



Flow-injection chemiluminescence determination of dihydralazine sulfate in serum using luminol and diperiodatocuprate (III) system

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ARTICLE INFO

Article history:

Received 14 January 2009

Received in revised form 23 August 2009

Accepted 25 September 2009

Keywords:

Chemiluminescence
Diperiodatocuprate
Dihydralazine sulfate
Serum

ABSTRACT

A novel flow-injection chemiluminescence (CL) method for the determination of dihydralazine sulfate (DHZS) is described. The method is based on the reaction of luminol and diperiodatocuprate ($K_2[Cu(H_2IO_6)(OH)_2]$, DPC) in alkaline medium to emit CL, which is greatly enhanced by DHZS. The possible CL mechanism was first proposed based on the kinetic characteristic, CL spectrum and UV spectra. The optimum condition for the CL reaction was in detail studied using flow-injection system. The experiments indicated that under optimum condition, the CL intensity was linearly related to the concentration of DHZS in the range of 7.0×10^{-9} to 8.6×10^{-7} g mL⁻¹ with a detection limit (3σ) of 2.1×10^{-9} g mL⁻¹. The proposed method had good reproducibility with the relative standard deviation 3.1% ($n=7$) for 5.2×10^{-8} g mL⁻¹ of DHZS. This method has the advantages of simple operation, fast response and high sensitivity. The special advantage of the system is that very low concentration of luminol can react with DPC catalyzed by DHZS to get excellent experiment results. And CL cannot be observed nearly when luminol with same concentration reacts with other oxidants, so luminol–DPC system has higher selectivity than other luminol CL systems. The method has been successfully applied to determine DHZS in serum.

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1. Introduction

Dihydralazine sulfate (DHZS, Fig. 1), which contains two hydrazine groups, is a well-known antihypertensive compound. It can induce peripheral vasodilatation, thereby reducing peripheral vascular resistance and thus lowering elevated blood pressure. Several methods have been reported for its determination in pharmaceutical preparations, including spectrophotometry [1,2], liquid chromatography [3–5] and also CL method [6–10].

Flow-injection CL method is known to be a powerful analytical technique that possesses low detection limit, a wide linear dynamic range and relatively simple and inexpensive instrumentation [11,12]. Trivalent copper is in the highest oxidation state which can be stabilized by chelating with suitable polydentate ligands. Although there are many reports concerning the use of diperiodatocuprate (III) (DPC) as oxidant, the use of DPC in CL analysis is relatively few [13–15]. In recent studies, it was found that CL phenomena accompanied with reaction between DPC and luminol in alkaline medium with low concentration of luminol, which could be significantly enhanced by DHZS. According to previously study, it was found that the reaction of DPC and luminol can emit CL with low concentration of luminol, but CL cannot be observed nearly when luminol with same concentration reacts with other

oxidants. In the experiment, it was found that the CL intensity of luminol–DPC reaction can be greatly enhanced by DHZS. Under the same condition, the CL intensity of luminol–H₂O₂–metal ion system, which is one of the most important luminol CL systems, was much lower than luminol–DPC–DHZS. So this method possesses particular advantage which is less luminol consumption than other luminol CL systems. So the method holds higher selectivity than other luminol CL systems because of using low luminol concentration. Based on these observations, a novel flow-injection CL method for the determination of DHZS was developed. Under optimum conditions, the relative CL intensity was linearly related to the concentration of DHZS in the range of 7.0×10^{-9} to 8.6×10^{-7} g mL⁻¹ with a detection limit (3σ) of 2.1×10^{-9} g mL⁻¹. The method has been successfully applied to determine DHZS in serum. The possible CL mechanism was first proposed briefly.

2. Experimental

2.1. Reagents

Potassium persulfate (Shanghai Aijian Chemical Reagent Company), potassium hydroxide, Hydrogen peroxide, Sodium nitrate, sodium periodate, nickel sulfate, calcium chloride (Shanghai Chemical Reagent Company). All the reagents were of analytical grade. Deionized and doubly distilled water was used throughout the work.

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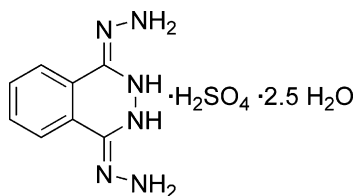


Fig. 1. The structure of DHZS.

A stock solution of $1.0 \times 10^{-4} \text{ g mL}^{-1}$ DHZS (Wuhan Yuancheng Technology Development Co., Ltd.) was prepared by dissolving appropriate amount of DHZS in warm water and diluting to the mark with water. The $1.0 \times 10^{-2} \text{ mol L}^{-1}$ luminol stock solution was prepared by dissolving 1.772 g luminol in 1 L 0.1 mol L^{-1} carbonate buffer and left to stand for approximately 24 h before use. The luminol solution was stable for at least 1 month when stored in dark.

2.2. Apparatus

The flow system used in this work is shown in Fig. 2. Two peristaltic pumps (HL-2, Shanghai Huxi, China) were used to deliver all flow streams. Polytetrafluoroethylene (PTFE) tubing (0.8 mm i.d.) was used as connection tubing in the flow system. Sample solution was injected by a eight-way injection valve into the carrier stream (H_2O) and then merged with CL reagents in a spiral flow cell in the front of a photomultiplier tube (PMT). The CL signal was monitored by IFFM-A multifunction chemiluminescence analyzer (Remex Analytical Instrument Co. Ltd., Xian, China). The UV absorbance was detected by the TU1901 UV-vis spectrophotometer (Beijing Purkinje General Instrument Co., Ltd., China). The chemiluminescence spectrum was monitored using F-4600 fluorescence spectrophotometer (Shimadzu, Japan).

Not less than 20 tablets were weight, ground to a fine powder, and mixed. A sample equivalent to approximately 10 mg of DHZS was weighed accurately and dissolved with 50 mL of double-distilled warm water. The resulting mixture was filtered and the filtrate was transferred into a 100 mL flask and diluted to the mark with water. This solution was further diluted with water appropriately so that the final DHZS concentration was within the working range.

2.3. Preparation of DPC

The diperiodatocuprate (III) was prepared by oxidizing Cu (II) in the alkaline medium [16]. $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (1.56 g), NaIO_4 (2.67 g), $\text{K}_2\text{S}_2\text{O}_8$ (1 g) and KOH (8 g) were added in 100 mL water. The mixture was heated to boiling for about 20 min on a hot plate with constant stirring. The boiling mixture turned intensely red and the

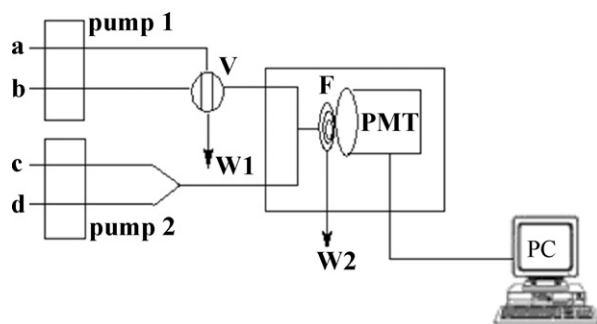


Fig. 2. Schematic diagram of the CL-FIA system a: DHZS solution or samples; b: distilled water; c: luminol solution; d: DPC solution; V: injection valve; F: spiral glass flow cell; PMT: photomultiplier tube; pump1, pump2: peristaltic pump.

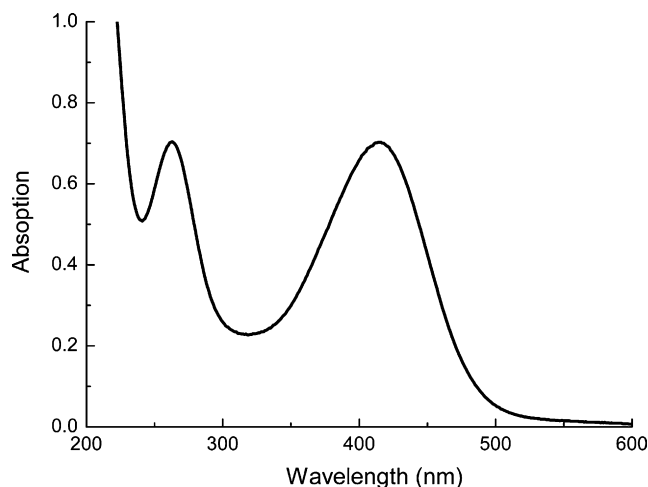


Fig. 3. The UV-vis absorption spectra of DPC.

boiling was continued for another 20 min for the completion of the reaction. The mixture was then cooled, filtered through sintered glass crucible. The solution was cooled in an ice bath to eliminate as much of potassium sulfate as possible and filtered again while it was cold. The resulting brown clear filtrate was left to attain room temperature. In order to isolate the complex, 40 mL of NaNO_3 solution (50%, in excess) was added to the solution and the mixture left to crystallise. Almost immediately dark brown crystals started appearing and crystallisations were complete when the supernatant liquid was colorless. The crystals were filtered and washed several times with doubly distilled water until the complex itself started dissolving, which was indicated by the brown drops being formed under the crucible. Then the dark brown crystals of DPC were obtained.

The DPC solutions were freshly prepared by dissolving an amount of complex in $1.0 \times 10^{-2} \text{ mol L}^{-1}$ KOH solution before use. The complex was characterized by its UV/visible spectrum, which exhibits a broad absorption band at 415 nm (Fig. 3). The aqueous solution of DPC was standardized by a standard procedure [17].

2.4. General procedure

The FIA-CL configuration used is outlined in Fig. 2. In order to achieve good mechanical and thermal stability, the instruments were allowed to run for 10 min before the first measurement was made. The flow line were connected with DHZS standard solution (a), a carried H_2O (b), $6.0 \times 10^{-8} \text{ mol L}^{-1}$ luminol solution in $1.0 \times 10^{-3} \text{ mol L}^{-1}$ potassium hydroxide (c), $1.0 \times 10^{-4} \text{ mol L}^{-1}$ DPC solution in $4.0 \times 10^{-2} \text{ mol L}^{-1}$ potassium hydroxide (d). Luminol solution was firstly mixed with DPC solution to give stable base-line. The 100 μL solution of standard DHZS was injected into the carrier stream via the sample injection valve which pumped continuously. The mixture passed through the flow cell, while the CL signal was recorded by IFFS-A multifunction chemiluminescence analyzer.

3. Result and discussion

3.1. Kinetics curve of the CL reaction

In order to determine the life of the CL, the dynamical profile of the CL reaction was tested with a static system. In static mode, the experimental parameters were kept constant, the CL intensity-time profile of luminol ($1.0 \times 10^{-7} \text{ mol L}^{-1}$) CL reaction catalyzed by DHZS ($5.2 \times 10^{-8} \text{ g mL}^{-1}$) in the present DPC ($1.0 \times 10^{-4} \text{ mol L}^{-1}$)

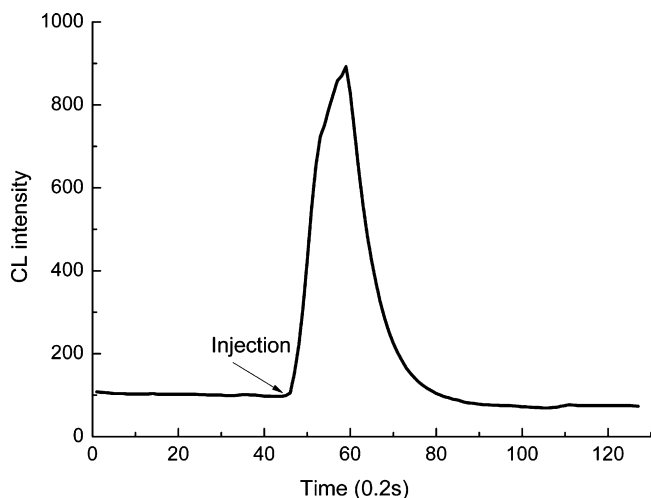


Fig. 4. Kinetics curves of luminol–DPC catalyzed by DHZS luminol: $1.0 \times 10^{-7} \text{ mol L}^{-1}$; DPC: $1 \times 10^{-4} \text{ mol L}^{-1}$; DHZS: $8 \times 10^{-8} \text{ g mL}^{-1}$.

was recorded to study the kinetic characteristic. Fig. 4 demonstrates that the CL reaction was very quick. The CL intensity peak appeared within 3 s since the DHZS solution was injected. The CL signal would decrease to baseline at within 2 s. The kinetic curve indicated the CL system is rapid and sensitive enough and suitable to perform determination of DHZS.

3.2. Stability of DPC

Trivalent copper is in the highest oxidation state which should be stabilized by chelating with suitable polydentate ligands due to the fact of its limited stability. The stability of DPC in aqueous solution was studied by the variety of CL intensity of luminol–DPC–DHZS within 2 h (Fig. 5). As can be seen, the CL intensity varied little within 2 h when DPC concentration was up to $6.0 \times 10^{-5} \text{ mol L}^{-1}$. The stability can achieve the test requirement.

3.3. Possible reaction mechanism

In order to explain the possible reaction mechanism, the CL spectra of the luminol–DPC reaction in the absence and presence of DHZS were measured using an F-4600 fluorescence spectropho-

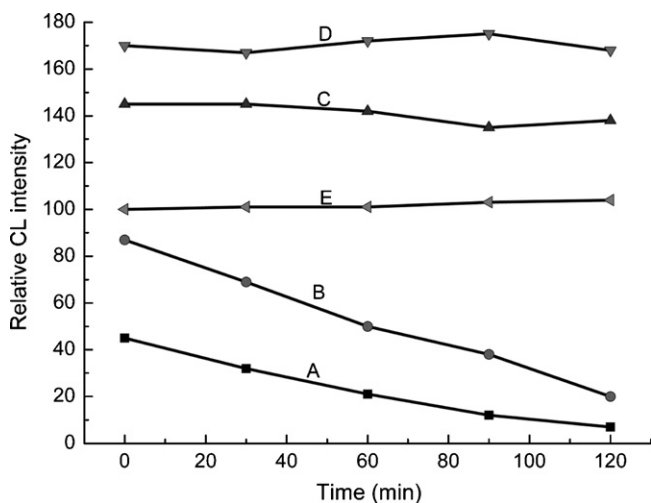


Fig. 5. The stability of DPC luminol: $1.0 \times 10^{-7} \text{ mol L}^{-1}$; DHZS: $4.0 \times 10^{-8} \text{ g mL}^{-1}$; DPC: $1.0 \times 10^{-5} \text{ mol L}^{-1}$ (A); $2.0 \times 10^{-5} \text{ mol L}^{-1}$ (B); $6.0 \times 10^{-5} \text{ mol L}^{-1}$ (C); $1.0 \times 10^{-4} \text{ mol L}^{-1}$ (D); $2.0 \times 10^{-4} \text{ mol L}^{-1}$ (E).

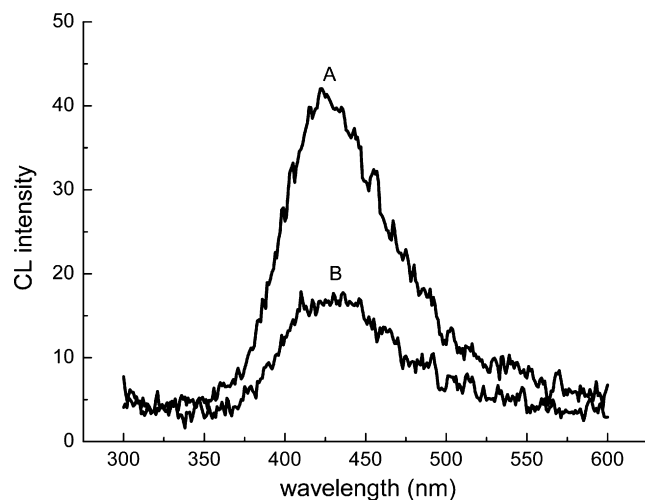


Fig. 6. CL spectrum of luminol and DPC catalyzed by DHZS in the presence (A) and absence (B) conditions luminol: $1.0 \times 10^{-4} \text{ mol L}^{-1}$; DPC: $1.0 \times 10^{-4} \text{ mol L}^{-1}$; DHZS: $2.0 \times 10^{-4} \text{ g mL}^{-1}$.

tometer (Shimadzu, Japan) combined with flow-injection system, whose light entrance slot was shut. Both CL spectra were almost identical with a maximum wavelength at about 425 nm (Fig. 6). It is well known that 3-aminophthalate is the luminophor, and the maximum emission of CL reaction is at 425 nm. This indicated that the CL spectra were independent of DHZS. So the CL emitter in the both CL reactions between luminol and DPC with and without DHZS is 3-aminophthalate, which is the oxidation product of luminol.

Series experiments have been performed to know more details of luminol–DPC–DHZS CL reaction. Firstly, the UV–vis absorption spectra of DHZS, DPC and their mixture were made in basic medium. The result showed (Fig. 7) that the absorption peaks of DHZS and DPC almost disappeared as they were mixed. Secondly, when DPC and DHZS were mixed in alkaline medium, the color of DPC faded immediately. However, the primary color of DPC recovered when strong oxidant ($\text{K}_2\text{S}_2\text{O}_8$ or HNO_3) was added into the near colorless solution. Considering of above experiment, it is obvious that a redox reaction took place between DHZS and DPC. What is more, no CL enhancement could be observed when the mixture of DHZS and DPC was injected into luminol. The observation implied the existence of a intermediate product which maybe a free radical (DHZSox^{\bullet}) [18–20], although more evidences are not available. Based on above analysis, reactions (1) and (2) were proposed.

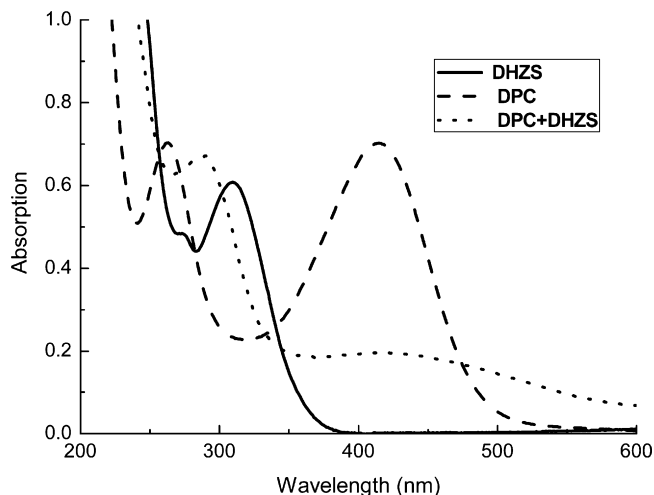


Fig. 7. UV–vis absorption spectra.

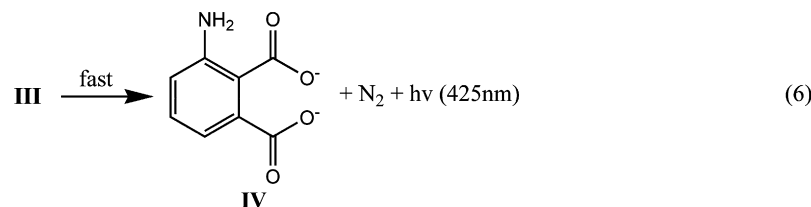
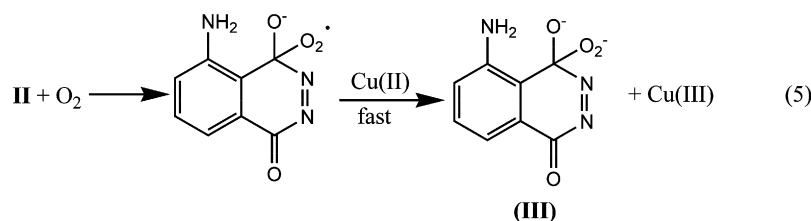
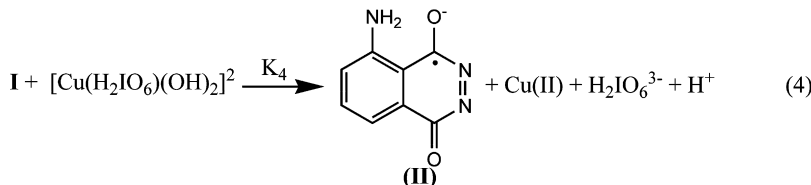
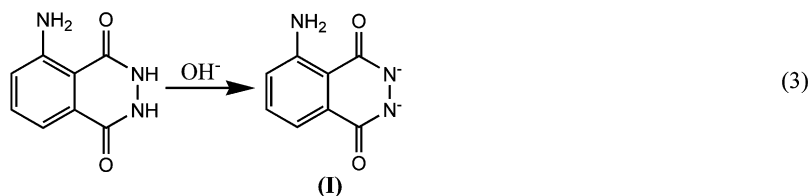
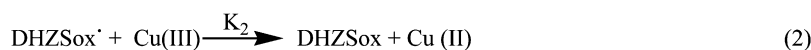


Fig. 8. The most possible reaction mechanism.

More experiments to evaluate reactions (1) and (2) were carried out. When DHZS standard solution was firstly mixed with DPC flow instead of luminol in the present flow system (Fig. 2), the CL intensity was much lower than that obtained without above flow system change. And by varying the tube length from DPC–DHZS confluence point to luminol confluence point, it was found that the longer the tube length, the weaker CL was observed. The experimental results coincide with what it has been suggested in reactions (1) and (2). And it can be concluded the CL difference observed in above experiments is attributed to the instability of proposed DHZSox[•].

Table 1
Result of determination of DHZS in tablet samples.

Sample	Amount labeled (mg)	Amount found (mg) ^a	
		Proposed method	HPLC method
Tablet 1	10	9.8 ± 3.2	9.9 ± 1.0
Tablet 2	10	10.1 ± 2.8	10.2 ± 2.1

^a Average of three measurements (±R.S.D.).

It is known luminol forms the dianion of luminol (I) as shown in reaction (3) in basic aqueous. And in this paper, it is considered that the dianion (I) can be oxidized by DPC to the semidione structure shown in one of its resonance form (reaction (4)). The semidione (II) reacts with oxygen to give the proxy radical, the proxy radical is subsequently reduced in a fast step to give proxy anion (III) (reaction (5)). The proxy anion decomposes to electronically excited (IV) with loss of nitrogen and then, contributes CL emission (reaction (6)) [21]. Based on the CL enhancement of DHZS on DPC–luminol reaction, it is suggested that DHZSox[•] could oxidize the luminol dianion (I) to semidione structure (II) as shown in reaction (7), and this reaction performs as the competing reaction with reaction (4). It also enabled us to conclude that $K_1K_7 \gg K_4$ and $K_1 > K_2$, otherwise the CL enhancement of DHZS should not be observed. Based on the above discussions, the most possible reaction mechanism is shown in Fig. 8, although more evidences are not available.

3.4. Optimization of CL reaction conditions

A series of experiments was conducted to select optimum analytical condition using $3.5 \times 10^{-7} \text{ mol L}^{-1}$ DHZS solution. The

Table 2

Results of recovery tests on human serum.

Sample	Found (10^{-8} g mL $^{-1}$)	Added (10^{-8} g mL $^{-1}$)	Total found (10^{-8} g mL $^{-1}$)	Recovery/%	R.S.D./%
No. 1	1.8	2.0	3.9	105	2.7
		4.0	5.7	97.5	1.2
		6.0	7.9	102	3.7
No. 2	5.1	6.0	11.0	98.3	1.2
		8.0	13.4	104	0.3
		10.0	15.0	99	2.0
No. 3	19	20.0	40.0	105	3.0
		40.0	56.9	94.8	0.8
		60.0	80.0	102	1.1

optimized conditions included flow system, flow rate and CL reagents concentration.

Several flow systems were designed in order to obtain the maximal CL signal. When employing the system shown schematically in Fig. 2 and water as carrying stream, the reagent solution could mix adequately with sample solution as soon as they met and a strong CL signal with good repeatability was obtained. So, flow system in Fig. 2 was selected.

The flow rate is an important parameter in the experiment, which influences the analytical sensitivity. The effect of the flow rate of pump on CL intensity was examined in the range of 0.5–1.5 mL min $^{-1}$. The results showed that the CL intensity increased with increasing of flow rate, because the CL reaction is rapid. So, a flow rate of 1.5 mL min $^{-1}$ which was the maximal flow rate under present conditions was selected.

DPC is the oxidant in the CL reaction whose concentration influences the CL intensity greatly. The effect of DPC concentration on the CL intensity was examined in the range of 6.0×10^{-5} to 4.0×10^{-4} mol L $^{-1}$. The experiments showed the maximal CL intensity could be obtained when the concentration of DPC was 1.0×10^{-4} mol L $^{-1}$.

DPC should be used as oxidant in alkaline medium. The effect of potassium hydroxide in DPC solution on the CL intensity was examined. The concentration of potassium hydroxide was studied in a concentration range 2.0×10^{-2} to 2.0×10^{-1} mol L $^{-1}$. It was found that the CL intensity increased with potassium hydroxide concentration up to 1.2×10^{-1} mol L $^{-1}$, then increased little. For obtaining the highest sensitivity, 1.2×10^{-1} mol L $^{-1}$ potassium hydroxide was selected as an optimum concentration.

The effect of luminol concentration on the signal/noise (S/N) ratio was investigated in the range 5.0×10^{-9} to 2.0×10^{-7} mol L $^{-1}$. It was found that S/N ratio reached the maximum value when the concentration of luminol was 1.0×10^{-7} mol L $^{-1}$. Therefore, 1.0×10^{-7} mol L $^{-1}$ luminol was used as an optimum concentration.

The luminol CL reaction should occur in alkaline solution. In the experiments, the alkalinity of the reaction medium was adjusted by preparing luminol with suitable concentration of potassium hydroxide. The effect of potassium hydroxide concentration in the range of 4.0×10^{-4} to 4.0×10^{-3} mol L $^{-1}$ was examined. When 1.0×10^{-3} mol L $^{-1}$ potassium hydroxide was used, the CL reaction had the maximum CL intensity.

Table 3

Figures of merit of comparable methods of CL determination of DHZS.

CL system	Analytical range (ng mL $^{-1}$)	Detection limit (ng mL $^{-1}$)	References
Luminol–DPC	7–860	2.1	This work
MnO $_4^-$ + RhB + H $^+$	5–800	1.9	[7]
Fe(CN) $_6^{3-}$ + eosin Y + OH $^-$	20–2800	12	[8]
Peracetic acid + OH $^-$	20–4000	1.2	[9]
ONOO $^-$ + CO $_3^{2-}$	10–3000	3.6	[10]

3.5. Analytical parameters

Under the optimum condition given above and using the flow-injection system described in Fig. 2, the relative CL intensity was linearly proportional to the DHZS concentration in the range of 7.0×10^{-9} to 8.6×10^{-7} g mL $^{-1}$ and the detection limit was 2.1×10^{-9} g mL $^{-1}$ (3σ). The regression equation was $\Delta I = 7.57C - 98.83$ (ΔI being the relative height of CL intensity and C being the DHZS concentration (ng mL $^{-1}$)) with $R^2 = 0.9933$ ($n = 12$). The relative standard deviation (R.S.D.) ($n = 7$) for 5.2×10^{-8} g mL $^{-1}$ DHZS standard solution was 3.1%.

3.6. Interference studies

The interference of foreign species was studied by analyzing a standard solution 6.0×10^{-8} g mL $^{-1}$ DHZS to which increasing amounts of foreign species was added. A substance was considered no interference if the variation of the CL intensity was within $\pm 5\%$. The influence of some inorganic ions and organic compounds were studied. The tolerable concentration ratios of foreign species to 6.0×10^{-8} g mL $^{-1}$ DHZS was over 1000-fold Na $^+$, Ca $^{2+}$, Cl $^-$, SO $_4^{2-}$, NO $_3^-$, CO $_3^{2-}$, pyruvic acid, 500-fold C $_2$ O $_4^{2-}$, creatinine, carbamide, starch, 100-fold Fe $^{3+}$, 50-fold citrate, 10-fold lactic acid, 5-fold lactose, glucose, Co $^{2+}$, Cu $^{2+}$, Cr $^{3+}$, 1-fold Mn $^{2+}$, 0.1-fold ascorbic acid, uric acid.

3.7. Sample analysis

3.7.1. Determination of DHZS in pharmaceutical preparations

Following the procedure detailed in Section 2.4, the proposed method was applied for the determination of DHZS in commercially available compound antihypertensive, Compound DHZS Tablets (10 mg DHZS, 12.5 mg hydrochlorothiazide, 0.1 mg reserpine). The results are listed in Table 1, which agreed well with those obtained by the HPLC method [5]. The HPLC procedure used as follows, using ODS column, the mobile phase consisted of 0.06 mol L $^{-1}$ potassium phosphate monobasic solution–methanol–acetonitrile (86:9:5), the flow rate was 1 mL min $^{-1}$ and detecting wavelength was 240 nm.

3.7.2. Determination of recovery of DHZS in human serum

The proposed method was attempted to determine DHZS in serum which was provided by Shaanxi normal university hospital. 2 mL blank serum sample was collected and transferred into ultra-filtration tube, then centrifuged at 10,000 rpm for 10 min at 4 °C to eliminate the potential influence of proteins. The 1 mL filtrate was transferred into a 100 mL volumetric flask and diluted to the mark with doubly distilled water. The blank serum was injected to the CL system, and then recorded the blank signal. A known amount of DHZS standard solution was added to 10 mL diluted serum. The DHZS concentration of serum samples were determined by the procedure detailed in Section 2.4. The amount

of DHZS in human serum, and the recovery obtained are shown in Table 2.

3.7.3. Comparison with other CL systems

Some reported CL methods for the determination of DHZS are compared with the proposed CL method in this paper and the results are shown in Table 3. From Table 3, it can be seen that under the optimum conditions, the proposed CL method for the determination of DHZS has considerable or lower detection limit comparable with other CL methods.

4. Conclusions

The potential application of DPC as inorganic CL oxidizing agents has been demonstrated in the work. The important advantage of the oxidant over other common oxidants is that very low concentration of luminol can react with DPC catalyzed by DHZS to get excellent experimental results. So the method holds higher selectivity than other luminol CL systems because of using low luminol concentration.

The work has shown that the proposed FIA–CL method based on DPC as oxidants can be successfully used for the determination of DHZS. The analytical performance in assay of DHZS in pharmaceutical preparation and human serum demonstrates that the proposed method can be utilized in routine determination of DHZS and clinical

applications. The method is simple, fast, and needs little luminol consumption and inexpensive instrumentation. The possible CL reaction mechanism was investigated.

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