Research Article

Study of Silver Nanoparticles Sensitized Fluorescence and Second-Order Scattering of Terbium(III)-Pefloxacin Mesylate Complex and Determination of Pefloxacin Mesylate

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α-Keto acid of pefloxacin mesylate (PFLX) can form the complex with Terbium(III). The intramolecular energy from PFLX to Terbium(III) ion takes place when excited, and thus Terbium(III) excited state is formed and then emits the characteristic fluorescence of Terbium(III), locating at 490, 545, 580, and 620 nm. The second-order scattering (SOS) peak at 545 nm also appears for the complex with the exciting wavelength of 273 nm. When the silver nanoparticles are added to the system, the luminescence intensity at 545 nm greatly increased. So, with the adding of nanoparticles to the Terbium(III)-PFLX complex, not only is the intramolecular energy promoted but also the SOS intensity is enhanced. The experimental results show that it is the silver nanoparticles with certain size and certain concentration which can greatly enhance the fluorescence-SOS intensity, and the relative intensity at 545 nm is proportional to the amount of PFLX. Based on this phenomenon, a novel method for the determination of PFLX has been developed and applied to the determination of PFLX in capsule and serum samples.

1. Introduction

In recent years, researches on noble metals nanoparticles have got considerable attention in chemistry and physics [1–3] especially silver nanoparticles, which exhibit an enhancement of some potential properties including electrical conductivity [4], catalysis [5, 6], magnetic and optical polarizability [7], photonic technologies [8–11], and antimicrobial activity in surface-enhanced Raman scattering (SERS) [12]. Particle size may influence the physical properties of silver nanoparticles [13–15]. With the progress of nanotechnologies and the spectrum theories, more studies have been attracted to the luminescence of the role of silver nanoparticles [16, 17].

Terbium ions have unique fluorescent properties when complexed with organic ligands. The strong ion emission of these complexes originates from an intrachelate energy transfer from the triplet state of the ligand to the excited energy levels of the lanthanide ion. Methods for the determination of several organic compounds, which serve as energy donors to Terbium ions, have been developed [24].

Ofloxacin (OFLX), (±)-9-fluoro-2,3-dihydro-3-methyl-10-(4-methyl-1-piperazinyl)-7H-oxo-7H-pyrido[1,2,3-de]-1,4-benzoxazine-6-carboxylic acid (as shown in Figure 1), is one of the third-generation members of quinolone synthetic antibiotics, with a broad spectrum of activity against Gram-positive and Gram-negative bacteria [25, 26]. It is widely used in therapies against inflammation [27]. The drug’s effect is concentration dependent and its antibacterial effect is closely related to its plasma concentration.

Pefloxacin mesylate (PFLX), 1-ethyl-6-fluoro-1,4-dihydro-7-(4-methylpiperazin-1-yl)-4-oxoquinolone-3-carboxylic acid (as shown in Figure 1), is a fluoroquinolone antibacterial agent. It is used for the treatment for diseases of the skin and various kinds of urinary tract infections [28] and has been widely applied in clinical medicine. Determination methods for PFLX include spectrofluorometry [24, 29, 30], HPLC [31], TLC-fluorescence [32], and capillary electrophoresis [33, 34]. But using the silver nanoparticles sensitized fluorescence and second-order scattering (SOS) for the determination of PFLX has not been reported.
In this paper, the influence of silver nanoparticles on the SOS and fluorescence of Terbium(Tb)(III)-PFLX complex is studied through using the SOS and fluorescence spectrum. The results show that the size and concentration of nanoparticles can greatly affect the fluorescence-SOS intensity of the complex. Based on this phenomenon, a novel method has been developed for the determination of PFLX, and the determination comparison between PFLX and OFLX is also proposed.

2. Material and Methods

2.1. Apparatus. A transmission electron microscopy (TEM) image of the silver nanoparticles was acquired using a Hitachi H-600 (Japan) transmission electron microscope. A Shimadzu RF-5301 PC spectrofluorometer (Japan) was used for fluorometric and SOS measurements. All absorption spectra were recorded with a Cintra 10e UV-vis spectrophotometer (GBC). A 420A plus pH meter (Orion Research Inc) is used to measure pH of the solutions. All reagents were of analytical reagents grade and doubly distilled water was used throughout.

Stock standard solution (1.0×10^{-3} M) of PFLX and OFLX (Institute of Medical Biotechnology, Beijing, China) was prepared by dissolving them in proper solvent (dilute acid or alkali) and then was diluted to the desired concentration with water.

2.2. Reagents. A standard stock solution of the Tb(III) ion (1.0×10^{-2} M) is prepared by dissolving 934.5mg Tb_4O_7 in 15 mL HCl (12 M) at 100℃ and evaporating the solution to be almost dry; it is then diluted to 500 mL with water.

The preparation of the silver colloids followed the same procedure as originally proposed by Lee and Meisel [35]. AgNO_3 is used as precursor of silver nanoparticles and sodium citrate is used as both reducing and protecting reagent. A concentration of 1.0×10^{-4} M colloidal solution is prepared in terms of the silver atoms. The morphology and size distribution of silver nanoparticles are obtained by a transmission electron microscopy (TEM) and were shown in Figure 2. The particles are almost spherical with a mean diameter of 42 nm, and the silver nanoparticles had an absorption maximum at 420 nm, which is consistent with the literature [35].

The drug content of five capsules is weighed, finely powdered, and mixed. The average mass per capsule can be determined. Transfer an accurately weighted amount of the powder equivalent to 200 mg corresponding to one capsule into a 100 mL calibrated dark flask, in which the deionized water is added to dissolve the powder. The solution is then filtered so as to separate out the insoluble excipients. The desired concentration for the drug thus is obtained by accurate dilution with deionized water and the analysis is followed up as the general analytical procedure.

2.3. Procedures. As for a 10 mL test tube, 1.0 mL of HAc-NaAc buffer solution, 0.2 mL of 1.0×10^{-2} M Tb(III) ion solution, and an appropriate working solution or sample solution of PFLX, followed by 0.5 mL of 1.0×10^{-4} M silver nanoparticles are added. This mixture is diluted to 10 mL with water, mixed thoroughly, and stood for 25 min.

The SOS intensity is recorded with the different excited wavelength from 220 to 400 nm and reached the maximum at 545 nm with λ_ex = 273 nm. The enhanced SOS and fluorescence intensities are represented as ΔI = I − I_0; here, I and I_0 are the intensities of the system with and without PFLX or OFLX. All the data are obtained with 5.0 nm excitation and emission slit-widths.

3. Results and Discussion

3.1. UV-Vis Spectrum. UV-vis absorption spectra of the system (Figure 3) are recorded. It can be found that the absorption peaks at 275 nm and 323 nm for Tb(III)-PFLX complex increased along with adding silver nanoparticles to the system, and the absorption peak at 420 nm for the nanoparticles appeared. The results indicate that there exist
interactions between Tb(III)-PFLX and silver nanoparticles and it can be concluded that silver nanoparticles incorporate with the complex of Tb(III)-PFLX, while the particle aggregates are formed in the ternary complex [16].

3.2. Second-Order Scattering Spectra and Fluorescence Spectra. α-Keto acid of PFLX supplies a coordination site binding to Tb(III) ion and has two aromatic rings that can absorb energy, resulting in intramolecular energy from PFLX to Tb(III) ions; thus, Tb(III) excited state is formed and then emits the characteristic emission of Tb(III), locating at 490, 545, 580, and 620 nm, corresponding to the transitions of the Tb(III) 5D4 → 7F6, 5D4 → 7 F5, 5D4 → 7F4, and 5D4 → 7F3, respectively [36]. The maximum fluorescence peak locates at 545 nm when it is excited; the silver nanoparticles can enhance the fluorescence of Tb(III)-PFLX complex, especially at 545 nm. At the same time, the SOS peak is also enhanced at 545 nm when the excited wavelength is at 273 nm, so the intensities conclude the fluorescence and SOS intensity. Figure 4 shows the fluorescence and SOS spectra, and the UV-35 filter is added to eliminate the scattering of the system [37].

3.3. Comparison between Silver Nanoparticles-Tb(III)-PFLX and Silver Nanoparticles-Tb(III)-OFLX System. From the fluorescence-SOS spectra above, the difference between silver nanoparticles-Tb(III)-PFLX and silver nanoparticles-Tb(III)-OFLX system could be observed (as shown in Figure 5). Silver nanoparticles can enhance the fluorescence-SOS intensity at 545 nm of Tb(III)-PFLX complex, while it can slightly increase the intensity of Tb(III)-OFLX system.

The observed spectral differences seem to be dependent on the structural variation of the fluoroquinolone and especially on the nature of the N1 substituent. The benzoxazine group of OFLX appears as an efficient electron-attracting system acting as a quencher of the fluorescence process. In contrast, the PFLX system has strong intensity owing to the electron-donating character of the N1 ethyl substituent [38]. The molecular structures of PFLX and OFLX are shown in Figure 1.

On the other hand, according to the theory of “the trivial of radiative mechanism for electronic energy transfer” [39], the efficiency of energy transfer is related to the capability of absorbing photon (ε) for donor and the overlap of the emission spectrum of donor and the absorption spectrum of acceptor. In Tb(III)-PFLX and Tb(III)-OFLX complexes, εPFLX > εOFLX, at the same time, the emission spectrum of...
Figure 6: Absorption spectrum of Tb(III) (1) and emission spectra of PFLX (2) and OFLX (3) Conditions: Tb(III), $2.0 \times 10^{-4}$ M; PFLX and OFLX, $1.0 \times 10^{-6}$ M.

Table 1: Tolerance of coexisting substance.

| Substance       | Concentration coexisting $(\times 10^{-6}$ M) | Intensity change (%) | Substance       | Concentration coexisting $(\times 10^{-6}$ M) | Intensity change (%) |
|-----------------|-----------------------------------------------|----------------------|-----------------|-----------------------------------------------|----------------------|
| Hemoglobin      | $10^b$                                        | +0.4                 | Fe$^{3+}$, NO$_3^-$ | 10                                            | +3.4                 |
| Myoglobin       | $1^b$                                         | −0.1                 | Mg$^{2+}$, SO$_4^{2-}$ | $1000$                                          | +2.4                 |
| Vitamin B1      | 5$^b$                                         | −4.7                 | NH$_4^+$, Cl$^-$ | $10000$                                         | +4.5                 |
| Glucose         | $500^b$                                       | +4.8                 | K$^+$, Cl$^-$ | $1000$                                          | −1.3                 |
| Fructose        | $500^b$                                       | +4.4                 | Co$^{2+}$, SO$_4^{2-}$ | 100                                            | −1.1                 |
| Starch          | $100^b$                                       | +4.0                 | Na$^+$, Cl$^-$ | $10000$                                         | +4.6                 |
| β-alanine       | $100^b$                                       | 0.7                  | Mn$^{2+}$, SO$_4^{2-}$ | $1000$                                         | +4.8                 |
| β-CD            | $100^b$                                       | +2.7                 | Ca$^{2+}$, Ac$^-$ | $100$                                          | −3.2                 |
| Uric acid       | 5                                             | −6.2                 | Zn$^{2+}$, SO$_4^{2-}$ | $100$                                          | −0.7                 |
| β-Dextrin       | 5                                             | +1.2                 | Pb$^{2+}$, NO$_3^-$ | $100$                                          | +1.9                 |
| Al$^{3+}$, SO$_4^{2-}$ | 10                                            | +5.1                 | K$^+$, H$_2$PO$_4^-$ | 10                                            | +4.1                 |
| Ni$^{2+}$, NO$_3^-$ | 10                                            | +3.0                 | Ca$^{2+}$, Cl$^-$ | $100$                                          | −4.0                 |
| Cu$^{2+}$, SO$_4^{2-}$ | 10                                            | −4.9                 | Ca$^{2+}$, Cl$^-$ | $1000$                                         | +4.8                 |

*Conditions: PFLX, $1.0 \times 10^{-6}$ M; Tb(III) ion, $2.0 \times 10^{-4}$ M; silver nanoparticles, $5.0 \times 10^{-6}$ M; pH, $6.0 \times 10^{-6}$ g mL$^{-1}$.

Table 2: Analytical parameters for the determination of PFLX.

| Linear range $(\times 10^{-7}$ M) | Linear regression equation $(c \times 10^{-7}$ M)$^a$ | $r^b$ | LOD$^c$ $(3\sigma_c \times 10^{-10}$ M) |
|-----------------------------------|------------------------------------------------------|-------|---------------------------------------|
| 0.008–10.0                        | $\Delta I = 7229.5c - 9.2828$                       | 0.9991| 2.5                                   |
| 10.0–80.0                         | $\Delta I = 4653c + 419.95$                         | 0.9973|                                       |

*a* $\Delta I$ is the enhanced intensity of SOS and fluorescence.

*b* Correlation coefficient.

*c* Detection limit.

3.4. Influence of pH. Fluorescence and SOS intensity of the system is pH dependent. The effect of pH was investigated over the range of 3.0–8.0, and the optimum pH is about 6.0. Then a HAc-NaAc buffer solution of pH 6.0 with a concentration of 0.1 M was found to be suitable for the measurements. Maybe the reason is that Ac$^-$ replaces H$_2$O which quenches fluorescence of the Tb(III) complex and incorporates with Tb(III)-PFLX complex [40].

3.5. Effect of Tb(III) Ion Concentration. The effect of Tb(III) ion concentration in the range from $1.0 \times 10^{-5}$ to $5.0 \times 10^{-4}$ M on the analytical signal for the system was studied. As the concentration of Tb(III) ion increased, the relative intensity was enhanced; when the concentration was over $2.0 \times 10^{-4}$ M, the relative intensity remains constant. So a Tb(III) ion concentration of $2.0 \times 10^{-4}$ M was selected for further research.

PFLX has a larger overlap with the absorption spectrum of Tb(III) than that of OFLX (see Figure 6); thus the efficiency of energy transfer of Tb(III)-PFLX system is much higher than that of Tb(III)-OFLX system, resulting in notable difference between them when the silver nanoparticles are added.
Table 3: Results for the determination of PFLX in capsules (n = 5).

| Sample          | Labeled (mg) | Amount found ± R.S.D (%) | Added (×10⁻⁷ M) | Found (×10⁻⁷ M) | Recovery ± R.S.D (%) |
|-----------------|--------------|--------------------------|-----------------|-----------------|----------------------|
| PFLX (capsule 1)| 200.0        | 200.4 ± 3.6, 197.2 ± 1.2 | 1.00            | 1.04            | 104.0 ± 3.60         |
|                 |              |                          | 2.00            | 2.04            | 102.0 ± 2.90         |
|                 |              |                          | 4.00            | 4.06            | 101.5 ± 2.92         |
| PFLX (capsule 2)| 200.0        | 200.2 ± 1.5, 196.9 ± 3.9  | 6.00            | 6.10            | 101.7 ± 2.46         |
|                 |              |                          | 8.00            | 8.20            | 102.5 ± 3.63         |
|                 |              |                          | 10.00           | 9.88            | 98.8 ± 3.92          |

Table 4: Analytical recoveries of PFLX in serum samples (n = 5).

| PFLX | Added (×10⁻⁸ M) | Found (×10⁻⁸ M) | Recovery ± R.S.D (%) |
|------|----------------|----------------|----------------------|
| Serum 1 | 1.00          | 1.03           | 103.0 ± 3.21         |
|       | 2.00          | 2.03           | 101.5 ± 3.89         |
|       | 3.00          | 3.02           | 100.7 ± 4.53         |
| Serum 2 | 3.00          | 3.12           | 104.0 ± 3.96         |
|       | 5.00          | 4.79           | 95.8 ± 2.43          |
|       | 7.00          | 6.92           | 98.8 ± 3.36          |

3.6. Effect of Silver Nanoparticles Concentration. From the experiments, it can be inferred that not only the size but also the concentration of nanoparticles (namely, the numbers of particles in the unit volume) can affect the luminescence intensity of the system. The silver nanoparticles are prepared by AgNO₃ solutions of 1.0 × 10⁻³ M, 1.0 × 10⁻⁴ M, and 1.0 × 10⁻⁵ M, respectively. The results show that if AgNO₃ was 1.0 × 10⁻³ M, the silver nanoparticles have very high SOS scattering and the relative intensity is not proportional to the concentration of drug; if AgNO₃ is 1.0 × 10⁻⁴ M, the scattering intensity of silver nanoparticles was very low and the fluorescence-SOS could not be enhanced by the silver nanoparticles. The silver nanoparticles are suitable for this system if AgNO₃ is 1.0 × 10⁻⁵ M and the mean diameter is 42 nm, and thus they are chosen in the experiments.

Fixing the size of silver nanoparticles mentioned above, the effects of the concentration on the intensity of SOS and fluorescence are also studied. A concentration of 5.0 × 10⁻⁶ M of silver nanoparticles is used for further experiments.

4. Stability

Under the optimum conditions, the results showed that ΔI reached a maximum after all reagents were mixed for 25 min and the intensity was stable for at least 3 h, so that 25 min was set as the standard for all the SOS and fluorescence measurements.

4.1. Tolerance of Foreign Substances. In order to assess the possibility of analytical application of the method, the effects of some common excipients, metal ions, and organic compounds on signals intensity are investigated. The tolerable concentration ratios for the interference are < ±5%. The results are presented in Table 1. It can be seen from Table 1 that most of metal ions can be allowed at higher concentrations, but some organic species such as myoglobin, Vitamin B1, and uric acid have a relatively high interference. In sample determinations, starch and dextrin which exist in capsules can be eliminated through filtration, while in the serum samples, ZnSO₄ and Ba(OH)₂ can be added in order to precipitate the interference before the determination [40]. So it can be successfully applied to determine PFLX in capsules and serum samples.

4.2. Calibration and Detection Limitation. The calibration graphs for the determination of PFLX are conducted under the optimal conditions, and the results are given in Table 2. The detection limit (3σ) is 2.5 × 10⁻¹⁰ M for PFLX.

4.3. Samples Determination. The proposed method is applied to the determination of PFLX in capsules and compared with UV-vis method; the results are given in Table 3. There are no significant differences between labeled contents and those obtained by this method. Recoveries range from 98.8% to 104.0%.

Moreover, analytical recoveries were assessed by analyzing serum samples which contain PFLX and required only separation of the precipitated protein with centrifugation [41]. In order to make the sample concentrations of the drug within the linear range of the determination, serum samples were properly diluted and the recoveries were determined by the standard addition method [42]. The results are shown in Table 4.

5. Conclusion

The proposed silver nanoparticles sensitized fluorescence and SOS method for the determination of PFLX is simple, rapid, and could be easily automated. At the same time, this method shows high sensitivity and wide linear response for the determination of PFLX; the sensitivity of this method is higher than that of most other methods summarized in Table 5. Since nanoparticles have unique physical and
chemical properties, applications of nanoparticles in analytical chemistry are very potential. But the mechanism needs further study.

Conflict of Interests

No conflict of interests is involved in this paper.

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References

[1] V. A. Grover, J. Hu, K. E. Engates, and H. J. Shipley, "Adsorption and desorption of bivalent metals to hematite nanoparticles," Environmental Toxicology and Chemistry, vol. 31, no. 1, pp. 86–92, 2012.

[2] A. De Giacomo, M. Dell’Aglìo, A. Santagata, R. Gaudìuso, O. De Pascale, and P. Wagener, "Cavitation dynamics of laser ablation of bulk and wire-shaped metals in water during nanoparticles production," Physical Chemistry Chemical Physics, vol. 15, pp. 3083–3092, 2013.

[3] A. Ivask, O. Bondarenko, N. Jepishina, and A. Kahr, "Profiling of the reactive oxygen species-related ecotoxicity of CuO, ZnO, TiO₂, silver and fullerene nanoparticles using a set of recombinant luminescent Escherichia coli strains: differentiating the impact of particles and solubilised metals," Analytical and Bioanalytical Chemistry, vol. 398, no. 2, pp. 701–716, 2010.

[4] H. Wang, X. Qiao, J. Chen, and S. Ding, "Preparation of silver nanoparticles by chemical reduction method," Colloids and Surfaces A: Physicochemical and Engineering Aspects, vol. 256, no. 2-3, pp. 111–115, 2005.

[5] M.-M. Jose Luis, G.-M. Maria del Mar, G.-M. Francisco et al., "Catalysis and inactivation of tyrosinase in its action on o-diphenols, o-amino phenols and o-phenylenediamines: potential use in industrial applications," Journal of Molecular Catalysis B: Enzymatic, vol. 91, pp. 17–24, 2013.

[6] S. J. Hayes, D. W. Knight, M. D. Menzies, M. O’Halloran, and W.-F. Tan, "An efficient furan synthesis using heterogeneous catalysis," Tetrahedron Letters, vol. 48, no. 43, pp. 7709–7712, 2007.

[7] F.-K. Liu, F.-H. Ko, P.-W. Huang, C.-H. Wu, and T.-C. Chu, "Studying the size/shape separation and optical properties of silver nanoparticles by capillary electrophoresis," Journal of Chromatography A, vol. 1062, no. 1, pp. 139–145, 2005.

[8] H. Y. Fu, D. R. Chen, and Z. P. Cai, "Fiber sensor systems based on fiber laser and microwave photonic technologies," Sensors, vol. 12, pp. 5395–5419, 2012.

[9] M. H. Ullah, K. Il, and C.-S. Ha, "Preparation and optical properties of colloidal silver nanoparticles at a high Ag concentration," Materials Letters, vol. 60, no. 12, pp. 1496–1501, 2006.

[10] C. P. Lai, N. Alan, O. Peter et al., "Energy-efficient colourless photonic technologies for next-generation DWDM metro and access networks," in Proceedings of the International Conference on Photonics in Switching (PS ’12), September 2012.

[11] P. Tuthill, N. Jovanovic, S. Lacour et al., "Photonic technologies for a pupil remapping interferometer," in Optical and Infrared Interferometry II, vol. 7734 of Proceedings of SPIE, July 2010.

[12] C. Dong, Z. Yan, J. Kokx, D. B. Chrisey, and C. Z. Dinu, "Antibacterial and surface-enhanced Raman scattering (SERS) activities of AgCl cubes synthesized by pulsed laser ablation in liquid," Applied Surface Science, vol. 258, pp. 9218–9222, 2012.

[13] S. K. Mwili, A. M. El Badawy, B. Karen et al., "Changes in silver nanoparticles exposed to human synthetic stomach fluid: effects of particle size and surface chemistry," Science of the Total Environment, vol. 447, pp. 90–98.

[14] S. Hegde, S. Kapoor, S. Joshi, and T. Mukherjee, "Self-assembly of Ag nanoparticle-biotin composites into long fiber-like microstructures," Journal of Colloid and Interface Science, vol. 297, no. 2, pp. 637–643, 2006.

[15] M. M. Oliveira, D. Ugarte, D. Zanchet, and A. J. G. Zarbin, "Influence of synthetic parameters on the size, structure, and stability of dodecanethiol-stabilized silver nanoparticles," Journal of Colloid and Interface Science, vol. 292, no. 2, pp. 429–435, 2005.

[16] H. Nabika and S. Deki, "Enhancing and quenching functions of silver nanoparticles on the luminescent properties of europium complex in the solution phase," Journal of Physical Chemistry B, vol. 107, no. 35, pp. 9161–9164, 2003.

[17] J. A. Jiménez, S. Lysenko, H. Liu, E. Fachini, and C. R. Cabrera, "Investigation of the influence of silver and tin on the luminescence of trivalent europium ions in glass," Journal of Luminescence, vol. 130, no. 1, pp. 163–167, 2010.

[18] Y. Zhao, L. J. Gao, X. H. Sun, and H. M. Chai, "Determination of pefloxacin mesylate by water-soluble CdTe quantum dots,"
[30] Liao, X. M. Cao, L. M. Du, and H. Wu, "Determination of Pefloxacin by terbium(III) ion fluorescence probe sensitized by the surfactant," Journal of Analytical Science, vol. 24, pp. 95–97, 2008.

[31] B. Zhang and H. H. Lin, "Spectrophotometric determination of pefloxacin mesylate based on the charge-transfer reaction," Huaxue Shi, vol. 31, pp. 625–627, 2009.

[32] J. Veipopoulou, P. C. Ioannou, and E. S. Lianidou, "Application of terbium sensitized fluorescence for the determination of fluoroquinolone antibiotics pefloxacin, ciprofloxacin and norfloxacin in serum," Journal of Pharmaceutical and Biomedical Analysis, vol. 15, no. 12, pp. 1839–1844, 1997.

[33] S. Swoboda, K. Oberdorfer, F. Klee, T. Hoppe-Tichy, H. von Baum, and H. K. Geiss, "Tissue and serum concentrations of levofloxacin 500 mg administered intravenously or orally for antibiotic prophylaxis in biliary surgery," Journal of Antimicrobial Chemotherapy, vol. 51, no. 2, pp. 459–462, 2003.

[34] E. F. Samanidou, C. E. Demetriou, and I. N. Papadoyannis, "Direct determination of four fluoroquinolones, enoxacin, norfloxacin, ofloxacin, and ciprofloxacin, in pharmaceuticals and blood serum by HPLC," Analytical and Bioanalytical Chemistry, vol. 375, no. 5, pp. 623–629, 2003.

[35] M. Ooishi and M. Miyao, "Antibiotic sensitivity of recent clinical isolates from patients with ocular infections," Ophthalmologica, vol. 211, no. 1, pp. 15–24, 1997.

[36] A. M. Beltagi, "Determination of the antibiotic drug pefloxacin in bulk form, tablets and human serum using square wave cathodic adsorptive stripping voltammetry," Journal of Pharmaceutical and Biomedical Analysis, vol. 31, no. 6, pp. 1079–1088, 2003.

[37] M. E. El-Kommos, G. A. Saleh, S. M. El-Gizawi, and M. A. Abou-Elwaal, "Spectrofluorimetric determination of certain quinolone antibacterials using metal chelation," Talanta, vol. 60, no. 5, pp. 1033–1050, 2003.

[38] L. M. Du, H. Y. Yao, and M. Fu, "Spectrofluorimetric study of the charge-transfer complexation of certain fluoroquinolones with 7,7,8,8-tetracyanoquinodimethane," Spectrochimica Acta A: Molecular and Biomolecular Spectroscopy, vol. 61, no. 1-2, pp. 281–286, 2005.

[39] M. I. R. M. Santoro, N. M. Kassab, A. K. Singh, and E. R. M. Kedar-Hackmam, "Quantitative determination of gatifloxacin, levofloxacin, lomefloxacin and pefloxacin fluoroquinolone antibiotics in pharmaceutical preparations by high-performance liquid chromatography," Journal of Pharmaceutical and Biomedical Analysis, vol. 40, no. 1, pp. 179–184, 2006.

[40] P.-L. Wang, Y.-L. Feng, and L. Chen, "Simultaneous determination of trace norfloxacin, pefloxacin, and ciprofloxacin by TLC-fluorescence spectrophotometry," Microchemical Journal, vol. 56, no. 2, pp. 229–235, 1997.

[41] Z. Yang, X. Wang, W. Qin, and H. Zhao, "Capillary electrophoresis–chemiluminescence determination of norfloxacin and prulifloxacin," Analytica Chimica Acta, vol. 623, no. 2, pp. 231–237, 2008.

[42] C. Fierens, S. Hillaert, and W. Van den Bossche, "The qualitative and quantitative determination of quinolones of first and second generation by capillary electrophoresis," Journal of Pharmaceutical and Biomedical Analysis, vol. 22, no. 5, pp. 763–772, 2000.

[43] P. C. Lee and D. Meisel, "Adsorption and surface-enhanced Raman of dyes on silver and gold sols," Journal of Physical Chemistry, vol. 86, no. 17, pp. 3391–3395, 1982.

[44] Z. Tieli, Z. Huichun, and J. Linpei, "Photochemical fluorescence enhancement of the terbium-lomefloxacin complex and its application," Talanta, vol. 49, no. 1, pp. 77–82, 1999.

[45] G. Z. Chen, Z. Z. Huang, Z. Z. Zheng, J. G. Xu, and Z. B. Wang, Fluorescence Analysis Method, Science Press, Beijing, China, 1990 (Chinese).

[46] A. Rietoruda, L. Vazquezb, M. SOURSACa et al., "Fluoroquinolones as sensitizers of lanthanide fluorescence: application to the liquid chromatographic determination of ciprofloxacin using terbium," Analytica Chimica Acta, vol. 290, pp. 215–225, 1994.

[47] M. J. Turro, Modern Molecular Photochemistry, Benjamin/ Cummings Publishing, 1978.

[48] E. E. DiBella, J. B. Weissman, M. J. Joseph, J. R. Schultz, and T. J. Wenzel, "Lanthanide ions as luminescent chromophores for liquid chromatographic detection," Journal of Chromatography A, vol. 328, pp. 101–109, 1985.

[49] Y. Huang, C. Zhang, X. Zhang, and Z. Zhang, "Chemiluminescence analysis of menadione sodium bisulfite and analgin in pharmaceutical preparations and biological fluids," Journal of Pharmaceutical and Biomedical Analysis, vol. 21, no. 4, pp. 817–825, 1999.

[50] C. T. Kenner and K. W. Bush, Quantitative Analysis, Macmillan, New York, NY, USA, 1979.