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ORIGINAL PAPER

A Batch Chemiluminescence Determination of Enoxacin Using a Tris-(1,10-phenanthroline)ruthenium(II)–Cerium(IV) System

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Abstract A batch type chemiluminescence (CL) determination of enoxacin is described. In this work, it was observed that enoxacin could enhance the chemiluminescence (CL) emission $Ru(phen)_3^{2+}$–Ce(IV) system and this enhancement effect was dependent on the concentration of enoxacin, based on which, CL system was established for the determination of enoxacin. Under the optimum experimental conditions, the linear range and detection limit are 0.6406–64.06 μg/ml and 0.0210 μg/ml, respectively. The R.S.D. is 1.75%. ($n = 10$). The proposed method has been applied to detect the content of enoxacin in pharmaceutical formulation and human serum with satisfactory results. The possible mechanism of the CL reaction was discussed.

Keywords Batch chemiluminescence · Enoxacin · Ruthenium · Cerium · Serum

Introduction

Enoxacin (Enox), an antibiotic in the class of fluoroquinolone drugs, is used in the treatment of urinary tract, respiratory, gastro-intestinal and skin infections because of its excellent activity against bacteria, low frequency of adverse effect and good absorption on oral administration. Structurally (Fig. 1(a)), it is an amino compound containing piperazine moiety at 7 and fluorine at 6 positions. Fluorine at position 6 confers greater antibacterial potency and piperazine moiety at position 7 confers antipseudomonal activity [1]. The extensive use of this compound and the need for clinical and pharmacological study require fast and sensitive analytical techniques for determination of its presence in biological fluids and pharmaceutical formulations. Numerous methods have been reported for the determination of enoxacin including differential pulse polarography [2], single-sweep polarography [3], reversed-phase high-performance liquid chromatography [4], capillary electrophoresis using solid-phase extraction [5], liquid chromatography-tandem mass spectrometry [6], spectrophotometric [7], micellar liquid chromatography [8], partial least squares multi component fluorimetry [9], fluorimetric method using Tb^{3+}-enoxacin [10], HPLC-PIF [11]. Application of chemiluminescence method is gaining interest in analytical chemistry because it shares a number of advantages [12] including (1) low detection limits (in the nanogram-or even subnanogram-per-milliliter region, (2) wide dynamic ranges (up to six orders of magnitude), (3) high signal to noise ratios resulting from the absence of a light source and the consequent absence of noise, (4) absence of Rayleigh and Raman scattering, (5) instrumental simplicity and affordability and (6) absence of toxic effects from the usual CL reagents. Electrochemiluminescence using Tb^{3+}-enoxacin-Na_2SO_3 system [13] and chemiluminescence using $KMnO_4$-/Na_2SO_3-Tb^{3+}-ENX [14] for enoxacin determination have already been reported. $Ru(phen)_3^{2+}$ (Fig. 1(b)) is a sensitive chemiluminescence reagent and has been used to determine many chemicals, such as organic acids [15] sulfite [16], nucleic acids [17], barbituric acid [18] and so on. The luminescence properties of Tris-(1,10-phenanthroline)ruthenium(II) ($Ru(phen)_3^{2+}$)

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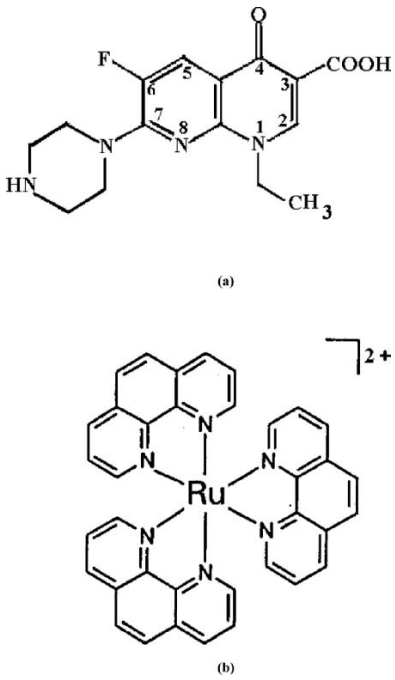


Fig. 1 Structures of enoxacin (**a**) and Tris-(1,10-phenanthroline) ruthenium(II) (**b**)

is similar to $Ru(bipy)_3^{2+}$ and exhibits higher sensitivity comparing to $Ru(bipy)_3^{2+}$ [19].

A flow-injection chemiluminometric method for the determination of ciprofloxacin (CIP), norfloxacin (NOR) and ofloxacin (OFL) based on the CL reaction of the studied drugs with $Ru(bipy)_3^{2+}$ using Ce(IV) in sulfuric acid medium as an oxidant [20] has been published. To the best of our knowledge a batch type chemiluminescence using $Ru(phen)_3^{2+}$–Ce(IV) system for the determination of enoxacin has not been yet reported.

In our experiment, it was observed that enoxacin could enhance the CL emission of $Ru(phen)_3^{2+}$–Ce(IV) system and the enhancement degree was linearly related to the amount of enoxacin added. Under the optimum experimental conditions, the CL intensity is linear to the concentration of enoxacin in the range of 0.6406–64.06 μg/ml and the detection limit is 0.0210 μg/ml.

Experimental

Materials and reagents

Enoxacin (Sigma-Aldrich Co, USA) has limited solubility in water; all enoxacin solutions were prepared in 95% methanol (Duksan pure chemical Co., Ltd, Korea). Methanol was degassed by boiling prior to dissolution of the enoxacin in order to obtain best results. Enoxacin solutions were preserved in refrigerator when not in use. Cerium (IV) sulfate, $Ce(SO_4)_2$ (Aldrich, USA) working solution (1×10^{-2} M) was prepared by dissolving 0.08306 g of the salt in 25 ml of 0.5 M H_2SO_4. A 1×10^{-2} M stock solution of Ru $(phen)_3$ Br_2 was prepared by dissolving a required amount of the salt in water. The working solution was prepared by appropriate dilution with deionized water. Tris (1,10-phenanthroline) ruthenium(II) (as bromide salt) was synthesized using procedure described in the literature [21] and purified by means of re-crystallization from acetonitrile/toluene mixtures.

Apparatus

A Spex (Edison, NJ, USA) Model FL111 spectrofluorimeter was used to accomplish the batch type chemiluminescence measurements. An Ismatec Model 404 peristaltic pump was used to convey the one CL reagent for initiation of the reaction. During the measurements, the light source of the excitation monochromator was switched off. Slit width of emission monochromator was fixed with 0.25 mm. The photomultiplier tube (PMT) used was a Hamamatsu Model R 928 (Hamamatsu, USA) powered at 950 V. Spectra data were collected by Spex DM 3000 spectroscopy computer. The instrument lay out is shown in the Fig. 2.

Basic procedure

The basic analysis procedure of the batch type CL consisted of addition of the following quantities of the equilibrated solutions into the reaction cell: 1.0 ml $Ru(phen)_3^{2+}$ (1.6×10^{-3} M) solution, 1 ml enoxacin (4×10^{-4} M) solution. The contents of the reaction cell were allowed to mix for 10 s in the cell compartment prior to injection of 0.5 ml (2×10^{-3} M) Ce(IV) solution with peristaltic pump. The analytical signal was taken as the difference in the CL peak height between a blank and analyte run.

Procedure for sample preparation (tablet)

Five tablets were weighed and ground to powder. An accurate amount of the powdered drug equivalent to 200 mg of enoxacin was dissolved in methanol and filtered. In order to make the concentrations of the drug within the linear range, the solution was properly diluted and the nominal content of the tablet was calculated by the calibration equation.

Results and discussion

Effect of $Ru(phen)_3^{2+}$concentration on the CL intensity

It is well reported that for the CL system involved in $Ru(phen)_3^{2+}$ the emission is observed from the excited $[Ru(phen)_3^{2+}]^*$ which is the reaction product of $Ru(phen)_3^{3+}$ with a radical amine, therefore $Ru(phen)_3^{2+}$ is the

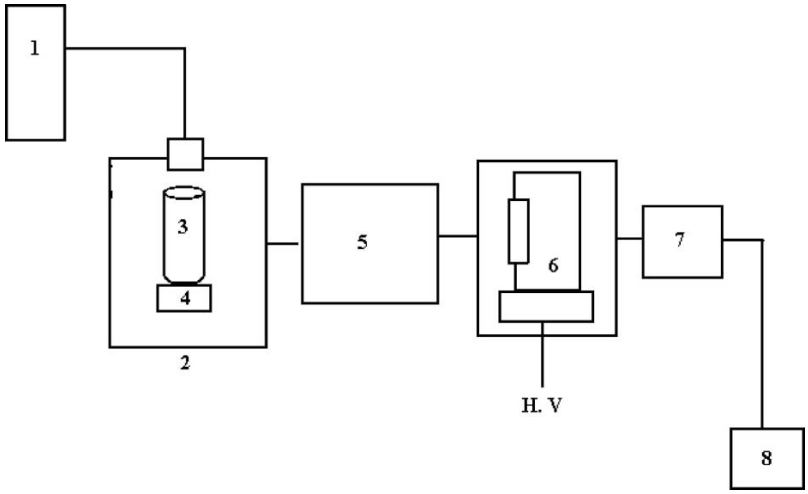


Fig. 2 Schematic diagram of batch chemiluminescence **1**. Peristaltic pump, **2**. Light-tight housing, **3**. Reaction cell, **4**. Magnetic stirring bar, **5**. Emission monochromator, **6**. Photomultiplier tube, **7**. Amplifier, **8**. Spectroscopy computer

luminophor of the system [22]. With the solutions containing a variable amount of $Ru(phen)_3^{2+}$ from 2.0×10^{-4} to 4.0×10^{-3} M, 4.0×10^{-4} M enoxacin, and 2.0×10^{-3} M Ce(IV) (0.1 M H_2SO_4), (all cell concentrations) the effect of the concentrations of $Ru(phen)_3^{2+}$ on the system was investigated by determining the CL intensity of $Ru(phen)_3^{2+}$–Ce(IV) system (blank) and $Ru(phen)_3^{2+}$–Ce(IV)-enoxacin and the results are shown in the Fig. 3. The experimental results showed that with the concentration of $Ru(phen)_3^{2+}$ increasing, the chemiluminescence intensity increased from 2.0×10^{-4} to 1.6×10^{-3} M. The phenomenon may result due to the rapid chemiluminescence reaction kinetics because of the increased reagent to analyte radical ratio. The CL intensity then started to fall off from 1.6×10^{-3} to 4.0×10^{-3} M with substantial increase in the blank value. Therefore the optimum concentration of $Ru(phen)_3^{2+}$ is 1.6×10^{-3} M with best signal to background ratio (this represents a precell concentration of 4.0×10^{-3} M).

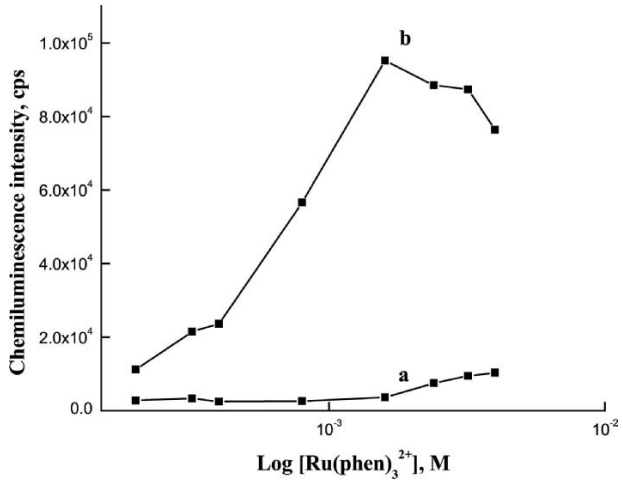


Fig. 3 $Ru(phen)_3^{2+}$ optimization: (**a**) Blank, (**b**) $Ru(phen)_3^{2+}$–Ce(IV) -enoxacin. Conditions [Enoxacin] = 4×10^{-4} M, [Ce(IV)] = 2×10^{-3} M, [H_2SO_4] = 0.1 M, [λ_{em}] = 578 nm

Effect of $Ce(SO_4)_2$ concentration on the CL intensity

Ceric sulfate being a non luminescent and strong oxidizing agent [23] was utilized as the oxidant in this CL system. The effect of $Ce(SO_4)_2$ concentration on CL intensity was studied over the range 6.0×10^{-5}–1.8×10^{-2} M $Ce(SO_4)_2$ (cell concentrations) under the optimum conditions, and the results are shown in Fig. 4. This shows that the CL intensity was increased with $Ce(SO_4)_2$ concentration when the concentration of $Ce(SO_4)_2$ was under 2.0×10^{-3} M. The maximum intensity was obtained when the concentration of $Ce(SO_4)_2$ was 2.0×10^{-3} M. At higher $Ce(SO_4)_2$ concentrations, the CL intensity decreased, which might be due to the effect of the color of the $Ce(SO_4)_2$ solution and the scattering of light emitted by the unsolvable hydrolysis product of Ce(IV) in acidic media. For this reason, an optimum point was selected at 2.0×10^{-3} M Ce $(SO_4)_2$ (this represents a precell concentration of 1.0×10^{-2} M). The blank CL signal was independent of the $Ce(SO_4)_2$ concentrations.

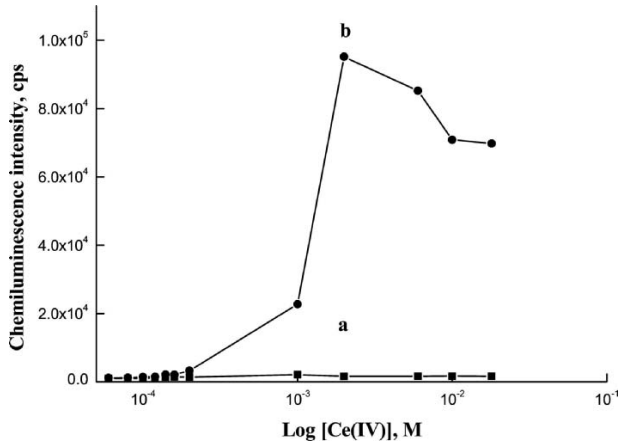


Fig. 4 Ce(IV) optimization: (**a**) Blank, (**b**) $Ru(phen)_3^{2+}$–Ce(IV)-enoxacin. Conditions: [$Ru(phen)_3^{2+}$] = 1.6×10^{-3} M, [H_2SO_4] = 0.1 M, [Enoxacin] = 4×10^{-4} M, [λ_{em}] = 578 nm

Effect of H_2SO_4 concentration on the CL intensity

The chemiluminescence intensity depends on the concentration of H_2SO_4. The experiment was performed in the range of 1.6×10^{-2}–0.2 M H_2SO_4 (cell concentration) under the standard conditions mentioned. The maximum intensity reached at 0.1 M H_2SO_4. When the H_2SO_4 concentration was above this level, the light intensity started to decrease upto 0.2 M H_2SO_4 (cell concentration) (Fig. 5). In the range of the used H_2SO_4 concentration, the Ce(IV) species exist as sulfated complexes, such as, $Ce(SO_4)^{2+}$, $Ce(OH)(SO_4)^{1+}$, $Ce(SO_4)_2$, $Ce(SO4)_3^{2-}$, $HCe(SO_4)_3^{-}$, $HCe(SO_4)_4^{3-}$ and $Ce(SO_4)_4^{4-}$ [24, 25] and these species are in a series of equilibria with HSO_4^{-}. It has already pointed out that the reactive species of the oxidants are Ce(IV), $Ce(SO_4)_2$ and $HCe(SO_4)_3^{-}$ [26]. So, the reactive species of Ce(IV) decrease with increasing H_2SO_4 concentration, and the intensity decreases. Further more the rate of reaction is inversely proportional to the concentration of H_2SO_4 [17]. The reason behind the lower extent of oxidation with the increase of H_2SO_4 concentration is the less oxidizing power of Ce as SO_4^{2-} content is increased. For this reason, 0.1 M H_2SO_4 (this represents a precell concentration of 0.5 M) solution was used in the work. It was noted that no change in blank signal was observed at varying concentration of H_2SO_4.

Effect of mixing order of reagents on the CL intensity

In the batch system the chemiluminescence intensity was influenced by the mixing order of the reagents into the reaction cell. It has shown that the chemiluminescence intensity was the highest when $Ru(phen)_3^{2+}$ and enoxacin were added into the reaction cell at first, mixed well, and then Ce(IV) was injected after 10 s interval. The major effect is caused by the oxidant [27].

Kinetic curves

The CL intensity of $Ru(phen)_3^{2+}$–Ce(IV) system in the absence of and in the presence of enoxacin were recorded batch wise with the emission monochromator using time base scanning, respectively, and the obtained CL kinetic curves were shown in Fig. 6. The experimental results indicated that when Ce(IV) was added to the cell the reaction was initiated and that CL emission of the investigated system was weak but could be enhanced proportionally by the addition of enoxacin into the ruthenium solution. The CL reaction for enoxacin is faster and the intensity reached maximum at residence time of 37 s, after which the signal decreased slowly.

Analytical parameters

Calibration curve for enoxacin run under the aforementioned optimum conditions such as $[Ru(phen)_3^{2+}] = 1.6 \times 10^{-3}$ M, $[Ce(IV)] = 2 \times 10^{-3}$ M, $[H_2SO_4] = 0.1$ M, $[\lambda_{em}] = 578$ nm was obtained by using a series of ten standard solutions. The calibration curve was found to be linear in the range of 0.6406–64.06 μg/ml. The equation for calibration graph is $X = 0.001503Y - 2.6784$ ($R = 0.99974$), where X is the concentration of enoxacin expressed in μg/ml and Y is the chemiluminescence intensity (cps unit). The limit of detection as defined by IUPAC, $C_{LOD} = 3\ S_b/m$ (where S_b is the standard deviation of the blank signals and m is the slope of the calibration graph) was found to be 0.0210 μg/ml. The relative standard deviation (R.S.D) for 10 repeated measurements of 12.812 μg/ml enoxacin was 1.75%.

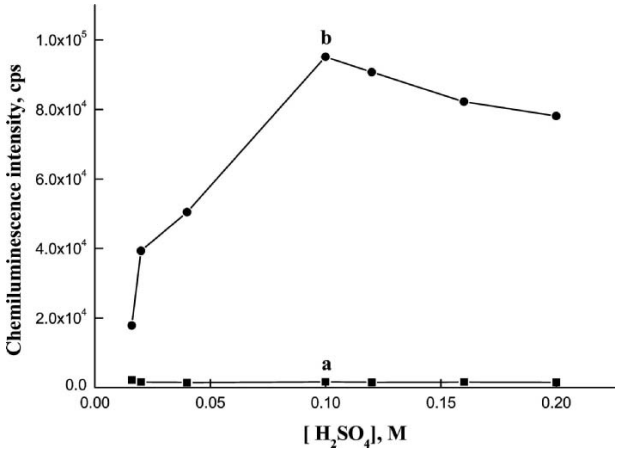


Fig. 5 H_2SO_4 optimization: (**a**) Blank, (**b**) $Ru(phen)_3^{2+}$–Ce(IV)-enoxacin. Conditions: $[Ru(phen)_3^{2+}] = 1.6 \times 10^{-3}$ M, $[Ce(IV)] = 2 \times 10^{-3}$ M, $[Enoxacin] = 4 \times 10^{-4}$ M, $[\lambda_{em}] = 578$ nm

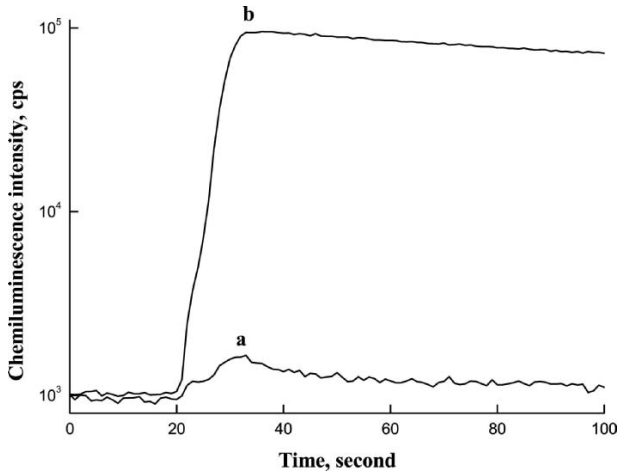


Fig. 6 Typical peak shapes for $Ru(phen)_3^{2+}$ signals using optimized reagent concentrations. (**a**) Blank, (**b**) $Ru(phen)_3^{2+}$–Ce(IV)-enoxacin. Conditions: $[Ru(phen)_3^{2+}] = 1.6 \times 10^{-3}$ M, $[Ce(IV)] = 2 \times 10^{-3}$ M, $[Enoxacin] = 4 \times 10^{-4}$ M, $[\lambda_{em}] = 578$ nm

Interference studies

In a real sample, the analyte under investigation will be in the presence of interferents. They may suppress or enhance the CL, although they have no significant effect on the CL reaction of $Ru(phen)_3^{2+}$. The influence of several metal ions, anions and organic compounds on the determination of 12.812 μg/ml (0.00004 M) enoxacin by the proposed method was studied. A foreign ion was considered to interfere seriously when it showed a determination error of more than 5%. The experimental results indicate that 1000-fold K^+, Na^+, Al^{3+}, Ca^{2+}, Cl^-, Zn^{2+}, SO_4^{2-}; 200-fold glucose, dextrin, starch; 50-fold Ni^{2+}, Fe^{3+}, Pb^{2+} and 10-fold Mn^{2+}, Cu^{2+}, Co^{2+} had no interference on the determination of 12.812 μg/ml of enoxacin.

Analytical applications

The proposed method was applied to the determination of enoxacin in one pharmaceutical preparation. The results obtained and the labeled content is given in the Table 1. Enoxacin is a fluoroquinolone with maximum serum content reported of 1.3 ± 0.4 μg/ml [28]. Serum sample was collected from a healthy person who received a single oral dose of 200 mg of enoxacin. The preparation of the serum was followed by the procedure described by Aly *et al*. [20]. The drug content in serum was determined by calibration method and the recovery test was also performed from spiked serum sample by standard addition method. Both results are shown in the Table 2.

Reaction mechanism

The luminescence properties of Tris-(1,10-phenanthroline) ruthenium(II) ($Ru(phen)_3^{2+}$) is similar to $Ru(bipy)_3^{2+}$ and exhibits higher sensitivity comparing to $Ru(bipy_3^{2+}$ [19]. The proposed reaction mechanism for the CL detection of enoxacin is presumably analogous to that of the fluoroquinolone/$Ru(bipy)_3^{2+}$–Ce(IV) system [20]. The CL reaction mechanism in this present work involves the oxidation of $Ru(phen)_3^{2+}$ and the secondary amine present on the piperazine moiety of enoxacin by Ce(IV) in acidic media. The oxidation product of enoxacin undergoes deprotonation to form a radical, which is highly reducing intermediate. This intermediate is the source of the chemical energy to produce $Ru(phen)_3^{2+}$ by reduction of $Ru(phen)_3^{3+}$ which subsequently emits light at 578 nm similar to the data obtained by Veening and Brandt [29]. A detail CL reaction mechanism is suggested in Scheme 1.

Table 1 Results for the determination of enoxacin in tablet

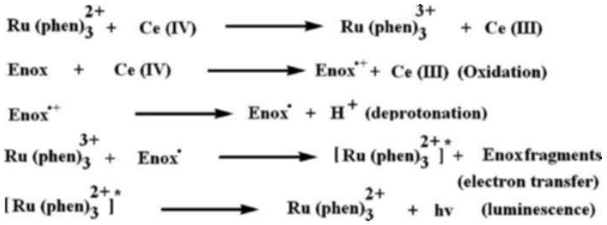
Sample	Amount (mg)	
	Label	Found[b]
Enoxacin	100 mg enoxacin per tablet[a]	97.5 ± 0.44

[a] Active ingredient in 200 mg tablet powder.

[b] Average value $\pm$ 95% confidence limits of three determinations.

Table 2 Results for the determination of enoxacin in serum sample

Sample	Calibration method	Standard addition method		
	Amount found (μg/ml)	Spiked (μg/ml)	Found (μg/ml)	Recovery (%)
Enoxacin	1.05 ± 0.25	0.60	0.59	98.33
		0.70	0.67	95.70
		0.80	0.76	95.01
		0.90	0.88	98.0
		1.0	0.98	98.0



Scheme 1

Conclusion

This preliminary study shows that enoxacin exhibits analytically useful chemiluminescence upon reaction with Tris-(1,10-phenanthroline)ruthenium(II) and acidic Ce(IV). The linear range and detection limit are 0.6406–64.06 μg/ml and 0.0210 μg/ml, respectively. The CL method proposed here is relatively simple and showed significant selectivity. The results indicated that the proposed CL reaction system is not only appropriate for flow injection analysis but also convenient for batch type systems due to intense CL signal. Utilizing the proposed method, the enoxacin content of human serum can be determined with reasonable selectivity and sensitivity.

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