

Account

Investigation of Chemiluminescence with Electrogenerated Reagents and Its Analytical Application

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In this paper, studies on chemiluminescence (CL) systems with electrogenerated reagents, including BrO^- , ClO^- , Br_2 , $[\text{Cu}(\text{HIO}_6)_2]^-$, H_2O_2 , Mn^{3+} , Co^{3+} and Ag^{2+} , are described. The analytical applications of the CL system with electrogenerated reagents are reviewed.

Keywords chemiluminescence, electrogenerated reagents, flow injection

Introduction

Although the first chemiluminescence (CL) phenomenon was reported more than 100 years ago,¹ application of the CL method in analysis became possible with appearance of the highly sensitive photomultiplier tube (PMT) in the 1950s. The high sensitivity and the simple instrumentation of modern CL analysis have attracted much interest in this field during the last 40 years. CL can easily be obtained by mixing a variety of redox reagents. Since Abbott *et al.*² reported the CL determination of morphine and its modification by oxidation with potassium permanganate, there have been increasing interest in the application of inorganic oxidate-based CL reactions to analytical chemistry. Inorganic oxidants, such as H_2O_2 , Br_2 , KMnO_4 , $\text{Ce}(\text{IV})$, $[\text{Ru}(\text{bpy})_3]^{2+}$, $[\text{Fe}(\text{CN})_6]^{3-}$, IO_4^- , ClO^- , BrO^- and BrO_3^- , were frequently used in a CL reaction. However, this method can not be employed if the reagents are not stable within the duration of the experiment. For example, the disproportionation of ClO^- or BrO^- is very easy in solution, so their applications in CL analysis are limited.

The application of strongly oxidizing agents in quantitative analysis has in general been restricted to those reagents that are not or only very slowly reduced by water, thus making possible the storage of standard solutions. Permanganate and cerium(IV) in acid solution, although thermodynamically unstable, fulfill this requirement. Stronger oxidants, such as cobalt(III), silver(II) and manganese(III), are quickly reduced by water, so their applications in quantitative analysis under normal condi-

tions are not possible.

The success of flow injection analysis (FIA) can be attributed to the reproducibility of the operations involved in the systems, such as injection, pumping and timing, allowing quantitative analysis without the necessity of completeness of the chemical reaction.³ As a complete chemical reaction is unnecessary, the idea arises that instability of the reagent also might be no objection as long as the reaction rate is reproducible. This would open possibilities for the application in quantitative analysis of these reagents, which are unstable under normal condition,⁴ by generating them in flow systems, starting from a stable oxidation state of the same element. In flow system, the unstable solution generated by chemical oxidation contains some superfluous oxidants, which interfere with the subsequent reaction. The electrochemical generation does not have the drawback mentioned above.

In our laboratories, the aim of the research work was focus on the development of new oxidants in CL analysis to extend the analytical applications or to improve the analytical performance of some CL systems relating to unstable oxidic reagents by combining flow-injection technique. Some reagents needed for the CL reaction are electrochemically produced and used as soon as they are formed. This is achieved by the sequential anodic oxidation of suitable and stable precursors. Therefore, these unstable oxidants, such as BrO^- , Br_2 , ClO^- , $[\text{Cu}(\text{HIO}_6)_2]^-$, H_2O_2 , Mn^{3+} , Ag^{2+} and Co^{3+} have been *on-line* or *in-situ* electrogenerated for this purpose. This not only eliminates the inconvenience of their instability, but also obtains some highly active and nascent reagents.

Electrogenerated chemiluminescence (ECL) has important advantages over more conventional CL. In early 1990s, Lin *et al.*^{5,6} firstly reported some ECL systems in China. Nowadays, Lin *et al.*⁷ reported some research about ECL in China. In this paper, the newly proposed ECL method is discussed in detail and recent progress in our group on this ECL and its analytical applications are reviewed.

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On-line electrogenerated BrO^- and ClO^- as the CL oxidant

Although the unstable CL oxidants such as ClO^- , BrO^- have been already used in CL analysis, the procedure for the preparation of its solutions often is time-consuming, complicated and even harmful. Thus, the further applications of these reagents in CL analysis were cumbrered.

In order to overcome this drawback, Teckentrup *et al.*⁸ designed a flow-through electrolytic cell to *on-line* electrogenerate BrO^- for this purpose in 1981. But their flow-through electrolytic cell was designed poorly, in which the two electrolytic chambers were at the same stream, and it only provided a low concentration of BrO^- . So this technique was not been paid much attention.

Up to 1999, Zhang *et al.*⁹ reported a flow-injection electrogenerated chemiluminescence (ECL) analysis. In this method, a novel flow-through electrolytic cell was designed (Fig. 1), in which its two electrolytic chambers were separated each other by the frit glass in order to keep away from the interference of H_2 bubbles generated on the face of the counter electrode. With this flow-through electrolytic cell, BrO^- was *on-line* electrogenerated quantitatively. Based on this flow-injection ECL system, some of the CL performance of BrO^- in CL analysis was then explored. For example, since the CL signal of BrO^- with luminol was very weak and the isoniazid can greatly enhance this weak CL signal, a more sensitive ECL method for the determination of isoniazid (Fig. 2) was developed.⁹ Furthermore, the sulfide ion with more reducing ability can react selectively with BrO^- to produce sulfide intermediate, which can further reduce the dissolving oxygen to generate active oxygen, thus the sulfide ion presents the enhance effects for the weak CL signal arising from the BrO^- with luminol. Based on this observation, a sensitive ECL method for the determination of sulfide ion was proposed.¹⁰

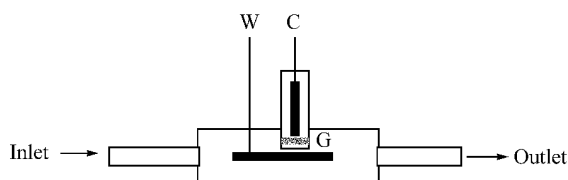


Fig. 1 Structure of the flow electrolysis cell : W, working electrode ; C, counter electrode ; M, frit glass.

Thereafter, ClO^- was also electrogenerated *on-line* with the similar way. ClO^- was *on-line* electrogenerated from KCl ($0.10 \text{ mol} \cdot \text{L}^{-1}$)- PBS ($0.01 \text{ mol} \cdot \text{L}^{-1}$) (pH 10.0). It was found that NH_4^+ and some drugs can enhance or inhibit the CL emission from the luminol- ClO^- system. The CL systems with electrogenerated ClO^- were applied to the determination of NH_4^+ ¹¹ and many drugs, such as etamsylate, dopamine, adrenaline and iso-

preenaline.¹²⁻¹⁴

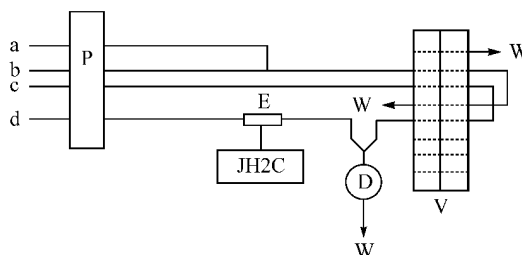


Fig. 2 Schematic diagram of FIA-CL system : a, luminol ; b, sample ; c, carrier stream ; d, KBr electrolyte ; P, peristaltic pump ; E, electrolytic flow cell ; JH2C, potentiostat ; D, detector ; V, six-way valve ; W, waste.

In-situ electrogenerated Br_2 as the CL oxidant

It is an important aspect of CL analysis to develop the sensitive CL analytical method for different analytes. For this purpose, many useful schemes, such as using the highly quantum yield fluorophore species to amplify the weak CL signal based on energy-transfer CL mechanism, using surfactant to change, or to modify the microenvironment of some emitters to improve the analytical performance of CL analysis, have been proposed.

In our previous paper,¹⁵ a novel flow-through CL reaction cell was designed (Fig. 3), in which an electrode was introduced into the cell to *in-situ* generate Br_2 in the near surface of the electrode by constant current oxidizing KBr in H_2SO_4 medium. Then, the electrogenerating Br_2

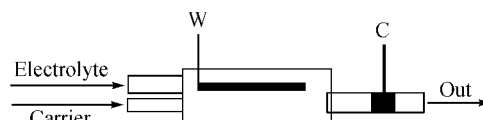


Fig. 3 Construction of the flow-through electrolytic cell : W, working electrode ; C, counter electrode.

could react with analyte (isoniazid), which was injected into the cell, in the diffusion layer of the electrode accompanying by the fast and stronger CL signal. Because the all CL reaction procedure, including the initial mixing point of electrogenerated Br_2 with isoniazid and the zone of making the subsequent CL reaction, not only was located on the near surface of the electrode, but was made in the front of the window of the photomultiplier tube, this novel flow-through electrolytic cell also can thus afford greater spatial and temporal control over this fast CL reaction initiation for analytical purpose. At the same time, the result (as shown in Fig. 4¹⁵) showed that the CL signal of *in-situ* electrogenerated Br_2 with isoniazid was nearly twenty times that of reagent Br_2 with isoniazid. Among these Br_2 solutions, the *in-situ* electrogenerated Br_2 possessed the highest reaction activity. This nascent state CL reaction active of the *in-situ* electrogenerated Br_2 was depended upon the electrogenerating time of Br_2 (as shown in Fig. 5¹⁵). After 30

min, this nascent state CL reaction active of *in-situ* electrogenerated Br_2 decreased dramatically. Based on this observation, one scheme by employing nascent state oxidant as the CL reagent to improve the sensitivity of CL analysis was also proposed firstly.

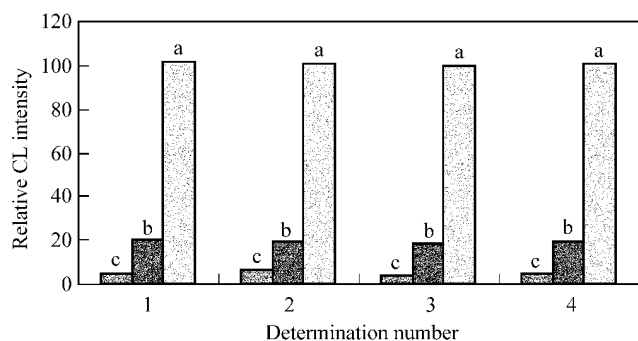


Fig. 4 CL contrast of nascent Br_2 (a), on-line electrogenerated Br_2 (b) and reagent Br_2 (c) with isoniazid: isoniazid, $3 \text{ g} \cdot \text{mL}^{-1}$; electrolytic current for generating Br_2 , 9 mA; reagent Br_2 , $1.5 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$.

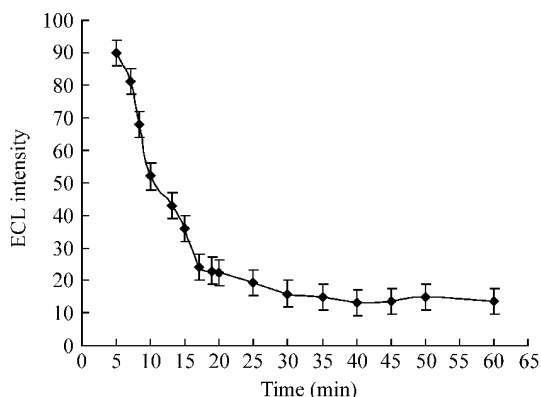


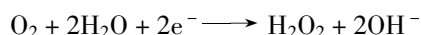
Fig. 5 Nascent Br_2 CL activity-time profile.

In addition, it was found that the *in-situ* electrogenerated Br_2 can oxidize H_2O_2 to generate strong CL emission signals. Based on this observation, a new, repeatable, rapid and selective FI-based ECL method for the determination of H_2O_2 was proposed.¹⁶ Compared with other ECL methods for the determination of H_2O_2 , the proposed method presented the followings advantages: (1) the Br_2 concentration and the zone of CL reaction of Br_2 with H_2O_2 can be well adjusted and controlled, respectively by adjusting both the electrolysis current and flow-rates of electrolyte or carrier stream. Thus, the areas of the subsequent CL reaction was extended and the sensitivity was improved; (2) the proposed FIA-based ECL method for the determination of H_2O_2 is rapid and simple, and present the better selectivity.

In-situ electrogenerated H_2O_2 as the CL oxidant

In recent years, the CL flow sensors based on immo-

bilized or solid-state reagents with obvious operational advantages have received much attention. The immobilization of reagent is a key problem in the design of these CL sensors. As a CL oxidant, H_2O_2 can not be immobilized by some conventional methods. It was suggested¹⁷ that H_2O_2 could be electrochemically generated at a negatively-based electrode from dissolved oxygen in the flow cell based on the following reaction:



So H_2O_2 was electrochemically immobilized *in-situ*. The flow cell was made of a mini-glass column ($20 \text{ mm} \times 3 \text{ mm}$ i. d.), which contained a gold working electrode with an area of $2 \text{ mm} \times 15 \text{ mm}$ exposed to the detector and a screw-in Ag/AgCl reference electrode. To complete the electrochemical cell, a stainless-steel tube placed at the exit of the flow cell was used as the counter electrode. For all experiments, the cell potential required to generate hydrogen peroxide was held at -0.5 V vs. Ag/AgCl . Furthermore, luminol was immobilized electrostatically on an anion-exchange column. By passing sodium phosphate through the column with immobilized luminol, luminol was eluted from the resin and then mixed and reacted with cobal(II) which was liberated from vitamin B_{12} by acidification and hydrogen peroxide in the flow cell under basic condition to produce the CL signal, by which vitamin B_{12} can be sensed. The CL emission was transduced to an electric signal by a Hamamatsu R456 photomultiplier tube placed close to the flow cell. The sensor for vitamin B_{12} described here (Fig. 6¹⁷) offers advantages of simplicity, rapidity as well as high sensitivity for the determination of vitamin B_{12} . The design of the sensor suggests a new ideal that the reagent can be immobilized by electrochemical method.

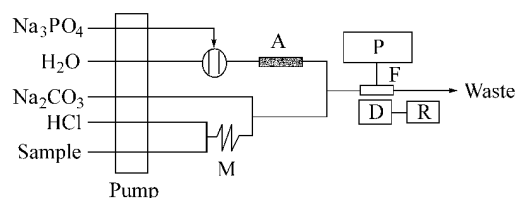


Fig. 6 Schematic diagram of the flow sensor for the determination of vitamin B_{12} : M, mixing coil; A, anion exchange column; P, potentiostat; F, flow cell; D, detector; R, recorder.

On-line electrogenerated Mn^{3+} as the CL oxidant

In general, the CL reaction can be achieved by the direct CL mechanism or energy-transfer mechanism. Compared with the direct CL analytical method, the energy-transfer CL analytical method presents the better analytical performance, such as the better selectivity inherent to fluorescence method and the wider analytical application

fields. Moreover, the investigation of the fluorescence analysis has provided the wider basic knowledge in this kind of CL method.

One typical example of these CL systems is the SO_3^{2-} -based weak CL system, many fluorophore species such as riboflavin, quinine and Rhodamine B, can amplify the weak CL signals arisen from the excited state SO_2^* .

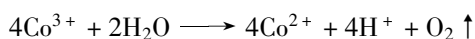
As reviewing those analytical results obtained in SO_3^{2-} -based CL systems, it can be found that the same weak CL precursor (SO_3^{2-}) can be oxidized to generate the same weak CL emitter of SO_2^* (excited state) by different oxidants such as MnO_4^- , hydrogen peroxide, O_2 and Ce^{4+} ,¹⁸⁻²¹ then this weak CL emitter can selectively and effectively transfer its energy to co-present fluorophore compounds to amplify the weak CL signals.

Quinine was selected as the testing fluorophore compound and the proposed ECL flow system was used to offer some unconventional oxidants, which might be more suitable to chemical-exciting quinine. The Mn^{3+} was then found to be the most suitable oxidant for chemical excitation of quinine in the SO_3^{2-} -based CL system. Based on this observation, a sensitive CL-based method for the determination of quinine was proposed,²² and a new concept of improving the sensitivity of some energy-transfer CL methods by modulating the oxidant used was also proposed.

As one useful CL oxidant, MnO_4^- has been widely used in CL analysis and many sensitive CL methods for the determination of many analytes were proposed. For improving the analytical performance of MnO_4^- -based CL system, many interesting efforts on the CL system have been made. Mn^{3+} was proposed as a key and effective oxidant in the CL reaction, but the CL analytical performance of Mn^{3+} was not reported. Based on this consideration, we firstly developed the direct CL analytical method based on CL reactions of Mn^{3+} with isoniazid.²³

On-line electrogenerated Co^{3+} as the CL oxidant

The $\text{Co}^{3+}/\text{Co}^{2+}$ system has a high redox potential (1.81 V) in mineral acid solution. As a stronger oxidant, Co^{3+} can oxidize a large number of organic and inorganic substances, but the application of Co^{3+} in analytical chemistry is few. The main reason is that Co^{3+} is very unstable in solution and is rapidly reduced by water,



We designed a novel electrolytic flow cell, and Co^{3+} was electrogenerated via a positive Pt-electrode from CoSO_4 in H_2SO_4 medium by constant-current electrolysis.²⁴ Furthermore, the condition of electrogeneration of Co^{3+} was optimized. CoSO_4 was used as the precursor of Co^{3+} . The concentration of CoSO_4 was expected to affect that of electrogenerated Co^{3+} , and $0.03 \text{ mol} \cdot \text{L}^{-1}$ was chosen as opti-

imum CoSO_4 concentration. In sulfuric acid medium, oxidation with Co^{3+} are often more rapid than with hydrated Co^{3+} .²⁵ So H_2SO_4 was used as the medium of the supporting electrolyte. The effect of H_2SO_4 concentration in the range of $3.0\text{--}10.0 \text{ mol} \cdot \text{L}^{-1}$ was investigated. The Co^{3+} concentration increased with the of increase H_2SO_4 concentration. The possible reason is that the reaction, $4\text{Co}^{3+} + 2\text{H}_2\text{O} \rightarrow 4\text{Co}^{2+} + 4\text{H}^+ + \text{O}_2 \uparrow$, can be suppressed by increasing the sulfuric acid concentration. That is to say, the ability to oxidize water decreases with acid concentration increasing. However, because of the durability of the tube and the occurrence of leakage in the connection, sulfuric acid concentration should be as low as possible for practical application in a flow system. So $7.0 \text{ mol} \cdot \text{L}^{-1}$ H_2SO_4 was chosen for further work. In this flow system, the electrolysis current could control the concentration of electrogenerated Co^{3+} . Too higher electrolysis current would result in decline of the current efficiency. The flow rate also affects the generation of Co^{3+} . Because the nascent Co^{3+} is very unstable and the half-life of Co^{3+} determined is about 60 s in the flow system, the flow rate would not lower than $2.0 \text{ mL} \cdot \text{min}^{-1}$. But the flow rate more than $4.0 \text{ mL} \cdot \text{min}^{-1}$ would lead to greater consumption of reagents and unacceptable reproducibility.

The electrogenerated Co^{3+} can oxidise directly quinine,²⁴ pipemidic acid²⁶ and gentamycin²⁷ in sulfuric acid medium to produce strong CL. In order to get an idea about the reaction generating the CL, the CL spectrum of the reaction was examined by a series of interference filters. The results indicated that there were two luminescence peaks at 480 nm and 580 nm, respectively. When nitrogen or oxygen was bubbled through the solutions, the CL intensity decreased with nitrogen and increased with oxygen. Furthermore, it was found that the CL spectrum of the reaction between Co^{3+} and pipemidic acid was the same as that of the reaction of Co^{3+} and quinine. The results showed that the reaction involved dissolved oxygen. The CL spectrum coincides with the emitting wavelength (480 and 580 nm) of excited double molecular oxygen (O_2)₂^{*}.²⁸ Since Khan and Kasha²⁹ reported the CL of hypochlorite-oxygen reaction as due to the liberated single oxygen, there have been many CL system^{30,31} concerned with (O_2)₂^{*}. It is proposed that (O_2)₂^{*} is the luminous species in this system. In this work, the formation of (O_2)₂^{*} may be two steps: one is generating HO_2^- free radicals, then HO_2^- can attack each other, giving a molecular pair (O_2)₂^{*}.³²

On-line electrogenerated Ag^{2+} as the CL oxidant

In the basic design of the ECL cell,³³ the electrolytic flow cell lay directly in front of the photomultiplier. Obviously, the electrolytic cell has an optical interference as a result of scattering, reflectance or absorbent by the electrode, and the optimum condition of the electrochemical

reaction would disagree with the optimum of the CL reaction.

An ECL cell was designed (Fig. 7), in which the electrolytic flow cell and the CL cell were separated each other and placed at different sites in the flow line, and the optical signal was detected in the CL cell. The new design avoided two main problems: the lack of reproducibility and the fouling of electrodes, when CL emission occurred directly on the surface of the electrode.³³ In this novel ECL cell, the unstable Ag^{2+} is *on-line* electrogenerated via a positive Pt-electrode from AgNO_3 in HNO_3 media by constant current electrolysis, so the Ag^{2+} has the property of the nascent state. The nascent Ag^{2+} is a powerful oxidizing reagent because the $\text{Ag}^+/\text{Ag}^{2+}$ system has a high redox potential (+1.91 V) in nitrate acid solution. Furthermore, it is found that nascent Ag^{2+} can oxidize sulfite to produce strong CL in nitrate acid media.³⁴ Based on this observation, an ECL flow system for sulfite was proposed. Compared with these reported CL systems for sulfite, in which various sensitizers were used such as Riboflavin, Tween-85, Rhodamine 6G, SDBS and 3-cyclohexylaminopropanesulfonic acid, the present method does not need any sensitizers and has been proved to be simple, rapid, sensitive, and suitable for automatic and continuous analysis. This method has been applied successfully to the determination of sulfur dioxide in air. Furthermore, Ag^{2+} can also oxidize captopril to produce CL in HNO_3 media.³⁵ The CL intensity emission intensity was linear with captopril concentration in the range of $0.02\text{--}10\ \mu\text{g}\cdot\text{mL}^{-1}$; The detection limit was $6 \times 10^{-9}\ \mu\text{g}\cdot\text{mL}^{-1}$ (3σ). The proposed method is suitable for automatic and continuous analysis and has been applied successfully to the analysis of captopril in pharmaceutical preparation.

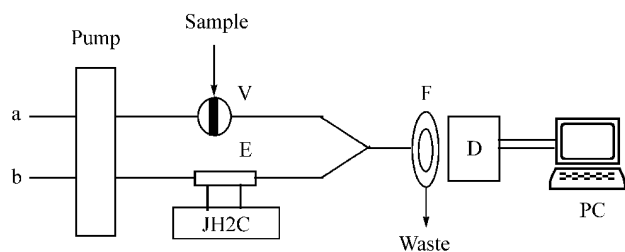
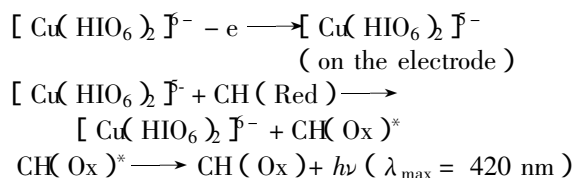


Fig. 7 Flow-injection manifold for quinine determination: a, H_2O carrier stream; b, $\text{CoSO}_4\text{-H}_2\text{SO}_4$ electrolyte; E, flow electrolysis cell; JH2C, galvanostat; F, CL reaction cell; V, valve; D, detector; PC, personal computer.

On-line electrogenerated $[\text{Cu}(\text{HIO}_6)_2]^-$ as the CL oxidant

$[\text{Cu}(\text{HIO}_6)_2]^-$ as the CL oxidant was reported in 1997,³⁹ but the procedure of $[\text{Cu}(\text{HIO}_6)_2]^-$ prepared by chemical oxidation with $\text{K}_2\text{S}_2\text{O}_8$ is time-consuming and very complicated. We *on-line* electrogenerated $[\text{Cu}(\text{HIO}_6)_2]^-$ from $\text{Cu}(\text{NO}_3)_2$ ($0.01\ \text{mol}\cdot\text{L}^{-1}$), KIO_4 ($0.2\ \text{mol}\cdot\text{L}^{-1}$) and KOH ($1\ \text{mol}\cdot\text{L}^{-1}$) by constant current electrolysis. Furthermore, its concentration can be *on-line* controlled with flow injection analysis technique and regulation of electrolytic current. It is found that $[\text{Cu}(\text{HIO}_6)_2]^-$ can oxidize chlortercyclini hydrochloridum to generate CL signal. Based this phenomenon, the CL method for determination of chlortercyclini hydrochloridum in the range of $1 \times 10^{-4}\text{--}1 \times 10^{-6}\ \text{g}\cdot\text{mL}^{-1}$ was presented.⁴⁰ The CL spectrum was obtained ($\lambda_{\text{max}} = 420\ \text{nm}$), which coincides with the fluorescence spectrum of the production of chlortercyclini hydrochloridum oxidized by the $[\text{Cu}(\text{HIO}_6)_2]^-$. So, the CL mechanism of the reaction in its simplest form may be attributed to the following reactions:



where CH is chlortercyclini hydrochloridum, Ox is the oxidized form, Red is the reduced form and $h\nu$ is the light emission.

Conclusion

The unstable and nascent reagents required for the CL reactions can be easily electrogenerated *on-line* or *in-situ* and lead to the method for many analytical applications. Table 1 summarizes some applications of CL with electrogenerated reagents. The electrogenerated strong oxidants Mn^{3+} , Co^{3+} and Ag^{2+} are first used as the CL oxidant. The methods improve the analytical performance of the CL systems of $[\text{Cu}(\text{HIO}_6)_2]^-$, BrO^- , Br_2 and ClO^- , and easily immobilized H_2O_2 in flow CL sensor. Further work on this subject is now in progress, aiming at capillary electrophoresis and HPLC applications. On the other hand, this ECL method is promising to be one detection method for micro total analysis system because of its high sensitivity and simplify.

Table 1 Application of CL with electrogenerated reagents

Analyte	Oxidant system	Detection limit	Ref.
Isoniazid	ClO^- -luminol- OH^-	$6 \times 10^{-9}\ \text{g}\cdot\text{mL}^{-1}$	12
Etamsylate	ClO^- -luminol- OH^-	$6 \times 10^{-10}\ \text{g}\cdot\text{mL}^{-1}$	13
Catecholamines	ClO^- -luminol- OH^-	$8 \times 10^{-10}\ \text{g}\cdot\text{mL}^{-1}$	14

Analyte	Oxidant system	Detection limit	Ref.
<i>L</i> -Dopamine	ClO ⁻ -luminol-OH ⁻	8 × 10 ⁻¹⁰ g·mL ⁻¹	36
NH ₄ ⁺	ClO ⁻ -luminol-OH ⁻	0.4 × 10 ⁻⁶ mol·L ⁻¹	11
Isoniazid	BrO ⁻ -luminol-OH ⁻	7.0 × 10 ⁻⁹ g·mL ⁻¹	9
S ²⁻	BrO ⁻ -luminol-OH ⁻	1.00 × 10 ⁻⁷ mol·L ⁻¹	10
Persantin	BrO ⁻ -luminol-OH ⁻	0.004 mg·L ⁻¹	37
Hydrazine	BrO ⁻ -luminol-OH ⁻	0.003 μg·mL ⁻¹	38
Vitamin B ₁₂	H ₂ O ₂ -luminol-OH ⁻	3.5 × 10 ⁻⁴ mg·L ⁻¹	17
Isoniazid	Br ₂ -H ⁺	1.2 × 10 ⁻⁸ g·mL ⁻¹	15
H ₂ O ₂	Br ₂ -H ⁺	3.3 × 10 ⁻⁷ mol·L ⁻¹	16
Isoniazid	Mn ³⁺ -H ⁺	3.2 × 10 ⁻² μg·mL ⁻¹	23
Quinine	Mn ³⁺ -H ⁺	1.0 × 10 ⁻⁷ mol·L ⁻¹	24
Gentamycin	Co ³⁺ -H ⁺	0.5 × 10 ⁻² μg·mL ⁻¹	27
Pipemidic acid	Co ³⁺ -H ⁺	3.3 × 10 ⁻⁹ g·mL ⁻¹	26
Quinine	Co ³⁺ -H ⁺	3.3 × 10 ⁻² μg·mL ⁻¹	24
Captopril	Ag ²⁺ -H ⁺	6 × 10 ⁻⁹ g·mL ⁻¹	35
Sulfite	Ag ²⁺ -H ⁺	1.4 × 10 ⁻⁷ mol·L ⁻¹	34
Chlortercyclini	[Cu(HIO ₆) ₂] ⁻ -OH ⁻	4.4 × 10 ⁻⁷ g·mL ⁻¹	40

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