



Microemulsion-enhanced electrochemiluminescence of luminol-H₂O₂ for sensitive flow injection analysis of antioxidant compounds

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ABSTRACT

A microemulsion enhanced electrochemiluminescence (ECL) of luminol-H₂O₂ was studied with the flow-injection (FI) technique. The results revealed that the microemulsion composed with cetyltrimethylammonium bromide (CTAB), n-butanol, n-heptane and water greatly enhanced the ECL especially in acidic medium. The ECL emission increased for 20 to 2 times in this microemulsion medium over the pH range of 5.0–8.0 compared to that in aqueous solution. The mechanism of enhancement of surfactant and microemulsion for luminol-H₂O₂ ECL was discussed. It is mainly based on the electrostatic interaction between luminol anion and the head group of surfactant, which causes the adsorption and promotes the dissociation of luminol on the surfaces of the microemulsion droplets, favors the oxidation of luminol by the yielded reactive oxygen species (ROSs) during electrolysis. This research is very significant for ECL applications because of the extended practicable pH range which was suitable for environmental and biological systems. As an example, this FI-ECL technique can be applied for determination of oligo proanthocyanidin (OPC) because of its antioxidant property and to evaluate the total antioxidant activity of the grape skin using OPC as an index.

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1. Introduction

Electrochemiluminescence (ECL) is a well-known high sensitive method for analytical purpose depending on the generation of luminescent signal triggered by an electrochemical reaction [1]. For ECL of luminol, compared with traditional chemiluminescence (CL), the application of an electric potential to oxidize luminol can successfully replace the catalyst to provoke its luminescence with inherent high sensitivity and wide linear responding range [2,3]. But, for a long time, the ECL application of luminol has been limited in alkaline solution [4–9] just as its CL, principally due to its less dissociation in neutral or acidic solution.

How to fulfill the ECL of luminol which was facily occurred in acidic or neutral medium has practical significance since many biomolecules can only exist in acidic or neutral mediums. So far, there is only one report about luminol ECL in acidic solution. Fang and co-workers [10] proposed an ECL method for determination of Co²⁺ based on its catalysis for electrochemiluminescence of luminol-H₂O₂ in acidic solution. In recent years, our researches have revealed that the ECL of luminol was oxygen related [11] and was more efficient in near neutral medium through modifying the electrodes with nano-materials [12] or changing the solution

medium [13], thus expanded the applicable acidity range of luminol ECL to apply it in biological analysis. It supplied a powerful tool for monitoring of reactive oxygen species (ROSs) [14] and further bio-applications such as in biosensors [15,16]. Also we developed a flow injection ECL analytic technique (FI-ECL) [17] in previous work which was facile for ECL detection with high performance.

In aqueous medium, the coexistence of surfactant, cosurfactant and organic matters by certain contents will result in the formation of microemulsion, a spontaneously formed perfectly clear, thermodynamically stable and optically isotropic medium [18]. Presently, it is widely employed in drug delivery [19], oil recovery [20], synthesis of nano materials [21], preparation of cosmetics [22] and organic synthesis [23] and so on. Its unique property mainly includes the low interfacial tension, high interfacial area and the ability to dissolve immiscible liquids.

Refer to the reports that the formation of surfactant micelles would enhance the solubility and sensitivity for many analytical purposes [24,25], the effects of the surfactant and microemulsion medium on the ECL performance were studied in this paper with coexisted luminol and H₂O₂ as luminescent signal. We obtained higher ECL emission in both cases but more efficient in later. It is very significant that the enhancement was more prominent in acidic and neutral conditions, which greatly extended the applicable pH range of luminol ECL to acidic condition.

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Oligo proanthocyanidin (OPC) is a typical free radical scavenger and is believed to be an important contributor to the health benefits of fruits and vegetables [26,27]. It shows the ability to protect the human body against the UV light-induced carcinogenesis and to prevent the immune suppression [28]. Grape is one genus of the most consumed fruits in the world, and they also stand out as a source of antioxidants such as OPC for human health [29,30]. So it is very significant to develop the efficient technique for quantitative assay of OPC in biological samples. The proposed method was successfully applied to evaluate the total antioxidant activity of the grape skins using OPC as an index.

2. Experimental

2.1. Instruments

The lab-built flow-injection analytical system was described in our previous paper [17], which contained a flow ECL cell connected with a double-way commixing cell, and a sample injector with a 5 μ L injection loop. An RST600 Electrochemiluminescent Workstation (custom-built, Risetest Instrument Co. Ltd., Suzhou, P.R. China) was used to provide the electrolytic potential for exciting the ECL signal and to record it. An R212 photomultiplier tube (Hamamatsu, Japan) was connected to act as an ECL detector with a -800 V bias potential. An indium tin oxide (ITO) working electrode, a platinum wire auxiliary electrode and an Ag/AgCl reference electrode were used in experiments. The ITO was cleaned in an ultrasonic bath with dilute ammonia, ultrapure water, ethanol and ultrapure water in sequence and dried with nitrogen-blowing. Cyclic voltammetry was performed with a RST-3000 Electrochemical Workstation (Risetest Instruments Co. Ltd., Suzhou, China). The fluorescence spectra were recorded using an F-4500 Fluorescence Spectrophotometer (Hitachi, Japan).

2.2. Materials and reagents

ITO glass was purchased from Suzhou Nippon Sheet Glass Electronics Co. Ltd. (Suzhou, China). Luminol was purchased from Fluka (Buchs, Switzerland). Cetyltrimethylammonium bromide (CTAB), sodium dodecyl sulfate (SDS), polyvinylpyrrolidone (PVP), n-heptane (Hep), n-butanol (Buta), hydrogen peroxide (30%, v/v), pyrogallol, gallic acid and ascorbic acid were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). OPC (UV $\geq 95\%$) was purchased from Shanghai Shunbo Biology Engineering Technology Co. Ltd. (Shanghai, China). Resveratrol (HPLC $> 98\%$) was purchased from Nanjing TCM Institute of Chinese Materia Medica (Nanjing, China). All of the reagents are analytical grade and used without further purification. Ultrapure water (prepared by an ALH-6000-U ultrapure water machine, Aquapro, China) was used throughout the experiment.

2.3. Preparation of CTAB/Buta/Hep/H₂O microemulsion

The mass ratio of co-surfactant to surfactant ($\omega = m_{\text{Buta}}/m_{\text{CTAB}}$) is an important factor for formation of CTAB/Buta/Hep/H₂O microemulsion within the scale of 1 to 3. In this study, we selected the conditions of $\omega = 1$ and 4 g of the total quantity of CTAB, Buta and Hep. This oil-in-water microemulsion was prepared by the titration [31] of mixed solution of surfactant, co-surfactant and oil into the buffer under stir until a clear solution was obtained. In this case, equal quantities of CTAB and Buta were mixed with Hep in the designed concentrations, and then titrated into phosphate buffer at 70 °C.

2.4. Pretreatment of real sample

The Jufeng grapes (a famous variety of grape in China) were collected from Donghai County (Lianyungang, China). The skins of those grapes were flensed off carefully and dried by insolation, then ground in a Wiley mill to pass through a 20 mesh (840 μ m) bould. Every 2 g portions of the powder were extracted with 3 times of 10 mL acetone/water (7:3) under mechanical agitation for 1 h at 20 °C, and then the total extracts was vacuum filtered with Whatman 41 paper on a Büchner funnel. The filtrate was finally rotary evaporated under vacuum at 40 °C, then freeze-dried to obtain the extract [32].

2.5. The operation procedure and parameters

The microemulsion was pumped through the sampling injector into the commixing cell, the mixed solution of luminol and hydrogen peroxide was directly pumped into the commixing cell. Their mixture flowed into the ECL cell, and the ECL was generated while the working electrode was powered by consecutive rectangular pulsed electrolytic potential. The signal was simultaneously detected by the PMT. The duty factor, upper and lower limiting potentials, period of pulse and flow rate are most important factors which greatly influenced the ECL performance. In experiments, those parameters were optimized for best ECL response.

3. Results and discussion

3.1. The effect of surfactants on ECL performance of luminol

Surfactants have been widely applied in spectral analysis, electrochemical analysis and other fields due to solubilization and sensitization resulting from the micelle formation. In our previous work, we have pointed out that the ECL intensity of luminol can be enhanced by the action of surfactants under neutral and alkaline conditions [13]. In this work, the effects of surfactant type and concentration on the ECL behavior of luminol-H₂O₂ were studied in detail over the range of pH 5.0–9.0.

The most popular surfactants as CTAB, SDS and PVP are the representatives of cationic, anionic and nonionic surfactants. The ECL performances of luminol-hydrogen peroxide system in the presence of these surfactants in the phosphate buffer were investigated. As shown in Fig. 1, under optimized electric parameters as 10% of duty factor, 1.0 V and -0.5 V of upper and lower limiting potentials, 2.0 s of period and 1.5 mL/min of flow rate, besides the quenching effect from SDS (curve c) and non-effective of PVP (curve b), only

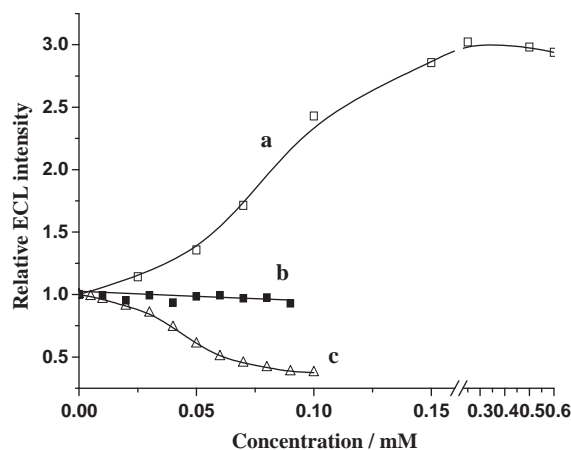


Fig. 1. The effect of surfactant concentration of (a) CTAB, (b) PVP and (c) SDS on the ECL response of luminol-H₂O₂.

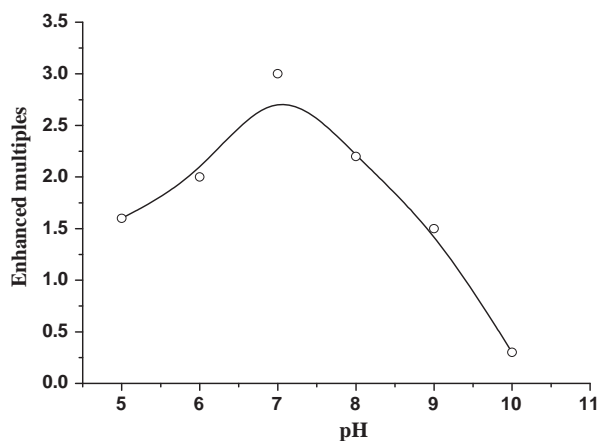


Fig. 2. The effect of pH value of buffer solution on enhanced multiples. $C_{H_2O_2} = 0.01$ mM, $C_{luminol} = 0.1$ mM, flow rate = 1.5 mL/min.

the cationic surfactant CTAB can obviously enhance the ECL intensity (curve a). The ECL intensity increased with increasing CTAB concentration up to the critical micelle concentration (CMC) of about 0.2 mM and resulted in a threefold increase in ECL intensity. The influence of pH value of buffer solution on the sensitization of CTAB was of vital importance. As illustrated in Fig. 2, the maximum enhancement was observed at pH 7.0.

3.2. Investigation of the effect of microemulsion on ECL performance of luminol- H_2O_2

The cationic surfactant was demonstrated to enhance the ECL emission of luminol- H_2O_2 by prior research. However, the overall efficiency is not very satisfactory. The microemulsion system containing cationic surfactant can result in a more significant enhancement. A microemulsion comprised of CTAB, Buta and Hep is investigated. Several factors that influenced the ECL signals were optimized, including mass ratio of emulsifier to Hep, water content and pH value.

The effect of the mass ratio of emulsifier to Hep on the ECL intensity of luminol- H_2O_2 was studied over the range of 1–6. As shown in Fig. 3A, the ECL intensity decreased with increasing mass ratio. A mass ratio of 1 can be seen to give the highest ECL intensity. Unfortunately, however, there the phase separation was observed when the mass ratio was less than 1, which suggested the destruction of microemulsion. Therefore, a mass ratio of 1 was decided for further research.

The effect of water content on the ECL signal was studied in the range of 30–70 mL. As can be seen from Fig. 3B, the relative intensity increased with the increase of water content, whereas it was reduced when higher than 50 mL. 50 mL was therefore selected as suitable water content.

The pH value is a crucial aspect because the ECL reaction of luminol with hydrogen peroxide was a pH-dependent process. Under optimized conditions, the sensitization of microemulsion at various pH values from 5.0 to 9.0 was investigated. As shown in Fig. 3B,

enhanced multiple increased with the decrease of pH and the maximum enhanced multiple of 20.0 was obtained at pH 5.0, and about 2 times of enhancement was obtained at pH 8.0. However, the ECL intensity was attenuated in microemulsion medium at higher pH than 9.0. The distinguishable significance of this result is that the applicable pH range of luminol- H_2O_2 ECL was extended to acidic range of pH 5.0 for the first time. Although the attempt to further extend the applicable pH range is blocked now because of the detection threshold of instruments, it is in promising if we do well on continuous progress on the enhancement of ECL intensity. The detection performances for H_2O_2 in microemulsion medium at different pH values were shown in Table 1. It demonstrated that the present method was a very sensitive method in neutral and acidic medium.

3.3. The mechanism of enhancement from microemulsion

Cyclic voltammetry was applied to verify the action of microemulsion for this ECL procedure. As shown in Fig. 4, the oxidation potential of luminol decreased rapidly with CTAB concentration increasing up to 0.5 mM meanwhile the peak current reached its highest around this concentration. This suggested that the CTAB played an uppermost role to promote the electrochemical oxidation of luminol, by which the ECL was enhanced greatly.

The mechanism of the ECL enhancement also can be unraveled by fluorescence quenching research. The analysis of fluorescent quenching data according to the Stern–Volmer equation [33] is helpful for understanding of the principle pathway of the interaction between fluorophore luminol and quenching matters as CTAB. The Supplementary Fig. 1A displays a 35% of fluorescent intensity decrease upon the addition of microemulsion (CTAB up to 4.5 mM) but almost no shift on the emission band. In addition, the fluorescence spectra of luminol were almost identical in both the

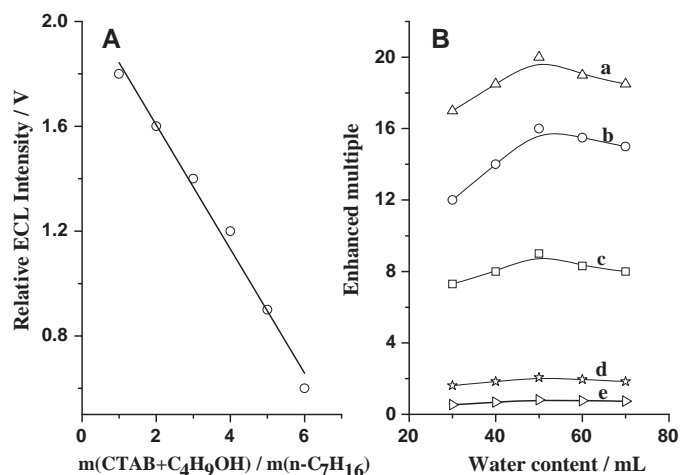


Fig. 3. (A) Effect of the mass ratio of emulsifier to $n-C_7H_{16}$ on ECL response. The water volume is 40 mL, total quantity of emulsifier and $n-C_7H_{16}$ is 4.0 g, 0.2 M phosphate buffer (pH 7.0). (B) Effect of water content and pH of (a) 5.0, (b) 6.0, (c) 7.0, (d) 8.0 and (e) 9.0 on enhanced multiples. Other conditions are same as in Fig. 1.

Table 1

The detection performance for H_2O_2 in microemulsion medium at different pH.

pH	Microemulsion medium			Phosphate buffer
	Linear equation	LOD (M)	RSD ($n=5$)	
6.0	$\Delta ECL = -0.285 + 0.665C_{H_2O_2} (10^{-5}M)$	1.68×10^{-7}	3.94%	8.73×10^{-6}
7.0	$\Delta ECL = 0.109 + 0.989C_{H_2O_2} (10^{-5}M)$	7.75×10^{-8}	3.43%	6.23×10^{-7}
8.0	$\Delta ECL = -0.0533 + 1.554C_{H_2O_2} (10^{-6}M)$	3.02×10^{-8}	2.96%	1.05×10^{-7}
9.0	$\Delta ECL = 0.0229 + 0.291C_{H_2O_2} (10^{-7}M)$	9.59×10^{-9}	4.02%	1.20×10^{-8}

Table 2
The comparison of total antioxidant content in different grape varieties.

Grape varieties	Total antioxidant content	Method	Ref.
Bordô grape	1130 ± 105 mg/kg (gallic acid), fresh grape	Folin–Ciocalteu method	[38]
<i>Vitis vinifera</i> red grape	731 – 3486 mg/kg (gallic acid), fresh grape	Folin–Ciocalteu method	[39]
<i>Vitis rotundifolia</i> grape	3.59 – 5.04 mg/g (gallic acid), fresh skin	Folin–Ciocalteu method	[40]
Jufeng grape	4450 ± 410 mg/kg (OPC), fresh skin	The proposed method	

presence or absence of n-butanol, indicating there was no interaction between luminol and n-butanol.

By the linear regression for $[F_0/F]$ upon CTAB concentration ($F_0/F = 1.015 + 0.0121C_{CTAB}$, see [Supplementary Fig. 1B](#)), the Stern–Volmer constant (K_{SV}) could be calculated from its slope as $1.21 \times 10^2 \text{ L mol}^{-1}$, indicates a static quenching process. Also there

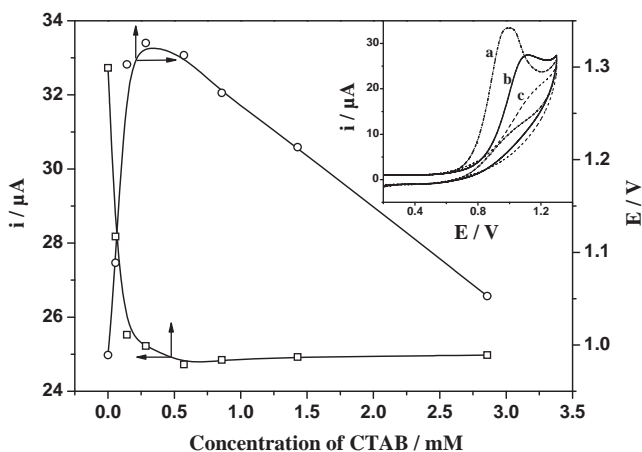
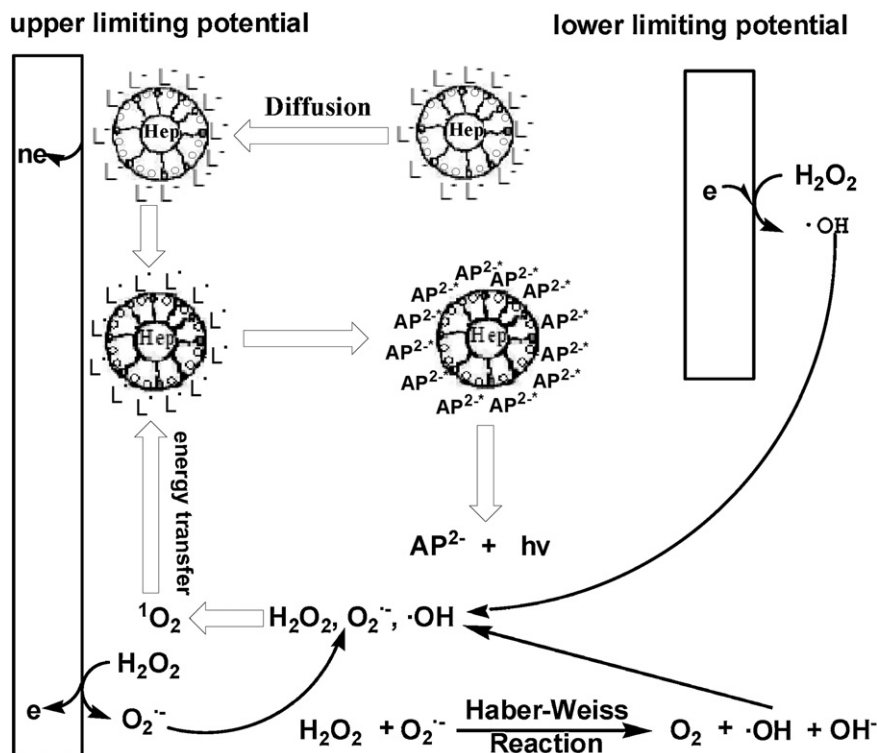


Fig. 4. Effect of CTAB concentration on the redox peak current and potential of luminol in microemulsion. The inset is the cyclic voltammograms of 0.1 mM luminol in (a) 0.1, (b) 0.02, (c) 0 mM of CTAB in 0.2 M phosphate buffer containing 0.1 mM H_2O_2 at scan rate of 0.1 V/s.

is another linear regression ($\log[(F_0 - F)/F] = 2.083 + 0.991 \log C_{CTAB}$, see [Supplementary Fig. 1C](#)). From it the binding constant (K), binding number (n), and the free energy of binding ($\Delta G_{\text{binding}}^0$) have been calculated for $1.21 \times 10^2 \text{ L mol}^{-1}$, 0.99 and $-11.9 \text{ kJ mol}^{-1}$, respectively. These thermodynamic values indicate the spontaneous and very strong interaction to form the coupled molecular assemblies between luminol anion (L^-) and the positive charged cation group (CTA^+) [34] by electrostatic force. These assemblies exhibited typical effects as fluorescent quenching, metachromasy and accumulation in phase boundaries, etc. [35].

From previous researches [24,36], in surfactant medium, the CTAB plays a pivotal role for enhancement of the luminol- H_2O_2 ECL, due to the formation of assemblies between CTA^+ and luminol anion (L^-) by attractive electrostatic interaction. This interaction promoted the dissociation of luminol molecules to form the anions in neutral or acidic medium and concentrated them, which made them react more effectively to generate higher ECL emission.

As to microemulsion medium, the mechanism of enhancement is illustrated in [Scheme 1](#). On the one hand, more luminol molecules would be adsorbed onto the droplet surfaces because of the larger surface area of microemulsion droplets than micelles due to the coexistence of co-surfactant and oil. Thus, they are more easily to be delivered to electrode surface by those droplets as the carrier, which resulted in more efficient enhancement for ECL emission. On the other hand, H_2O_2 can be further oxidized to yield $\text{O}_2^{\cdot-}$ under upper limiting potential and reduced to yield the more oxidative $\cdot\text{OH}$ under lower limiting potential during the ECL



Scheme 1. The mechanism of enhanced ECL of luminol- H_2O_2 from microemulsion.

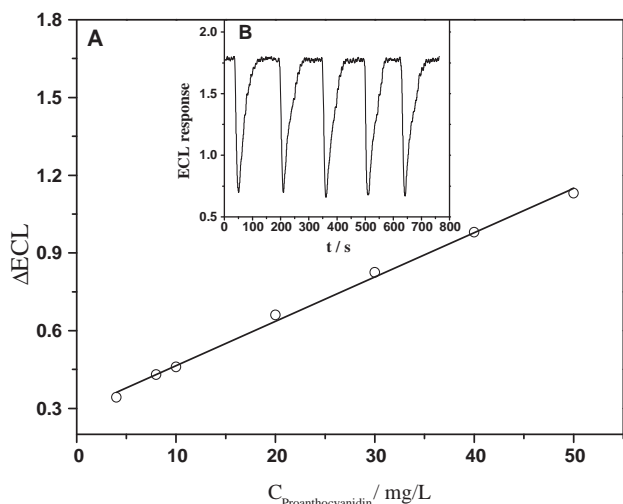


Fig. 5. (A) The ECL response upon OPC and (B) the ECL signal of five sequential injections of 50 mg L⁻¹ OPC in microemulsion buffered at pH 7.0.

process. Meanwhile, a Haber–Weiss reaction will take place between H₂O₂ and O₂^{•-} to yield •OH. Finally, the singlet oxygen (¹O₂) will be produced from the reactions of those ROSS and transfer the energy to the oxidized intermediate of luminol to enhance the ECL emission, just like the discussions in our previous paper [14,37].

3.4. Analysis of total antioxidant capacity of grape skin

Based on the above discussion, the microemulsion enhanced ECL of luminol–H₂O₂ is related to ROSS. So, it could be applied to evaluate the antioxidant efficiency of some radical scavengers. Grape skin extracts were tested in this experiment.

Under optimized conditions (C_{Luminol} = 0.1 mM, C_{H₂O₂} = 0.1 mM, pH 7.0), the OPC quenched the ECL with the linear response (Fig. 5A) within the concentration ranging from 4.0 to 50 mg L⁻¹ (ΔECL = 0.294 + 0.0171C_{OPC} (mg L⁻¹), r = 0.9981) and a detection limit of 1.12 mg L⁻¹ (S/N = 3). Fig. 5B shows the ECL curve for successive five injections of 50 mg L⁻¹ OPC. The RSD thus been calculated for 1.14% (n = 5), suggested an adequate repeatability.

The total antioxidant content in the fresh grape skin with OPC as index was therefore determined as 4450 ± 410 mg/kg, agreed with different grape varieties shown in Table 2. Although the data in Table 2 are not totally the same, it is agreeable about the differences between the grape varieties or parts (fresh flesh or fresh skins), the results suggest that Jufeng grape must be a remarkable source of antioxidants. Recovery tests were performed for three samples by standard addition method. As shown in Table 3, the recoveries from 96.5 to 102.1% and the RSD (n = 5) ranged from 2.63 to 4.10% demonstrated the good performance of proposed method. Also, the content of total antioxidant in grape skin

Table 3
Recovery tests of OPC for grape skin samples.

Sample conc. (mg L ⁻¹)	Added (mg L ⁻¹)	Found total (mg L ⁻¹)	Recovery (%)	R.S.D. (%) (n = 5)
10.20	20	29.5	96.50	3.19
	30	40.68	101.60	2.63
9.51	20	29.15	98.20	3.16
	30	40.14	102.10	2.94
11.36	20	30.84	97.40	4.10
	30	41.87	101.70	3.62

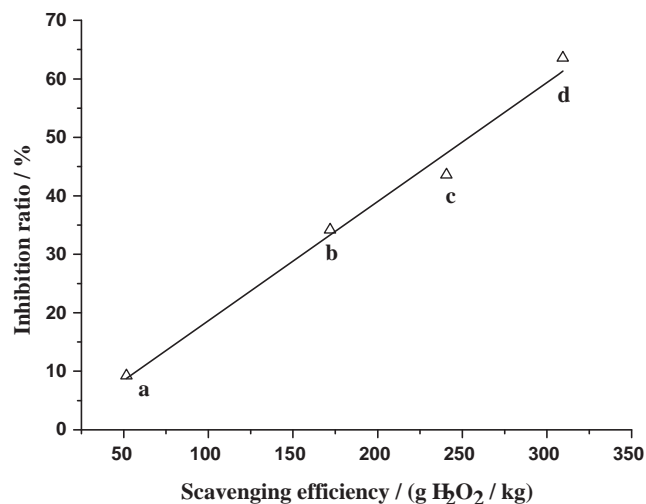


Fig. 6. Correlation of antioxidant activity determined by pyrogallol autoxidation method and proposed method for (a) ascorbic acid, (b) resveratrol, (c) OPC and (d) gallic acid.

can be convert to the antioxidant activity, namely the gross ROSS scavenging efficiency with H₂O₂ as index, by the linear equation ΔECL = 0.109 + 0.989C_{H₂O₂} (10⁻⁵M) which was obtained in experiments, for 430 mg (H₂O₂)/kg of fresh skins. For validation of the practicability of proposed method, some other typical antioxidants were tested and compared with the traditional pyrogallol autoxidation method. Here Fig. 6 shows the linear correlation between antioxidant activity (from proposed method) and the reference method (with inhibition ratio as index) of ascorbic acid, resveratrol, OPC and gallic acid. The good correlation coefficient of 99.01% suggests the excellent coherence of proposed method with reference method.

4. Conclusion

The combination of microemulsion-enhanced electrochemiluminescence of luminol–H₂O₂ with a flow-injection technique has been proved to be a sensitive and feasible means of ECL application. In this paper, we successfully achieved 20 times enhancement of ECL intensity in acidic medium of pH 5.0. It largely extends the applicable domain of ECL analysis. The performance of proposed technique has been validated by the application to determine the OPC. There is a linear response upon the concentration of OPC in the range of 4.0–50 mg L⁻¹ and a detection limit of 1.12 mg L⁻¹. The total antioxidant content in grape skin with OPC as index was therefore evaluated for 4450 ± 410 mg/kg, and further converted into the gross ROSS scavenging efficiency of 430 mg H₂O₂ per kg fresh weight skins. Also the comparing between present method and traditional pyrogallol autoxidation method shows the excellent coherence with 99.01% of correlation coefficient.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.talanta.2012.03.042>.

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