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## Quantitative Detection of Levofloxacin Hydrochloride by Differential Pulse Stripping Voltammetry with Electrodeposited Bismuth Film Electrodes

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**Abstract:** In this study, differential pulse stripping voltammetry was developed for the quantitative detection of levofloxacin hydrochloride indirectly. Levofloxacin hydrochloride contains organic amine, which can be precipitated upon interaction with  $Zn(SCN)_2$ . By means of differential pulse stripping voltammetry, the concentration of  $Zn^{2+}$  can be determined using an in-situ formed bismuth film electrode, which allows determining indirectly the amount of levofloxacin hydrochloride. The linearity equation,  $I = 1.1401c - 0.5309$  with the correlative coefficient  $R = 0.9979$ , was presented in the experiment. The results showed that this approach is very sensitive, having a limitation of detection of  $3.18 \times 10^{-5} \mu\text{g} \cdot \text{mL}^{-1}$  in a linearity range of  $5.0 \sim 60 \mu\text{g} \cdot \text{mL}^{-1}$ .

**Key words:** bismuth film electrode; differential pulse stripping voltammetry; levofloxacin hydrochloride; zinc ion; ion-association compound

**CLC Number:** O646

**Document Code:** A

Antibiotics are indispensable therapeutic agents for microbial infectious diseases. However, a sharp rise of antibiotic usage has been a recent concern worldwide since inappropriate disposal of these drugs not only contaminates the environment, but also brings chances for development of antibiotic resistance strains within our surrounding. Therefore, the detection of antibiotics is an important aspect by which the threshold concentration of drugs in environment can be estimated and necessary measures can be taken to combat the spread of pharmaceuticals in the environment<sup>[1]</sup>.

Levofloxacin hydrochloride (LV·HCl), named (-)-(S)-9-fluoro-2,3-dihydro-3-methyl-10-(4-ethyl-1-piper-azinyl)-7-oxo-7H-pyrido [1,2,3-de]-4-benzoxazine-6-carboxylic acid hemihydrates hydrochloride, as seen in Fig. 1, is an oral fluoroquinolone anti-microbial agent which exhibits broad-spectrum bactericidal activity against gram-positive and gram-nega-

tive bacteria<sup>[2]</sup>. LV·HCl is used for the treatment of infections of the respiration and urinary tract, skin, and soft tissues.

Numerous analytical methods have been developed for the detection of LV including HPLC<sup>[3-5]</sup>, microdialysis<sup>[6-7]</sup>, spectro-fluorometry<sup>[8-9]</sup>, capillary electro-phoresis<sup>[10]</sup>, enzyme-linked immuno-sorbent assay<sup>[11]</sup> and molecularly imprinted polymer<sup>[12]</sup>. However, with these methods, the analysis is often complex, time-consuming, and requires expensive apparatus. In contrast, electrochemical methods offer not only the advantages of rapidity, simplicity and low cost, but also diverse possibilities for the development of new portable sensor devices adapted for on-site analysis of untreated samples. So far, some electrochemical methods have been developed for LV·HCl detection by using various sensing elements such as glassy carbon electrode<sup>[13]</sup>, DNA sensor<sup>[14-15]</sup>, modified electrode, e.g. poly(o-aminophenol)/multi-walled carbon nano-

tubes (MWCNTs)<sup>[16]</sup>, MWCNT-SnO<sub>2</sub><sup>[17]</sup>, CeO<sub>2</sub>-Au<sup>[18]</sup>. Another type of sensing element such as bismuth film electrodes (BiFEs) can be interesting candidates for such applications. BiFEs consist of electrochemically generated thin bismuth film and currently they are widely used in electroanalysis thanks to their good repeatability, low residual current and high hydrogen overpotential. Moreover, BiFEs have a wide range of interesting environmental and clinical applications in trace metal analysis in combination with advanced electrochemical stripping techniques<sup>[19-23]</sup>. Unfortunately, the performance of BiFEs for direct LV·HCl detection is poor due to the organic nature of LV·HCl.

To overcome this problem, in the present work, we developed a novel approach using Zn(SCN)<sub>4</sub><sup>2-</sup> as an intermedium to detect LV·HCl. It was reported that levofloxacin hydrochloride containing organic amine can protonate with Zn(SCN)<sub>4</sub><sup>2-</sup> by 1:1 molar ratio and consequently produce ion-association compound precipitation under pH < 7<sup>[24-25]</sup>. The precipitation can be separated and dissolved to produce Zn<sup>2+</sup>. Then we used differential pulse stripping voltammetry with BiFEs to determine the amount of Zn<sup>2+</sup> in precipitation, based on which the content of LV·HCl was calculated. To the best of our knowledge, this is the first report based on the indirect detection of LV·HCl by electrochemical measurement with BiFEs.

## 1 Experimental

### 1.1 Reagents

All solutions were prepared with double-distilled water. The Zn<sup>2+</sup> standard stock solution (1 mol·L<sup>-1</sup>) was obtained from Standard Center of China and diluted as required. Bismuth nitrate and potassium

cyanide were of analytical grade obtained from Aladin without further purification. Standard levofloxacin hydrochloride sample was supplied from National Institutes for Food and Drug Control. API Samples A and B were obtained from the local pharmaceutical companies.

### 1.2 Experimental Procedures for the Analysis of Levofloxacin

Experimental procedures for the analysis of levofloxacin: 0.0501 g levofloxacin hydrochloride was added in 10 mL nessler tube, and then dissolved with 1 mL 6.0 × 10<sup>-2</sup> mol·L<sup>-1</sup> hydrochloride solution. The as prepared solution was diluted to a desirable volume, and stored in a refrigerator. 0.50 mL standard LV solution was added in a 10 mL centrifugal tube, and then mixed with 0.50 mL 0.04 mol·L<sup>-1</sup> Zn<sup>2+</sup> solution, 0.50 mL 0.50 mol·L<sup>-1</sup> KSCN and 0.50 mL 6.0 × 10<sup>-2</sup> mol·L<sup>-1</sup> hydrochloride solutions. A white precipitation was observed immediately in the tube. Shaking tube is helpful for the complete reaction. After 10 min stationary sitting, the solution was centrifuged, upper clear liquid was removed. The precipitation was washed three times with 0.60 mol·L<sup>-1</sup> KSCN solution. After that, the precipitation was dissolved in water, and then diluted to 50 mL volumetric flask. The half of the above solution was moved to another volumetric flask, mixed with 5.00 mL 1.0 × 10<sup>-5</sup> mol·L<sup>-1</sup> Bi(NO<sub>3</sub>)<sub>3</sub> and 30.00 mL 0.50 mol·L<sup>-1</sup> KSCN solutions. Finally, the obtained solution was diluted to 250 mL in which the stripping peak current was measured.

All the experiments were performed with a CHI660E electrochemical workstation (Shanghai Chenhua Instrument Co., Ltd) in connection with a three-electrode cell. A saturated calomel electrode and a platinum electrode were used as the reference and auxiliary electrodes, respectively. Prior to use, a 3 mm-diameter glassy carbon was polished with 0.05 μm alumina powder and then washed under sonication for 5 min. Stripping voltammetric measurements were performed by *in-situ* deposition of bismuth film and Zn metal after removing dissolved oxygen. A deposition potential (-1.60 V) was applied to the glass carbon (GC) electrode while the solution was stirred.

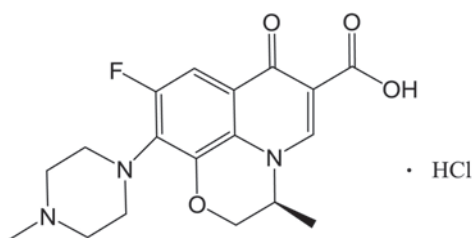


Fig. 1 Molecular structure of levofloxacin hydrochloride (LV·HCl)

Afterwards, the stirring was stopped and the voltammogram was recorded after 2 min of equilibrium. After each measurement, the working electrode potential was adjusted at 0.8 V and electrodes were rinsed for 60 s in order to remove the bismuth films. All the experiments were performed at  $20 \pm 1$  °C after removing dissolved oxygen.

## 2 Results and Discussion

### 2.1 Materials Characterization

As a common technique for examining the conformation of material, FT-IR spectroscopy could provide ample information on the material structure. Due to forming stable ion-association compound precipitation of  $\text{LV} \cdot \text{HCl}$  and  $\text{Zn}(\text{SCN})_4^{2-}$ , the precipitation was characterized with IR spectrum. The IR spectrum comparison of  $\text{LV} \cdot \text{HCl}$  and  $[\text{Zn}(\text{SCN})_4]^{2-} \cdot (\text{LVH})^{2+}$  is shown in Fig. 2. The IR spectrum of  $\text{LV} \cdot \text{HCl}$  was almost identical to the standard spectrum. There were two regions in FT-IR spectra:  $4000 \sim 1330 \text{ cm}^{-1}$  of functional group region and  $1330 \sim 400 \text{ cm}^{-1}$  of fingerprint region<sup>[26-28]</sup>. Two distinct regions (Parts 1, 2) of two IR spectra are seen in Fig. 2. The multiple absorptions in the range of  $2400 \sim 3100 \text{ cm}^{-1}$  were stretching vibrations absorption of the  $\text{NH}^+$  ionic associate. When forming ion association compounds of  $(\text{LVH})^{2+}$  and  $\text{Zn}(\text{SCN})_4^{2-}$ , these absorptions disappeared (Part 1). In part 2, a very strong characteristic band was present around  $2000 \text{ cm}^{-1}$ , suggesting the characteristic absorption of strong coordination of

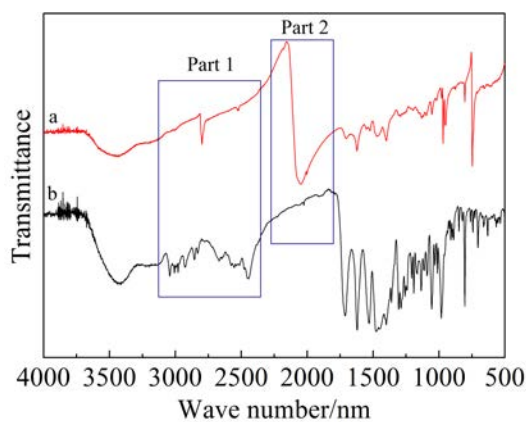


Fig. 2 FT-IR spectrum comparison of (a)  $\text{LV} \cdot \text{HCl}$  and (b)  $[\text{Zn}(\text{SCN})_4]^{2-} \cdot (\text{LV})^{2+}$

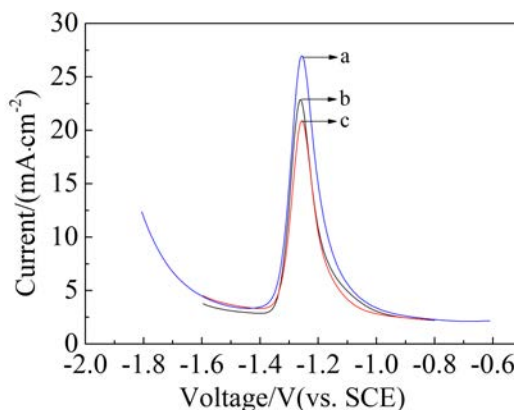


Fig. 3 The differential pulse stripping voltammetric curves of  $\text{Zn}^{2+}$  ( $2.5 \times 10^{-6} \text{ mol} \cdot \text{L}^{-1}$ ) on the electrodeposited a: Bi film, b: Hg film and c: bare GC. The sample width: 0.005 s; incr E: 4 mV; pulse amplitude: 50 mV; pulse width: 40 mV; pulse period: 0.5 s

thiocyanate anion<sup>[29]</sup>.

The electrochemical response comparison of BiFE, bare GC and usually used Hg film electrode is shown in Fig. 3. It is found that the BiFE exhibited the highest response current, indicating that the Bi film electrode is superior to other electrodes for detecting  $\text{Zn}^{2+}$ . SEM can take useful insights into the growth patterns of the Bi film. The morphology and the structure of electrodeposited particles were obtained by SEM. Fig. 3 shows the *in-situ* electrodeposited Bi film with different magnifications ( $50\times$ ,  $500\times$ ,  $2000\times$  and  $5000\times$ ). As can be seen from Fig. 2a, at applied deposition potentials, partial GC surface coverage was achieved. The Bi islands ranging with diameters ranging from  $5 \sim 30 \mu\text{m}$  were formed Fig. 4 (A, B). The SEM image of the Bi-coated GCE with a large magnification indicates a highly porous, three-dimensional sponge-like network. As shown in Fig. 4 (C, D), the pores were observed with diameters ranging from 100 to 500 nm, which could greatly enhance the electrochemically active surface area of the modified electrode.

Firstly, the instrument parameters were optimized to achieve good stripping potential graphs for  $\text{Zn}^{2+}$ , with nice signal curve, good sensitivity, and high peak current values. The parameters in the experiments were chosen as follows: sample width:

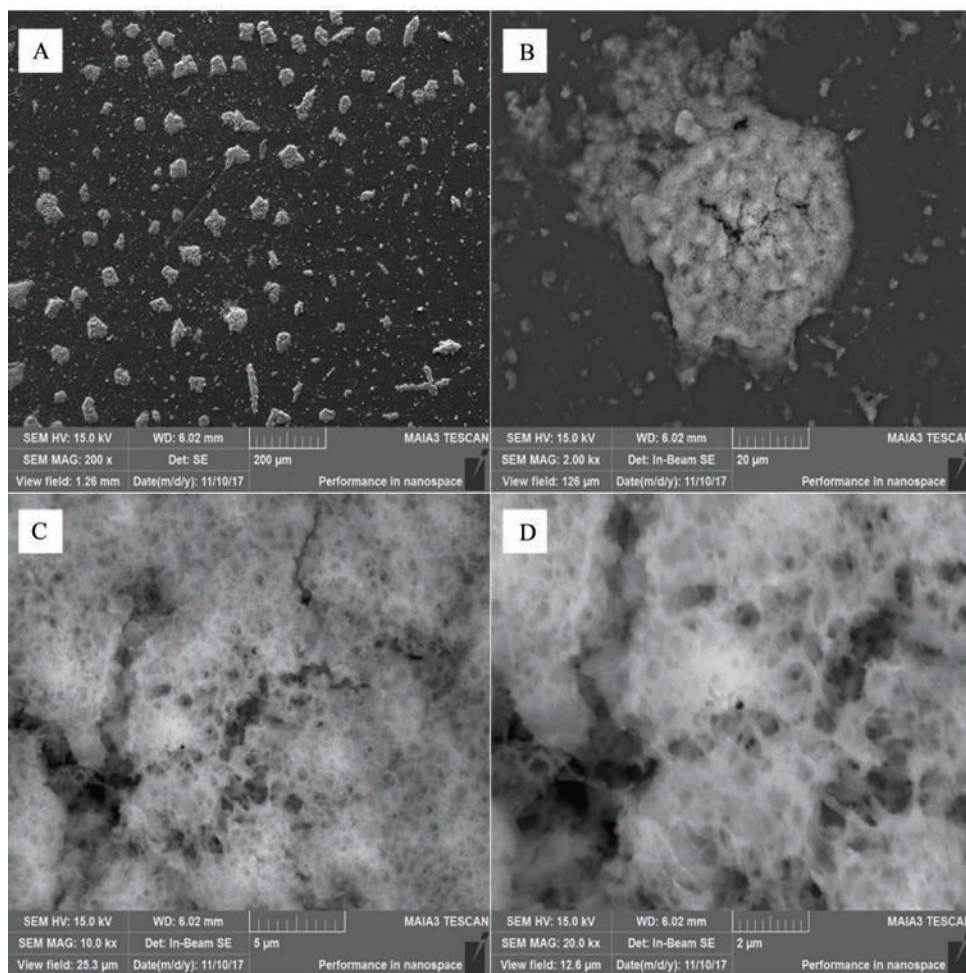


Fig. 4 SEM images of the *in-situ* electrodeposited Bi film at GC electrodes showing different magnifications under optimization conditions.

0.005 s; incr E: 4 mV; stationary time: 5 s; pulse amplitude: 50 mV; pulse width: 40 mV; pulse period: 0.25 s.

## 2.2 Optimization of Experimental Conditions for the Analysis of Levofloxacin

Moreover, various experimental conditions were optimized for the analysis of levofloxacin, including accumulation potential, accumulation time, precipitation and stationary time, concentration of KSCN solution,  $Zn^{2+}$  solution and bismuth nitrate, as well as pH. When the accumulation potential ( $E$ ) decreased from -1.40 to -1.80 V, the peak current in solution slightly decreased with potential being positively displacing. As seen in Fig. 5 (A, B), at  $E = -1.60$  V, the signal reached its maximum value. With increasing the accumulation time, more  $Zn^{2+}$  ions were reduced,

and the current peak values increased. When the accumulation time was longer than 140 s, the variation of peak current gradually decreased. Selection of the accumulation time should follow a principle: the accumulation time can increase remarkably sensitivity, and thus, longer accumulation time should be adopted for lower concentration of  $Zn^{2+}$ . In the present work, the accumulation time of 140 s was used (Fig. 5 (C, D)). In the experiment, five precipitations were produced, and placed statically for 5, 10, 20, 30 and 40 min. Then the effect of the stationary time on peak current was studied. The results showed that the peak current was maximum and peak shape was fairly well when the placement time was 10 min (Fig. 5 (E, F)). Therefore, the placement time of deposition was fixed at 10 min in the following experiments.

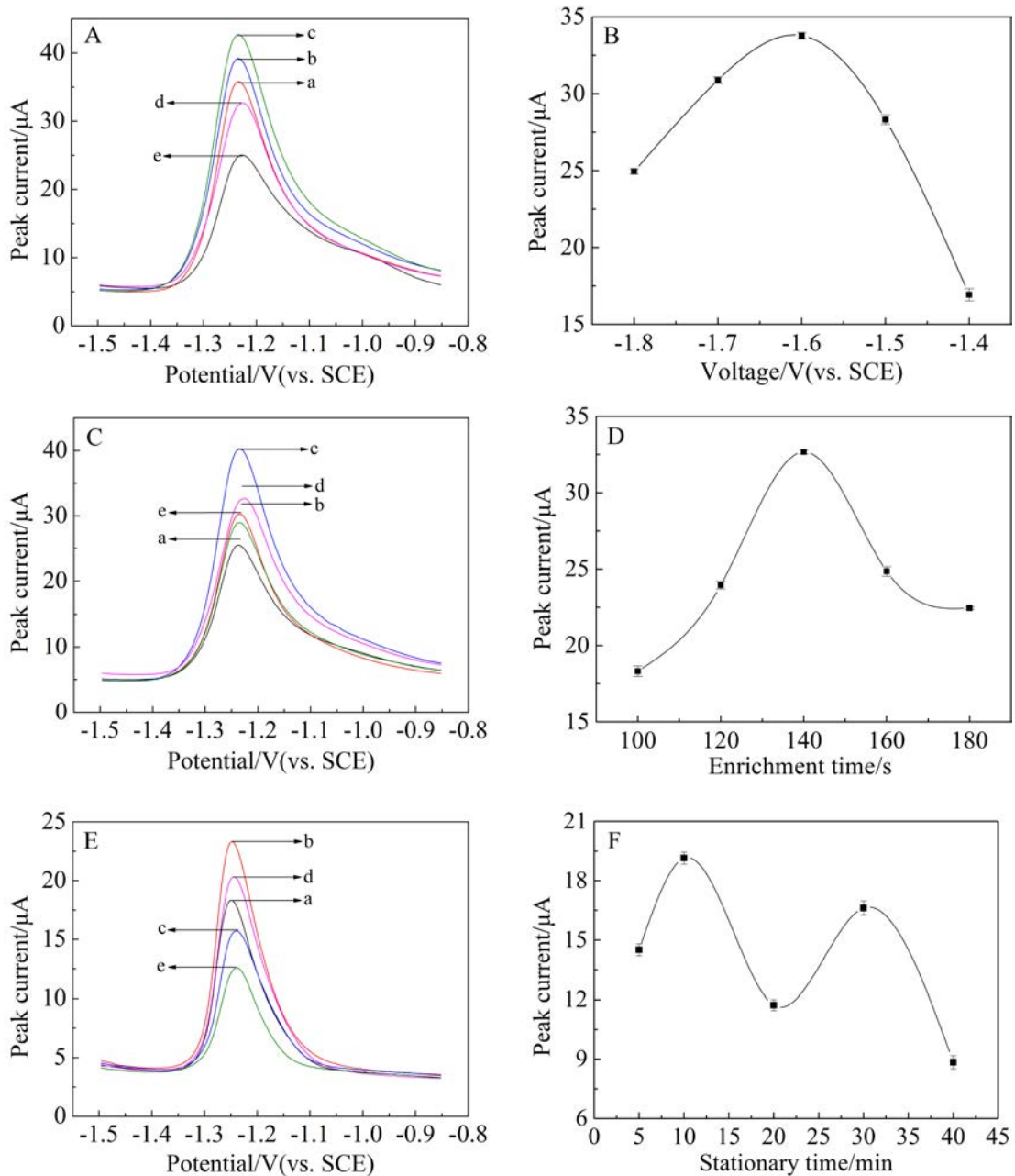


Fig. 5 Optimization of experimental conditions on BiFE of Zn<sup>2+</sup> ( $2.5 \times 10^{-6} \text{ mol} \cdot \text{L}^{-1}$ ) accumulation potential (A, B): potential a: -1.40 V, potential b: -1.50 V, potential c: -1.60 V, potential d: -1.70 V, potential e: -1.80 V; accumulation time (C, D): a: 100 s, b: 120 s, c: 140 s, d: 160 s, e: 180 s; stationary time (E, F): a: 5 min, b: 10 min, c: 20 min, d: 30 min, e: 40 min.

At the constant concentrations of LV·HCl and Zn<sup>2+</sup>, the effect of KSCN solution concentration used in the precipitation was studied. As seen in Fig. 6 (A, B), the peak current reached the maximum with good peak shape when the concentration of KSCN solution was 0.50 mol·L<sup>-1</sup>. Therefore, 0.50 mol·L<sup>-1</sup> KSCN solution was adopted in this study. On the other hand, the precipitated compound had higher solubility in

water but lower solubility in KSCN solution, thereby, 0.50 mol·L<sup>-1</sup> KSCN solution was also used to wash the precipitation. With the constant concentrations of LV·HCl and KSCN solutions, but varying the concentration of Zn<sup>2+</sup> solution, the Zn<sup>2+</sup> effects was investigated. The result showed that in 0.04 mol·L<sup>-1</sup> Zn<sup>2+</sup> solution the peak current became the maximum with good peak shape (Fig. 6 (C, D)). Therefore, 0.04 mol·L<sup>-1</sup>

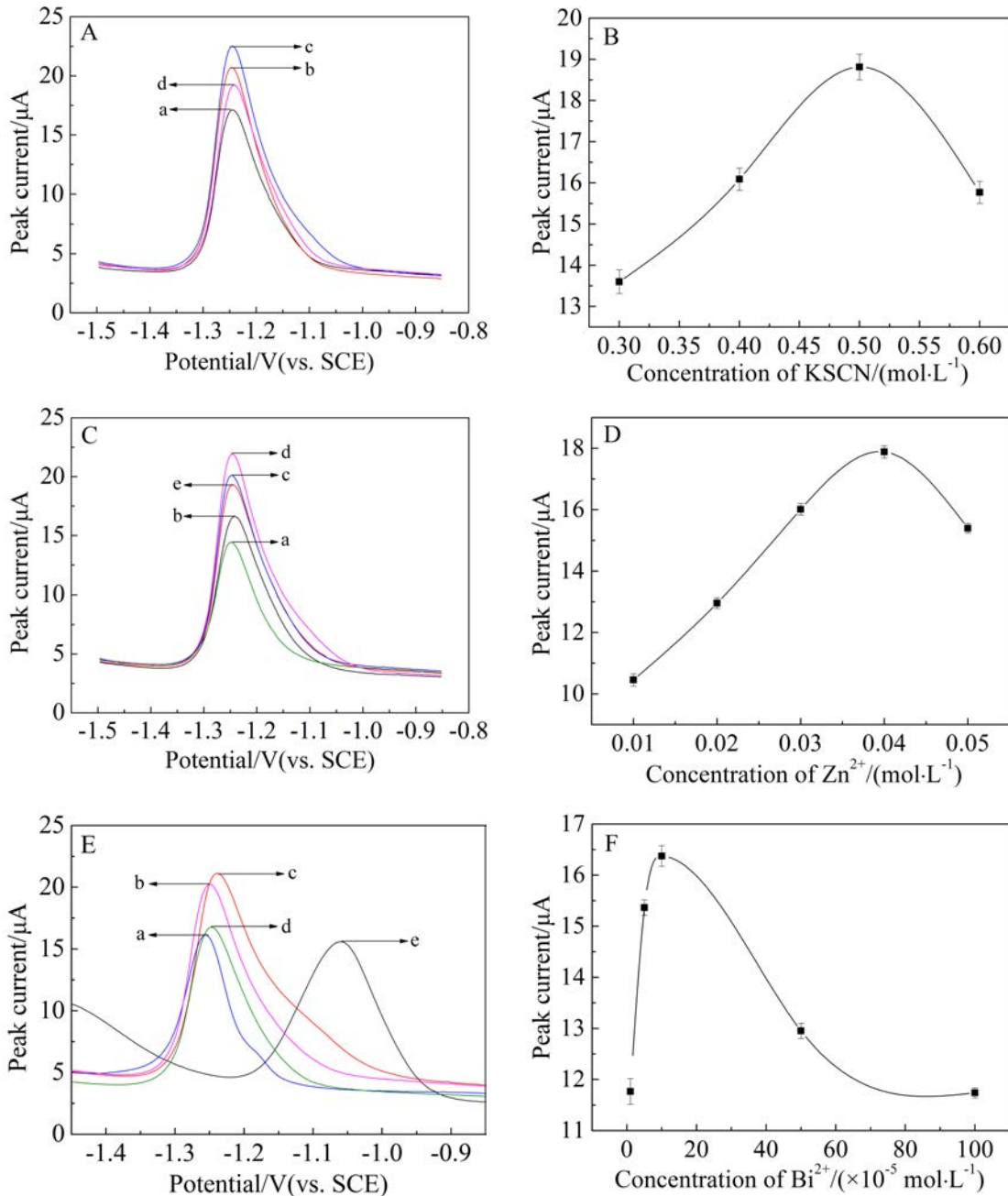


Fig. 6 Optimization of experimental conditions for KSCN solution concentrations (A, B): 1: 0.30, 2: 0.40, 3: 0.50, 4: 0.60 ( $\text{mol}\cdot\text{L}^{-1}$ );  $\text{Zn}^{2+}$  solution concentrations (C, D): 1: 0.01, 2: 0.02, 3: 0.03, 4: 0.04, 5: 0.05 ( $\text{mol}\cdot\text{L}^{-1}$ ); and bismuth nitrate solution concentrations (E, F): 1:  $1.0\times 10^{-6}$ , 2:  $5.0\times 10^{-6}$ , 3:  $1.0\times 10^{-5}$ , 4:  $5.0\times 10^{-5}$ , 5:  $1.0\times 10^{-4}$  ( $\text{mol}\cdot\text{L}^{-1}$ ).

$\text{Zn}^{2+}$  solution was used here. At the constant concentrations of LV·HCl and KSCN solutions, as shown in Fig. 6 (E, F), when the concentrations of bismuth nitrate solution increased from  $1 \times 10^{-6}$  to  $1 \times 10^{-4} \text{mol}\cdot\text{L}^{-1}$ , the current peak increased initially and then decreased afterwards. When the  $\text{Bi}^{3+}$  concentration was  $1 \times 10^{-5} \text{mol}\cdot\text{L}^{-1}$ , the peak current reached the maximum with

fine peak shape. The reason was that the thickness of Bi film increased with a higher concentration of  $\text{Bi}^{3+}$  being used, which could inhibit the diffusion and reduction of  $\text{Zn}^{2+}$ . Therefore, the concentration of  $1 \times 10^{-5} \text{mol}\cdot\text{L}^{-1} \text{Bi}^{3+}$  was adopted in the present work. Further work was carried out for investigating the effect of solution pH on voltammetric signal. As

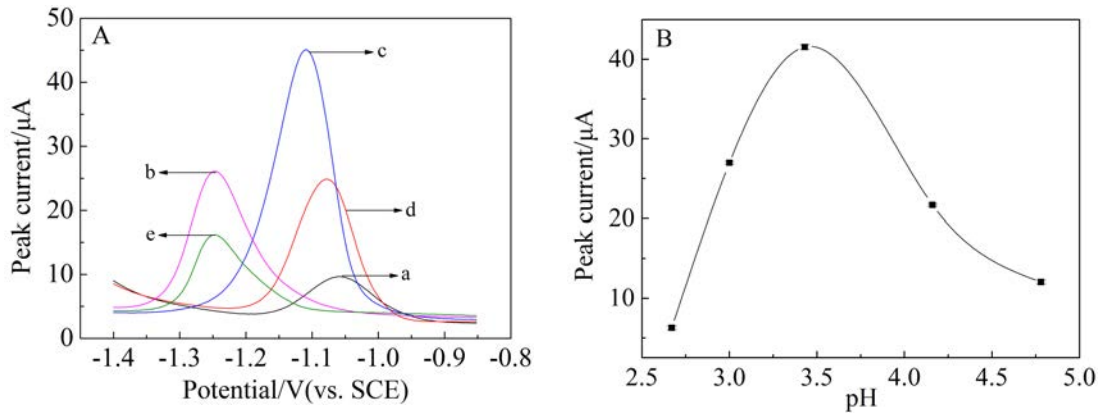


Fig. 7 A) The differential pulse stripping voltammograms of Zn<sup>2+</sup> ( $2.5 \times 10^{-6} \text{ mol} \cdot \text{L}^{-1}$ ) under different pH values. Curves a: 2.67, b: 3.00, c: 3.43, d: 4.16; e: 4.78; B) The relationship between peak current and pH value.

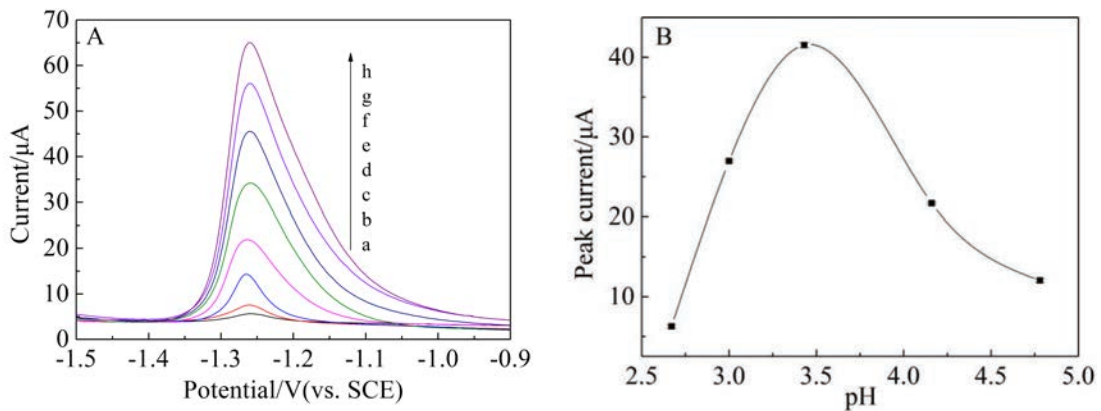


Fig. 8 (A) The differential pulse stripping voltammograms of Zn<sup>2+</sup> with different concentrations of LV·HCl. Curves a: 5.0, b: 10, c: 15, d: 20, e: 30, f: 40, g: 50, h: 60  $\mu\text{g} \cdot \text{mL}^{-1}$ ; (B) The relationship between peak current and LV·HCl concentration.

can be seen in Fig.7, the peak current showed the maximum with good peak shape at pH = 3.43.

### 2.3 Interfering Ions Experiments

For 25  $\mu\text{g} \cdot \text{mL}^{-1}$  LV·HCl solution within  $\pm 5\%$  relative error, the effects of different interfering ions with different concentration were studied. The results showed that as compared to the concentration of LV, the following concentrations of various metal ions have no interference in the experiments: 585 times of Ca<sup>2+</sup>, 3 times of Cr<sup>3+</sup>, 1800 times of K<sup>+</sup>, 10 times of Mg<sup>2+</sup>, and 825 times of Na<sup>+</sup>.

### 2.4 Quantitative Detection of Levofloxacin Using *in-Situ* Bismuth Film Electrodes

According to the above-mentioned experimental procedures, LV·HCl solutions of 0.50 mL, 1.00 mL, 1.50 mL, 2.00 mL, 3.00 mL, 4.00 mL, 5.00 mL, and 6.00

mL were added into six centrifugal tubes separately to prepare various concentrations from 5.0  $\mu\text{g} \cdot \text{mL}^{-1}$  to 60  $\mu\text{g} \cdot \text{mL}^{-1}$ . Under the optimized conditions described above, the peak currents were found to be linearly related to the concentration of LV·HCl solution. The correlation equation is  $I = 1.1401c - 0.5309$  with the relativity coefficient  $R = 0.9979$ , as seen in Fig. 8. The RSD value from the thirteen parallel determinations of standard LV·HCl solutions at 25  $\mu\text{g} \cdot \text{mL}^{-1}$  was 2.87%. The result indicated that this method is very reliable with good reproducibility. A blank test was carried out with 25  $\mu\text{g} \cdot \text{mL}^{-1}$  standard LV·HCl and 0.5 mol·L<sup>-1</sup> KSCN solutions. After the measurements were repeated for 24 times, the standard deviation  $Sb$  value was calculated to be  $1.21 \times 10^{-8}$ . The slope  $k$  of working curve according to the linear



equation was obtained, i.e.,  $k = 1.1401$ . The detection limit ( $D$ ) of this method was  $D = 3Sb/k = 3.18 \times 10^{-5} \mu\text{g} \cdot \text{mL}^{-1}$ .

## 2.5 Determination of the Concentration for Unknown LV Samples

1) Recovery ratio experiment. Under the optimization conditions, the LV·HCl solutions were measured, and the recovery ratio experiment was performed. The results are shown in Tab. 1.

2) Determination of API samples. Under the optimized conditions, the results are shown in Tab. 2 ( $n = 3$ ).

## 3 Conclusions

BiFEs were successfully used to measure the content of LV·HCl in precipitation in KSCN-HSCN medium indirectly based on differential pulse stripping voltammetry. The optimized conditions were determined. The accumulation potential and accumulation time were  $-1.60 \text{ V}$  and  $140 \text{ s}$ , respectively; the stationary time was  $10 \text{ min}$ ; the solution concentrations of  $\text{Zn}^{2+}$ , KSCN and  $\text{Bi}^{3+}$  were  $0.04 \text{ mol} \cdot \text{L}^{-1}$ ,  $0.50 \text{ mol} \cdot \text{L}^{-1}$  and  $1 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$ , respectively; the pH of the solution was  $3.43$ . The linear function was  $I = 1.1401c - 0.5309$  and the relativity coefficient  $R =$

$0.9979$ . The detection limit of this method was  $3.18 \times 10^{-5} \mu\text{g} \cdot \text{mL}^{-1}$ . Notably, the Bi film is non-toxic, environment friendly electrode material. This method provides a new, easy, cheap and fast pathway with advantages of high sensibility, easy renew ability of electrode surface, good reproducibility for concentration determination of LV·HCl, which is hopeful for laboratory and industrial applications.

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Tab. 1 Recovery test results

API Sample	Amount/mg	Measured value/mg	Recovery ratio/%
	0	1.716	-
A	0.1	1.817	101.0
	0.250	1.964	99.2
	0	1.821	-
B	0.1	1.916	95.0
	0.350	2.162	97.4

Tab. 2 Determination results of unknown concentration for LV·HCl sample ( $n = 3$ )

API Sample	Peak current/ ( $\times 10^{-5} \cdot \text{A}$ )	Measured value/mg	Content/%
A	6.866602	433.5	90.3
B	7.118436	468.7	92.6

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# 电沉积铋膜电极差示脉冲溶出伏安法 测定盐酸左氧氟沙星

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**摘要:**盐酸左氧氟沙星分子中含有弱酸性有机胺结构,可与  $\text{Zn}(\text{SCN})_4^{2-}$  形成离子缔合物沉淀.将沉淀分离溶解后,用差示脉冲溶出伏安法在原位形成铋膜电极上测定沉淀中锌(II)的含量,间接测定盐酸左氧氟沙星的含量,结果表明,采用铋膜电极伏安曲线峰形好、灵敏度高、峰电流值大,方法的线性回归方程为  $I = 1.1401c - 0.5309$ ,相关系数  $R = 0.9979$ ,线性范围为  $5.0 \sim 60 \mu\text{g} \cdot \text{mL}^{-1}$ ,检出限为  $3.18 \times 10^{-5} \mu\text{g} \cdot \text{mL}^{-1}$ ,回收率为  $95\% \sim 101\%$ ,相对标准偏差  $\text{RSD} = 2.87\%$ 。

**关键词:**铋膜电极;差示脉冲溶出伏安法;盐酸左氧氟沙星;锌离子;离子缔合物