Talanta 85 (2011) 1304–1309

Contents lists available at ScienceDirect

Talanta

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

A luminol-based micro-flow-injection electrochemiluminescent system to determine reactive oxygen species

Chen Ming, Wei Xiuhua, Tu Yifeng*

Institute of Analytical Chemistry, Department of Chemistry, Dushu Lake Campus, Soochow University, Dushu Lake Higher Education Town, Suzhou Industrial Park, Suzhou, 215123, PR China

ARTICLE INFO

Article history:
Received 10 March 2011
Received in revised form 25 May 2011
Accepted 1 June 2011
Available online 12 June 2011

Keywords:
Flow injection analysis
Electrochemiluminescence
Reactive oxygen species
Luminol
Water sample

ABSTRACT

A flow injection analysis (FIA) system with electrochemiluminescent (ECL) detection has been established. Based on a specially designed flow-through ECL cell with a very simple structure, the system possesses rapid response and high sensitivity. With luminol as the ECL reagent, the response of hydrogen peroxide (H_2O_2) was investigated on the developed FIA-ECL system. After optimizing the experimental conditions, such as the electric parameters, the buffer condition and the flow rate, it was demonstrated that the developed FIA-ECL system works well for quantified assays. Compared with reported works, the present results indicate that the developed FIA-ECL system has the lowest limit of detection (S/N = 3) of 3.0×10^{-9} mol/L for H_2O_2, which is equal to the level of chemiluminescence (CL). The developed system was successfully used to monitor the yield of reactive oxygen species (ROSs) in water vapour during the work of an ultrasonic humidifier with H_2O_2 as index. And the amount of ROSs in some other real samples, including tap water, drinking water and river water was detected with recoveries from 92.0% to 106%.

1. Introduction

Chemiluminescence (CL) is a very sensitive method for the determination of trace analytes [1]. It is initiated by the mixing of reagents and controlled by careful manipulation of fluid flow. Therefore, the transient luminescence of CL is somewhat difficult to detect using the dynamic mixing procedure of CL reagents [2]. A recently developed analytical method, electrochemiluminescence (ECL) is similar but superior to CL. This method consists of a rapid process that involves a light emission from a species that undergoes a high-energetic electro-transfer reaction and/or concomitant reactions [3]. In ECL, luminescence is initiated and controlled by a programmable electrolytic voltage so that it is induced on the electrode surface and measured synchronously by a photon detector. The energy required for the excitation of a luminescent reagent can be easily controlled by adjusting the applied potential. ECL is used in a wide range of analytical applications, including clinical diagnostics, environmental assays, food and water testing and biowarfare agent detection [4].

Reactive oxygen species (ROSs), with higher reactivities than molecular oxygen, have attracted attention in many fields, such as life science, environmental chemistry and organic synthesis. As a typical index of ROSs, hydrogen peroxide is important in the gas-phase and aqueous atmospheric chemistry [5,6]. Hydrogen peroxide is found in all natural aquatic environments and is predominantly formed by photochemical generation via free-radical intermediates and dissolved organic chromophores [7,8]. It is widely agreed that hydrogen peroxide is toxic in vivo, and high levels of hydrogen peroxide is cytotoxic to a wide range of animals, plants and bacteria [9]. In recent years, much attention has been paid to the determination of hydrogen peroxide by CL [10–13] due to the capability of the CL intensity enhancement of luminol [14–18].

Luminol, one of the most prevalent CL reagents [19], is also widely used for ECL assays [18]. The application of an electric potential oxidises the luminol to induce luminescence with inherently high sensitivity and a wide linear range [20–23]. The ECL of luminol has been applied to determine hydrogen peroxide [24,25]. Our previous study shows that all species of ROSs and hydrogen peroxide can enhance the ECL of luminol [26]. Therefore, the ECL of luminol is a powerful analytical method with some particular advantages, such as a wider dynamic range, excellent sensitivity and facile instruments [27].

The flow injection analysis (FIA) systems based on CL detection have once been developed as an analytical methodology with fast, effective and applicable response. It has also drawn much attention for determination of scavenging capacity against ROSs [28,29]. However, the CL-FIA system requires complicated equipment and a very strict controlling system to ensure the precision and reproducibility. ECL can be applied to both static and dynamic systems.

* Corresponding author. Tel.: +86 13812768378; fax: +86 512 65101162.
E-mail address: tuyf@suda.edu.cn (T. Yifeng).

0039-9140/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.talanta.2011.06.002

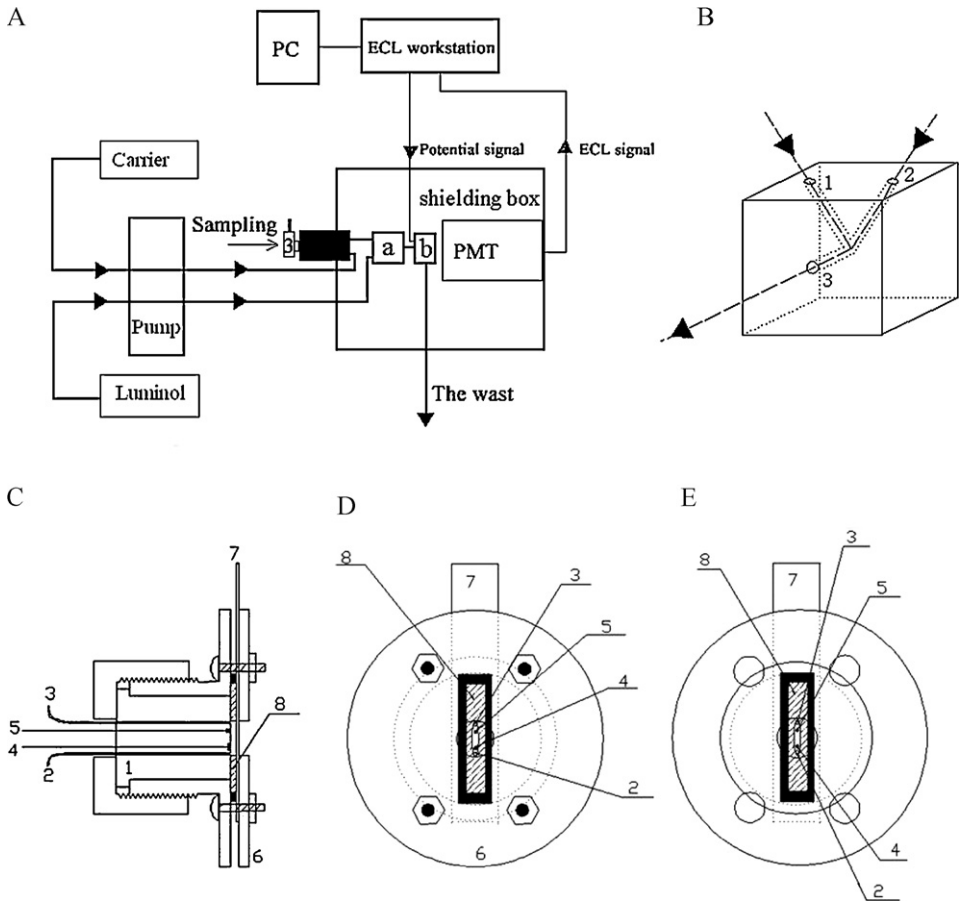

Fig. 1. (A) is the installation of ECL-FIA system there the (a) for commixing cell, (b) for ECL cell. (B) is the structure of commixing cell there (1) for carrier inlet, (2) for background solution inlet and (3) for mixture outlet. (C–E) are the side view, bottom view and top view of the ECL cell, respectively, there (1) for plexiglass subassembly, (2, 3) for inlet and outlet channels, (4) for Ag/AgCl reference electrode, (5) for Pt counter electrode, (6) for plexiglass pedestal, (7) for ITO working electrode and (8) for incised latex film.

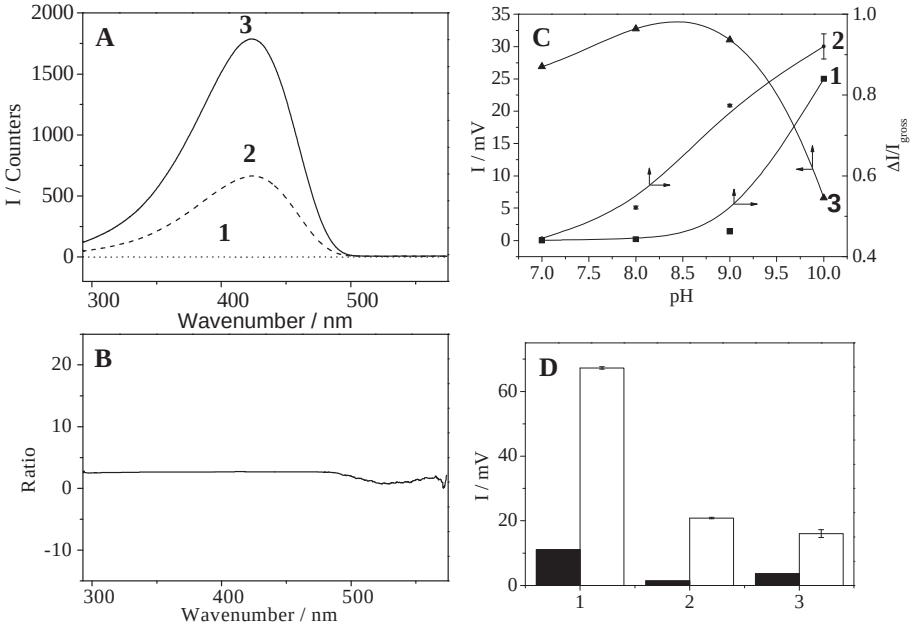

Fig. 2. (A) for ECL spectra of (1) 5×10^{-6} mol/L H_2O_2, (2) 5.0×10^{-3} mol/L luminol and (3) their mixture in 0.1 mol/L Na_2CO_3–$NaHCO_3$ (pH 9.16, 20 °C). (B) The ratio of curve (3) to (2) in (A). (C) For effect of the buffer pH on ECL intensity of (1) 1×10^{-4} mol/L luminol, (2) 1×10^{-4} mol/L luminol + 1×10^{-6} mol/L H_2O_2 and (3) the quotient of response (ΔI) to gross intensity (I_{gross}), at 0.15 mL/min of flow rate. (D) For effect of buffer component on ECL response there (1) for 0.1 mol/L Na_2CO_3–$NaHCO_3$ (pH 9.16), (2) for PBS (pH 9.01) and (3) for 0.2 mol/L borax (pH 9.20).

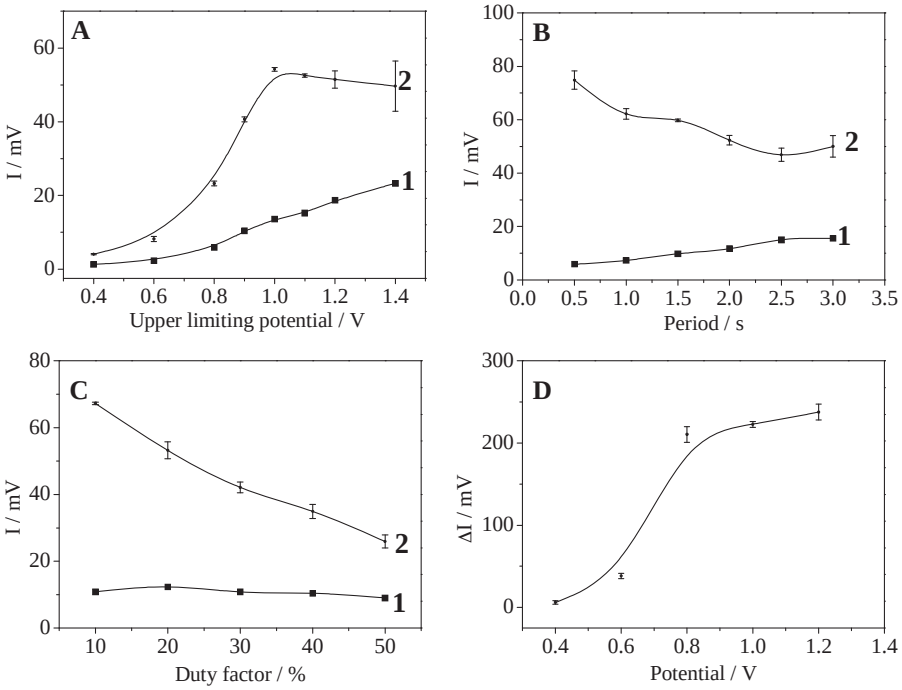

Fig. 3. In pulsed mode, the influence of (A) the upper limiting potential, (B) period and (C) duty factor on the ECL response of (1) for 1×10^{-4} mol/L luminol and (2) for the ΔI from 1×10^{-6} mol/L H_2O_2 in 0.1 mol/L Na_2CO_3–$NaHCO_3$ (pH 9.16, 20 °C) with flow rate of 0.15 mL/min. (D) In potentiostatic mode, the effect of electrolytic potential on ECL response of H_2O_2.

A facile and smart luminol-based FIA system with ECL detection (ECL-FIA) for the determination of ROSs was developed in this research. It was built by equipping an FIA device combined with a newly designed ECL flow cell with indium tin oxide (ITO) glass as the working electrode. Compared with conventional ECL flow cells [2], where some limitations as (1) large dead volumes, when the reference electrode was placed near the inlet [30] and (2) difficult to remove away possible gas bubbles because of the high flow resistance [31] presented, our design has overcame those limitations and possessed the advantages including the simplicity of its structure, high sensitivity and easy assembly. The response of the developed ECL-FIA system to hydrogen peroxide was then investigated. The mass detection limit of hydrogen peroxide is as low as 15 fmol (femtomols). Furthermore, it was used to determine ROSs in water and to monitor the yields of ROSs in water vapour from an ultrasonic humidifier.

2. Experimental

2.1. Instruments

An RST600 Electrochemical Workstation (custom-built digital instrument, RST Instrument Co. Ltd, Suzhou, P.R. China) was used to provide the electrolytic potential for exciting the ECL and to record the ECL signals. A R212 photomultiplier tube (Hamamatsu, Japan) was connected to act as an ECL detector with a −800 V potential. A Sci-Q 400 peristaltic pump (Watson-Marlow Bredel Pumps, USA) and a 7725(i) manual sample injector (six-way valve, Rheodyne, USA) with a 5 μL injection loop were applied to construct the flow-injection system. An Acton SP2300 grating monochromator/spectrograph with a PIXIS 100 CCD detector (Princeton Instruments, USA) was used to record the ECL spectrum.

The ECL-FIA system, which is illustrated in Fig. 1A, consists of a pump/injection system and two self-built cells (i.e., the commixing cell and ECL cell). As indicated in Fig. 1B, the commixing cell is a plug-in unit between the injection unit and the ECL cell. There are two inlet-channels from the pump and the valve, respectively, for the background and sample solutions as well as an outlet-channel to output the mixed solution to the ECL cell, the background solution and sample are mixed at the trifurcate junction and then flow through the outlet channel. The inner diameter of the inlet and outlet channels is 0.6 mm. The microlitre ECL-cell was designed for ECL-FIA detection. Its structure can be seen as side-view, bottom-view and top-view (Fig. 1C–E). On a plexiglass subassembly (1), two stainless steel pipes were fixed in to act as the inlet (2) and outlet (3) channels, and an Ag/AgCl reference electrode (RE) (4) and a Pt counter electrode (CE) (5) were also fixed in. The obverse plane of this subassembly also served as one wall of the ECL cell. The other plexiglass subassembly (6) is a pedestal to support the fastener. The opposite wall of the cell is a piece of ITO glass (7), which also acts as the working electrode (WE). The third component of the ECL flow cell is an incised latex film (8) (thickness of 0.5 mm) with a narrow elliptic hollow in its centre. All parts were firmly integrated together with four bolts to create the cell. The inlet and outlet pipes were fixed at two ports of the thin cell, ensuring no dead volume. The volume of this ECL cell is about 5 μL, nearly to those of the ECL flow cells reported by other authors [32,33]. The FEP tubes (0.6 mm i.d.) were used to connect all components of the system. By using ITO glass as both the working electrode and optical window, the sample solution made contact with the entire WE area when flowing through the cell. Thus, the analytes have a greater reaction opportunity, allowing a greater response. Unlike Pt and other electrode materials used in other ECL flow cells, the washing and replacement of ITO glass is more convenient.

2.2. Chemicals

5-Amino-2,3-dihydro-1,4-phthalazinedione (luminol) was purchased from Fluka. Other chemicals were all of analytical grade. Ultra pure water (prepared by an ALH-6000-U ultra pure water

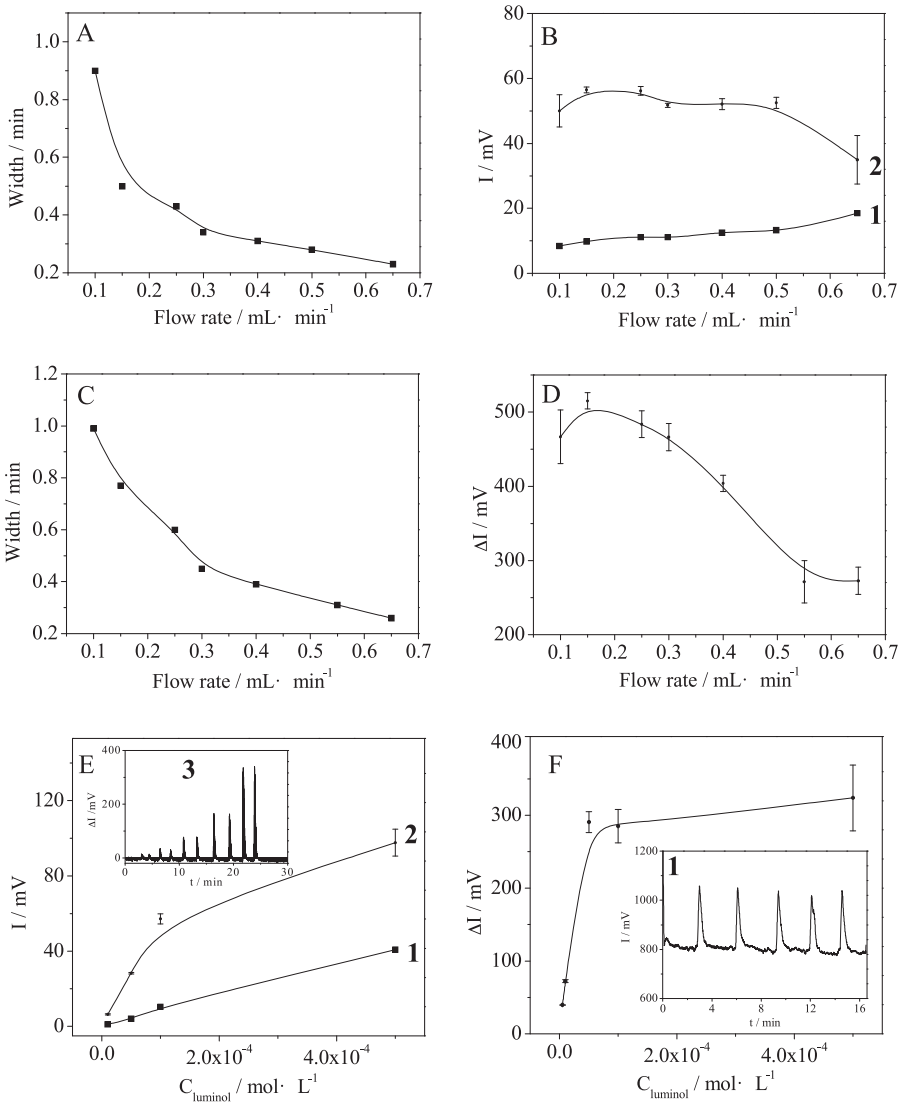

Fig. 4. The influence of flow rate on peak width (A, C) and ECL response (B, D) of 1×10^{-6} mol/L H_2O_2. There (A, B) for pulsed mode, (C, D) for potentiostatic mode. In (B), (1) is for background and (2) is for ΔI. (E, F) are the influence of luminol concentration on ECL response in pulsed and potentiostatic mode, respectively. In (E), (1) is for background ECL, (2) for ΔI and (3) for ECL response of 2×10^{-7}, 5×10^{-7}, 1×10^{-6}, 2×10^{-6} and 4×10^{-6} mol/L H_2O_2. In (F), the insert is the ECL response of 5×10^{-7} mol/L H_2O_2 during five sequential injections.

machine, Aquapro, China) was used. The 0.01 mol/L luminol stock solution was prepared and stored in the refrigerator.

2.3. ECL measurement

The ITO glass was cleaned in an ultrasonic bath with acetone, ethanol, dilute ammonia and ultra pure water in sequence and dried with nitrogen-blowing before being fixed into the ECL cell. The carrier solution was pumped through the sampling injector into the commixing cell, and luminol solution 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 an electrolytic potential. The signal was simultaneously detected by the PMT.

2.4. The determination of ROSs in real samples

Different water samples, including tap water, drinking water and river water, were sampled. The distillates of atomised water vapour produced by an ultrasonic humidifier (UH-1011, AUP Co., China) were also collected according to a schedule. The gross amounts of ROSs in those samples were detected with H_2O_2 as the index.

3. Results and discussion

3.1. Performance optimization of the FIA system

As shown in Fig. 1A, the manual sample injector (six-way valve) was mounted on the wall of the shielding box. The length of the tube from the injector to the commixing cell was 30 mm, and the length of the tube between the commixing cell and the ECL cell was 20 mm. With this short length, the system worked well at a very low flow rate (less than 0.5 mL/min), whereas other reported ECL-FIA systems cannot work with less than 1.0 mL/min [2,34,35]. The RSD of the ECL signal under different flow rates (0.15, 0.4 and 0.65 mL/min) was 1.61%, 3.33% and 21.33%, respectively, which indicated that a lower flow rate is beneficial for obtaining a more stable ECL signal. Meanwhile, the short connecting tube ensures the limited longitudinal diffusion of the analytes.

Table 1
The comparison of LOD of developed ECL-FIA system with some reported CL (A) and ECL (B) systems.

	CL/ECL system	LOD (mol/L)	Ref.
A	Luminol-Co(II)-H_2O_2, Co(II) as a catalyst	5.0×10^{-9}	[36]
	Luminol-KIO_4-H_2O_2, KIO_4 catalytic-cooxidative reagent	2.0×10^{-6}	[37]
	Luminol-horseradish peroxidase (HRP)-H_2O_2, HRP as a catalyst	8.0×10^{-6}	[38]
	Luminol-Co(II)-H_2O_2, Co(II) as a catalyst, enhanced by ultrasound	1.0×10^{-9}	[39]
	Luminol-dowex-50W-X4-Co(II)-monoethanolamine-H_2O_2, Dowex-50W-X4-Co(II)-monoethanolamine as a catalyst	1.0×10^{-7}	[40]
B	Luminol-H_2O_2	1.0×10^{-5}	[41]
	Amphiphilic luminol derivative-H_2O_2	1.0×10^{-7}	[42]
	$Ru(bpy)_3^{2+}$-H_2O_2	2.7×10^{-5}	[43]
	ZnSe quantum dots-H_2O_2	2.0×10^{-7}	[44]
	CdS nanocrystals/hemoglobin multilayers-H_2O_2	2.0×10^{-8}	[45]
	CdSe nanocrystal-H_2O_2	1.0×10^{-7}	[46]
Developed method	In pulse mode	6.0×10^{-8}	
	In potentiostatic mode	3.0×10^{-9}	

3.2. Investigation of the ECL response of hydrogen peroxide on developed FIA system

The experimental results show that hydrogen peroxide does not exhibit ECL activity but effectively enhances the ECL emission of luminol in 0.1 mol/L Na_2CO_3–$NaHCO_3$ (pH 9.16) buffer solution (see Fig. 2). In Fig. 2A, curve 1 is the recorded signal of hydrogen peroxide in the buffer medium; no indication of luminescence is observed. Curve 2 is the ECL spectrum of luminol in the buffer medium, which is a typical luminescence spectrum of luminol. Curve 3 is the ECL spectrum when hydrogen peroxide was piped into the luminol solution. In this curve, the intensity is obviously greater, but the spectral character remains the same. The latter is proven by Fig. 2B, in which there is a basically constant ratio between the ECL spectra of the enhanced and unenhanced luminol.

The ECL response of hydrogen peroxide (ΔI, the difference of ECL intensity with and without hydrogen peroxide) responds to its concentration. Similar to luminol, the ECL response of hydrogen peroxide is highly dependent on the pH and the buffer component. In weakly alkaline buffer (pH from 7.0 to 10.0), the gross ECL increases with the pH, but the signal quotient ($\Delta I/I_{gross}$) peaks between pH 8.0 and 9.0 (line 3 in Fig. 2C). The response of the buffer component was also compared, and the result is shown in Fig. 2D. Therefore, considering the discrimination and intensity of response, the 0.1 mol/L Na_2CO_3–$NaHCO_3$ (pH 9.16) buffer was selected.

The experimental results prove that both the pulsed and static modes of the potential worked well for exciting the ECL in this ECL-FIA system. For the pulsed potential, the period, upper and lower limiting potentials and the duty factor were optimized. As shown in Fig. 3A, despite the increasing background ECL with the increasing upper potential, the ECL response of hydrogen peroxide reached the highest level at the potential of 1.0 V. When the higher potential exceeded 1.0 V, it did not provide more sensitivity and caused poor repeatability. As indicated in Fig. 3B, the ECL background increased slightly with the pulse period from 0.5 s to 3 s, but the response for hydrogen peroxide somewhat decreased. When the pulsing period was very short (0.5 s), ΔI was larger but unstable. As the pulse period got longer, ΔI decreased, especially when exceeding 2.5 s. Between 1.0 s and 1.5 s, it changed less with good repeatability. Finally, 1.5 s was chosen as the pulse period for optimally counterbalanced ΔI and reproducibility. Fig. 3C describes the effect of the duty factor, ranging from 10% to 50%, on the ECL response; the ECL background barely changed, whereas ΔI became small. Thus, a 10% duty factor was chosen for the following experiments.

For the potentiostatic mode, the working potential was also optimized. The ECL response of hydrogen peroxide was strongly dependent on the voltage of the applied potential at the ITO working electrode. In Fig. 3D, the ECL response of H_2O_2 upon the applied potential from 0.4 V to 1.2 V is shown. The response was weak when the potential was below 0.6 V then increased sharply when the potential was more than 0.6 V. The final applied potential was set at 1.0 V for the optimization of both the response and repeatability.

In both two electrolytic modes, the influences of the flow rate on the ECL response of hydrogen peroxide were similar. As shown in Fig. 4, the higher flow rate resulted in a narrower peak (Fig. 4A and C) but a lower response (Fig. 4B and D). Considering a suitable peak width and the best response, 0.15 mL/min of flow rate was adopted.

The concentration of luminol in the background solution is also an important factor for the optimization of the ECL response of H_2O_2. Based on the consideration of the response distinguishable from the ECL background of luminol (Fig. 4E and F), 1.0×10^{-4} mol/L and 5.0×10^{-5} mol/L of luminol are befitting for pulsed mode and potentiostatic mode, respectively.

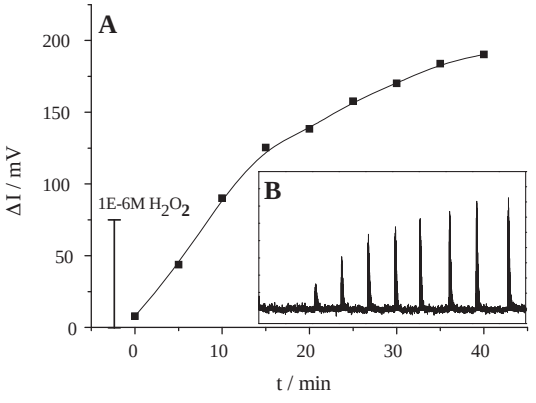

Fig. 5. The dynamic concentration of ROSs in the water vapour of ultrasonic humidifier.

3.3. The analytical performance of the developed ECL-FIA system

Under the abovementioned optimal conditions, the ΔI responded proportionally to the concentration of hydrogen peroxide in both electrolytic modes. The linear response range for H_2O_2 and the limit of detection (LOD) that was calculate from the 3 multiples of standard deviation of background divided by the slope of calibration curve of two ECL exciting modes have all been characterized. In the potentiostatic mode, there is a wide linear range from 5.0×10^{-9} mol/L to 5.0×10^{-6} mol/L ($\Delta I = 0.0259 + 3.50 \times 10^5 C_{H_2O_2}$, $r = 0.998$) with an LOD of 3.0×10^{-9} mol/L. In pulsed mode, there is a linear response for hydrogen peroxide from 2.0×10^{-7} mol/L to 4.0×10^{-6} mol/L ($\Delta I = -8.10 + 8.62 \times 10^7 C_{H_2O_2}$, $r = 0.999$) with an LOD of 6.0×10^{-8} mol/L. Compared to

Table 2
The detected results of trace amount ROSs in real water samples[a]..

Sample	ROSs concentration (mol/L)	Recovery (%)
Tap water	2.0 ± 0.8	106.0
Drinking water	7.1 ± 0.35	92.0
River water	No found	

[a] The amount of ROSs is indexed by the concentration of hydrogen peroxide and the recovery is gained by standard addition method.

potentiostatic mode, the absolute value of ECL intensity in pulsed mode is greater, and thus one third of the integration time is needed compared to as potentiostatic mode. Therefore, the detection takes less time and the stability of the ITO WE is better in pulsed mode. The ITO WE had to be replaced about weekly in potentiostatic mode but only every few months in pulsed mode. The comparison of the analytical performance of the developed ECL-FIA system to other reported systems is shown in Table 1. These data clearly indicate that the LOD of the developed system is significantly lower than other ECL systems and reaches to the level of CL methods. From another perspective, the mass detection limit, which was calculated from the concentration and 5 μL of sampling volume, reached to as low as 15 fmol, which is much lower than that of CL works [39,47].

3.4. Applicability to real samples

To demonstrate the applicability of the developed ECL-FIA system for the determination of ROSs, the developed system was used to monitor the ROSs yielding of an ultrasonic humidifier during its use, as illustrated in Fig. 5. In addition, samples of tap water, drinking water and river water around the campus were sampled and analysed. After filtration with a 0.22 μm cellulose acetate filter, the samples were injected into the system. With hydrogen peroxide as an index and a standard, the contents of ROSs in samples were quantified. The results are shown in Table 2. As can be seen, the recovery is between 92% and 106%.

4. Conclusion

A newly designed ECL-FIA system was constructed using a home-made flow-through ECL cell as the detector. By applying ITO glass as both the working electrode and the optical window for the ECL cell, a larger electro-active area was obtained. In addition, the ECL cell succeeded in reducing the dead volume. After the optimization of the mechanical, electrical and medium parameters, the response of hydrogen peroxide based on the enhancement for ECL of luminol was studied. Thus, the system was successfully used to establish a more sensitive and reproducible method for ROSs determination in various water samples.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (nos. 20275025, 20675055), the Natural Science Foundation of Jiangsu Province (BK2009111) and the Project of Science and Technology of Suzhou (SYJG0901). Thanks for helps from Dr. Liu Feng in National University of Singapore.

References

[1] G.D. Mendenhall, Angew. Chem. Int. Ed. Engl. 16 (1977) 225–232.
[2] K. Arai, K. Takahashi, F. Kusu, Anal. Chem. 71 (1999) 2237–2240.
[3] M.M. Richter, Chem. Rev. 104 (2004) 3003–3036.
[4] A.W. Knight, G.M. Greenway, Analyst 119 (1994) 879–890.
[5] C. Lu, G. Song, J. Lin, Trends Anal. Chem. 25 (2006) 985–995.
[6] D.W. Gunz, M.R. Hoffmann, Atmos. Environ. Part A 24 (1990) 1601–1633.
[7] W.J. Cooper, C.H. Shao, D.R.S. Lean, A.S. Gordon, F.E. Scully Jr., in: L.A. Baker (Ed.), Environmental Chemistry of Lakes and Reservoirs, American Chemical Society, Washington, DC, 1994, pp. 391–442.
[8] W.J. Cooper, R.G. Zika, R.G. Petasne, J.M.C. Plane, Environ. Sci. Technol. 22 (1988) 1156–1160.
[9] B.H. Halliwell, M.V. Clement, J. Ramalingam, H.L. Lee, IUBMB Life 50 (2000) 251–257.
[10] A. Tanhirovic, A. Copra, E.O. Miklicanin, K. Kalcher, Talanta 72 (2007) 1378–1385.
[11] S.H. He, W.B. Shi, X.D. Zhang, J. Li, Y.M. Huang, Talanta 82 (2010) 377–383.
[12] T.M. Freeman, W. Rudolf Seitz, Anal. Chem. 50 (1978) 1242–1246.
[13] Q.L. Ma, H.M. Ma, Z.H. Wang, M.H. Su, H.Z. Xiao, S.C. Liang, Talanta 53 (2001) 983–990.
[14] T.G. Burdo, W.R. Seltz, Anal. Chem. 47 (1975) 1639–1643.
[15] K. Hool, T.A. Nieman, Anal. Chem. 60 (1988) 834–837.
[16] F.J. Pérez, S. Rubio, Plant Growth Regul. 48 (2006) 89–95.
[17] O. Nozaki, H. Kawamoto, Luminescence 18 (2003) 203–206.
[18] J.Z. Li, P.K. Dasgupta, Anal. Chim. Acta 442 (2001) 63–70.
[19] F. Barni, S.W. Lewis, A. Berti, G.M. Miskelly, G. Lago, Talanta 72 (2007) 896–913.
[20] C.A. Marquette, L.J. Blum, Anal. Bioanal. Chem. 385 (2006) 546–554.
[21] T. Kuwana, B. Epstein, E.T. Seo, J. Phys. Chem. 67 (1963) 2243–2244.
[22] V.C. Tsafack, C.A. Marquette, B. Leca, L.J. Blum, Analyst 125 (2000) 151–155.
[23] B. Leca, L.J. Blum, Analyst 125 (2000) 789–791.
[24] A. Sassolas, L.J. Blum, B.D. Leca-Bouvier, Anal. Bioanal. Chem. 390 (2008) 865–871.
[25] D.W. King, W.J. Cooper, S.A. Rusak, B.M. Peake, J.J. Kiddle, D.W. O'Sullivan, M.L. Melamed, C.R. Morgan, S.M. Theberge, Anal. Chem. 79 (2007) 4169–4176.
[26] H.H. Chu, W.Y. Guo, J.W. Di, Y. Wu, Y.F. Tu, Electroanalysis 21 (2009) 1630–1635.
[27] Z. Chang, X.W. Zheng, J. Electroanal. Chem. 587 (2006) 161–168.
[28] M.A. Segundo, L.M. Magalhaes, J.P. Ribeiro, M. Lucio, S. Reis, Methods Mol. Biol. 704 (2011) 91–104.
[29] L.M. Magalhaes, M. Lucio, M.A. Segundo, S. Reis, J.L. Lima, Talanta 78 (2009) 1219–1226.
[30] C.Q. Yi, Y. Tao, B. Wang, X. Chen, Anal. Chim. Acta 541 (2005) 75–83.
[31] Y.W. Chi, J.P. Duan, Z.F. Zhao, H.Q. Chen, G.N. Chen, Electroanalysis 15 (2003) 208–218.
[32] Y.W. Chi, Y.Q. Dong, G.N. Chen, Anal. Chem. 79 (2007) 4521–4528.
[33] A.F. Martin, T.A. Nieman, Biosens. Bioelectron. 12 (1997) 479–489.
[34] Y.W. Chi, J.P. Duan, S.D. Lin, G.N. Chen, Anal. Chem. 78 (2006) 1568–1573.
[35] J.S. Littig, T.A. Nieman, Anal. Chem. 64 (1992) 1140–1144.
[36] D. Price, P.J. Worsfold, R. Fauzi, C. Mantoura, Anal. Chim. Acta 298 (1994) 121–128.
[37] Y.X. Zhou, T. Nagaoka, F. Li, G.Y. Zhu, Talanta 48 (1999) 461–467.
[38] J. Li, K.M. Wang, X.H. Yang, D. Xiao, Anal. Commun. 36 (1999) 195–197.
[39] G.M. Greenway, T. Leelasattarathkul, S. Liawruangrath, R.A. Wheatleya, N. Youngvises, Analyst 131 (2006) 501–508.
[40] J.M. Lin, X.Q. Shan, S. Hanaoka, M. Yamada, Anal. Chem. 73 (2001) 5043–5051.
[41] A. Chovin, P. Garrigue, N. Sojic, Electrochim. Acta 49 (2004) 3751–3757.
[42] T.F. Jiao, B.D. Leca-Bouvier, P. Boullanger, L.J. Blum, A.P. Girard-Egrot, Colloids Surf., A: Physicochem. Eng. Aspects 321 (2008) 143–146.
[43] B.Q. Yuan, H.W. Du, T.Y. You, Talanta 79 (2009) 730–733.
[44] X.F. Hu, H. Han, L.J. Hua, Z.H. Sheng, Biosens. Bioelectron. 25 (2010) 1843–1846.
[45] C.G. Shi, J.J. Xu, H.Y. Chen, J. Electroanal. Chem. 610 (2007) 186–192.
[46] G.Z. Zou, H.X. Ju, Anal. Chem. 76 (2004) 6871–6876.
[47] S. Sakura, Anal. Chim. Acta 262 (1992) 49–57.