

Chemiluminescence Behavior of Luminol-KIO₄-Ag Nanoparticles System and Its Analytical Applications

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Abstract

It was found that silver nanoparticles could strongly enhance the chemiluminescence (CL) of the luminol-KIO₄ system in the presence of Co²⁺. The most intensive CL signals were obtained with silver nanoparticles in diameter of 22 nm. The studies of UV-visible spectra and CL spectra were carried out to explore the possible CL enhancement mechanism. Moreover, the influences of 17 amino acids and 25 organic compounds on the luminol-KIO₄-Co²⁺-Ag NPs CL system were studied by a flow injection procedure, which led to an effective method to detect these compounds.

Keywords

Flow Injection, Luminol, Chemiluminescence, Silver Nanoparticle

1. Introduction

Chemiluminescence (CL) has received many chemists' attention due to its advantages: high sensitivity, simplicity, wide linear detection range and rapidity in signal detection [1]-[6]. In recent years, nanoparticles (NPs) have been widely studied for their excellent performance [7]-[11]. They display special optical, mechanical, electrical, magnetic and catalytic properties. Nanoparticles contained quantum size effect, volume effect, and surface effect that traditional solid material does not have [12]-[19]. It has been reported that metal nanoparticles have been applied to many fields, such as chemical engineering, biomedicine, environment, and electromagnetics. Using

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nanoparticles, especially metal nanoparticles, as catalysts for the chemiluminescence system has attracted considerable interest.

Recently, the combination of nanoparticles with chemiluminescence has attracted substantial interest because the noble metal nanoparticles have been found to participate in CL reactions as a catalyst, reductant, luminophor, and energy acceptor [20] [21]. For example, Lin *et al.* [22] [23] have reported that metal nanoparticles can enhance the CL of the luminol-H₂O₂ and NaHCO₃-H₂O₂ system. Cui's group applied noble metal nanoparticles to the CL reactions of lucigenin and potassium permanganate system [24] [25].

In this study, we examined the response of Ag NPs for CL intensity of the luminol-KIO₄-Co²⁺ system. The prepared Ag NPs displayed much stronger catalytic activity in presence of Co²⁺ on the luminol CL than single Ag NPs or Co²⁺. The effects of reaction conditions on the CL intensity were examined. Moreover, the possible enhancement mechanism of Ag NPs on luminol-KIO₄-Co²⁺ CL reaction was investigated in terms of the UV-visible and CL spectra in detail. In addition, the influences of amino acids and organic compounds on the luminol-KIO₄-Co²⁺-Ag NPs CL system were reported in extension.

2. Experimental Section

2.1. Reagents and Materials

All chemicals and reagents were analytically pure and used without further purification, and the deionized and triple-distilled water was used throughout.

A $2.5 \times 10^{-2} \text{ mol}\cdot\text{L}^{-1}$ stock solution of luminol (3-aminophthalhydrazide) was prepared by dissolving luminol (Fluka) in $0.1 \text{ mol}\cdot\text{L}^{-1}$ sodium hydroxide solution. Working solutions of luminol were prepared by diluting the stock solution with water. The $1.0 \times 10^{-2} \text{ mol}\cdot\text{L}^{-1}$ stock solution of periodate was prepared by dissolving 0.23 g KIO₄ (Shanghai, China) in $0.01 \text{ mol}\cdot\text{L}^{-1}$ sodium hydroxide solution, and stored in a brown bottle to avoid photochemical decomposition. Silver nitrate, trisodium citrate, hydroborate, amino acids and organics were obtained from Sinopharm Group Chemical Reagent Co. Ltd. (Shanghai, China).

2.2. Measurements

The CL measurements were conducted on a model IFFM-E flow injection CL Analysis system (Ruimai Electronic Science Co., Xi'an, China). The chemiluminescence signals were monitored by the PMT adjacent to the flow CL cell. The concentrations and flow rates of all the solutions were optimized. The CL spectra of this system were recorded with a Hitachi FL-4500 spectrofluorometer (Hitachi, Tokyo, Japan) combined with a flow-injection system, and its excitation light source being turned off. The UV-visible spectra were measured on a Hitachi UV-4100 PC spectrophotometer (Hitachi, Tokyo, Japan).

2.3. Synthesis of Ag NPs

Ag NPs (~5 nm in diameter) were obtained according to the literature [26]. First, 100 mL of a solution containing AgNO₃ and Na₃C₆H₅O₇, both in a concentration of $0.25 \text{ mmol}\cdot\text{L}^{-1}$, was prepared and stirred for 30 s. Then, 3 mL $1.0 \text{ mmol}\cdot\text{L}^{-1}$ solution of NaBH₄ (freshly prepared) was added quickly to the mixture. The solution immediately turned to yellow and was stirred for 60 s and then stored in refrigerator at 4°C before use.

Ag NPs (~16 nm in diameter) were prepared by following the previous reported method [27]. Briefly, 250 μL of AgNO₃ ($100 \text{ mmol}\cdot\text{L}^{-1}$) and 250 μL of sodium citrate ($100 \text{ mmol}\cdot\text{L}^{-1}$) were added into 100 mL water followed by the addition of 6 mL fresh NaBH₄ solution ($5 \text{ mmol}\cdot\text{L}^{-1}$) under vigorous stirring. The mixed solution was stirred for an additional 30 min and was left overnight before use.

Ag NPs (~22 nm in diameter) were synthesized according to the literature [28]. Shortly, 25 mL silver nitrate solution ($1.0 \text{ mmol}\cdot\text{L}^{-1}$) was added dropwise into 75 mL NaBH₄ solution ($2.0 \text{ mmol}\cdot\text{L}^{-1}$) under vigorous stirring. Ten minutes later, 5 mL 1% (w/w) sodium citrate aqueous solution was added to stabilize the colloid. The colloid was stirred for another 20 min and aged for 2 days at 4°C before use.

Ag NPs (~40 nm in diameter) were prepared according to the previous reported method [29]. Briefly, 2.0 mL of 1% (w/w) trisodium citrate was added into a boiling 50.0 mL AgNO₃ ($1.0 \text{ mmol}\cdot\text{L}^{-1}$) solution in a conical flask with continuous stirring and boiling for about 30 min; the aqueous mixture gradually changes into brown-yellow via yellow, indicating the formation of large Ag NPs. The colloidal solution of Ag NPs was continuous stirred until it had cooled down to room temperature.

2.4. Procedures

A diagram shown in **Figure 1** illustrates the flow injection chemiluminescence detection system employed in this work. The solutions of luminol, KIO_4 and carrier water were pumped into the flow cell by the peristaltic pump at the rate of $3.0 \text{ mL}\cdot\text{min}^{-1}$, respectively. The Ag NPs colloid solution mixed with Co^{2+} was injected by a valve injector with a sample loop of $100 \mu\text{L}$. The light output from the CL reaction was detected and amplified by the PMT and luminometer. The signal was imported to the computer for data acquisition. The net CL intensity $\Delta I = I_s - I_0$ was used for the quantitative determination, where I_s and I_0 were the CL intensity of sample and blank solutions, respectively.

3. Results and Discussion

3.1. CL Kinetic Characteristics

In this work, we have studied the kinetic characteristics of the CL reaction system, no obvious CL emission was observed when luminol was mixed with KIO_4 in the absence of Ag NPs or Co^{2+} . But when the Ag NPs with Co^{2+} solution was injected, a strong CL was detected from the luminol- KIO_4 system, as shown in **Figure 2**. All the prepared Ag NPs in diameters of 5, 16, 22, and 40 nm could initiate the CL, and the most intense CL signal occurred for 22 nm Ag NPs. Although NaBH_4 and AgNO_3 solutions could enhance the luminol CL signal from the figure, their enhancement effects were much lower than that of the Ag NPs and Co^{2+} solution. Therefore, it can be concluded that Ag NPs mix with Co^{2+} can initiate the CL emission of luminol- KIO_4 system.

3.2. Effect of Media and Concentration of Luminol

The effect of NaOH concentration was investigated. The range of NaOH concentration was from 0.01 to $0.2 \text{ mol}\cdot\text{L}^{-1}$. As shown in **Figure 3(A)**, (curve D), the luminous intensity of this system has significantly enhanced with the increase of NaOH concentration, but when the higher NaOH concentration led to a decrease in the CL intensity of this system. So a $0.05 \text{ mol}\cdot\text{L}^{-1}$ NaOH concentration in luminol was used in consequent research work.

The effect of luminol concentration on the increased CL intensity was examined in the range of $1 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$ to $7.5 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$. As can be seen in **Figure 3(B)**, the optimum concentration for the luminol maximum signal was $2.5 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$. Thus, this concentration was selected for further measurements.

3.3. Effect of Media and Concentration of KIO_4

The effect of the NaOH concentration on the CL signal was studied from $0.005 \text{ mol}\cdot\text{L}^{-1}$ to $0.2 \text{ mol}\cdot\text{L}^{-1}$. It was found (**Figure 3(A)**, curve II) that the relative CL intensity increased then got a maximum by increasing NaOH concentration up to $0.025 \text{ mol}\cdot\text{L}^{-1}$. Lower or higher concentration of NaOH caused a decrease of the CL signal. Therefore, this concentration was chosen for further study.

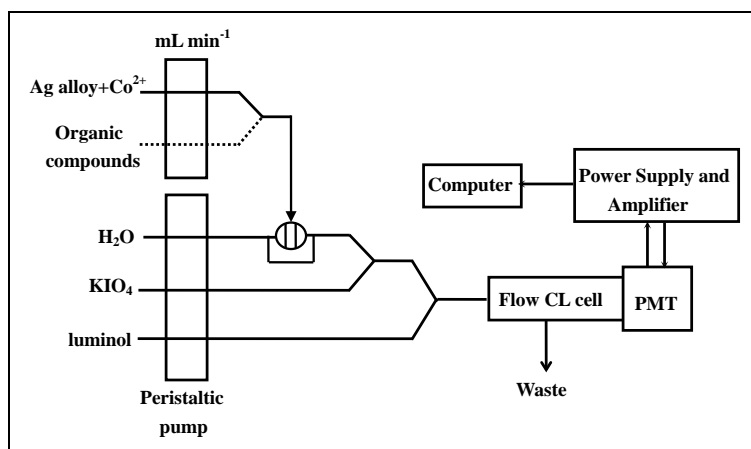


Figure 1. Schematic diagram of flow injection CL system.

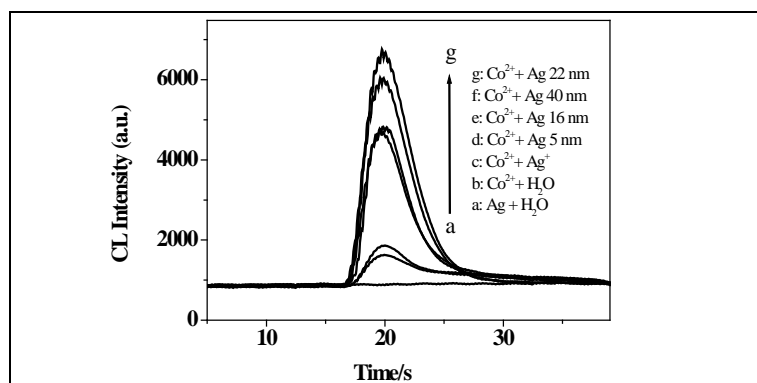


Figure 2. Kinetic characteristics of the luminol-KIO₄ CL system mixed with nanoparticles and blank solutions. Luminol solution: 2.5×10^{-4} mol·L⁻¹, 0.05 mol·L⁻¹ NaOH; KIO₄ solution: 3×10^{-4} mol·L⁻¹, 0.025 mol·L⁻¹ NaOH; Ag⁺ solution: 5×10^{-5} mol·L⁻¹; Co²⁺ solution: 2.5×10^{-5} mol·L⁻¹; silver colloids: 5×10^{-5} mol·L⁻¹ mol·L⁻¹.

In this CL system, KIO₄ was the oxidant, the concentration will affect the CL intensity. A study (shown in Fig. 3c) was carried out for the range of 5×10^{-5} mol·L⁻¹ to 4×10^{-4} mol·L⁻¹ KIO₄. The CL emission increased with the concentration of KIO₄, reaching a maximum for 3×10^{-4} mol·L⁻¹. The higher concentrations led to a decrease in the CL signal. Therefore, 3×10^{-4} mol·L⁻¹ KIO₄ was adopted for further use.

3.4. Effect of Ag NPs Concentration

The effect of Ag NPs concentration on CL reaction of luminol was investigated. As shown in Figure 3(D), the CL intensity increased with the concentration of Ag nanoparticles. Considering the CL intensity and the consumption of the reagents, the Ag NPs solution with concentration of 5×10^{-5} mol·L⁻¹ was chosen as the optimum concentration in this study.

3.5. Effect of Co²⁺ Concentration

It was known that the luminol-KIO₄ system produces weak CL, the intensity of the CL was slightly increased in the presence of Ag NPs. After adding different metal ions, we found that chemiluminescence intensity was greatly increased by adding Co²⁺. CL intensity increased multiplied with concentration of Co²⁺ and the maximum value occurs at 2.5×10^{-5} mol·L⁻¹. Thus, this concentration was chosen as the optimum concentration in this study.

3.6. Effect of Negative High Voltage and Flow Rate

The effect of negative high voltage and flow rate on the CL reaction was also examined. The relative CL intensity continued to increase with increasing negative high voltage and the flow rate, may be due to the reaction was very fast. However, a high negative high voltage and flow rate might lead to excessive consumption of the reagents. Therefore, 450 V negative high voltage and 3 mL·min⁻¹ of flow rate were adopted in this system.

3.7. Possible CL Mechanism Discussion

In order to explain the possible reaction mechanism of this CL enhancing phenomenon, the UV-Vis absorption spectra of the luminol-KIO₄-Ag NPs-Co²⁺ CL reaction were recorded, as shown in Figure 4(A). It could be seen that KIO₄ had no absorption (curve a), 22 nm Ag NPs (curve b) had a maximum absorption peak at around 398 nm, and luminal-KIO₄ (curve c) system had two absorption peaks at 296 nm and 346 nm. Whereas, the light absorption of the mixed system (curve e) was approximately equal to the sum of the light absorption of the two individual systems, which implied that no change was taken between the species after the reaction. Therefore, the enhancement of CL signals may have originated from the catalytic effects of Ag NPs and Co²⁺.

Thus the CL emission spectrum of the system was obtained using the modified FL-4500 fluorescence spectrophotometer, with the light source taken off, combined with a flow-injection system. The reaction mechanism

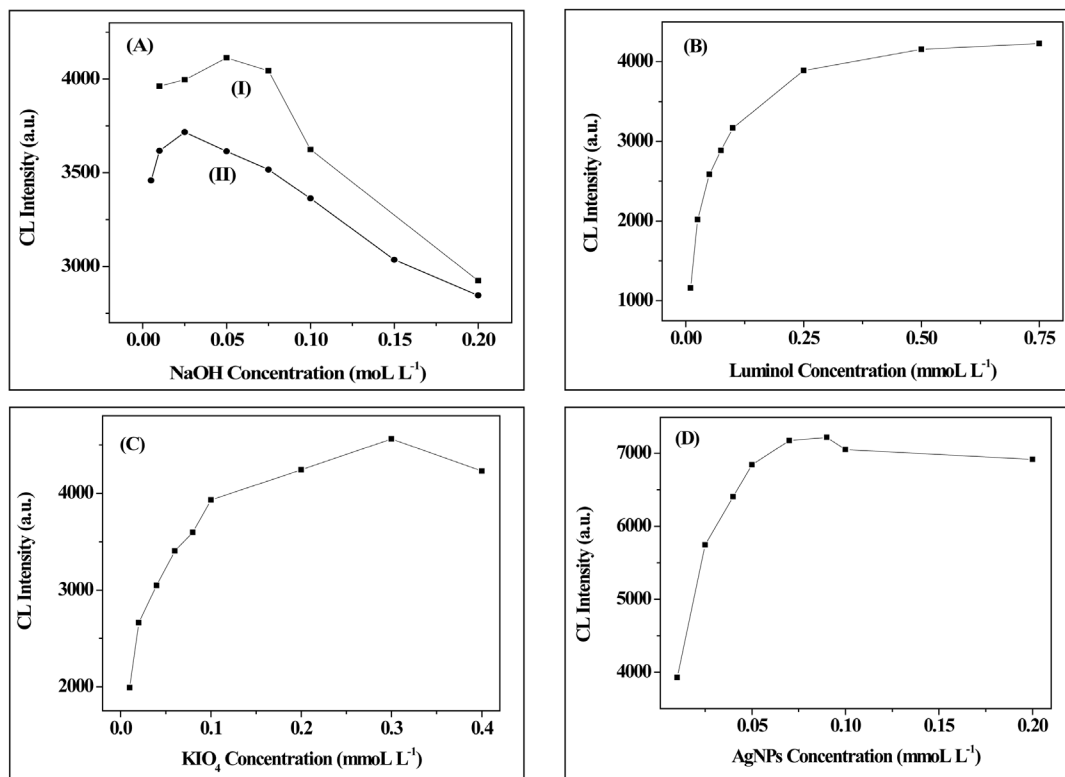


Figure 3. Effects of the reactant conditions on the luminal-KIO₄-Ag NPs-Co²⁺ colloids CL system. (a) Effect of NaOH concentration in luminol (curve I) and KIO₄ (curve II): 1.0×10^{-4} mol·L⁻¹ luminol, 5.0×10^{-4} mol·L⁻¹ KIO₄, 2.5×10^{-5} mol·L⁻¹ 22 nm Ag NPs, 2.5×10^{-5} mol·L⁻¹ Co²⁺; (b) Effect of luminol concentration: 0.05 mol·L⁻¹ NaOH in luminol, 5.0×10^{-4} mol·L⁻¹ KIO₄ (0.025 mol·L⁻¹ NaOH), 2.5×10^{-5} mol·L⁻¹ 22 nm Ag NPs, 2.5×10^{-5} mol·L⁻¹ Co²⁺; (c) Effect of KIO₄ concentration: 0.025 mol·L⁻¹ NaOH in KIO₄, 2.5×10^{-4} mol·L⁻¹ luminol (0.05 mol·L⁻¹ NaOH), 2.5×10^{-5} mol·L⁻¹ 22 nm Ag NPs, 2.5×10^{-5} mol·L⁻¹ Co²⁺; (d) Effect of 22 nm Ag NPs concentration: 2.5×10^{-4} mol·L⁻¹ luminol (0.05 mol·L⁻¹ NaOH), 3×10^{-4} mol·L⁻¹ KIO₄ (0.025 mol·L⁻¹ NaOH), 2.5×10^{-5} mol·L⁻¹ Co²⁺.

of oxidation of luminol is believed to involve the superoxide radical $O_2^{\bullet-}$ or hydroxyl radical OH^{\bullet} as the important intermediates leading to luminescence. During the luminol oxidation processes, the presence of oxygen-related radicals (for example, OH^{\bullet} , $O_2^{\bullet-}$, and other radical derivatives) as oxidants is expected to occur. The reaction of luminol with periodate in alkaline solution in the absence of a catalyst underwent weak CL. It is assumed that the catalyst Ag NPs and Co²⁺ may interact with the reactants or the intermediates of the reaction of luminol with KIO₄. When Ag NPs and Co²⁺ were used as the catalysts, active oxygen-containing reactant intermediates, such as superoxide anion ($O_2^{\bullet-}$), hydroxyl radical (OH^{\bullet}), formed. So in this system it can be concluded that the enhancement effect on CL by Ag NPs and Co²⁺ is attributed to the formation of $O_2^{\bullet-}$. Then, the resulting products such as superoxide anion reacted with luminol to form luminol radical and diazaquinone, giving rise to light emission. As a result, the emission enhanced [7] [9].

The results (Figure 4(B)) showed that the maximum emission wavelength of the luminal-KIO₄-Ag NPs-Co²⁺ CL system was 425 nm. It is well known that aminophthalate is the luminophor, and the maximum emission of the CL reaction is at 425 nm [30] [31]. Thus, the luminophor in the both CL reactions between luminol and KIO₄ with and without Ag NPs and Co²⁺ was the same species, which was the oxidation product aminophthalate of luminol. The schematic reaction mechanism could be expressed as Scheme 1.

3.8. Influence of Organics and Amino Acids

In the luminal-KIO₄-Ag NPs-Co²⁺ CL system, some intermediate radicals such as $O_2^{\bullet-}$ and HO^{\bullet} were formed during the reaction. The reducing groups of NH₂, OH, or SH is likely to compete with luminol for active oxygen intermediates, leading to a decrease in CL intensity. Therefore, these compounds may interact with Ag nanopar-

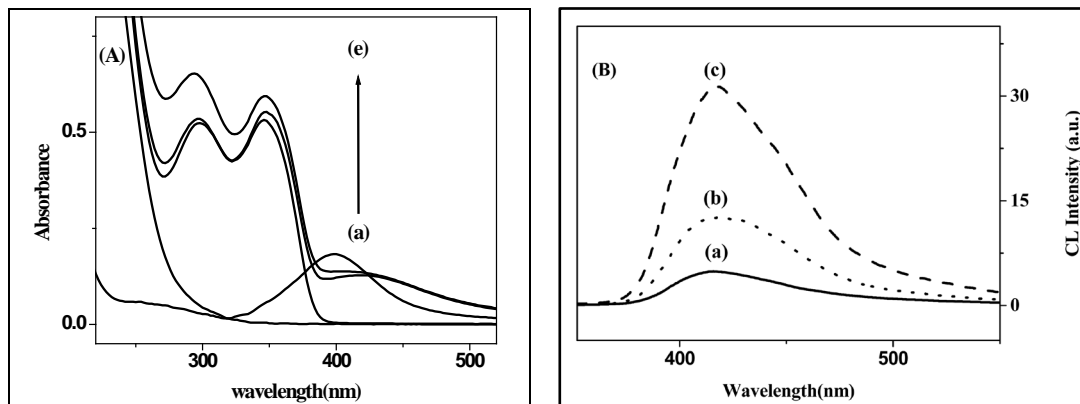
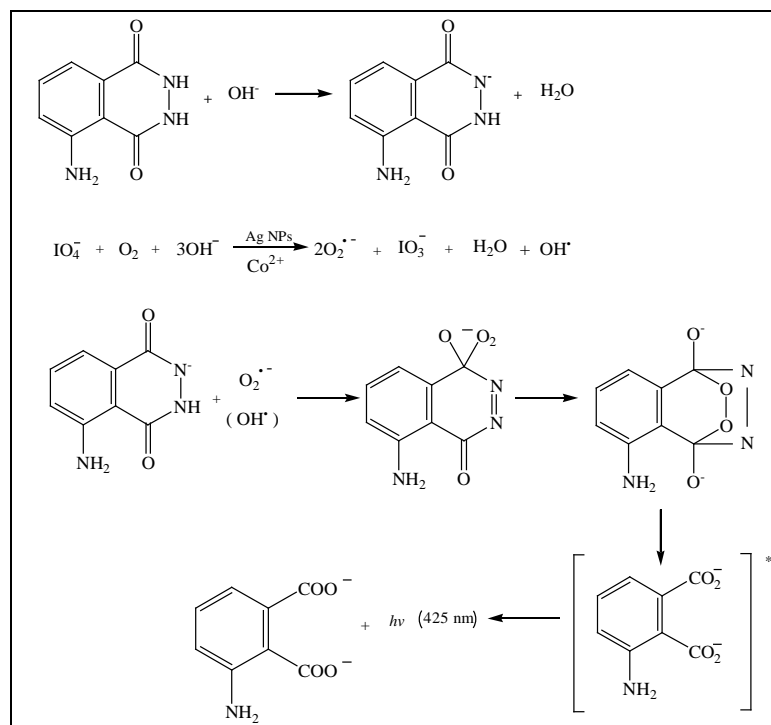


Figure 4. (A) UV-visible absorption spectra of (a) KIO_4 ; (b) 22 nm Ag NPs; (c) luminol- KIO_4 ; (d) luminol- KIO_4 -Ag NPs; (e) luminol- KIO_4 -Ag NPs- Co^{2+} ; (B) CL spectra for luminol- KIO_4 -Ag NPs- Co^{2+} CL system (a) luminol- KIO_4 ; (b) luminol- KIO_4 -Ag NPs (22 nm); (c) luminol- KIO_4 -Ag NPs (22 nm)- Co^{2+} .



Scheme 1. Possible mechanism for the luminol- KIO_4 -Ag NPs- Co^{2+} CL system.

ticles to interrupt the formation of luminol radicals ($\text{L}^{\bullet-}$) and superoxide radical anion ($\text{O}_2^{\bullet-}$), resulting in a decrease in CL intensity. Under the selected optimum conditions given above, the effects of 17 amino acids and 25 organic compounds on the luminol- KIO_4 -Ag NPs- Co^{2+} system were investigated. As can be seen in **Table 1**, some amino acids and organic compounds have an intensive influence on this system. The results demonstrate that the luminol- KIO_4 -Ag NPs- Co^{2+} CL system has a wide application for the determination of such compounds.

The analytical potential of the enhanced and inhibited effects for seven selected compounds are presented in **Table 2**. The regression equation, correlation coefficients were also summarized. It can be seen that the luminol- KIO_4 -Ag NPs- Co^{2+} CL system has a wide application for the determination of these organics.

3.9. Application

Under the best analytical conditions, the content of pyrogallal acid in synthesized samples were determined. The

Table 1. Effects of amino acids and organic compounds on the luminol-KIO₄-Ag NPs-Co²⁺ CL system.

Organic compounds	ΔI	Organic compounds	ΔI
Pyrogalllic acid	11,467	L-cysteine	8330
L-epinephrine	2457	L-histidine	43
Gallic acid	425	L-asparagine	-513
Riboflavin	355	L-tryptophan	-466
Hydroquinone	-3231	L-glycine	-307
Pyrocatechol	-3209	L-tyrosine	-222
L-dopamine	-3202	L-iso-leucine	-216
p-t-butylpyrocatechol	-3159	L-arginine	-147
L-ascorbic acid	-2800	L-proline	-124
Resorcinol	-2742	L-cystine	-112
p-aminophenol	-1580	L-threonine	-110
5-sulfosalicylic acid	-1547	L-leucine	-92
Ethyl naphthol	-1097	L-aspartic acid	-81
Aniline	-917	L-valine	-70
p-aminobenzoic acid	-567	L-phenylalanine	-35
o-aminobenzoic acid	-538	L-serine	-6
p-nitroaniline	-447	L-methionine	-2
o-methoxyphenol	-404	Benzoic acid	-317
p-nitrylbenzoic acid	-377	2,4-dihydroxybenzoic acid	-315
3,5-dinitrylbenzoic acid	-345	Salicylic acid	-186
Sulfanilic acid	-339	Acetanilide	-99

Concentration of organic compounds: 1×10^{-5} g·mL⁻¹, ΔI : net CL Intensity. CL conditions: luminol: 2.5×10^{-4} mol/L (0.05 mol·L⁻¹ NaOH), KIO₄: 3×10^{-4} mol·L⁻¹ (0.025 mol·L⁻¹ NaOH), 22 nm Ag NPs: 2.5×10^{-5} mol·L⁻¹, Co²⁺: 2.5×10^{-5} mol·L⁻¹, Flow rate: 3.0 mL·min⁻¹, Negative high voltage: 450 V, I_0 obtained by luminol-KIO₄-Ag-Co²⁺ CL system was 3111.

Table 2. Analytical parameters of the proposed luminol-KIO₄-Ag NPs-Co²⁺ CL system.

Organic compounds	Linear range (g·mL ⁻¹)	Regression equation (C: g·mL ⁻¹)	Correlation coefficient
Pyrocatechol	3×10^{-10} - 1×10^{-8}	$\lg(-\Delta I) = 6.6832 + 0.3947 \lg C$	0.9937
L-dopamine	9×10^{-11} - 5×10^{-8}	$\lg(-\Delta I) = 6.8107 + 0.4610 \lg C$	0.9933
L-ascorbic acid	6×10^{-11} - 2.5×10^{-7}	$\lg(-\Delta I) = 4.4666 + 0.2619 \lg C$	0.9932
Hydroquinone	6×10^{-11} - 2.5×10^{-8}	$\lg(-\Delta I) = 10.0460 + 0.8444 \lg C$	0.9904
Resorcinol	6×10^{-11} - 2.5×10^{-8}	$\lg(-\Delta I) = 3.5072 + 0.1571 \lg C$	0.9951
Pyrogalllic acid	1×10^{-10} - 1×10^{-5}	$\lg \Delta I = 6.9787 + 0.5314 \lg C$	0.9971
L-cysteine	5×10^{-8} - 1×10^{-5}	$\lg \Delta I = 8.5024 + 0.8499 \lg C$	0.9929

results shown in **Table 3** indicated that this new flow injection chemiluminescence method was sensitive and accurate for the pyrogalllic acid detection.

Table 3. Determination of pyrogalllic acid in synthesized samples.

Sample	Initially present (g·mL ⁻¹)	Added (g·mL ⁻¹)	Found (g·mL ⁻¹)	Recovery (%)
1	0.99 × 10 ⁻⁸	2.0 × 10 ⁻⁸ 3.0 × 10 ⁻⁸	2.93 × 10 ⁻⁸ 3.96 × 10 ⁻⁸	98.0 99.2
2	1.46 × 10 ⁻⁸	1.0 × 10 ⁻⁸ 3.0 × 10 ⁻⁸	2.42 × 10 ⁻⁸ 4.48 × 10 ⁻⁸	98.4 100.4
3	2.03 × 10 ⁻⁸	2.0 × 10 ⁻⁸ 3.0 × 10 ⁻⁸	4.07 × 10 ⁻⁸ 4.97 × 10 ⁻⁸	101.0 98.8
4	2.49 × 10 ⁻⁸	1.0 × 10 ⁻⁸ 2.0 × 10 ⁻⁸	3.46 × 10 ⁻⁸ 4.55 × 10 ⁻⁸	99.1 101.3
5	3.03 × 10 ⁻⁸	1.0 × 10 ⁻⁸ 2.0 × 10 ⁻⁸	4.11 × 10 ⁻⁸ 4.93 × 10 ⁻⁸	102.0 98.0

4. Conclusion

In the present study, Ag NPs could strongly enhance the CL of the luminol-KIO₄ system in the presence of Co²⁺. Based on the studies of UV-visible spectra, PL spectra and CL spectra, the possible CL enhancement mechanism is proposed. Moreover, we studied the effects of 17 amino acids and 25 organic compounds on the luminol-KIO₄-Ag NPs-Co²⁺ system, most of which showed a strong inhibition effect, and others had an enhancing effect. So we could establish a novel CL method to determinate these organic compounds.

Acknowledgements

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