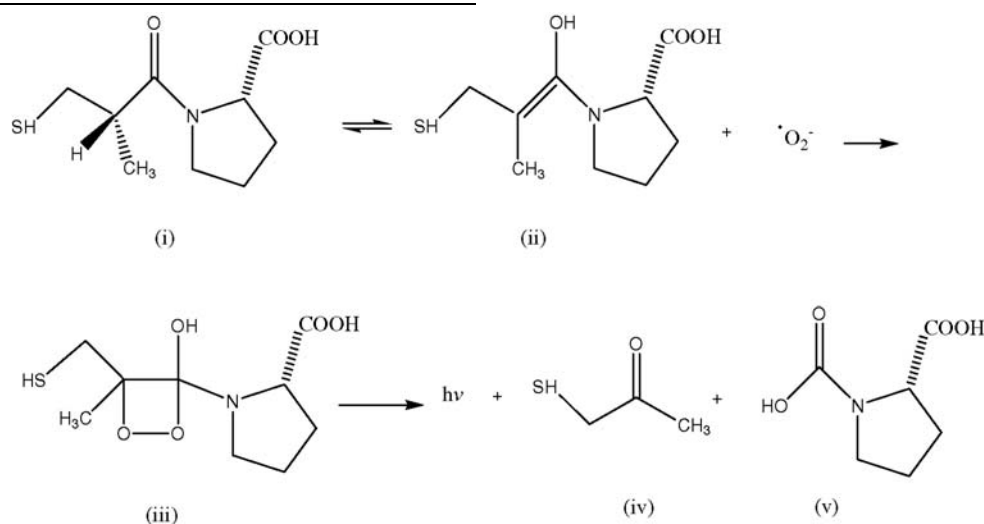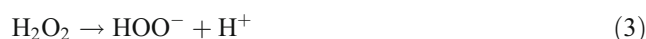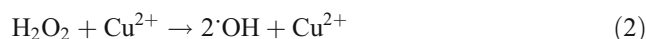
Applications

We have examined the applicability of the proposed analytical method for the selective determination of trace amounts of Cu(II) in human scalp hair, wheat flour, and rice flour as some typical cases of potential applications. Taking into account the results of interference examinations and the reported concentration of metal ions in human hair, wheat flour, and rice flour [34, 35], led us to the conclusion that selective determination of Cu(II) in these natural matrices can be achieved by this novel CL system. The results obtained by the proposed method, were compared with that of flame atomic absorption spectrometry (FAAS) standard method (Table 2) by two-tailed t-test [36]. Statistical comparison of the two sets of results at 95% confidence level proved the null hypothesis holds true.

Summary of possible CL reaction mechanism

Based on the mechanisms present in the literature for the similar compounds [15, 37–39], the following mechanism is proposed as a possible route for the new CL reaction. Transition metal ions with two available oxidation states usually catalyze the radical decomposition of H_2O_2, so they can be detected by CL reaction [15, 38]. The superoxide ion (anion radical) is produced by the radical decomposition of H_2O_2 [15, 37, 38]. It is proposed that the superoxide ion, $^{\bullet}O_2^-$, reacts with captopril (i, ii) to form an intermediate product (iii), which emits light by fragmenting into two parts (iv, v). Enhancement of CL by added cationic micellar solutions (CTMAB) is thought to involve more efficient reaction of captopril with the $^{\bullet}O_2^-$ in the Stern region of the micelles [16, 32].

$$H_2O_2 \rightarrow 2\,^{\bullet}OH \tag{1}$$

$$H_2O_2 + Cu^{2+} \rightarrow 2\,^{\bullet}OH + Cu^{2+} \tag{2}$$

$$H_2O_2 \rightarrow HOO^- + H^+ \tag{3}$$

$$HOO^- + \,^{\bullet}OH \rightarrow OH^- + \,^{\bullet}O_2H \tag{4}$$

$$^{\bullet}O_2H \leftrightarrow \,^{\bullet}O_2^- + H^+ \tag{5}$$

Last step of the CL reaction mechanism

In this mechanistic discussion, the involvement of $^{\bullet}OH$ and $^{\bullet}O_2^-$ in the CL reaction is assumed. With a view to verifying this involvement, we examined the effect of some specific scavengers for these two radicals: ascorbic acid [40] and superoxide dismutase [41] for $^{\bullet}O_2^-$, and mannitol [41] for $^{\bullet}OH$. These scavengers had inhibiting effect on the CL emission, which accords with the proposed mechanism.

Conclusions

The CL method proposed here is quite simple and demonstrates improved selectivity and satisfactory sensitivity. The results reveal that the proposed CL reaction is not only suitable for automated flow-stream systems, but also for simple batch-type systems by virtue of its relatively long-lasting light emission. Utilizing the proposed method, the copper content of human hair, rice flour, and wheat flour can be directly determined with quite acceptable selectivity and sensitivity, with no need for any preconcentration step. This novel reaction may unravel fresh horizons and perspectives in the field of oscillatory CL reactions. The system may also be employed for indirect determination of any ligand capable of forming a stable chelate with Cu(II).

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